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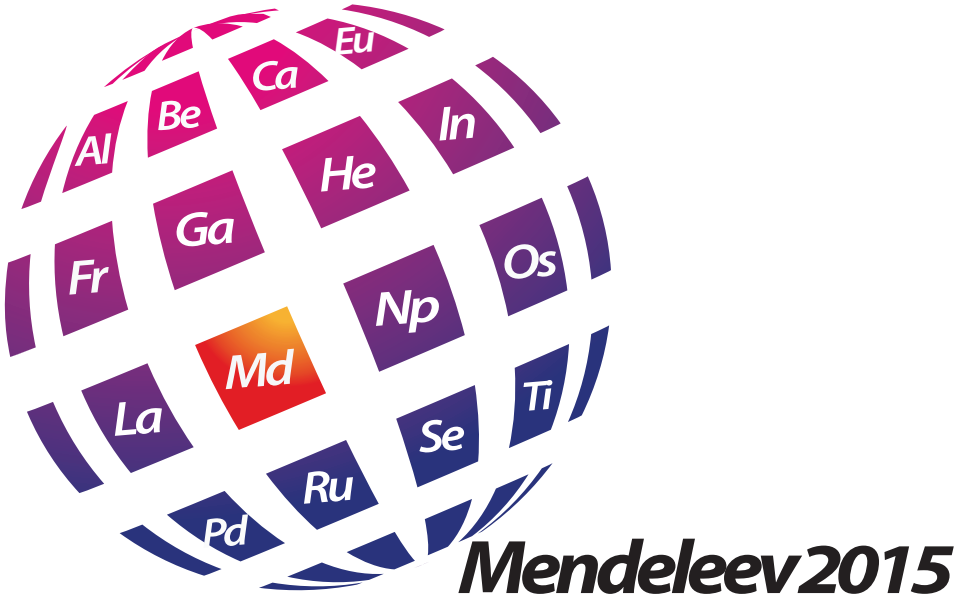

Book of abstracts

7-10 of April 2015
Saint Petersburg

Saint Petersburg State University
Mendeleev Russian Chemical Society
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**IX INTERNATIONAL CONFERENCE
OF YOUNG SCIENTISTS ON CHEMISTRY**

«MENDELEEV 2015»

Book of abstracts

Section 1
Inorganic materials and nanotechnology
Section 2
Polymeric materials: methods of production and processing
Section 3
Bioorganic and medical chemistry
Section 4
Quantum chemistry and computer modeling
Section 5
Modern techniques in analytical chemistry

Saint Petersburg
2015

Mendeleev 2015. Section 1: Inorganic materials and nanotechnology; Section 2: Polymeric materials: methods of production and processing; Section 3: Bioorganic and medical chemistry; Section 4: Quantum chemistry and computer modeling; Section 5: Modern techniques in analytical chemistry. IX Iinternational conference of young scientists on chemistry. Book of abstracts. Saint Petersburg. 2015.

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INVITED SPEAKERS
CONFERENCE “MENDELEEV-2015”

Gleb B. SUKHORUKOV

Head of the laboratory "Remotely controlled systems for theranostics" at the National Research Saratov State University (Saratov, Russia); Head of the Department of Biomaterials at the School of Engineering and Materials Science of the Department of Materials, Queen Mary University of London (UK).

In 1994 he defended his thesis at the Physics Department of Moscow State University on a specialty "Biophysics". First showed the possibility of forming a polymeric shell on colloidal microparticles by successive adsorption of polyelectrolyte microcapsules creation and encapsulation of various substances. He is the author and co-author of over 200 articles and 12 patents, the total number of citations is greater than 15,000 per year, h-factor is 71. He acts as reviewer of highly cited international journals such as Nature Materials, Angewandte Chemie, Advanced Materials, Journal of Controlled Release, Journal of American Chemical Society, Biomacromolecules and others. Also he was a coordinator and head of a large number of research projects, including grants of the European Union, Alexander von Humboldt Foundation and the Ministry of Education and Research of Germany (2001-2005). He has been ranked inside the top 10 world's most famous Russian scientists, according to the magazine «Forbes» (2011). His research comprises physics and (bio)-chemistry on submicron dimensions and design of multifunctional capsules.

Professor Sukhorukov was visiting researcher at the Institute of Physical Chemistry, University of Mainz (Mainz, Germany), research fellow at the Institute of Crystallography of RAS (Moscow, Russia), research fellow at the Department of phase boundaries Max Planck Institute of Colloids and phase boundaries (Golm - Potsdam, Germany), head of the research group "multifunctional nanostructured polymeric microcapsules" in the Max Planck Institute of Colloids and phase boundaries (Golm - Potsdam, Germany), a visiting professor at the Institute of Materials Research and Engineering A

STAR (Singapore). He is a head of research and production company «CapsulutionNanoScience» AG (Berlin, Germany), since 2000; Professor, Head of the Department of Biomaterials at the School of Engineering and the Department of Materials Science, Queen Mary University of materials (London, UK), since 2005; also a scientific head of the laboratory "Remotely controlled systems for theranostics" National research Saratov State University (Saratov, Russia).

MULTIFUNCTIONAL COMPOSITE POLYELECTROLYTE BASED CAPSULES AS THERANOSTIC SYSTEM WITH REMOTE CONTROLLING PROPERTIES

One of the challenges in the bionanotechnology field is development of nano-sized delivery systems comprising different functionalities. These systems should enable to ship and to carry bioactive substances to pre-defined site and unload it in designed time and place. Layer-by-layer assembled capsules are have been intensively studied in last few years owing to their ability to encapsulate a wide range of chemicals, for their permeability to be modified and their responsiveness to different factors and functionalities to be tailored in one capsule entity. Current research leads to the fabrication of carriers with remote guiding and activation by optical, magnetic and ultrasound addressing, what envisages unique applications as multifunctional biomaterials in-vivo. Microcapsules display a broad spectrum of qualities over other existing microdelivery systems such as high stability, longevity, versatile construction and a variety of methods to encapsulate and release substances. Release and encapsulation of materials by light and ultrasound and their navigation with magnetic field is a particularly interesting topic. Microcapsules can be made sensitive to light by incorporation of light sensitive polymers, functional dyes and metal nanoparticles. Optically active substances can be inserted into the shell during their assembly as a polymer complex or following the shell preparation. Visible- and infrared- addressable microcapsules offer a large array of release strategies for capsules, from destructive to highly sensitive reversible approaches. The paper demonstrates application for intracellular delivery of compounds and cellular response as well as in vivo perspectives.

Submicron sized capsules are good model to mimicking bio-chemical processes in a confined geometry imitating cell organelles, whilst delivered inside cell (including neurons) and tissues the capsules could serve as intracellular reporter or enzymatic reactor. Biophotonic approaches are envisaged to enhance the possibilities for multifunctional use of capsules. The talk discusses possible solutions and promising applications.

Alexander V. GARABADZHIU

Doctor of Chemistry, professor, head of the department of technology of microbiological synthesis, vice rector for scientific work of the St. Petersburg State Institute of Technology (Technical University). The winner of the award of the Government of the Russian Federation of 2006 in the field of science and equipment.

Author more than 200 scientific works, 3 monographs, 5 textbooks, more than 20 patents.

Prepared 15 candidates of science and 2 doctoral candidates, member of the editorial boards of "General Chemistry", "Applied Chemistry" and "Scientific Equipment Making" magazines of the Russian Academy of Sciences, editor-in-chief of the "Ecological Chemistry" magazine.

Areas of scientific interests: biopharmaceutics, ecological biotechnology, biomedicine, bioorganic chemistry, combinatory chemistry.

DESIGN OF SMALL-MOLECULE MODULATORS OF PROTEIN - PROTEIN INTERACTIONS AS THERAPEUTIC TARGETS

Detlef W. BAHNEMANN

Professor Detlef W. Bahnemann is one of the world leading researchers in the area of photocatalysis. He is a Head of Photocatalysis and Nanotechnology Research Unit at the Institute of Technical Chemistry, Leibniz University of Hannover. In 2014 Prof. Bahnemann received megagrant from the Government of the Russian Federation to create new laboratory "Photoactive Nanocomposite Materials " at the Saint-Petersburg State University. His main research topics include photocatalysis, photoelectron-chemistry, solar chemistry and photochemistry focused on the synthesis and the detailed investigation of the physical-chemical properties of semiconductor and metal nanoparticles.

Prof. Bahnemann holds an Honorary Professorship at the Robert Gordon University in Aberdeen/Scotland (United Kingdom), an Honorary Professorship at the Xinjiang Technical Institute of Physics and Chemistry (Chinese Academy of Sciences) in Urumqi (China), the Erudite Professorship at the Mahatma Gandhi University in Kottayam (India), a Guest Professorship of Tianjin University (China) and a DeTao Master of Photocatalysis, Nanomaterials and Energy Applications (China).

He has written more than 250 publications in refereed journals with a current Hirsch-Factor (h-Index) of 66 (papers have been cited more than 30,000 times altogether). He has presented over 300 lectures at scientific meetings at various universities, research institutes and industrial research development centers.

Andrei V. SHEVELKOV

Chair of the Department of Inorganic Chemistry and Head of Inorganic Synthesis Laboratory, Chemistry Faculty, Lomonosov Moscow State University, Moscow, Russia

CATIONIC CLATHRATES: ON THE WAY FROM AESTHETICALLY BEAUTIFUL STRUCTURES TO ADVANCED THERMOELECTRIC MATERIALS

Inorganic clathrates comprise a vast family of inclusion compounds that feature sequestering of guest atoms or molecules in large cavities of tracery frameworks. Ten varieties of their crystal structures are known to scientists, each delighting by their aesthetical beauty. First discovered as "anomalous ice" by Davy and then found in many hydrates as well as in solid-state compounds of p-elements, clathrates have long remained a fascinating object of scientific curiosity. It was only in the middle of the 1990th that Slack realized that clathrates, with their profound separation of host and guest substructures, might provide a base for creating thermoelectric materials of a new generation. Thermoelectric materials convert heat into electrical power or, vice versa, electrical power into a temperature gradient. The efficiency of the conversion rests with the ability of a compound to provide an efficient transport of charge carriers along with a poor transport of heat. Two weakly interacting substructures of clathrates, a host and guests, are ideally suited for decoupling charge carriers and heat-carrying phonons, leading to a property of a phonon glass and electronic crystal. In this lecture, we will focus on cationic clathrates and clathrate-like compounds that exhibit positively charged frameworks of different chemical nature and structure, which trap electronegative anions to form complex symmetric patterns. Their crystal and electronic structures as well as structure-related thermoelectric properties will be the central points of discussion.

Irina Yu. GORYACHEVA

Professor, D.Sc. in Chemistry (Analytical Chemistry), is a specialist in the development of new formats of rapid tests for clinical analysis, food and environment control.
The main goal of her research is to make assay simple, fast, user friendly and sensitive. In the course of her interest also is answering for questions, such as how to make visible substances at low concentration, how visualize processes in living organism, how add contrast to biological samples.

As an answer for these questions luminescent semiconductor nanoparticles (quantum dots) were developed and applied as biolabels in immunoassay, and for bioimaging.

Other scientific interests: Food & environment control, Immunochemical methods for sensitive detection of contaminants, Quantum dots synthesis, modification and application, room temperature phosphorescence and sensitized room temperature phosphorescence, Triplet-triplet energy transfer, kinetics of the photo-physical processes of singlet and triplet states, Cloud point extraction with surfactants.
Author of 60 articles and 6 RU patents.

BIOLABELS BASED ON LUMINESCENT QUANTUM DOTS: ANALYTICAL APPLICATION

Presentation will cover state of the art of the luminescent quantum dots development and application as biolabels in analytical chemistry. Luminescent quantum dots are semiconductor light-emitting particles of nanometer scale that have emerged as a new class of luminescent labels for chemical analysis (first of all bio- and immunoassay), molecular imaging and biomedical diagnostics. Small size, bright luminescence, photostability and turnable spectral characteristics are well suited for the detection of multiple analytes with ultrahigh sensitivity. For successful development of new immunoassay methods two basic aspects for obtaining satisfactory sensitivity and reproducibility exist. The first key point is to exploit highly efficient

signal-transduction labels (tags). Another important issue is to adapt a simple and sensitive signal-transduction method.

Properties of quantum dots, their synthesis and modification, variants of quantum dots' based labels, conditions of signal generation together with advantages and disadvantages will be discussed. Firstly used for bioimaging, they later became useful tools for immunoassay in the traditional microtiter plate format (fluorescent-linked immunoassay, FLISA) and after in sensors and rapid tests. The interest to this kind of labels for analytical applications could be even wider because the related toxicity (the main restriction of QDs application for in vivo imaging) is not so critical for in vitro goals.

Narrow symmetrical QD's luminescent peaks make it possible to use QDs as labels for the simultaneous detection of multiple analytes. This possibility is especially important for analysis of more than one analyte on a single test spot. Multiplex systems based on QDs which emit in different parts of spectrum without any mathematical or statistical processing of the obtained results, were already successfully described for multicolour bioimaging, multiplex electrochemiluminescence immunoassay, multiplex luminescent microarrays and rapid tests.

Small QD's size (units or tens nanometers) grants possibility to comsolidate multiple QDs into one structure. Numerous QDs instead of one single QD involved in each molecular recognition event amplify the analytical signal output. Moreover several QD based techniques, such as luminescent, electrogenerated chemiluminescent and electrochemical detection can offer high sensitivity. The combination of association of numerous QDs into one label with a highly sensitive detection of each QD enables to detect analytes at low concentrations. One advantage of enhanced labels is the possibility to use the same signal generation and signal-transduction methods as for the single QDs.

Examples of luminescent quantum dots applications in analysis will be presented, perspectives for rapid tests, sensors as well as for modification of classical methods

The work was supported by Russian Scientific Foundation (project 14-13-00229).

Gerd MAURER

Retired professor of Thermodynamics in the Department of Mechanical and Process Engineering at the University of Kaiserslautern

Academic Education:
1962/1963 to 1966/1967 - Process Engineering at University of Karlsruhe/Germany
1967 to 1971 - Research for Doctoral Thesis at University of Karlsruhe/Germany Supervisor: Prof. Dr. K. Bier
06.02.1971 - PhD (Dr.-Ing.) examination
1971 to 1977 - Research for Habilitation at University of Karlsruhe/Germany
25.06.1977 - Habilitation for „Applied Thermodynamics“

Professional experience:
1967 to 1980 - In various positions at Faculty of Chemical Enginnering, University of Karlsruhe/Germany
(1977 to 1978 - Scholarship by DFG for doing research with Prof. J. M.Prausnitz/University of California, Berkeley/USA)
1980 to 1985 - BASF AG Ludwigshafen a.Rh./Germany
1985 to 2008 - Full Professor for Applied Thermodynamics, Department of Mechanical and Process Engineering, University of Kaiserslautern/Germany
Since 04/01/2008 - Professor emeritus

Research interests: Fluid Phase Thermodynamics and its applications in various industries (chemical, petrochemical, biochemical, pharmaceutical etc.)

Publications: more than 300 in reviewed international journals

GAS SOLUBILITY: PHENOMENA AND MODELLING

The lecture discusses the phenomena of “physical” and “chemical” gas solubility, gives a short introduction on the thermodynamic modelling – without going into details – presents experimental techniques to investigate such phenomena, prediction and correlation tools and presents some applications. The first part of the lecture deals with “physical” gas solubility phenomena which – under certain conditions - result in interesting phenomena, such as the formation of gas hydrates, the salting-out of gases by electrolytes in aqueous solutions, the vice-versa phenomenon of reduced salt solubility due to well soluble gases and the SONG –phenomenon (Salting-Out by Near-critical Gases). In the second part, examples of “chemical” gas solubility phenomena are presented. All examples come from applications in the chemical (and related) industries (for example, the removal of carbon dioxide from gaseous effluents in the chemical and electric power industries).

Section 1.

Inorganic materials and nanotechnology

SYNTHESIS OF IRON OXIDE IN THE PRESENCE OF $HAuCl_4$

Abakshonok A.V.[1], *Kashevsky S.B.*[2]

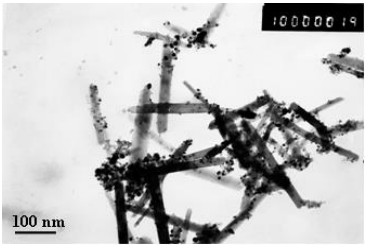
[1]Institute of Chemistry of New Materials of NAS of Belarus,
[2]A.V. Luikov Heat and Mass Transfer Institute of NAS of Belarus,
Graduate student
nura2007@tut.by

Composite nanomaterials including gold and iron oxides are promising for applications in biotechnology and catalysis. The purpose of our work is to determine the effect of the concentration of $HAuCl_4$ on the synthesis of iron oxides particles by co-precipitation method. The cooled solution 1, containing 0.04 N HCl, 25 (or 150) mM $FeSO_4$, 50 (or 300) mM $FeCl_3$ and 0 - 20 mM $HAuCl_4$, and solution 2 including 100 mM $N_2H_4 \cdot 2HCl$ and 2.2 M $NH_3 \cdot H_2O$ were prepared. One part of solution 1 was added to 9 parts of solution 2 and resulting mixture was treated for 3 hours in the ultrasonic bath Elmasonic S30H (Germany).

Table 1. Characteristics of iron oxides particles.

$[FeCl_3]$, mM	$[FeSO_4]$, mM	$[HAuCl_4]$, mM	Specific magnetization, $G \cdot cm^3/g$	Length	Width	Length / width
5	2.5	0	0	70±7	13±3	5.4
5	2.5	0.3	<1.0	110±13	13±2	8.5
5	2.5	1.6	2.4	261±21	21±2	12.4
30	15	0	41.1	16±2	16±1	1.0
30	15	0.3	34.5	18±8	14±7	1.3
30	15	2.0	6.7	61±16	16±6	3.8

Morphology and magnetic properties of the forming particles depend on the concentration of iron salts and $HAuCl_4$ in the co-precipitation medium (table 1). As a result of reduction of $HAuCl_4$, finely dispersed gold nanoparticles are formed, which effectively bind to iron oxides particles (figure 1).



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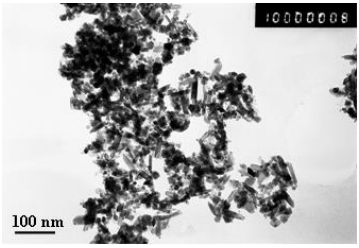

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Figure 1. TEM-images of iron oxides particles prepared in the medium containing *1* – 5.0 mM $FeCl_3$, 2.5 mM $FeSO_4$ and 1.6 mM $HAuCl_4$, *2* – 30.0 mM $FeCl_3$, 15.0 mM $FeSO_4$ and 2.0 mM $HAuCl_4$.

PHASE AND STRUCTURE FORMATION OF COMBUSTION PRODUCTS AT γ-AlON SYNTHESIS WITH THERMAL CONJUGATED REACTIONS OF BORON, ALUMINUM AND SILICON COMBUSTION IN GASEOUS NITROGEN

T.G. Akopdzhanyan, I.P. Borovinskaya
Institute of Structural Macrokinetics and Materials Science, RAS
Chernogolovka, Russia
Ph.D. student
Tigi@yandex.ru

Nowadays high-temperature nitride ceramics takes one of the leading places among novel materials for various industries: electronics, radio, aircraft and space engineering, nuclear industry. The main materials among them are aluminum, silicon and boron nitrides, aluminum oxynitride (AlON), SiAlONs, etc. One of the efficient technologies for production of these materials is self-propagating high-temperature synthesis (SHS) based on exothermic reactions between metals and nonmetals with nitrogen (combustion reactions). Generally, these reactions have a high thermal effect and propagate spontaneously with high velocities. For low-caloric systems, the method of conjugated reactions was developed. It includes simultaneous combustion of low-exothermic and high-exothermic mixtures to obtain two or more target products. This paper demonstrates the results of investigation of combustion mechanism and development of the synthesis method in the conjugated mode of aluminum oxynitride which is considered very important for development of construction and optical ceramics along with aluminum or boron nitride.

The paper contains some literature data on well-known production methods of aluminum oxynitride and its phase composition. The experiments in Al-Al_2O_3 combustion without a preliminary heating were carried out in high pressure nitrogen. Also conjugated reactions with Al-AlN and B-BN systems were studied. Chemical and XRD analyses prove that combustion of Al-Al_2O_3 results in $Al_{2.81}O_{3.65}N_{0.44}$ and AlN formation. At combustion of conjugated systems at high temperatures, the main phase is cubic Al_5O_6N and the combustion products composition depends on nitrogen pressure slightly.

The paper demonstrates the results of phase and chemical composition investigations as well as the structure of “chemical furnace” combustion products based on boron, aluminum, and silicon at γ-AlON synthesis with thermal conjugated reactions of nitriding in high-pressure gaseous nitrogen. It is shown that at stiff terms of nitriding (nitrogen pressure – 10-40 MPa) and high temperatures (up to 3000°C) gas-phase reactions play the important role in formation of boron, aluminum and silicon combustion products and the structure of the obtained nitrides differ from the conventional structures of SHS

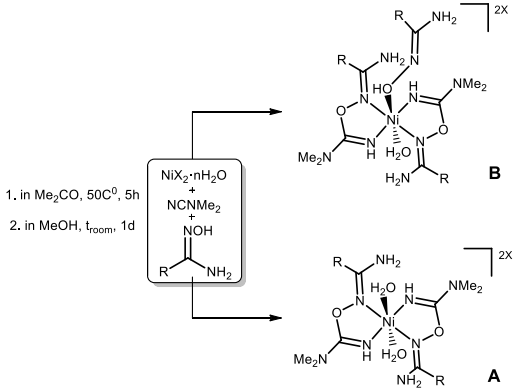
nitrides. For instance, BN nanotubes were discovered in boron-based combustion products.
Some suggestions are made on the mechanism of non-conventional structure formation of boron, aluminum and silicon nitrides within thermally conjugated reactions of nitriding.

Ni^{II}-MEDIATED DIMETHYLCYANAMIDE–AMIDOXIME COUPLING

Andrusenko E.V., Kabin E.V., Bokach N.A.

Saint Petersburg State University
Saint Petersburg, Russia
Ph.D. Student
e.andrusenko@spbu.ru

The reactivity of push-pull nitrile ligands, i.e. dialkylcyanamides, is different from that of alkyl cyanides, both quantitatively (high speed interaction), and in qualitative terms (different reaction products). In the present work Ni^{II}-mediated nucleophilic addition of amidoximes to dimethylcyanamide was chosen as an object of study. For our study we addressed the amidoximes $RC(NH_2)NOH$ (R = Me, Ph, $PhCH_2$, *p*-BrC_6H_4) and $NiX_2 \bullet nH_2O$ (X = Cl, *n* = 0; Br, *n* = 3; I, *n* = 6; OTf, *n* = 0). It should be noticed, that structure of the complex product depends on substituent R in amidoxime moiety (Scheme 1). Generally, the cationic complexes, bearing two coordinated carbimidoylamidoximes and two water molecules, viz. $[Ni\{HN{=}C(NMe_2)ONC(NH_2)R\}_2(H_2O)_2]^{2+}$, were obtained (products **A**). In some instances (R = $PhCH_2$, X = Br or I; R = Ph, X = I) products **B** were isolated. All compounds were characterized by $HRESI^+$-MS, X-Ray, FTIR, and CHN-analyses.



Scheme 1. Ni^{II}-mediated dimethylcyanamide–amidoxime coupling

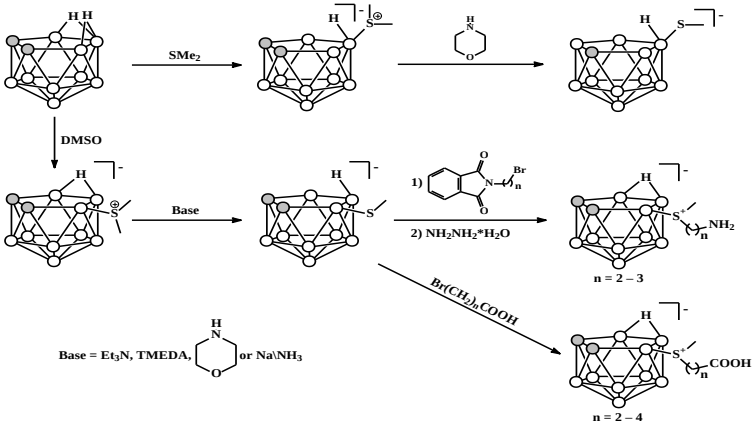
Acknowledgements: We thank Russian Science Foundation (grant 14-03-00060) for the support of this study. EVK is grateful for Saint Petersburg State University for postdoctoral fellowship (12.50.1190.2014). Physicochemical studies were performed at Center for X-ray Diffraction Studies, and Center for Chemical Analysis and Materials Research.

SYNTHESIS OF FUNCTIONAL DERIVATIVES OF CARBORANE

Anufriev S.A., Sivaev I.B., Bregadze V.I.

A. N. Nesmeyanov Institute of Organoelement Compounds
Russian Academy of Sciences, Moscow, Russia
trueMan476@mail.ru

Reactions of the protonated *nido*-carborane [7,8-$C_2B_9H_{13}$] with dimethyl sulfide and dimethyl sulfoxide were studied. The reaction with dimethyl sulfide gives symmetrically substituted dimethyl sulfonium derivative [10-Me_2S-7,8-$C_2B_9H_{11}$], whereas the reaction with dimethyl sulfoxide produces asymmetrically substituted isomer [9-Me_2S-7,8-$C_2B_9H_{11}$]. Reactions of demethylation of the prepared sulfonium derivatives were studied. A series of new *nido*-carborane-based amines and carboxylic acids were prepared by alkylation of [9-SMe-7,8-$C_2B_9H_{11}$]$^-$ [1] with various ω-halogenalkyl N-phthalimides and ω-halogenalkyl carboxylic acids.



References

[1] M.V. Zakharova, I.B. Sivaev, S.A. Anufriev, S.V. Timofeev, K. Suponitsky, I. Godovikov and V.I. Bregadze, *Dalton Trans.*, 2014, 43, 5044-5053.

Acknowledgements

The authors thank the Russian Foundation for Basic Research (projects 13-03-00581 and 15-03-05822) for financial support.

PRODUCTION OF LONG-SIZED ITEMS BASED ON TI – AL – C MAX-PHASE BY SHS-EXTRUSION

O.A. Averichev [1], P.M. Bazhin, A.M.Stolin

[1]Institute of Structural Microkinetics and Materials Science RAS,
Chernogolovka, Russia
Postgraduate student
olegaverichev@gmail.com

Compounds based on MAX-phases take an intermediate position between metals and ceramics. This class of compounds is characterized by high thermal and electric conductivities on the one hand and excellent heat resistance, elastic modulus, crack resistance and flexural strength on the other. In order to obtain long steel items from these compounds, the SHS-extrusion method was used. The main advantages of this method are a low cost of production, high synthesis velocities and ability to preset the required shape and size. Furthermore, this method allows avoiding the powder technology method, especially sintering, which implies enormous power consumption.

The main goal of this study is to examine technological parameters of SHS-extrusion. It allows us to improve microstructure quality of long steel rods based on Ti – Al – C MAX-phase and maximize their length. The most important of them are time delay, velocity of pressing, pressure value, preliminary heating of initial templates and others.

Stoichiometric ratio of Ti, Al and C in the initial mixture was variable. Before SHS-extrusion, preliminary one-axial cold pressing was carried out in order to obtain initial mixture templates (tablets) of a cylindrical shape. These tablets were 50 and 70 g in mass, 40-45 mm in height; their relative density was 60%. The process of SHS-extrusion was realized at 10 MPa, the pressing velocity was 100 mm/sec, and the tablet was preliminarily heated up to 300 ^{o}C.

Within the work we obtained long steel rods and found out experimental dependences of the rod length, surface homogeneity and continuity on the technological parameters of SHS-extrusion. One of the principal parameters, which determines the material formation ability, is time delay (the time between the beginning of the combustion process and that of the plunger movement). The experiments prove that the optimal values of this parameter range from 3 to 8 sec depending on the stoichiometric ratio (if the formation part is 3 mm long). The material was under pressure during 5 sec, the optimal pressure was determined to range from 15 to 50 MPa.

Acknowledgements. This study was held within the financial support of Education and Science Department of Russian Federation, President's scholarship aimed to support young Russian scientists MK-4078.2014.8

CHEMICAL REGULATION OF INITIAL COMPONENTS CONSUMPTION AT HYDROGEN COMBUSTION WITH VARIOUS ADMIXTURES

G.V. Balayan, V.V. Azatyan
Institute of Structural Macrokinetics and Materials Science, RAS
Chernogolovka, Russia
Postgraduate Student
Gevorg_balayan@mail.ru

When studying hydrogen oxidation by experimental and calculation methods, we observe that in the case of gas ignition prevention with inhibitors the initial reagents are practically not consumed because the combustion is suppressed at the beginning of reaction chains development. When the flame propagates in the presence of inhibitors, the combustion is suppressed partially, the inhibitor is spent in the reactions of the chain interruption with active particles and retards the process. Besides, there is an additional consumption of oxygen. The same effect of the inhibitor is observed in the case of detonation wave suppression. Quantitative data on an inhibitor consumption at various combustion modes are shown.

It is well known that hydrocarbon mixtures suppress combustion in in the detonation wave of hydrogen-air mixtures; that results in stationary detonation wave breakdown. In our experiments we initiated the process by the falling detonation wave of hydrogen-oxygen stoichiometric mixture. The inhibitor reacts with the atoms and radicals of the initiating flame of hydrogen and oxygen mixture with the following formation of low-active products. The inhibitor is obvious to be consumed. But it occurs in the reactions of chain interruption.

The important result of the experiments is the absence of the reaction between the inhibitors and oxygen at high initial temperatures. The inhibitory effect of additives on hydrogen combustion is impossible to be explained, e.g. with the hypothesis of oxygen consumption at its reaction with the additive without participation of carriers of hydrogen combustion chains. The results of this experiment prove that at ignition prevention the initial components are not consumed, and correspondingly, there is no deficiency of an oxidizer with a basis point. It is also supported by the results of special experiments when hydrogen was replaced by helium. In the mixture of 6% O_2 + 3.5 % C_3H_6 + 90.5 % He the ignition does not occur at least to 1750 K. Meanwhile, the same and even smaller additions of propylene prevent hydrogen combustion within the temperature interval of 940 – 1450 K. If oxygen were also consumed in the reaction with an inhibitor not only hydrogen without participation of intermediate particles of hydrogen, the inhibitor would have to intensify the combustion by creating an independent parallel reaction of oxygen

consumption. But the inhibitor, on the contrary, prevents and suppresses the combustion from the very beginning.

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MOBILITY OF IONC CHARGE CARRIERS IN OXYFLUORIDES $Ba_4Ca_2Nb_2O_{11-x}F_{2x}$

Baskakova S.A., Belova K.G., Animitsa I.E.
Ural Federal University
Yekaterinburg, Russia
Student
baskakova.s.a@gmail.com

Oxide ceramic materials having proton and oxygen- ion conductivity show a great interest because of their potential applications as electrolytes, membranes, sensors and etc. in different electrochemistry devices. Among them, we can distinguish oxygen- deficient double perovskite $Ba_4Ca_2Nb_2O_{11}$. This compound can uptake a significant quantity of water and show a dominant proton transport below 500ºC. Under wet air, $Ba_4Ca_2Nb_2O_{11}$ exhibit mainly oxygen- ion transport at high temperatures and proton transport at low temperatures.

For optimization of its properties is carried introduction of fluorine ions into the anion sublattice $Ba_4Ca_2Nb_2O_{11}$ ($F^- \rightarrow O^{2-}$, $r(O^{2-})=1.40$ Å, $r(F^-)=1.33$ Å). It largely affects oxygen mobility and therefore of protons, as dynamics of the oxygen sublattice determines their mobility.

Powders of $Ba_4Ca_2Nb_2O_{11-x}F_{2x}[V_O]_{1-x}$, где $0 \le x \le 0.25$ were prepared by conventional ceramic methods from powder mixture of pre- dried oxides and carbonates at the temperature range 800-1300ºC with intermediate grinding. The mobility of charge carries is investigated by dependence of electrical conductivity versus oxygen partial pressure under dry and wet air (dry air $pH_2O=10^{-5}$ atm, wet air $pH_2O=0.02$ atm, $pO_2=0.21 \div 10^{-20}$ atm).

The pO_2- dependencies of a total conductivity in dry air are shown pO_2-independent plateau. This is an oxygen- ionic conductivity region. Also the curves have a positive slope at higher pO_2, which indicates the appearance of some contribution of p-type conductivity to the total conduction. Decrease in temperature led to an increase region of oxygen- ionic conductivity. The influence of wet atmosphere is observed at rather high temperature. Ion transport numbers were calculated.

THE EFFECT OF DELAMINATION OF SILICATE FILLER ON PHYSICAL AND MECHANICAL PROPERTIES OF POLYVINYL ALCOHOL/MONTMORILLONITE NANOCOMPOSITES

A. G. Belozerov, N. S. Karasev, N. L. Ovchinnikov, M. F. Butman

Ivanovo State University of Chemistry and Technology, pr. Sheremetevskii 7, Ivanovo, 153000 Russia
belozerovartem@rambler.ru

A concept that complete exfoliation can be achieved by the inclusion into the processing of polymer/layered silicate nanocomposites of the intermediate stage, which is connected with the preparation of a delaminated form of layered silicate that is then entered into a polymer matrix, is developed in the present work. Large cations can serve as delaminating agents.

This idea is approbated in the present studies on the example of a composite on the basis of polyvinyl alcohol (PVA) and montmorillonite (MM). Microscopic studies on the PVA/MM nanocomposites clearly have shown the presence of delaminated and exfoliated silicate layers [1]. The preliminary hydrophobization of MM is not required in this case, since PVA is a water soluble polymer and the large $[A1_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ polyhydroxocomplexes of aluminium, so called Keggin ions, which are easily intercalated into MM, increasing its basal distance by 0.4 to 0.6 nm [2], are suggested for use as delaminating agents.

The following aims were pursued in the present studies: (1) the preparation of natural PVA nanocomposites, nanocomposites intercalated with Keggin ions, and nanocomposites with pillared MM; (2) a comparison of the strength properties and thermal stability of composite films and pure PVA; and (3) comparing the exfoliation degree of different forms of silicate filler.

The three forms of montmorillonite, i.e., natural, intercalated with large $[A1_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ Keggin ions, and pillared, are chosen for the comparative studies. Their use as filler in the watersoluble polymer, specifically, polyvinyl alcohol, has revealed that the obtained nanocomposite films show significantly higher strength properties in the case of using a delaminated silicate component. Due to preliminary delamination, the nearly complete exfoliation of the silicate layers is observed.

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THE DYNAMICS STUDY OF Rh (III) POLYNUCLEAR HYDROXOCOMPLEXES FORMATION IN EXTREMELY BASIC SOLUTION

Berdyugin S.N.[1], *Vasilchenko D.B.*[2]

[1]Novosibirsk State University
[2] Nikolaev Institute of Inorganic Chemistry
Siberian Branch of Russian Academy of Sciences
Novosibirsk, Russia
Student
snberdyugin@gmail.com

A polynuclear hydroxocomplexes (PHC) are the complexes, which contain more than one central atom connected together with bridging hydroxoligands. The formation processes of PHC have been studied for the series of nontransition and transition elements whereas analogue chemistry of platinum group metal (PGM) ions has been studied weakly. Currently, these complexes (PHC PGM) are of wide interest because it has been shown that they can act as predecessors of heterogeneous catalysts active sites.

The aim of this work is the investigation of Rh (III) PHC formation dynamics from its chlorocomplexes in strongly basic solutions. Earlier polynuclear Rh (III) aquahydroxocomplexes was derived from $[Rh(H_2O)_6]^{3+}$ in basic solutions and its crystal structure was determined. However, the processes of PHC formation was not discussed, moreover, the hexaaquarhodium (III) ion preparation is not a simple experimental task. In the present work, Rh (III) chlorocomplexes were used as the starting compounds because they are traditional reagents for industry applications.

The Rh (III) clorocomplexes were shown to undergo the fast substitution Cl^- to OH^- in concentrated NaOH (> 1M) solution at room temperature with formation of $[Rh(OH)_6]^{3-}$ which was determined by spectrophotometry (hypsochromic shift of d-d band) and ^{103}Rh NMR. Quantitative conversion was proved by the measurements of Cl^- content in the solutions. Slow condensation process of $[Rh(OH)_6]^{3-}$ ion proceeds in the prepared basic solutions resulting in formation of PHC. The dynamics of this process was investigated by spectrophotometric method in a range of metal-to-ligand charge transfer bands (200-300 nm). The condensation process was shown to be temperature and concentration depended: increasing of temperature and (or) Rh (III) concentration results in increasing of condensation rate, while growing of NaOH concentration slows down the reaction. A method of $[Rh(OH)_6]^{3-}$ and Rh(III) PHC isolation in solid phase was developed.

FORMATION OF COBALT NANOPARTICLES IN MATRIX OF POLY(PERFLUOROSULPHONIC) ACID MEMBRANE

Bespalov A.V., Sokolov M.E.

Kuban State University,
Krasnodar, Russia
Senior Lecturer
bespalov-alex@mail.ru

The synthesis of nanocomposite materials, containing magnetic metal nanoparticles, is an actual problem of modern chemistry. The ion-exchange materials are intensively used for preparation of metal-containing nanocomposites as polymeric matrixes. The chemical structure of poly(perfluorosulfonic) acid membranes, such as Nafion and MF-4SC, consists of a polytetrafluoroethylene hydrophobic matrix and regularly spaced sulphonate ionic groups, which agglomerates to hydrophilic ionic domains. These domains are the centers of formation of metal nanoparticles [1]. Significant interest represents in an opportunity of synthesis of nanocomposites with various distribution of reduced metal in thickness of membrane. Such materials have a wide range of uses in many diverse applications. The purpose of this study was to prepare and investigate composite magnetic materials based on poly(perfluorosulfonic) acid membranes MF-4SC and cobalt nanoparticles. Cobalt nanoparticles in matrix of membrane have been prepared by well-known borohydride method [2,3]. The prepared nanocomposites are characterized by scanning electron microscopy, FMR spectroscopy and voltammetric method for measurement of surface resistivity. The average size of cobalt nanoparticles is 75 nm in diameter, with the size distribution standard deviation of 30 nm. It was shown that the reductant concentration don't strongly influence the size of formed particles. The thickness of cobalt-containing layer changes from 10 to ~120 micrometers for samples with difference initial quantity of Co^{2+}. The thin conductive layers of reduced cobalt are formed on surface of membranes under certain conditions. In summary, nanocomposite materials with various distribution of reduced cobalt in thickness of membrane can be prepared by borohydride reduction.

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THE BASIC LAWS OF THERMAL EXPANSION OF APATITE

Blokhina A.G.,Knyazev A.V., Bulanov E.N., Korokin V.Zh.

Lobachevsky State University
Nizhni Novgorod, Russia
Student
Al1ona.rom@yandex.ru

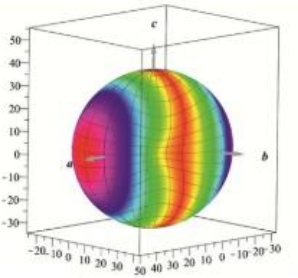
Thermal expansion is one of the thermophysical characteristics of matter and may characterized by linear (or volume) thermal expansion coefficient α_l. It provides information about the behaviour of materials in a wide range of temperatures. Here we produce the result of such a work for compounds with an apatite structure, as they are one of the most important substances from the industrial point of view.

The general formula of the apatites may be represented as follows: $M_5(AO_4)_3L$ (M – mono-, di-, tris- and tetravalent cations and their combinations; A= Si, Ge; P, V, Cr, Mn, As; S; L= Hal, OH, O, etc)

1. Thermal Expansion of Apatites with A = P, V, Cr, Mn

The primary direction of the thermal deformation for P- and V-apatites is crystallographic axis *c*; for Mn- and Cr-apatites it is the *a* axis. Anisotropy of the thermal expansion: α_a/α_c (s-element-apatites) > α_a/α_c (Cd- and Pb-apatites).

Some of such apatites have a polymorphic transition accompanied by lowering of the unit-cell symmetry from hexagonal ($P6_3/m$) to monoclinic ($P2_1/b$): in that case volume thermal expansion coefficient increase twice or thrice.



Picture 1. The general view for 3D thermal expansion diagram.

2. Thermal Expansion of Silicate Oxyapatite

The primary direction of the thermal deformations is crystallographic axis *c*. Anisotropy of the thermal expansion*:* α_a/α_c (Sr-oxyapatite) > α_a/α_c (Ca-oxyapatite).

3. Thermal Expansion of Sulfate Apatites

The primary direction of the thermal deformations is crystallographic axis ***c***. Sulfate apatites have two tipes of transitions: polymorphic $P6_3/m \rightarrow P2_1/b$ and morthotropic: $P6_3/m \rightarrow Pna2_1$ (not-apatite structure). In both cases volume thermal expansion coefficient significantly increase.

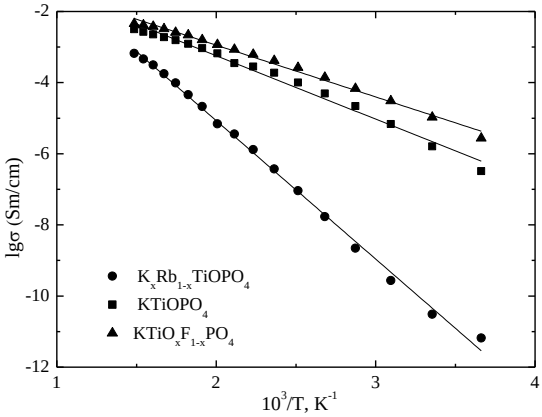
CONDUCTIVITY OF RUBIDIUM AND FLUORINE DOPED $KTiOPO_4$ CRYSTALS

BodnarV.A[1]., Glumov O.V[1]., Yakobson V.E.[2]

[1]Saint Petersburg State University
[2] Research and technological institute of optical materials all-russia scientific center «S.I. Vavilov State Optical Institute»
Saint Petersburg, Russia
Student
vikky95bodnar@gmail.com

Crystals of potassium titanyl phosphate $KTiOPO_4$ (KTP) and its solid solutions continues to attract attention as promising nonlinear materials for different applications, particularly as active elements of optical radiation transmitters and light modulators. Oxygen nonstoichiometry in KTP crystals along the crystallographic z-axis results the superionic conductivity of potassium ions K^+ in lattice.

KTP, KRTP ($K_xRb_{1-x}TiOPO_4$), KTPF ($KTiO_xF_{1-x}PO_4$) crystals were grown using a modified Czochralski method at varied temperature. The study of superionic conductivity of monovalent K^+ revealed the dependence of the ionic conductivity on the composition, conditions of growth and temperature. Activation energy (E_a) of process of potassium conductivity was calculated. The potassium conductivity was measured using impedance spectroscopy in the frequency range of 10 MHz - 100 Hz at temperature 0-400°C (Novocontrol Concept 40). A significant increase of the conductivity of fluorine doped $KTiOPO_4$ crystals was determined in this work.



Picture 1. Temperatures dependences of the electrical conductivity for few crystals.

The work carried out using equipment of the Resource Center for Innovative Technologies for Composite Nanomaterials, St. Petersburg State University.

SOLID-SOLUTION EQUILIBRIUM IN TERNARY SYSTEMS CONTAINING MIXED WATER-ORGANIC AND BINARY ORGANIC SOLVENT AND CADMIUM HALIDES

N. A. Bogachev, M. Yu. Skripkin, Nikolsky A. B.

Saint Petersburg State University
Postgraduate student
e-mail: allanfrack@yandex.ru

The development of an integrated physico-chemical way to approach to describe of the processes occurring in electrolyte solutions is the key to the prediction of the macroscopic properties of solutions, as well as to the creation of universal methods of purposeful synthesis of substances in liquid phase. The research relevance is connected with the lack of a common framework for the fundamental theory of solutions and a detailed model of such processes as dissolution, crystallization and solvation. The lack of the general theory makes quite actual the study of some particular problems among which solubility problem plays one of the key roles. In this report the results of the investigation of solid-solution equilibrium in the ternary aqueous-organic and double organic systems containing organic solvents with widely different properties such as DMSO, DMA, DMF, and dioxane, as well as cadmium halides are presented. The influence of salt ions association and the properties of the mixed solvents on the composition, structure and conditions of the solid phase formation are shown.

We acknowledge the support of resource centers "Centre for Optical and Laser Material Research" and “Centre for X-Ray Diffraction Studies” of St. Petersburg State University Research Park.
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CHARACTERIZATION OF BINARY SOLVENT MIXTURES CONSISTING OF DMSO, DMA, DMF AND 1,4 – DIOXANE

N. A. Bogachev, M. Yu. Skripkin, Yu. V. Kondratiev, Nikolsky A. B.

Saint Petersburg State University
Postgraduate student
e-mail: allanfrack@yandex.ru

The study of the properties of solvents mixture and the formation of intermolecular associates that they form in liquid phase is important for the understanding of the properties of liquid systems employed in organic synthesis or in the separation and concentration of solutes, and also for creating a real model, that is able to can predict observable macro properties of such a mixtures. In this study binary systems consisting of such oxygen-donating aprotic organic solvents as DMSO, DMA, DMF and 1,4-dioxane were investigated. Formation of intermolecular associates was characterized by vibrational spectroscopy, calorimetry and computer simulation potential intermolecular bonds in these mixtures. The determination of the dielectric constant, density and viscosity made it possible to estimate the structuredness of solvents in the whole concentration range. The compositions and fields of dominance of the most stable associates were detected.

We acknowledge the support of resource center "Centre for Optical and Laser Material Research" of St. Petersburg State University Research Park.
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THE INFLUENCE OF LiH AND NaH ON THERMAL STABILITY OF BH_3NH_3

Butlak A.V., Kazakov I.V., Krasnova I.S., Timoshkin A.Y.

Saint Petersburg State University,
Saint Petersburg, Russia
Postgraduate student, 1st year
a.v.butlak@gmail.com

Ammonia borane BH_3NH_3 (AB) is one of the widely used compounds for the hydrogen energetics [1]. Its decomposition proceeds in two steps and requires elevated (381-427 K) temperatures [2]. Reactions of metal hydrides with AB lead to the formation of amidoboranes MNH_2BH_3 (M=Li-K): $MH_{(s)} + BH_3NH_{3(s)} = MNH_2BH_{3(s)} + H_{2(g)}$. Such compounds decompose with the release H_2 at low temperatures (~358 K) [3]. In the present work reactions of LiH and NaH with AB were investigated at 293-343 K by tensimetry. In additional experiments, the gas phase composition at different temperatures was monitored by mass spectrometry (Thermo Scientific ISQ). The static tensimetric method with the glass membrane null-manometer was used to measure the pressure–temperature or pressure-time dependence without any contact of the studied substances with atmospheric air or moisture. The typical experiment was performed as follows: AB or equimolar amounts of MH and AB were placed in the membrane chamber under vacuum and then the system was sealed off. Series of measurements at constant temperatures allowed estimation of the reaction rate and the activation energy (Ea) of H_2 release. Noticeable pressure (~1 torr) appears at 320 K in case of AB and LiH+AB. Estimated at 320-343K activation energy for the dehydrogenation process in the system LiH+AB (95±65 kJ/mol) is very close to those of the first step of AB decomposition: $^1/_nBH_3NH_3 = [BH_2NH_2]_n + {}^1/_nH_2$ (94±11 kJ/mol). Those facts indicate that LiH does not significantly influence decomposition of AB below 343 K. In case of NaH+AB, hydrogen release started already at room temperature with formation of $NaNH_2BH_3$. The estimated activation energy for this process at 320-342K is 65±47 kJ/mol. Large experimental errors for Ea are attributed to the small number of data points and the narrow temperature range. Thus, addition of NaH significantly increases the rate of hydrogen release from AB, while LiH does not affect AB decomposition at 293-343 K. The major boron-nitrogen containing form in the mass-spectrum for all studied systems is BNH_5^+ ion, which indicates sublimation of AB at these conditions. This work was supported by Russian Science Foundation (project №14-13-00151).

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SYNTHESIS AND STUDY OF URANATES WITH GENERAL FORMULA $M^{III}U_2O_{7.5}$ (M^{III} – Y, Tb, Dy, Ho, Er, Tm, Yb, Lu)

K. A. Chaplieva, O. V. Nipruk, E. L. Kostrova
Lobachevsky State University of Nizhni Novgorod
Nizhni Novgorod, Russia
Postgraduate student
Kseniyachaplieva@yandex.ru

Method of synthesis of uranates with general formula $M^{III}U_2O_{7.5}$ (M^{III} – Y, Tb, Dy, Ho, Er, Tm, Yb, Lu) has been proposed in this work. The composition and structure of the synthesized compounds have been established by mean of high-temperature X-ray diffraction, IR spectroscopy, thermography, chemical analysis. The dimensional parameters of M(III) atoms which allow to prepare the crystalline phase the said composition have been determined.

The individual crystalline phases of uranates with general formula of $M^{III}U_2O_{7.5}$ were synthesized by the reaction of schoepite UO_3 $2.25H_2O$ with an aqueous solutions of $M^{III}(NO_3)_2$ under hydrothermal conditions at 200°C.

The values of the M^{3+} ionic radii increase from 0.80 for Lu^{3+} to 0.97 Å for Y^{3+}. These ionic radii are preferable for the octahedral coordination. All studied diuranates have similar composition and they are the crystallographic analogues. X-ray pictures of all compounds contain reflections with very close positions and intensities. The absence of maxima reflections in the region of small angles, which are characteristic for layered structure, shows the frame structure of the studied compounds.

The IR spectroscopic study was carried out in order to evaluate the function composition and structure of compounds. All uranates of yttric group are the functional analogs. IR spectrums of each diuranates contain the onely group of absorption bands of $\nu_{as}(UO_2^{2+})$ in the region of 868-871 cm^{-1}. Its position is a consequence of lengthening of the axial U-¨¨O bands. It can be caused by formation of-not-layered-type of structure of the compounds.

A thermographic study of $M^{III}U_2O_{7.5}$ has been carried out in tandem with high-temperature X-ray diffraction measurements in temperature range 20-1000°C. All the compounds are stable at high temperatures. The structure of $M^{III}U_2O_{7.5}$ decomposes to the oxide mixture ($M^{III}_2O_3$ and UO_3) at temperatures of over 800°C. This fact confirms our assumption that the compounds under study have a frame structure.

ADSORPTION-STRUCTURAL PROPERTIES OF MATERIALS BASED ON ZrO_2-Al_2O_3 SYSTEM

Chebotareva A.I.

Saint Petersburg State Electrotechnical University (LETU)
Saint Petersburg, Russia
Postgraduate student
a.tchebotareva@yandex.ru

Nanocomposite based on ZrO_2-Al_2O_3 was synthesized by precipitation of $Al(OH)_3$ in the suspension of nanoparticles ZrO_2 with an average size of 20±10 nm (70% tetragonal modification). The mixing ratio of components in terms of oxides (Al_2O_3:ZrO_2) varied over a wide range (10-80 mol% Al_2O_3). On the X-ray diffraction of the initial samples ZrO_2-$Al(OH)_3$ t-ZrO_2, m-ZrO_2 and peaks corresponding to aluminum hydroxide were registered. When the content of Al_2O_3 in the system is less than 50 mol%, aluminum hydroxide is represented by only γ-$Al(OH)_3$ (Gibbsite), while when Al_2O_3 content is 50 mol% or more, β-$Al(OH)_3$ (Nordstrandite) reflections are also observed.

Initial samples were exposed to hydrothermal (T = 480°C, P = 30 atm, τ = 4h) and thermal treatment in air (T = 500°C, τ = 2h), that led $Al(OH)_3$ diffraction reflexes to disappear. Besides, after processing the samples containing less than 50 mol% of Al_2O_3, there were not fixed any crystal phases except t-ZrO_2, m-ZrO_2. In the samples containing more than 50 mol% of Al_2O_3 there were observed reflections corresponding the trace amounts of γ- and θ-Al_2O_3. There were no significant changes in the crystallite size of zirconia dioxide and the ratio of its modifications (tetragonal and monoclinic) depending on the amount of Al_2O_3 in the system and their treatment method.

Stability of Al_2O_3 amorphous state was analyzed by thermal treatment of initial samples using "annealing-quenching" mode at 500-1200°C for 1 hour. It is shown that Al_2O_3 remains amorphous up to 800°C throughout the concentration range (10-80 mol% of Al_2O_3). Crystallization of θ-Al_2O_3 occurs at 1000°C. The sample containing 80 mol% of Al_2O_3 after heat treatment at 900°C contains several crystalline modifications of γ- and θ-Al_2O_3. Crystallization of thermodynamically stable α-Al_2O_3 was observed after heat treatment at 1200°C. Crystallization of Al_2O_3 is associated with a significant increase in crystallite size of zirconium dioxide.

Pycnometric density values of the samples decreases with increasing mol% of Al_2O_3 in the system, both for initial samples and for the samples hydrothermally and heat-treated in air. Specific surface area values of the initial and the samples heat treated in air grow with the increase of the mol% of Al_2O_3 in the system (from 90 to 260 g / cm^2). As for the samples after hydrothermal treatment, changes in the ratio of components do not affect the values of the samples' specific surface, and make about 50±10 g/cm^2.

This work was supported by RFBR № 13-08-01207

INTERRELATIONS OF STRUCTURAL FEATURES, OXYGEN NONSTOICHIOMETRY AND TRANSPORT PROPERTIES IN THE OXIDE SERIES $La_{0.5}Sr_{0.5}Fe_{1-x}Mn_xO_{3-d}$ (x = 0.1–0.33)

Chesnokov K.Yu., Markov A.A., Patrakeev M.V., Leonidov I.A., Kozhevnikov V.L.

Institute of Solid State Chemistry, Ural Branch of Russian Academy of Sciences
Yekaterinburg, Russia
PhD Student
chesnokov@ihim.uran.ru

Perovskite-like ferrites $La_{1-x}Sr_xFeO_{3-\delta}$ attract interest in a number of applications including electrochemical devices, oxidation catalysis and oxygen separation technologies [1]. The rather large oxygen ion conductivity (0.46 S/cm^2 at x = 0.5 and 950°C) is shown to be limited due to oxygen vacancy trapping and formation of local defect clusters that persist at high temperatures [2]. In this work we studied the impact of manganese doping upon structural features and ion-electron transport in $La_{0.5}Sr_{0.5}Fe_{1-x}Mn_xO_{3-\delta}$, where x = 0.1, 0.17, 0.25 and 0.33.

The specimens were obtained via Pechini process. X-ray powder diffraction evidenced single phase, rhombohedral (s.g. *R*-3*c*) perovskite-like oxides. The manganese substitution was observed to result in a decrease of the elementary unit parameters. The variations of oxygen non-stoichiometry (δ) were measured by making use of a coulometric titration technique in the oxygen partial pressure range 10^{-20} - 0.2 atm at 700-950°C. It was found that the capability of $La_{0.5}Sr_{0.5}Fe_{1-x}Mn_xO_{3-\delta}$ to exchange crystal lattice oxygen with the ambient gas phase tends to decrease with the increase in manganese content.

The four-probe d.c. conductivity measurements were carried out in oxygen partial pressure range 10^{-21} - 0.2 atm at 700-950°C. The partial contributions from oxygen ions, *n*- and *p*- type carriers were obtained from the analysis of the pressure dependent isotherms of the total conductivity. The ion contribution in the oxide x = 0.1 is smaller than in the parent ferrite. However, further doping results in a gradual increase of the ion conductivity. This behavior is explained as a manifestation of the doping induced decrease in the amount of tetrahedrally coordinated iron cations where oxygen vacancies are strongly trapped. As a consequence, the amount of movable oxygen vacancies tends to increase with manganese doping.

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PT-CONTAINING CATALYSTS FOR PRIMARY BIOMASS PRODUCTS CONVERSION INTO HYDROCARBONS

Chistyakov A.V.[1,2], *Zharova P.A.*[1], *Murzin V. Yu.*[1,3], *Kriventsov V.V.*[4], *Tsodikov M.V.*[1,2]

[1]Topchiev Institute of petrochemical synthesis RAS, Moscow, Russia
[2]Gubkin Russian State University of oil and gas, Moscow, Russia
[3]National Research Centre "Kurchatov Institute", Moscow, Russia
[4]Boreskov Institute of catalysis SB RAS, Novosibirsk, Russia
Moscow, Russia
Ph.D.
chistyakov@ips.ac.ru

Development of alternative approaches to fuel components and basic organic synthesis precursors producing based on biomass treatment products is important objective for ecology and chemistry. In the present work a number of industrial Pt-containing catalysts samples (AP-64, R-206, IP-62, PR-56) were used as well as an original Pt-Sn/Al2O3 catalysts based on heterometallic precursors providing the presence of Pt-Sn bonds.

Catalysts were observed to become more selective in hydrocarbons formation after the pretreatment procedure under 50 atm of H_2 and 450 °C during 12 hours. Industrial catalysts samples AP-64 and PR-51 were found to be the most active in ethanol conversion towards C_3-C_{12} alkanes or olefins. Ethanol conversion over Pt-Sn containing catalysts led to a number of ethers formation. By adding probable intermediates into reaction zone was found that hydrocarbon chain grow via ethylene oligomerization followed by olifins reduction.

Shown that over Pt-containing catalysts rapeseed oil converts into alkanes or olefins C_3-C_{28}. By temperature tuning was found the ability to adjust hydrocarbons chain length. The highest selectivity close to 100 % during rapeseed oil conversion into hydrocarbons C_3-C_{22} was found to be over Pd-Sn/Al2O3 catalyst with Pt:Sn molar ratio equal to 1:5.

Structural peculiarities of catalysts were characterized with X-ray diffraction and XAS technique. Relations between Pt clusters structure and its catalytic properties were determined.

Acknowledgements

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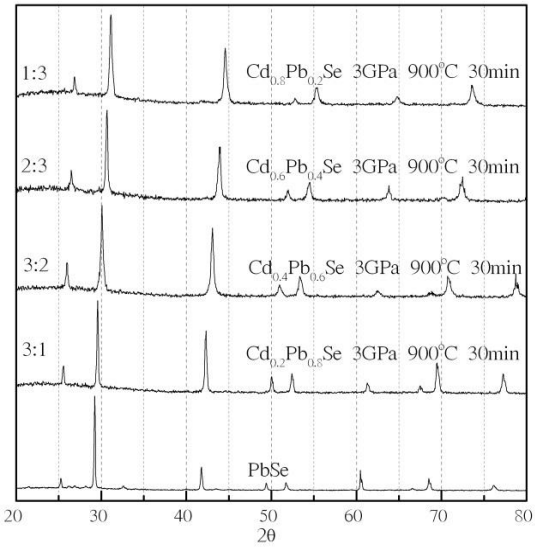
HIGH-PRESSURE/HIGH-TEMPERATURE PROCESSING OF PBSE/CDSE

Chufarov A.Yu., *Ermakov A.N.*, *Zaynulin Yu.G.*

Institute of solid state chemistry, Ural Branch of the Russian Academy of Sciences
Yekaterinburg, Russia
Research fellow
Circulchufa@google.com

Solid solutions of metal chalcogenides play an important role in semiconductor industry. It is supposed high pressure/high-temperature to use to increase in the solubility limit of the PbSe-CdSe systems. The powder mixtures of PbSe and CdSe with different molar ratios i.e. 3:1, 3:2, 2:3 and 1:3 were prepared under high temperature of 900°C and high pressure of 3.0 GPa for 30 min. The obtained powder was studied by the X-ray diffraction and scanning electron microscopy (SEM). SEM image show the homogeneous microstructure and no grain boundary. XRD patterns (pic. 1) show that obtained powder have a cubic NaCl-type structure with unit cell parameters a= 6.0485, 5.9476, 5.8334 and 5.7493 for molar ratios 3:1, 3:2, 2:3 and 1:3, respectively. The presence of only one crystal structure with decreasing unit cell parameters confirm completely transition of initial phases in solid solutions.



Picture 1. XRD patterns of solid solutions of the PbSe-CdSe systems with different ratios PbSe/CdSe

MONITORING ACTINIDES REDUCTION IN SPENT NUCLEAR REPROCESSING BY OPTICAL SPECTROSCOPY AND MULTIVARIATE CURVE RESOLUTION

Debus B.

Saint Petersburg State University, Saint Petersburg, Russia
Postdoc
b.debus87@gmail.com

In industrial processes, information regarding kinetics of transformation of various reactants is often of valuable interest to ensure the quality of the final product. This is especially true for spent nuclear fuel reprocessing where thorough control is a must to avoid various risks. Optical spectroscopy with modern probes appears to be a suitable instrument for on-line monitoring of technological streams in spent fuel reprocessing. However, due to variety of processes in this media, such as colloid particles and gas formation, temperature fluctuation etc. obtained spectra can have strong baseline curvature and excessive noise. Under these conditions, the separation of the various metal bands by UV-Visible spectroscopy becomes challenging and requires advanced preprocessing. In order to circumvent these difficulties, we applied a penalized least square procedure to estimate and correct baseline deviation and multivariate curve resolution [1] to restore actinides kinetics and spectra. The given procedure allows for the determination of important process information such as the time required for maximum accumulation of reduced forms of plutonium and neptunium in modeled solutions closely mimicking real industrial media conditions.

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THE INFLUENCE OF SILVER AND PLATINUM DEPOSITS ON ELECTRON TRANSFER FOR MODEL REDOX SYSTEMS

Doronin S.V., *Manzhos R.A, Krivenko A.G.*

Institute of Problems of Chemical Physics, Russian Academy of Sciences,
Chernogolovka, Moscow Region 142432, Russia
Chernogolovka, Russian Federation,
PhD student,
sedoronin@gmail.com,

The major goal of this work is to reveal the factors affecting the acceleration or deceleration of electron transfer. The estimation of deposit influence on electron transfer rate carried out by CV using the Nicholson method. Electrode coverage by deposits and its morphology will be investigated by CV, SEM and the laser temperature jump (LTJ) method.

A monolayer deposit of Ag on gold is shown to possess a number of specific properties. Its EDL structure is identical to the one for bare silver. There is no chemical binding of Ag atoms in monolayer with hexacyanoferrate from solution typical for massive silver. Also for multilayer deposits a dependence of a number of electrochemical characteristics on their thickness is established. In particular, properties of AgHCF(II) films formed in $Fe(CN)_6^{3-}$ solutions on silver deposits are appeared to be sensitive to the silver coating thickness. For $2 \leq n \leq \sim 20$, the film is sensitive for the $Fe(CN)_6^{3-}$ redox system. The increase of silver layers number up to ~20 causes more than one order of magnitude decrease in effective heterogeneous rate constant for $Fe(CN)_6^{3-/4-}$ system. This experimental fact is explained by the assumption that the observed kinetics are determined by the presence of two parallel processes with different rate constants. The first process corresponds to redox reaction on metal surface and the second one occurs on Ag hexacyanoferrate (II) structured film.

$Fe^{2+/3+}$ redox system is extremely convenient for experimental studies. Its heterogeneous rate constant on platinum is less than on gold in two orders of magnitude. Preliminary experiments show a decrease of the constant for $Fe^{2+/3+}$ with the increase in Pt amount on gold surface. More detailed analysis will clearly show the dependence of the electron transfer constant on Au electrode coverage by Pt deposits.

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Template Sol-Gel synthesis of magnetic sorbents based on porous iron oxides for the removal of U(VI) from aqueous media.

Dran'kov A.N.[1], Papynov E.K.[1,2], Tkachenko I.A.[2], Mayorov V.Yu.[2], Portnyagin A.S.[1,2], Kvach A.A.[2]
Sokol'nitskaya T.A.[1,2], Avramenko V.A.[1,2]

[1]Far Eastern Federal University
[2]Institute of Chemistry FEB RAS, Vladivostok, Russia
Vladivostok, Russia
Student of 4-th year
Artur.drankov@gmail.com

The integrated strategy for synthesis of magnetic sorbents based on porous iron oxides is presented. The keypoint of presented is a combination of sol-gel technology, providing the nonorganic framework of the material, and template synthesis, contributing to structuralization of porous space in solid body. Pore size and shape in template synthesis are controlled via colloid template – syloxane-acrilate emulsion (particle mean size 160 nm), formation of desired phase composition (magnetite or hematite) is obtained through thermal treatment at template removal stage under 600 and 900 ^{0}C temperatures. The influence of thermal treatment conditions on composition, structure and materials properties (magnetic and sorption) was studied.

Table-1. Structural and magnetic characteristics of porous iron oxides

Sample	Tsynthesis, ^{0}C	Phase composition	Ssp.(BET), m^2/g	Ms, e.m.u./g	Hc, Oe
1	600	γ-Fe_2O_3 (maghemite) α-Fe_2O_3 (hematite)	47,3	18,3	70
2	900	α-Fe_2O_3 (hematite)	6,2	0,8	1240

According to low-temperature nitrogen sorption data the trend of reduction of specific surface area (from 47,3 down to 6,2 m2/g) under high-temperature treatment conditions of xerogels was revealed (fig. 1A, table 1). Based on SEM images one can observe effect of porous structure distortion in oxide material, caused by crystal growth during phase transitions magnetite-hematite (Fig. 1B and C), that may lead to sintering of the material into monolith structure.

A

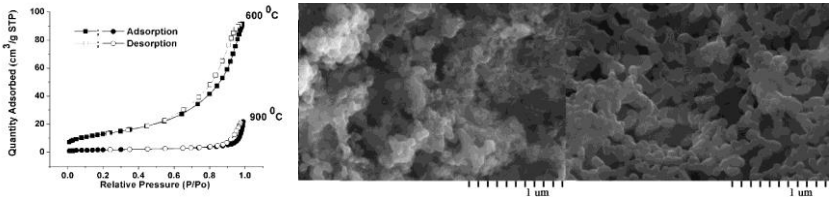

Figure 1. Results of analysis of structural characteristics: A – low-temperature nitrogen sorption, and scanning electrone microscopy of iron oxide based materials, fabricated at 600 ^{0}C (B) and 900 ^{0}C (C) annealing temperatures.

During magnetic investigations it was identified, that magnitude of magnetic saturation for iron oxide sample annealed at 600 0C is higher than that of hightemperature sample and reach 26 emu/g (table 1), that can be explained by the presence of maghemite and magnetite phases in the oxide's solid phase. According to sorption experiments it has been established, that behavior of investigated samples under sorption conditions of uranyl-ions from various media satisfies, in general, common sorption mechanisms.

Table-2. Results of quantitative sorption of uranil-ions from various media in the presence of porous magnetic iron oxides.

Sample	**A, µg U/ g of sorbent**		
	$UO_2(NO_3)_2$ in H_2SO_4 pH or. =2,50	**$UO_2(NO_3)_2$ in water** pH or. =4.92	**$UO_2(NO_3)_2$ in 0,02M Na_2CO_3** pH pH or.=10.93
1	729	712	109
2	930	715	272

It is revealed, that sorption capacity of fabricated samples is significantly higher in acid medium, than in alkali one (table 2). Studied materials are mechanically unstable (crashed), that can be explained by low stability of carbonate complexes of uranyl cation in solution.

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RECYCLING AG-ZN ACCUMULATORS CONTAINING LEAD

Ergashev N.U., Boboyev I.R., Rusalev R.E.

National University of Science and Technology "MISIS"
Moscow, Russia
Student
nurbek1991@mail.ru

Recycling used accumulators is an additional resource and helps to utilize dangerous for environment industrial waste, because accumulators have lead and alkali. Recycled material is plates of Ag-Zn accumulators. Scrap contains 20-57 % of silver, 20-40 % of zinc and 2-4 % of copper. The traditional scheme of scrap processing is the induction melting of waste with calcinated soda. But metal extraction equals 78-83 %. Also, another method of processing the material is cupellation. It is oxidative melting of enriched with silver lead at a temperature of furnace which equals 900 °C. But the process is of long duration and extraction of silver is low too [1].

Currently, chemical composition of accumulator scrap is changing. Scrap contains up to 10 % of lead for silver saving. This doesn't reduce accumulator capacity, but it complicates smelting process and electrolysis.

There is no information about processing this waste in literature. That's why, our purpose is to find an opportunity of processing the material. Thermodynamic calculations of reactions, which happened during the melting of Ag-Zn-Pb alloys, were calculated by using standard programs. Calculations confirmed our opinion. Oxidized lead takes only PbO form in high temperature, but silver oxide does not exist.

Two stage method of processing the material is offered. The first stage is melting of negative plates at a temperature of furnace which equals 1100 °C. Melting is performed by adding fluxes. Zinc is completely slagged, silver absorbs oxygen and lead is partly oxidized and removed after smelting process. Then crude metal is separated from the slag and quenched. It is necessary for saving maximal quantity of oxygen in silver, because this oxygen influences the content of lead in silver. The second stage is melting the crude metal without adding flux. When associated with silver, oxygen oxidizes lead and it is removed from the melt as oxide.

This method provides high concentration of silver in refined silver, which equals 97-99 % and extraction of silver is about 99 %. The advantages of the method are simple instrumentation, decrease of silver loss with sublimates and high performance.

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AMPHIPHILIC CALIX[4]RESORCINARENES IN THE NANOSYSTEMS WITH POLYMERS AND SILVER NANOPARTICLES

Ermakova A.M[1], Morozova Ju.E.[2], Shalaeva Ya.V.[2], Syakaev V.V.[2], Kazakova E.Kh.[2], Konovalov A.I.[2]

[1]Kazan (Volga region) Federal University
[2]A.E.Arbuzov Institute of Organic and Physical Chemistry, Kazan Scientific Centre, Russian Academy of Sciences
Kazan, Russia
Student
alinochka1201@mail.ru

Amphiphilic calix[4]resorcinarenes are molecules that a) are non-toxic, b) as a rule, able to forming self-associates, c) are preorganized and exhibit the enhanced receptor properties when guest associated with aggregates of macrocycle. All these properties make them promising components of nanosystems, useful, for example, in drug delivery formulations. To create such nanosystems we used the method of noncovalent adsorption of mixed macrocycle-substrate aggregates on the surface of the polyelectrolyte and silver nanoparticles. We formed the nanosized supramolecular polymer-colloid system in which the aggregates of amidoammonium calix[4]resorcinarene were immobilized on the hydrophilic polymer by non-covalent interactions. We have also received silver nanoparticles stabilized by amphiphilic calix[4]resorcinarenes. The potential to introducing of the substrate in the supramolecular nanosystems was shown on the example of immobilization of mixed aggregates of macrocycles with dyes.

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ISOBUTYLALUMINUM ARYLOXIDES AS NEW ACTIVATORS OF ZIRCONOCENES IN OLEFIN POLYMERIZATION

Faingold E.E., Babkina O.N., Saratovskikh S.L., Panin A.N., Bravaya N.M.
Institute of Problems of Chemical Physics RAS, Chernogolovka
PhD
fevgeny@mail.ru

The development of new efficient and cheap activators for metallocene catalysts alternative to methylalumoxane (MAO) is the actual task in ion-coordination catalysis of olefin polymerization. It was found that higher alumoxanes and aluminum trialkyls modified with phenols bearing bulky electron withdrawing substituents may work as effective activators [1-4]. Such activators provide greater activating ability than unmodified analogs and show high chemical stability [5].

Here we report synthesis and characteristics of new class of effective zirconocene activators based on isobutylaluminum aryloxides which provide high productivity to the system at low cocatalyst/precatalysts molar ratio (50-300 mol/mol). The series of isobutylaluminium aryloxides with tert-butyl group in 2,6 positions of aryloxy group have been synthesized by reaction of triisobutylaluminum with corresponding phenols. It was shown that such monoaryloxy- and diaryloxy compounds are very effective activators of zirconocenes in homo- and copolymerization of ethylene and propylene. It was found that new catalytic systems with isobutylaluminium aryloxides as cocatalyst are also effective in terpolymerization of ethylene, propylene, and 5-ethylidene-2-norbornene. Molecular weight characteristics, thermal and physicomechanical properties of co- and terpolymers obtained with new cocatalysts will be presented. Synthesized co- and terpolymers show good elastomeric properties.

Isobutylaluminum aryloxides in their efficiency are good alternative to MAO as cocatalysts and allow significantly reduce the cost of catalytic systems.

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STRUCTURE, COMPOSITION AND MORPHOLOGY OF HYDROCHEMICAL DEPOSITED POWDERS $Cu_{2-x}Se$

Fedorova E.A., Maskaeva L.N.

Ural Federal University named after the first President of Russia B.N. Yeltsin
Yekaterinburg, Russia
Postgraduate Student
ka_fed-ra@mail.ru

The growing interest directed to the study of copper(I) selenide $Cu_{2-x}Se$, is caused by the presence in them of specific photo and thermoelectric properties, which have wide practical application. Obtaining said semiconductor compound is carried out by hydro-chemical deposition from aqueous media, which is an environmentally safe, easy and affordable method.

Note, that a large number of variable parameters in the hydrochemical deposition have a significant influence on the crystal nanostructure, composition and morphology, and hence the functional properties of the deposited phases. Therefore, the search for new reaction mixtures, providing reception of highly functional semiconductor compounds of copper(I) selenide, is highly relevant.

The aim of this work was to chemical deposition of copper (I) selenide nanopowder compositions $Cu_{2-x}Se$, as well as the definition of its crystal structure, composition and morphological features.

Hydro-chemical deposition of powders $Cu_{2-x}Se$ was performed from the system containing copper chloride $CuCl_2 \cdot 2H_2O$, hydroxylamine hydrochloride $NH_2OH \cdot HCl$ and sodium selenosulfate Na_2SeSO_3.

Nanocrystalline powders were obtained by hydro-chemical deposition typical for copper(I) selenide $Cu_{2-x}Se$ dark gray.

X-ray diffraction of copper(I) selenide nanopowder has been found that the deposited material corresponds to the cubic phase $Cu_{2-x}Se$ (bertselianit) indicating on cubic (sp.gr. Fm3m) crystal structure of the test compound. The value of the lattice constant of the synthesized nonstoichiometric phase is 5,693 Å. Cubic phase Cu_2O (sp.gr. 224) with a lattice parameter 4,260 Å was also determined. This indicates the presence in the sample trace of cuprous oxide. The formation of this compound can be explained as synthetic hydro-chemical specificity well as interaction during storage nanopowder with oxygen and hence its slight oxidation.

According to the results of elemental analysis of copper(I) selenide freshly deposited nanopowder $Cu_{2-x}Se$ was found that the ratio of copper to selenium is 1.84. This value indicates some nonstoichiometry of synthesized powder and leads to the conclusion about the formation by hydrochemical deposition of nanopowder material $Cu_{1,84}Se$. According to SEM powder $Cu_{1,84}Se$ consists essentially of crystallites polyhedral shapes ranging in size from 80 to 500 nm.

INFLUENCE OF THE QUANTITY OF DOPANTS (Sr, Mg) ON THE STATE OF IRON ATOMS, MAGNETIC AND CONDUCTIVITY CHARACTERISTICS IN DOPED LANTHANUM GALLATE

Fedortsov A. I. , *Korolev D. A.*

Saint Petersburg State University
Saint Petersburg, Russia
Student
fedortsovai@gmail.com

Doped lanthanum gallate is known to be an ionic and/or electron-ionic conductor with a high value of conductivity, so it is a promising matrix for creation of solid oxygen fuel cells (SOFC). Perovskite-like structure of $LaGaO_3$ allows the synthesis of solid solutions over a wide concentration range.

The goal of this research is to study the influence of the quantity of dopants (Sr, Mg) on the state of iron atoms and intermolecular interactions. The magnetic, conductive and structural characteristics of lanthanum gallate doped with iron, magnesium, and strontium were explored over a wide range of concentrations.

The samples of the research were two solid solutions: $LaFe_xGa_{1-x}O_3$ and $La_{1-0.2x}Sr_{0.2x}Fe_xMg_{0.2x}Ga_{1-1.2x}O_{3-\delta}$ (x = 0.01 – 0.1). They were synthesized by ceramic procedure and appeared to be single-phase according to the X-ray diffraction method. The obtained dependence of the unit cell parameters on the concentration of dopants correlated with the Vegard law. According to the data of Mossbauer spectroscopy, all the iron atoms are trivalent. Conductivity of the samples was measured by the method of impedance spectroscopy. The dependence of conductivity on temperature is typical for semiconductors and for similar systems of solid solutions. Magnetic susceptibility was measured in temperature range from 77 to 400 K, and the values of paramagnetic component of magnetic susceptibility, and of the effective magnetic moment depending on the concentration of iron in the solid solution were defined. Anomalous values of the effective magnetic moment in the infinitely diluted solid solutions point to the formation of high nuclearity clusters containing iron atoms and also magnesium, strontium and associated vacancies.

Acknowledgements
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EXPANTION OF α-AgI EXISTENCE TEMPERATURE RANGE IN NANOLAYERED FILM

Fokina S.V., Tveryanovich Y.S., Borisov E.N., Tomaev V.V

Saint Petersburg State University
postgraduate student
Svetlanav.fokina@gmail.com

α–AgI is known to have an extremely high ion conductivity which is almost independent of temperature. Unfortunately, at temperatures lower than 147 °C AgI α–phase isn't stable as a bulk material and transitions to β or γ–phase occur. For stabilization purposes α–AgI at temperatures lower than 147 oC multilayered films of total thickness about 1 μm were obtained using laser ablation. Films are composed of alternating layers of AgI and chalcogenide glass. Each layer thickness is 10-30 nm. Chalcogenide glass was specially developed with this goal in mind [1]

Results of obtained films study showed that silver iodide phase transition from low-temperature β- и γ-phases to high-temperature α-phase takes place gradually. At cooling, α–AgI is preserved at temperatures up to 30°C according to XRD data and conductivity measurements.

Conductivity depending on temperature, hysteresis is observed when studying multilayered films. Instead of a rapid jump in conductivity during β→α phase transition (147 °C) smooth conductivity growth acceleration is observed in the 130 – 190°C temperature range. Conductivity value after http://www.google.ru/url?source=transpromo&rs=rssf&q=//translate.google.com/community?source=allseveral cycles of heating and cooling is far higher than initial value ($\sigma = 0.3$ S/cm).

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INFLUENCE OF CDS THIN FILM SURFACE TOPOGRAPHY ON SUBSTITUTION DEGREE OF METAL IONS AT THE PHASE BOUNDARY $CdS_{solid}/Pb^{2+}{}_{solution}$ IN THE ION-EXCHANGE PROCESS

Forostyanaya N.A.[1], *Markov V.F*[2], *Maskaeva L.N.*[2]

[1] Ural Federal University,
[2] Ural Institute of State Fire Service Russian Emergencies Ministry,
Yekaterinburg, Russia
Postgraduate student
natal-ku8@yandex.ru

There is very promising, relatively new method for preparing thin-film heterostructures of CdS – PbS system, called ion exchange process. It occurs at the border of thin polycrystalline films immersed in a solution of substitute metal salt.

Ion exchange is topochemical process, therefore, the surface morphology of the initial thin film plays a great role in this process. Thin films of cadmium sulfide were prepared from two different reaction mixtures, which differed in ligands for cadmium ions, to evaluate the influence of the surface morphology of CdS thin film obtained by the chemical bath deposition on the level of ions substitution on the interphase boundary $CdS_{solid}/Pb^{2+}{}_{solution}$ during the ion exchange process.

In the first case, the reaction mixture contaned sodium citrate and ammonia, in the second case, it was used ethylenediamine solution as a ligand. Temperature of synthesis was 353 K.

The results of electron microscopy research for obtained samples showed that the surface of the CdS film of ethylenediamine system was very homogeneous and consisted of spherical globules of about 150 nm or less, formed of a smaller particle (15 – 40 nm). And films composed of spherical aggregates with size ~ 350 nm, which formed of constituent particles varies in a wide range, from 30 to 150 nm, when ammonium - citrate system was used, due to stronger binding of cadmium ions in the complex and as a result, lower speed of the process, that's why this thin films has a bulker structure and more developed surface of contact with the solution.

At modification of cadmium sulfide films of ammonium-citrate system in the lead acetate solution the amount of lead entered at the film structure was 42.6 at.%, which is in 2.5 times higher than that in the ion exchange process at the surface of denser structure of ethylenediamine CdS due to heterogeneous processes at the interface CdS_{solid} / Pb^{2+} solution.

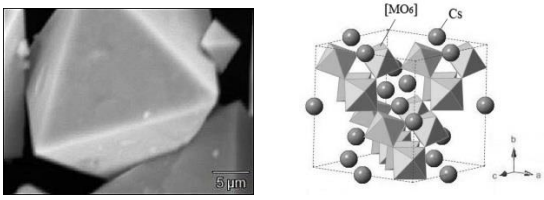
PREPARATION AND OPTICAL PROPERTIES OF $CsNbMoO_6$

Fukina D.G.[1], Suleimanov E.V.[1], Fukin G.K.[2], Boryakov A.V.[1], Titaev D.N.[1]

[1] Lobachevsky Nizhny Novgorod State University,
[2] Institute of Organometallic Chemistry of the Russian Academy of Sciences
Razuvaeva,
Nizhny Novgorod, Russia
Student
dianafuk@yandex.ru

Compounds with nonlinear-optical properties are of great interest for science and technology, because they are widely used in lasers and laser systems. Therefore, search these compounds is an important problem.

Single crystals of $CsNbMoO_6$ have been successfully synthesized by solid-state reactions (Picture 1, *a*). The composition of the compounds was refined using X-ray fluorescence analysis (*Shumadzu XRF-1800*). Their structures are determined by single-crystal X-ray diffraction methods (*Agilent Xcalibur Eos*). A high value of invariance of crystal electron density affects the X-ray reflections with the result that incorrect definition of the space group may occur. The degree of invariance of electron density with respect to inversion operation was calculated in the program PseudoSymmetry and has turned 0.99945. Spectrum of second harmonic generation (SHG) was recorded in order to check for the presence of inversion center in the $CsNbMoO_6$ structure. The sample $CsNbMoO_6$ under the influence of laser radiation (Nd: YAG, λ = 1064 nm) gave green emission (λ = 532 nm). The relative nonlinear susceptibility was calculated: $\chi_{rel}^{(2)}$ = 0.52. Thus, the space group can be determined unambiguously: *F-43m* without inversion center. The structure consists of chains of octahedral [MO_6], where M = Mo, Nb (Picture 1, *b*).



a *b*

Picture 1. *a* - SEM image of small crystals, *b* - The crystal structure of the $CsNbMoO_6$

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INFLUENCE OF TNE SOLVENTS NATURE ON THE SYNTHESIS OF SILVER NANOPARTICLES

V.N. Glushko, N.Y. Sadovskaya, O.A. Usova, L.I. Blokhina

Federal State Unitary Enterprise «State Scientific Research Institute of Chemical Reagents and High Purity Chemical Substances» (FSUE «IREA»),
Moscow, Russia
Head of Laboratory
tetrazoli@yandex.ru

It is necessary to obtain a dispersion of AgNPs in an organic solvent for the introduction in paints and polymer materials, whose surface is hydrophobic. The dispersions of nanoparticles were obtained for investigation the influence of the solvents nature on the reduction of silver ions. Electronic absorption spectra obtained stable dispersions were used to control the synthesis process.
Figure 1 shows the dependence of the optical density of the wavelength dispersions of the nanoparticles obtained by reacting silver trifluoroacetate with quercetin in the following solvents:a) ethyleneglycol methyl ether (fig.1, 1), b) ethylacetate - ethyleneglycol methyl ester (fig. 1, 2), c) ethyleneglycol - ethyleneglycol methyl ether (fig. 1, 3).

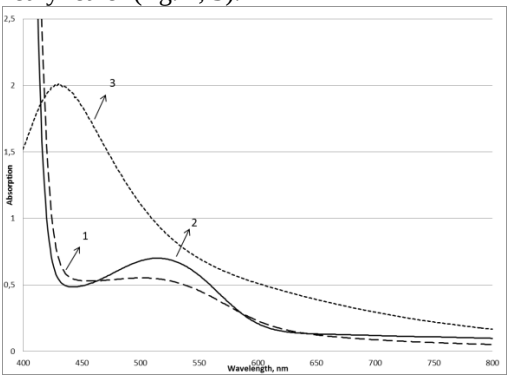

Figure 1 - The absorption spectra of the nanoparticles obtained by reacting silver trifluoroacetate with quercetin

The greatest stability (more than two months, was not investigated further) has a dispersion obtained by the reduction quercetin obtained in the ethylene glycol - ethylene glycol methyl ether.

Acknowledgements
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STUDY OF $MgAl_2O_4$ NANOPOWDERS FOR OPTICAL CERAMICS

Golyeva E.V.[1,3], *Tolstikova D.V.*[2,3], *Mikhailov M.D.*[3], *Sokolov I.A.*[1], *Dunaev A.A.*[3]

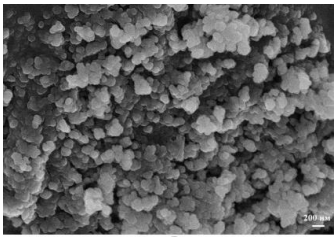
[1]Saint Petersburg State Polytechnic University,
[2]Saint Petersburg State University,
[3]Scientific and Technological Institute of Optical Materials Science, VNTs S.I. Vavilov State Optical Institute
Saint Petersburg, Russia
Postgraduate student
Lenysik_net@mail.ru, golyeva_elena@goi.ru

Magnesuim aluminum spinel, $MgAl_2O_4$, is a well known inorganic compound and it is widely used in optics. Spinel has a cubic crystal structure, thus optically isotropic and, besides its high melting point, excellent mechanical properties and corrosion resistance, it shows an outstanding transparency up the near-infrared frequency range even in the polycrystalline state [1].

The aim of this work is the synthesis and investigation of $MgAl_2O_4$ nanocrystalline powders. $MgAl_2O_4$ nanopowders were synthesized by Pechini method with additional heat treatment in molten salt KCl and by hydrolysis of Mg-Al isopropoxides.

Structural properties of obtained nanopowders were measured by X-ray diffraction (XRD). XRD patterns confirmed the formation of $MgAl_2O_4$ phase as the only crystalline phase.

The size and shape of the particles were determined by scanning electron microscopy and static light scattering. The powders consist of polycrystalline weakly agglomerated particles with size from 50 to 150 nm (Pic. 1).



Picture 1. SEM $MgAl_2O_4$ powder morphology

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Acknowledgements

Particle size was measured at the «Nanocomposite» center of Saint Petersburg State University.

MÖSSBAUER STUDY OF LOCAL STRUCTURE AND MAGNETIC HYPERFINE INTERACTIONS IN $BiFeO_3$ FERRITE

Gorchakov D.S. [1], , *Presniakov I.A.* [1], *Rusakov V.S.* [1], *Sobolev A.V.* [1], *Gapochka A.M.* [1], *Belik A.A*[2].

[1]Lomonosov Moscow State University
[2]International Center for Materials Nanoarchitectonics (MANA),
National Institute for Material Science (NIMS), Tsukuba, Japan
Moscow, Russia
Student
d-gorchakov@rambler.ru

The antiferromagnet ferrite $BiFeO_3$ is a "proper" multiferroic in which ferroelectricity and magnetism have different microscopic sources. The ferroelectricity is considered to primarily originate from displacements of the Bi^{3+} ions due to the stereochemically active $6s^2$ lone pair. The temperature-dependent evolution of the magnetic structure in $BiFeO_3$ is important subject with several currently unresolved issues. We report new results of ^{57}Fe Mössbauer studies on $BiFeO_3$ powder sample performed at various temperatures above and below of the point of magnetic phase transitions ($T_N \approx 650$ K). The ^{57}Fe Mössbauer spectra measured at $T > T_N$ consist of doublet with quadrupole splitting $\Delta_{660K} \approx 0.44$ mm/s corresponding to the Fe^{3+} sites in rhombohedral perovskite-like $BiFeO_3$ lattice with a strong electric field gradient (EFG) at ^{57}Fe nuclei. We have performed self-consistent calculations of the lattice contributions to the EFG tensor, taking into account dipole moments of the O^{2-} and Bi^{3+} ions. It was found that the induced dipolar moments of the oxygen and bismuth ions make a substational contribution to the EFG. Using the parameters of the crystal structure of $BiFeO_3$ for temperatures from 4.9 K to 663 K, we found the dependence $\alpha_{Bi}(T)$ reflecting that the displacement of the Bi^{3+} from the FeO_6 polyhedra, which influence the electric polarization, decreases with temperature. Low-temperature ^{57}Fe spectra recorded at $T < T_N$ were analyzed assuming an anharmonic cycloidal modulation of the Fe^{3+} magnetic moments. The cycloidal modulation of the iron spin was described with the elliptic Jacobi function $sn[(\pm 4K(m)/\lambda)x,m]$ (where m is its anharmonicity parameter, K(m) is the complete elliptic integral, λ is the modulation period, x is coordinate along the propagation direction). The good fit of the experimental spectra was obtained for the anharmonicity $m = 0.36 \pm 0.04$ ($T = 4.9$ K) resulting from easy-axis magnetic anisotropy, which was previously suggested by NMR and neutron diffraction studies [1, 2].
This work is supported by the RFBR grant № 14-03-00768a and № 14-02-01109a.

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SILICA-COATED LIPOSOMES WITH EMBEDDED QUANTUM DOTS

Goryacheva O.A.[1], *Beloglazova N.V.*[2]

[1] Saratov State University, 410012 Saratov Astrakhanskaya str., 83
[2] Ghent University, Belgium 9000 Ghent Harelbekestraat, 72
Saratov, Russia
student
olga.goryacheva.93@mail.ru

Quantumdots (QDs) are tiny particles or nanocrystals of a semiconducting material with diameters in the range of 2-10 nanometers. They are widely used in technique, analysis and diagnostics. For bioapplication QDs have to form stable colloid water solution. For this purpose we synthesized silica-coated liposomes loaded with QDs[1]. This structure is water-soluble and stable in time to mechanical stress. Active groups on the surface of silica shells provided possibilityfor conjugation with proteins allowing to use silica coated liposomes loaded with QDs as a luminescent label in the biochemical analysis. Conjugation of silica-coated liposomes was performed through the surface amino-groups provided by the silanization agent. Obtained conjugates were used as tracer for simultaneous detection of multiple mycotoxines.

Reference:
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Acknowledgements:
I express my gratitude to Prof. Irina Y. Goryacheva for project coordination and Prof. Sarah De Saeger for providing materials.

SYNTHESIS AND PHYSICO-CHEMICAL PROPERTIES EVALUATION OF HYPERBRANCHED POLYESTERPOLYOL STABILIZED IRON NANOPARTICLES

Grechkin Y.A., Evtugin V.G., Kutyreva M.P.,Ulakhovich N.A.

Kazan Federal University,
Kazan, Russia
Student
jaroslav.grechkin@gmail.com

Research and development of materials based on iron magnetic nanoparticles due to their use as cancer treatment agents. There are some problems, which are indicated of iron nanoparticles stability, shape, size and composition control; what finally allows to operate of the main characteristics of current materials. The main goals of this researching work were synthesis and characterization of the polymer-stabilized iron and iron oxide nanoparticles. In this work as polymer-stabilizer was used hyperbranched polyesterpolyol of second generation – Boltorn H20. Non-toxic, biosimilar, biodegradable and the hyperbranched structure features make polymer matrix as multifunctional, including nanoparticles stabilization and their transportation to the disease center. Iron pentacarbonyl was used as base compound for nanoparticles.

By chemical reduction method were synthesized Fe_xO_y /H2O composite nanoparticles in solid phase and in colloid solution. Thermal stability of the solid composite nanoparticles was observed in the range of from 30 to 200ºC.. Transmission electron microscopy data showed two phases of Fe_xO_y /H2O nanoparticles – nanopartciles with size from 26 to 53 nm, and spherical composite particles with size from 280 to 554 nm (fig. 1).

By sonochemical method were synthesized Fe_2O_3/H20 composite spherical particles; there are two phases in the system: oxide phase with sizes 145 – 370 nm (fig. 1) and spherical composite particles phase with sizes 370 - 777 nm (fig. 2).

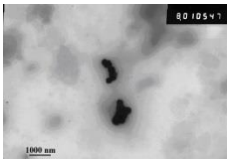

Fig.1. TEM microphotography of composite Fe_2O_3/H20nanoparticles

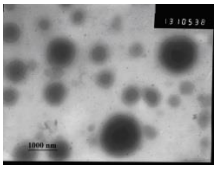

Fig.2. TEM microphotography of composite Fe_2O_3/H20nanoparticles

In this way, was proved effective stabilization properties of hyperbranched polyesterpolyols for the iron and iron oxide nanoparticles. Synthesis methods optimization allow to receive systems with one type of iron nanoparticles and evaluate its biomedical activity.

SYNTHESIS OF CISE NANOPARTICLES/PCBM THIN FILMS FOR SOLAR CELLS APPLICATION

Grevtsev A.S., *Muradova G.M.*, *Tver'yanovich A.S.*

Saint Petersburg State University
Saint Petersburg, Russia
Student
temaqwe@mail.ru

The new trends in solar energy materials science are obtaining of organic-inorganic hybrid solar cell. Among the $A^{I}B^{III}C^{VI}$-type materials investigated for photovoltaic applications, CISe (copper indium diselenide: $CuInSe_2$) is promising candidate for the development of low-cost organic-inorganic hybrid solar cells.

Technologically simple and efficient method for the synthesis of semiconductor nanoparticles is the polyol microwave assisted synthesis method. With this method it is possible to synthesize nanopowders of $CuInSe_2$. CuCl, $In(Ac)_3$, Se have been used to produce $CuInSe_2$ nanoparticles. PEG (polyethylene glychol) was used as the solvent and the reducing agent. Synthesis was carried out for one hour in a microwave field, the average temperature during synthesis was 280°C. $CuInSe_2$ films consisting of nanoparticles, were formed on ITO (SnO_2:In)-coated glass substrates (ITO/$CuInSe_2$) and also composite films ITO/$CuInSe_2$/PCBM (PCBM - [6,6]-phenyl C61 butyric acid methyl ester) were obtained. PCBM layer was spin-coated from chlorobenzene solution.

As a result the samples of $CuInSe_2$ films consisting of nano particles were obtained. The $CuInSe_2$ nanocrystals have the average size of 75-80 nm. Energy gap of $CuInSe_2$ films was defined ($Eg=0,98\pm0,05$ eV). $CuInSe_2$/PCBM layers were obtained and they photoelectric properties were investigated. Obtained films were photosensitive and they could be applied as absorber layer for solar cells formation.

THE STUDY OF KINETICS, STRUCTURAL AND MORPHOLOGICAL CHANGES DURING THERMAL DECOMPOSITION OF $Y_2(C_2O_4)_3 \cdot 10H_2O$

Gribov P.A.

Novosibirsk State University
Novosibirsk, Russia
Student
gribov_paviel@mail.ru

Thermal decomposition of solids is one of the traditional methods of preparative solid state chemistry for making nanoparticles of metals and metal oxides. However, despite the many works devoted to reactions of thermal decomposition of various precursors the possibility of influence on the size, shape and phase composition of the reaction product is still open.

The aim of this work was to study the mechanism of dehydration of decahydrate yttrium oxalate to corresponding hexahydrate and to investigate the effect of dehydration conditions on morphology and structure of the reaction product. The following methods were used: optical and scanning electron microscopy, thermogravimetry, powder and mono-crystal diffraction.

It was found that during dehydration the structural transformation proceeds by the deformation (martensitic) mechanism. The change of shape of initial crystal was observed in the experiment (Fig.1). The structure of hexahydrate obtained during rapid dehydration (heating on air) was determined. The product is triclinic with space group P-1. For process of rapid dehydration the mechanism of structural transformation was proposed and orientation correspondences were found. During dehydration in quasi-equilibrium conditions (slow removal of water) the monoclinic hexahydrate with space group $P2_1/c$ was produced. Morphologies of hexahydrates obtained in this two cases are differ. Also, it was studied the effect dehydration conditions on kinetics of the thermal decomposition of yttrium oxalate and the dispersion of final particles of yttrium oxide.

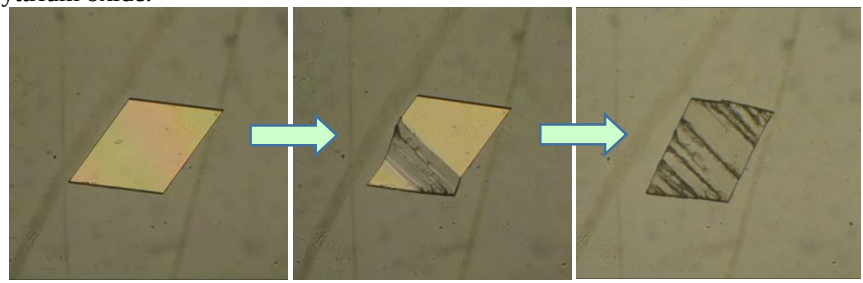

Fig.1. The change of shape of initial crystal of decahydrate yttrium oxalate during dehydration

SYNTHESIS CONDITIONS AND THE MORPHOLOGY DETERMINATION OF MANGANESE OXIDE MICROTUBES WITH THE BIRNESSITE STRUCTURE

Gurenko V.E.

Saint Petersburg State University
Saint Petersburg, Russia
Student
limeman14@gmail.com

The aim of this study was to investigate the possibility of obtaining tubular microstructures manganese oxide (IV), containing cations of nickel (II) in its composition. It was used a new, proposed in [1], method for synthesizing on the interface of aqueous solution – gas, which relates to the methods of the so-called "soft chemistry". First, the modeling of operating solutions through programs Hydra and Medusa and the optimal concentration and pH of the reagents solution was carried out. The next experimental stage aimed to study the effect of the duration of oxidation, thermal gradient etc. on the morphology of microtubules and the optimal synthesis conditions. Investigation of the synthesized samples by X-ray microanalysis demonstrated that the composition comprises oxygen, nickel and manganese with the ratio 1/7 for the last two elements. SEM analysis of microtube wall morphology revealed that it is formed 2D nanocrystals (Fig. 1b). The possibility of nickel-doped manganese oxide microtubes synthesis was proved. The influence of the purging organic-water mixture and thermal gradient on the microtubes morphological characteristics was investigated. For the first time ever, the conditions, under which the microtubules with diameter from 20 to 200 μm, 1-8 mm long (Fig. 1a) are formed, were acquired.

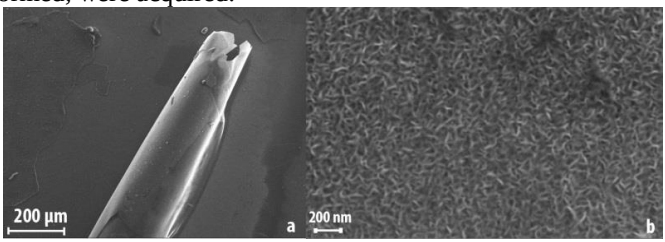

Figure 1a, 1b. SEM image of tube wall surface (a – general view, b – the inner surface).

References

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Acknowledgements

This work was supported by grant of St. Petersburg State University (№12.38.259.2014).

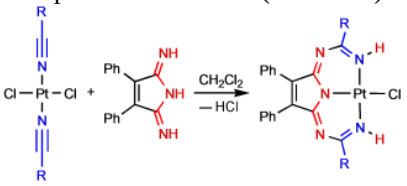
HALOGEN BONDS IN SOLVATES OF THE PANT CHLORIDE PLATINUM(II) COMPLEXES WITH HALOMETHANES

Ivanov D.M.[1], *Gushchin P.V.*[1]

[1]Saint Petersburg State University,
Saint Petersburg, Russia
Postgraduate Student
dan1510@rambler.ru

1,3,5-triazapentadienate platinum(II) complexes which can be synthesized by the interaction of amidines or guanidines with nitrile/dialkylcyanamide platinum(II) complexes are known to be used in the halogen and hydrogen bond investigations and crystal engineering [1,2].

The interaction of 2,3-diphenylmaleimidine with *trans*-dinitrile/*trans*-dicyanamide Pt^{II} complexes lead to the 1,3,5,7,9-pentaaza-1,3,6,8-tetraenate (PANT) platinum(II) complexes formation. (Scheme 1).



Scheme 1. R = *t*-Bu (1) R = NEt_2 (2)

These annulated 1,3,5-triazapentadienate platinum(II) complexes showed a tendency to cocrystallization with solvent molecules such as dichloromethane, chloroform, tetrachloromethane and dibromomethane. The Pt–Cl•••Hal–$CHalX_2$ short contacts (less than the sum of vdw radii) were detected in solvates **1**•1½CH_2Cl_2, **1**•CH_2Br_2 (Fig. 1), and **2**•CCl_4 by X-ray analysis in solid state. These contacts can be interpreted by the halogen bond (XB) formation, the chloride ligand being the XB acceptor and chlorine or bromine atom from the solvent molecule being the XB donor.

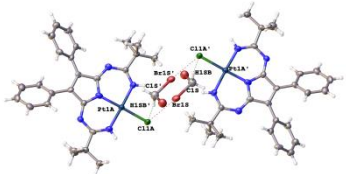


Fig. 1. Heterotetramers in 1•CH_2Br_2, linked by the halogen and hydrogen bonds

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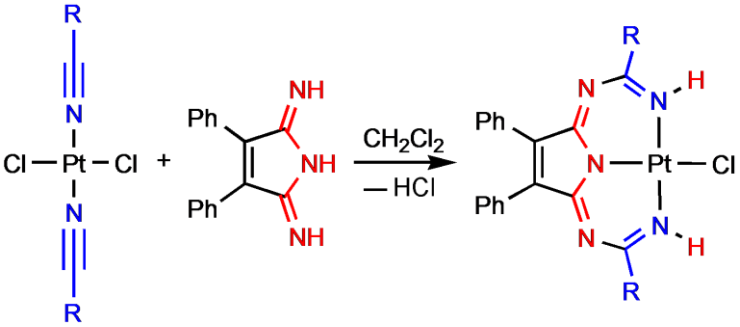
NUCLEOPHILIC ADDITION OF 2,3-DIPHENYLMALEIMIDINE TO NITRILE AND DIALKYLCYANAMIDE LIGANDS IN PLATINUM(II) COMPLEXES

Ivanov D.M.[1], *Guscshin P.V.*[1]

[1]Saint Petersburg State University,
Postgraduate Student
dan15101992@gmail.com

Nucleophilic addition to the nitrile/dialkylcyanamide triple carbon-nitrogen bond activated by coordination to Pt^{II} has been investigated for thirty years. [1] Various OH- (water, alcohols, oximes etc.) and NH-nucleophiles (amines, imines and more complicated amidines and guanidines) were employed in this reaction giving a great variety of platinum(II) complexes with imine ligands. The products of these interactions can be used as anticancer medicines, luminescent pH-indicators or systems for crystal engineering.

The interaction between various *trans*-dinitrile/*trans*-dicyanamide complexes Pt^{II} *trans*-[$PtCl_2(NCR)_2$] (R = Et, *n*-C_3H_7, *t*-Bu, CH_2Ph, Ph, *p*-$CF_3C_6H_4$, NMe_2, NEt_2, $N(CH_2)_5$) and 2,3-diphenylmaleimidine in CH_2Cl_2 at room temperature leads to the formation of 1,3,5,7,9-pentaaza-1,3,6,8-tetraenate (PANT) platinum(II) complexes (**Scheme 1**).



Scheme 1.

The synthesized compounds were thoroughly analyzed by a number of physico-chemical analytical methods (elemental analysis, ESI-MS mass-spectrometry, IR spectroscopy, ^1H and $^{13}C\{^1H\}$ NMR spectroscopy, and UV–Vis spectroscopy), and the structures of eight of them were confirmed by X-ray analysis in their solid state.

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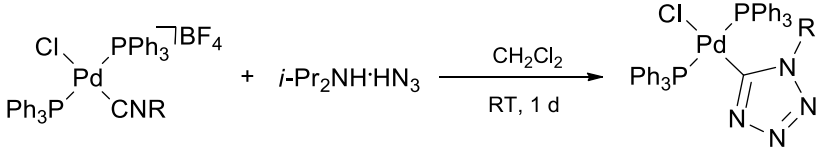
NEW APPROACH FOR PREPARATION OF CARBON-BONDED TETRAZOLATE COMPLEXES OF PALLADIUM

Mikhail A. Kinzhalov, Aleksandr S. Novikov, Konstantin V. Luzyanin
Institute of chemistry, Saint-Petersburg State University
Saint Petersburg, Russia
assistant professor
m.kinzhalov@spbu.ru

Organic azides have been frequently used as 1,3-dipoles. When coordinated to a metal, azide ligands undergo 1,3-dipolar cycloaddition with nitriles and isocyanides under mild conditions. With organonitriles NCR, this reaction gives metal-N^1- or metal-N^2-bonded tetrazolate complexes. With isocyanides, metal-C^1-carbon-bonded tetrazolates are generated. In this study, we propose an alternative approach toward preparation of C^1-tetrazolate complexes based on using of isocyanide complexes of palladium and free azides.



R = *t*-Bu **1**, R = Xyl **2** **3** R = *t*-Bu **4**, R = Xyl **5**

All obtained compounds were characterized by ^{1}H, ^{13}C{^{1}H} NMR and IR spectroscopies, ESI$^+$-MS, elemental analyzes (CHN), and by X-ray diffraction. In order to understand in more detail the mechanism of the azide–isocyanide coupling, the theoretical DFT study of this reaction for model systems was performed (CPCM-B3LYP/6-311+G(d,p)//gas-B3LYP/6-31G(d)). The mechanism of the cycloaddition of N_3^- to *trans*-[PdCl(PH$_3$)$_2$CNMe]$^+$ was found to be the stepwise, this is a charge-controlled process. It starts from the formation of an orientation complex, two transition states were located, the first one corresponds to the formation of the C–N bond and the second one is associated with the ring closure. The second step is the rate limiting one. Based upon our quantum chemical calculations we can state that the formation of the C^1-tetrazolate palladium complexes from coordinated isocyanides and free azides is very favorable from both a kinetic and thermodynamic point of view.

Acknowledgements. Financial support of Russian Foundation for Basic Research (grant 14-03-31204 мол_а) and Saint Petersburg State University (НИР 12.38.225.2014) is greatly appreciated. ASN is grateful to Saint Petersburg State University for the postdoctoral fellowship (grant 12.50.1190.2014). The authors are grateful to the Center for Magnetic Resonance, Center for X-ray Diffraction Studies, and Center for Chemical Analysis and Materials Research of Saint Petersburg State University.

LASER-INDUCED PROCESSES IN AQUEOUS COPPER AND NICKEL SOLUTIONS.

Khairullina E.M., Araslanova S.M., Borodulina O.V., Panov M.S., Kochemirovsky V.A.

Saint Petersburg State University,
Saint Petersburg, Russia
PhD Student
iskint@mail.ru

Laser-induced chemical liquid-phase metal deposition (LCLD) is a well-known method based on metal reduction in local volume of solution within the focal point of laser beam resulting in metal deposition on the surface of dielectric substrate [1]. This promising technique is of interest for many electronics applications, such as repairing of open lines, making customized interconnections, fabrication of small metallic conductors and others, and allows to deposit different types of metals on various substrates. In recent years the successful laser-induced deposition of copper [2] and nickel [3] has been demonstrated. In current study LCLD technique as well as the processes affecting the mechanisms of chemical and laser-induced deposition of copper and nickel local microstructures from aqueous solutions on the surface of dielectric substrates are reported. The influence of the composition of solution components, solvent, reducing agent and the properties of the dielectric substrate on the deposition process is discussed. Possible photochemical reactions induced by the laser irradiation and their role in photoreduction of copper and nickel from solution are considered. Experiment and theoretical considerations employed in this work are focused on a better understanding of all aspects involved in the laser-induced deposition process and provide ideas on future directions for development of the LCLD technique.

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THE HYDROXYAPATITE NANOPARTICLE WITH DIFFERENT MORPHOLOGY AND NANOCOMPOSITES BASED ON

Khramenkova E.V., Osmolowskaya O.M., Korzhikov V.A., Osmolowsky M.G.

Saint Petersburg State University
Saint Petersburg, Russia
Student
lena_khramenkova@mail.ru

Hydroxyapatite is the basic mineral of bone and teeth. Synthetic hydroxyapatite because of it biocompatibility, osteoconductivity and low biodegradability is extensively used as an artificial biomaterial for different biomedical applications, mostly for the recovery of the bone defects. The main HAP disadvantage is its fragility, which significantly limited the possibility of its application. This is why a lot of studies have been focused on improving HAP's properties by incorporating biodegradable synthetic and bio polymers. More studies showed the possibility of changing the mechanical properties of the scaffolds by varying the degree of porosity and mass content of hydroxyapatite, but the influence of particle shape on scaffolds characteristics is almost not studied. Up to now, many kinds of chemical synthesis methods for the preparation of HAP nanoparticles with different shape and sizes have been introduced. The wet chemical process is the most reported method for preparing HAP particles. This process is simple, low cost, and suitable for industrial production. It should be noted that formation of HAP nanoparticles is very sensitive to the synthesis conditions (pH, temperature, procedure). In addition the control the characteristics of the product suggested using chelating agents. The most promising is the use of amino acids as chelating agents because they are physiological substances and can be absorb on HAP surface.

In the present study the hydroxyapatite nanoparticles with different shape have been obtained via wet chemical process using glycine as a chelating agent. The morphology parameters have been determined by a number of methods including XRD, TEM, DLS and specific surface area estimation (the BET model). The influence of pH and temperature on NPs morphology at low level concentration of glycine were studied. The relation between the NPs shape and the acid-base equilibrium of the charged groups of the glycine molecule and zero point of HAP was shown. The 3D scaffold loaded by sphere, spindle- and needle-like HAP were prepared and were characterized by XRD, tomography and SEM measurement. The dependence of elastic coefficient value of scaffolds and the shape of its inorganic component were determined.

Acknowledgements

Scientific researches were performed at the Centre of X-ray Diffraction Studies, Centre for Geo-Environmental Research and Modelling (GEOMODEL), Innovate Technologies of Composite Nanomaterials of St. Petersburg State University.

COMPOSITE OXIDE MATERIALS OBTAINED BY TRANSIENT ELECTROLYSIS

Khramenkova A.V., *Bespalova Zh.I.*

Platov South-Russian State Polytechnic University (NPI)
Novocherkassk, Russia
Assistant Professor
anna.vl7@yandex.ru

At the present time obtaining of complicated inorganic materials with a whole set of properties seems to be very attractive due to expanding of possibilities of their using: as a catalytically active materials, sensory, solion, electrocatalytic devices, solid-phase light sensors and to protect metals from corrosion [1-2]. The properties of composite materials are determined by the composition, features of the structure and dimension of the particles of such materials.

In this paper the results of the study of composite oxide materials on the solid substrate obtained by transient electrolysis are presented [3]. The main components of the obtained materials are $Mo_{13}O_{33}$, MoO_3, $Mo_{18}O_{52}$, CoV_3O_8, $NiMoO_4$ and $CoMoO_4$. Investigation of the material in the process of electrochemical intercalation of lithium into oxide films by method of cyclic voltammetric curves and discharge – charge curves in 1 $mol \cdot dm^{-3}$ solution of $LiBF_4$ in acetonitrile showed the possibility of it's using as electrode material for symmetrical supercapacitor working with an upper voltage limit equal to 0.76 V. The composite oxide material also showed high catalytical activity in the process of liquid-phase oxidation of glyoxal to glyoxylic acid. During the testing it was found that the conversion is greater than conversion of the analogues by 13% and the selectivity is greater than selectivity of the analogues by 20% (Pt- and Pd - containing catalysts). Thus the developed composite oxide materials represent heterogeneous catalysts that may be used in oxidation processes and as cathode materials in chemical current sources.

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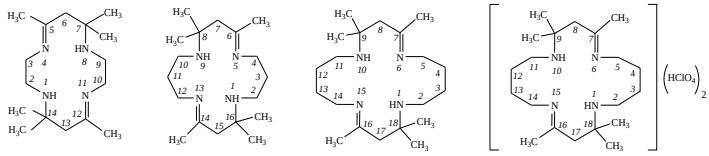
SYNTHESIS AND STRUCTURE OF 14-18-MEMBERED TETRAAZAMACROCYCLES COMPOUNDS

Khristoforova E. I., Anisimova N. A., Trishin Y.G., Duykova M. V.

Saint Petersburg State Technological University of plant polymers.
Saint Petersburg, Russia
KhristoforovaKate@yandex.ru

Interest in tetraazamacrocyclic compounds due to the presence of these unique properties, such as high electrical conductivity, lipophilicity, the formation of coordination compounds with metal ions, as well as the possibility of their use as active membrane-active substances, for removal of toxic and radioactive metals in the extraction and concentration of ions of noble and heavy metals [1].

Previously, we have obtained C-alkyl substituted 14-membered azamacrocycle the interaction of ethylene diamine-1,2 with acetone (C_2H_5OH, Δ, 10h) (**1**) [2]. In a similar and more mild conditions (18-20 °C, 24 h) in the interaction of propane-1,3– and butane-1,4-diamines with acetone were synthesized 16-and 18-membered azamacrocycle (**2,3**).



Picture 1. 14-18-membered tetraazamacrocycles and perchlorate salt of 18-membered cycle

In contrast to the literature [3], we have shown that 14-membered azamacrocycle (**1**) is a very stable compound; it is stored at room temperature during the year. Compared with 14-membered azamacrocycle (**1**) 16-and 18-membered cycles (**2, 3**) were less stable; they are hydrolyzed for 24 h and fixed by us only spectral (NMR^{1}H). Note that the 18-membered azamacrocycle (**3**) is unstable even in the form of perchlorate salt (**4**), which exposed to destruction in a few hours (for removal of IR and 1H NMR).

The structure of the obtained C-alkyl substituted tetraazamacrocycles (**1-4**) is proved using IR, NMR^{1}H, ^{13}C spectroscopy and heteronuclear experiments ^{1}H-^{13}C HMQC, ^{1}H-^{13}C HMBC.

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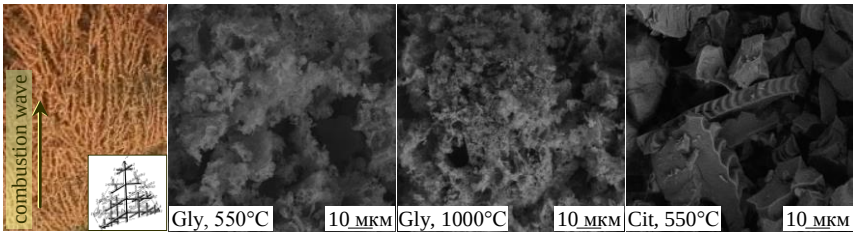
PHASE FORMATION IN THE Fe_2O_3–Al_2O_3 AND Fe_2O_3–SiO_2 SYSTEMS OBTAINED BY COMBUSTION AND SOL-GEL COMBUSTION

Kirillova S.A., *Sennikovskaya A.M.*

Saint Petersburg Electrotechnical University
Saint Petersburg, Russia
Researcher assistant
refractory-sveta@mail.ru

The combustion synthesis is an easy, safe, rapid and economic method used to synthesize various oxides or to prepare multi-component ceramics. The process is based on a rapid redox reaction between a fuel (urea, citric acid, glycine, sucrose, etc.) and oxidizers (generally metal nitrates), which starts under a moderated heating. This exothermic reaction can produce some fumes and/or a flame. The crystallization degree of the oxide and its intrinsic characteristics generally depend both on the type of fuel and on the fuel/oxidizer ratio [1-3]. The sol-gel combustion method combines the methodology of the sol-gel technique and the combustion technique, which favors the nucleation and crystallization of the product homogenously. The aim of the paper is to synthesize solid solutions (Fe_2O_3–Al_2O_3) and composite (Fe_2O_3–SiO_2) from precursors prepared by the nitrate/fuel combustion synthesis route using urea, glycine, citric acid, sucrose or their binary mixture as the fuel and also different fuel/nitrates ratios. In a first part, global reactions are proposed for each synthesis, which are useful to explain the differences in powder volume, morphology, crystallization state and specific surface area reported in the second part of the study (pic. 1). In a third part, the powders were further calcined at 550, 900, 1100°C in order to study of the phase formation in the Fe_2O_3–Al_2O_3 and Fe_2O_3–SiO_2 systems.



Picture 1. SEM images of 20 mol. % Fe_2O_3 powders in the Fe_2O_3–Al_2O_3 system

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SYNTHESIS AND REACTIVITY OF NEW *CLOSO*-DECABORATE ANION DERIVATIVES WITH BORON-OXYGEN BONDS

Klyukin I.N., Zhdanov A.P., Zhizhin K. Yu.

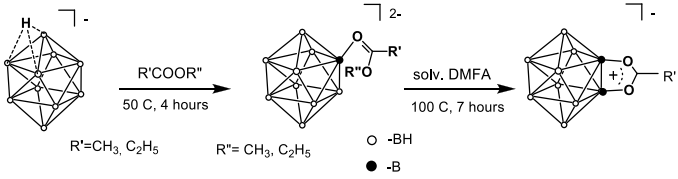
Kurnakov Institute of General and Inorganic Chemistry
of the Russian Academy of Sciences IGIS RAS,
Moscow, Russia
Postgraduate Student
klukinil@gmail.com

To date, a great number of *closo*-borate anion derivatives with *exo*-polyhedral boron-oxygen bonds are well known. Among these compounds, oxonium derivatives of polyhedral boron hydrides are most studied.

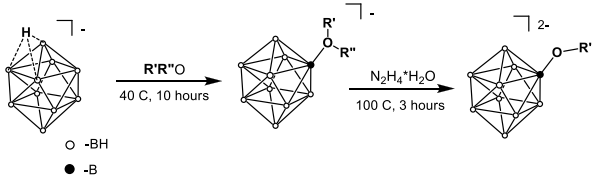
However, there are a few examples in which the boron is attached to the organic moiety by carbonyl oxygen atom. In a number of papers interactions of the *closo*-borate anions with carboxylic acids and their derivatives: esters, amides, acylchlorides were studied.

This work is devoted to the development of new methods for the synthesis of *closo*-decaborate anions with *exo*-polyhedral bonds B-O based on the reaction of anions $[B_{10}H_{10}]^{2-}$ with carboxylic acid derivatives and ethers.

The interaction between the anion $[B_{10}H_{11}]^-$ and carboxylic acids and esters has stepwise nature and depends on reaction temperature.



Also, we proposed a new method of the preparation of alkoxy-closo-decaborate $[B_{10}H_9OR]^{2-}$. This method of functionalization *closo*-decaborate anion involves two steps: obtaining oxonium derivatives of *closo*-decaborate anion and further cleavage of the CO bond.



Acknowledgements.
This work was supported by the Russian Foundation for Basic Research (project nos. 14-03-00864) the Presidential Grant Program "Leading Scientific Schools" (grant no. NSh 596.2014.3).

OXIDIZING LEACHING OF KUDRYAVYI VOLCANO RHENIUM-CONTAINING ROCK

Kolpakov I.E[1,2] Zanaveskin K.L.[2]
[1]National University of Science and Technology "MISIS",
[2]Karpov Institute of physical chemistry,
Moscow, Russia
Engineer
karovkas@gmail.com

Rhenium is one of the rarest earth core elements that finds it's application in various fields including air-spacecraft, petrochemistry and others. There is no source of rhenium in Russia now but Kudriaviy volcano (Iturup island) could be one of them. It is well known that this volcanic rock contain such elements as rhenium and molybdenum. A sample of volcanic rock was investigated and chemical analysis is presented in table 1.

Table 1 – Average chemical composition

Components	Al_2O_3	CaO	Fe_2O_3	MgO	Mo	Re*	SiO_2	S	Others
Content, % wt.	33,5	16,7	13,2	4,3	2,3	187 ppm*	25,2	4,1	0,68

It should be mentioned that rhenium and molybdenum concetrations are high. Rhenium exists as isomorfic impurity in molybdenite (MoS_2). Molybdenite particles are in the form of high-dispersive aggregates with volcanic rock.

Well-known methods of benefication (gravimetric, flotation) were un-efficient. Leaching and liquid-phase extraction with organic extragents could be used to extract rhenium and molybdenum from volcanic rock.

Oxidation leaching with nitric acid could be used to extract molybdenum (eq.1).

$$MoS_2 + 6HNO_3 \rightarrow H_2MoO_4 + 2H_2SO_4 + 6NO_{(r.)} \quad (1)$$

Leaching the volcanic rock with 10% nitric acid at the temperature 80 ^oC with 1/3 g/ml solid/liquid ratio for 2 hours resulted in 97% rhenium and 62% molybdenum conversion. Chemical compostion is shown in table 2.

Low molybdenum extraction is determined by the nitric acid concentration decrease due to the fact that it dissolves aluminum,iron, magnesium oxides and oxidizes sulfur. Moreover the solubility of H_2MoO_4 is 1,82 g/l in water and most of molybdenum precipitate as a crystallohydrate $MoO_3 \cdot 1/2H_2O$.

Leaching with sulfiric acid addition with the same conditions allows to decrease nitric acid concentration in solution and increase molybdenum extraction to 97%. In the presence of sulfiric acid H_2MoO_4 goes over the soluble form MoO_2SO_4 (eq. 2).

$$H_2MoO_4 + H_2SO_4 \rightarrow MoO_2SO_4 \quad (2)$$

$+2H_2O$

The decrease of calcium concetration is determined by calcium sulfate formation ($CaSO_4 \cdot 2H_2O$).

Table 2 – Chemical composition of leaching solution

	Components concentration in solution g/l						mg/l
Leaching agents	SO_4	Ca,	Mo,	Fe	Al	Mg	Re
HNO_3 10%	9,6	11,5	2,6	4,2	5,5	3,4	64,3
5% HNO_3 5% H_2SO_4	68,4	4,6	4,4	4,7	6	3,7	65,5

Results:

The use of nitric acid as a leaching agent is efficient for rhenium extraction from rhenium-containing volcanic rock. However molybdenum extraction is incomplete.

Sulfiric acid addition allows:

- To decrease the concentration of nitric acid
- To decrease the calcium concentration in solution
- To reach 100% molybdenum conversion

USAGE OF THE HIGH-PERFORMANCE LIQUID CHROMATIGRAPHY ASSESSMENT METHOD BY BENZO (A) PYRENE URBAN POLLUTION

Konysbayeva A.B.[1], *Bakhov Zh.K.*[2]
[1] M.Auezov South Kazakhstan State University Shymkent city, Kazakhstan
Postgraduate
a.konysbayeva@gmail.com
[2]M.Auezov South Kazakhstan State University, Shymkent city, Kazakhstan
Doctor of technical science, professor
zhbakhov@mail.ru

In recent years, Kazakhstan has been an intense increase in the number of vehicles. Shymkent is the third largest city by population in Kazakhstan. For instance, in Shymkent at the end of 2014 were 101,309 units of registered vehicles. Of these, cars are 88,835, cargo - 9651, buses - 2655, motorcycles - 168 units. This paper presents the results of experimental studies of environmental pollution (snow and soil) Shymkent benzo (a) pyrene under the influence of vehicles.

Atmospheric pollution of Shymkent recording by the system of state control. From 2008 to 2014 in the city, according to Kazhydromet, monitoring was carried out on four stationary observation points (PTZ). They are located at the following addresses: PTZ number 1 - Abay ave., 23 (near the lead plant); PTZ number 2 - Sq. Ordabasy; PTZ number 3 - at the intersection of Aldiyarov and Aknazarhan str. (District cement plant); PTZ number 8 - on the street Sairam (district brewery). Sampling and analysis provides by laboratory of monitoring environmental pollution of Kazhydromet.

Measuring the level of air pollution caused by emissions of vehicles, held in conjunction with the measurement of the level of pollution emissions from industrial sources, but it can be carried out independently. Evaluation of air pollution on the highways and in the surrounding residential area is based on the definition in the air content of the main components of exhaust gases (carbon monoxide, nitrogen oxides, sulfur dioxide, and formaldehyde).

In the course of research on the individual components of pollutants established qualitative and quantitative laws between the content of benzo (a) pyrene. There is shown the possibility of creating mutually complementary monitoring systems and obtaining on its basis more detailed assessment of the long-term environmental pollution. In determining benzo (a) pyrene in the environment used method of high performance liquid chromatography (HPLC) [1], which was implemented on the device “Varian Pro Star 500” in the test laboratory of engineering profile SKSU named after M. Auezov.

Snow cover is an inartificial natural tablet drives of aerosol. The study of the spatial dynamics of the distribution of contaminants in the snow reveals the

sources of aerosol emissions, to differentiate footprint and propagation distance, perform an assessment of the total output and the characteristics of the particulate composition [2]. The particular interests of the snow cover in the study of long-term pollution (month, season).

Analysis of the average annual concentrations (mg/m^3) of pollutants in the atmosphere of Shymkent for 2008-2014 year shows that the CO concentration is in the range between 1250-2100 mg/m^3, NO_2 - 40-55, SO_2 - 3-5 mg/m^3 Formaldehyde - 12.9 mg/m^3. In general, these figures though are the maximum permissible limits, in some periods, especially during adverse weather conditions, in the busiest transport stations in the city there is an excess of nitrogen dioxide and formaldehyde. For these areas of the city of Shymkent characterized by an increased content in the soil and snow cover benzo (a) pyrene. High degree of agreement in the data achieved under the following conditions: sampling carried out directly from the post of pristine snow, eliminated systematic errors as in sample preparation and chemical analysis of samples of snow and soil. The research results can be used to monitor mutual observations of the snow and the surface air of the city, to make decisions to improve the environmental situation in the city.

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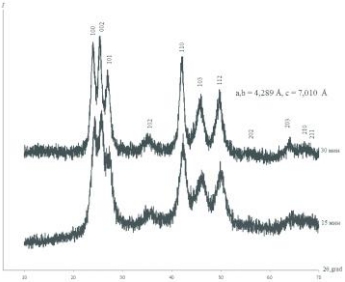
GREEN SYNTHESIS OF NANOCRYSTALLINE CADMIUM SELENIDE

Korobkova M.N., *Koryttseva A.K.*

Lobachevsky State University of Nizhny Novgorod, Nizhny Novgorod, Russia
Student
catfishsoup9@gmail.com

Cadmium selenide is a well-known n-type inorganic conductor and a very promising material for photovoltaics. Nanocrystalline CdSe has increasing applications due to the dependence of electro-optical properties on the nanoparticles size. The common way of their synthesis is a metal-organic route supplying toxic reagents and high temperatures. The aim of the present work is to develop a method for producing nanocrystalline CdSe in soft and environmentally friendly conditions. Aqueous solutions of cadmium nitrate, sodium selenite, D-glucose and ammonia were used as a starting reagents. Sodium selenite to glucose ratio was equal to 2, 3 and 10 in different syntheses. The resulting transparent solution was subjected to a hydrothermal or microwave hydrothermal treatment at 100-200ºC during a fixed period of time. The products obtained were characterized by X-ray powder diffraction, X-ray fluorescent analysis and also scanning and transmission electronic microscopy. All samples crystallize in hexagonal wurtzite structure.



Picture 1. XRD patterns of CdSe particles synthesized under microwave hydrothermal conditions (180 ° C).

Mean values of coherent scattering regions (CSR) were calculated from Sherrer equation, microstress contributions were not considered, x-ray diffraction patterns have been fitted with Gaussian function. The increase of the reaction time (from 15 minutes to 42 hours) results in the coarsening of nanoparticles (from 4.0 to 8.2 nm) and the increase of the D-glucose content in the solution results in the decrease of CSR.

The study was performed using equipment of the Center for collective use «New materials and energy saving technologies» of Lobachevsky State University of Nizhny Novgorod, and was supported by The Ministry of Education and Science of the Russian Federation, project FMEFI59414X0005.

THERMODYNAMIC PROPERTIES OF FULLERIDES C_{60} AND C_{70} WITH ORGANOELEMENT SUBSTITUTING GROUPS

Koryukina T.I., Markin A.V.

Lobachevsky Nizhny Novgorod State University (NSU)
Nizhny Novgorod, Russia
Student
koryukinatatyana@gmail.com

The study of donor-acceptor complexes of C_{60} and C_{70} fullerenes where the latter play the role of relatively strong acceptors is dictated by the search for new unique materials [1]. Such materials exhibit interesting optical, electrical conductivity and magnetic properties. Most often, fullerene complexes with aromatic hydrocarbons as donor partners were synthesized and their properties were studied.

The temperature dependences of heat capacities of fullerides C_{60} and C_{70} with organoelement substituting groups in the range from 6 to 360 K by precision adiabatic vacuum calorimetry were measured. For example, for $[(\eta^6\text{-}Ph_2)_2Cr]^{\bullet+}[C_{70}]^{\bullet-}$ the reversible endothermic transformation was detected and its thermodynamic characteristics were estimated. This transformation was caused by dissociation of $(C_{70}^-)_2$ and formation of fulleride $[(\eta^6\text{-}Ph_2)_2Cr]^{\bullet+}[C_{70}]^{\bullet-}$ during heating.

The low-temperature heat capacities (T < 50 K) were analyzed on based of the heat capacity solids Deby's theory and as results the hardness of structure for under study complexes was estimated. The temperature dependence of heat capacity in the low-temperature region (T < 20 K) is well described by the limiting Deby's law for the tested complexes as well as for fullerites C_{60} and C_{70}.

The experimental data were used to calculate the thermodynamic functions, namely heat capacity, enthalpy, entropy and Gibbs function in the range from 0 to 360 K. The standard thermodynamic properties of tested fullerides, studied earlier $(C_{60})_2$, C_{60} and C_{70} fullerites were compared and discussed. On the based of our thermodynamic data, information about the structure and the composition of these and the respective data for C_{60}, C_{70} and $(C_{60})_2$ the some conclusions about the bound nature between fullerene fragments in the fullerides were made.

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Acknowledgements

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SYNTHESIS AND STUDY OF CESIUM URANATE $Cs_3U_{12}O_7(OH)_{13}\cdot 3H_2O$

E. L. Kostrova, O. V. Nipruk, K. A. Chaplieva

Lobachevsky State University of Nizhni Novgorod
Nizhni Novgorod, Russia
Undergraduate student
kostrova90@inbox.ru

In this work the method of synthesis of cesium uranate $Cs_3U_{12}O_7(OH)_{13}\cdot 3H_2O$ is described. The chemical and functional composition of this compound has been studies; its crystallographic characteristics have been determined; the process of dehydration and thermal decomposition has bean researched.

The investigated compound is synthesized by reaction of shoepite $UO_3\cdot 2.25H_2O$ with aqueous solutions of cesium nitrate (pH of 10, CsOH) under hydrothermal conditions at 200°C. The synthesized cesium uranate is easily reproducible individual crystalline compound. The X-ray diffraction picture contains a series of reflections from planes with indices which, in combination with an intense reflection peak at $2\theta = 11.72°$ indicate a typical layered structure of the uranate.

For evolution of its functional composition of $Cs_3U_{12}O_7(OH)_{13}\cdot 3H_2O$, we have performed the IR spectroscopic research. The vibrations of H_2O are very characteristic. Band of vibrations $\delta(H_2O)$ are shown in the spectrums at 1621 cm^{-1}. The bands of vibrations ν_s and ν_{as} are represented in the spectra by a broad and intense band with weak maxima at 3511 and 3414 cm^{-1}. The stretching vibrations bands of ν(U(O-H)) are observed in the spectra at 3208 cm^{-1}. The corresponding bands deformation vibrations of the uranium-oxygen U-OH fragment can be attributed to a single unidentified band 1012 cm^{-1}.

Uranate cesium $Cs_3U_{12}O_{37.5}\cdot 9.5H_2O$ thermally is not stable compound. Three H_2O molecules per formula unit of the compound are removed at 122°C. Product dehydration of $Cs_3U_{12}O_{37.5}\cdot 6.5H_2O$ at further heating in the range of 61-425°C does not change the composition. The stretching vibrations bands of ν(U(O-H)) are observed in the spectra of $Cs_3U_{12}O_{37.5}\cdot 6.5H_2O$ at 3208 cm^{-1}. However, the band deformation vibrations $\delta(H_2O)$ in the area of 1600 cm^{-1} in the spectrum is not observed. This is possible when the compound has the composition $Cs_3U_{12}O_7(OH)_{13}$. Condensation of hydroxide groups and crosslinking of opposing layers occurs at 425-465°C. According to the results of chemical analysis the compound corresponds to the formula $Cs_3U_{12}O_{37.5}$. It is the crystalline phase. The compounds have a layer structure. As we could, weak diffraction peak intensity at small angles 2θ.

Co NANOPARTICLES: SYNTHESIS AND CATALYTICAL PROPERTIES

Kotel'nikova S.V., *Suslonov V.V.*, *Osmolowskaya O.M.*, *Osmolowsky M.G.*

Saint Petersburg State University
Saint Petersburg, Russia
Student
sofya.kotelnikova@gmail.com

Nowadays the study of cobalt nanoparticles (NPs) attracts much interest because they have a wide range of application such as recording media, electronic devices, MRAM memories, nanosensors, medicine, catalysis. This is caused by their unique magnetic, optical and electric properties which depend on the nanoparticles size and shape. One of the most important fields of NPs application is catalysis. Co NPs are perspective materials for the different types of industrial chemical reactions because they are cheaper that analogues and can be easily separate by magnetic separation. Therefore, the synthesis of NPs which meet the requirements for catalytic materials is very important task. In this work the chelating agents (CA) were used to inhibit the particle growth and the influence of its nature on NPs morphology, magnetic and catalytic properties were studied.

In aqueous medium the Co NPs can be easily oxidized and their surface needs to be protected. Therefore the synthesis was carried out by a polyol method using $NaBH_4$ as a reduction agent. As chelating agents phosphonic, oleic, succinic and salicylic acids were used.

The NPs were characterized by XRD, SEM and SSA estimation. The magnetic properties were studied by VSM. The catalytic properties were investigated by UV-VIS spectroscopy using the model reaction of reduction of p-nitrophenol to p- aminophenol.

It was shown that NPs sizes could be vary from 150 to 300 nm and depend on the CA nature. The magnetic and catalytic characteristics are also demonstrated the similar behavior. For all NPs the reaction of p-nitrophenol conversion starts with a delay which depend on the CA nature. In addition the more catalytic efficacy was detected for NPs with the higher coercivity value. These facts could be due to the different value of binding strength between CA and NPs and consequently the different surface composition and NPs interaction.

Acknowledgements
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LOW-DIMENSIONAL VANADIUM TETRASULFIDE: BULK, COLLOIDAL DISPERSIONS, THIN FILMS AND COMPOSITES

Kozlova M.N.[1,2],*Fedorov V.E.*[1,2]

[1]Novosibirsk State University,
[2]Nikolaev Institute of Inorganic Chemistry SB RAS
Novosibirsk, Russia
Student
kozlovamariia@list.ru

In the last few years preparation of nanosized low-dimensional metal chalcogenides attracted wide attention due to their improved electronic, optical, catalytic properties etc. Although many of the layered metal chalcogenides, such as MoS_2, are well-studied, some other chalcogenides have received less attention by comparison. In particular, there has been an emerging interest in vanadium tetrasulfide (VS_4), which displays useful properties as a component of hybrids [1]. The structure of VS_4 can be regarded as quasi-one-dimensional with metal chains which are bonded by weak van der Waals forces (interchain S…S distances >3.2 Å). We have synthesized VS_4 by a direct reaction between the elements. The bulk VS_4 was investigated by a set of methods and electrophysical properties of pressed samples were studied. We further demonstrate that the bulk may be ultrasonically dispersed in appropriate solvents to form colloids, similarly to the layered chalcogenides. VS_4 particles in colloids retain their phase identity and rod-shaped morphology with lengths in the range of hundreds of nanometers. Isopropanol dispersion exhibited the highest concentration (about 310 mgL^{-1}) and stability (over 10 days) [2]. Thin films of VS_4 were prepared from isopropanol dispersions by two methods: filtration throught membrane filters with pore size 0.02 μm and spray-method. Decorating the surface with nanoparticles of different types is an effective way to functionalize the material and bring new and enhanced properties for many areas such as energy storage, catalysis and surface enhanced Raman spectroscopy devices. Here we also report deposition of noble metal nanoparticles on the VS_4 interface.

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Acknowledgements.
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THERMAL DEFORMATION MODEL IN CERTAIN LAYRED PEROVSKITES

Krasheninnikova O.V., *Syrov E.V.*, *Knyazev A.V.*
Lobachevsky State University
Nizhny Novgorod, Russia
Graduate student
okkraska@gmail.com

Bismuth-containing ferroelectric with a layered structure of the mineral of perovskite, first described by Aurivillius, recently started to receive increasing attention from researchers. General formula for these compounds can be written as $A_{m-1}Bi_2B_mO_{3m+3}$, where m typically ranges from 1 to 5 and can take fractional values. Their structure have studied in detail in [1]. Most of them undergo phase transition from ferroelectric (with several symmetry-equivalent versions of structure) into paraelectric phase (with only type of structure) on heating. Last phase transition corresponds to the Curie temperature. The compounds Bi_2MoO_6 (m = 1), Bi_3NbTiO_9 (m = 2), $Bi_4Ti_3O_{12}$ (m = 3), $BaBi_4Ti_4O_{15}$ (m = 4), $Ba_2Bi_4Ti_5O_{18}$ (m = 5) and $Bi_5Nb_3O_{15}$ (m=1,5), $Bi_7Ti_4NbO_{21}$ (m = 2,5), $CaBi_8Ti_7O_{27}$ (m = 3,5) have been synthesized by solid state reactions. Phase transitions have been studied with differential scanning calorimetry together with high-temperature X-ray diffraction. We found a downward trend in the Curie temperatures and melting compounds through the increase of the number of octahedra in the packet of Aurivillius phase. $Bi_4Ti_3O_{12}$ has a general formula of $[Bi_2O_2]^{2+}[B_{m-1}M_mO_{3m+1}]^{2-}$, where B is the 12-fold coordinated cation with low valence in the perovskite sublattice, M denotes the octahedral site occupied by the ions with high valence, and m is the number of perovskite layers between the $[Bi_2O_2]^{2+}$ blocks. We decided to clarify the mechanisms of atomic displacements in the ferroelectric phase, which lead later to a second-order transition (T_C). Our research has shown that most “mobile” atoms of oxygen in slabs and Bi in blocks. The most significant displacement of the atoms is observed for the oxygen atoms in the outer octahedra of slabs. Bismuth atoms in the blocks move much less. All movements occur along the crystallographic c axis. We have noted that the direction of movement essentially depends on temperature. On the contrary, at higher temperatures occurs gradually alignment of the bond lengths in the octahedra. This process leads to an increase in the symmetry of the structure and phase transition. Thus, the symmetrization of the octahedra in the slab is the main reason of transition for ferroelectric Aurivillius phases in the paraelectric phase.

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SYNTHESIS AND MODELING OF HYDROSILICATE NANOSCROLLS

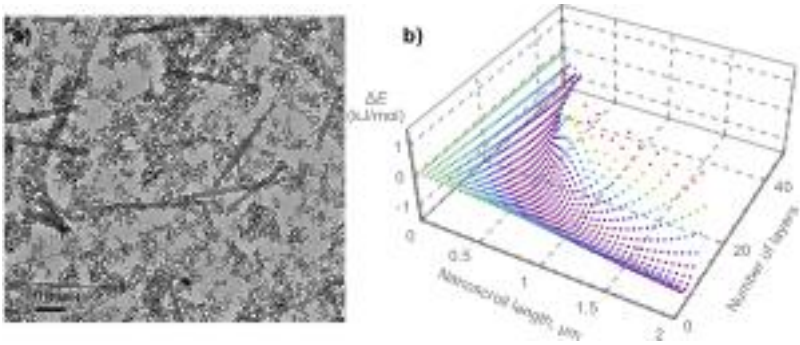
Krasilin A.A.

Saint Petersburg State Technological Institute (Technical University),
Saint Petersburg, Russia
Junior Research Fellow
ikrasilin@gmail.com

Hydrosilicate $(Mg,Ni)_3Si_2O_5(OH)_4$ nanoscrolls with chrysotile structure were synthesized via hydrothermal method. Structure and morphology of the nanoscrolls were investigated by X-Ray powder diffraction and transmission electron microscopy.

The phenomenological model of chrysotile nanoscroll formation was formulated as a concurrent action of strain and surface tension [1]. Influence of physical parameters – Young's modulus and specific surface energy – was investigated. Optimal morphological parameters – inner radius, number of layers and the nanoscroll length – were determined.

Correlations between real and theory-driven morphology are considered.



TEM-image of chrysotile nanoscrolls (a) and the results of modeling (b).

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Acknowledgements

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SYNTHESIS AND STUDY OF $Bi_{2-y}Li_xTi_2O_{7-\delta}$

Krasnov A.G.[1], *Baklanova Ya.V.*[2], *Denisova T.A.*[2]

[1] Institute of Chemistry Komi SC UB RAS
[2]Institute of Solid State Chemistry UB RAS
Syktyvkar, Russia
Postgraduate student
alexey-krasnov@rambler.ru

High dielectric constant and low leakage currents of $Bi_2Ti_2O_7$ make possible to use it as an insulating layer for advanced MOS transistors and for design storage capacitors in DRAM [1]. Low thermal stability of $Bi_2Ti_2O_7$ [2] can be improved by doping with metal cations. That also influences on the properties of resulting materials. The aim of this work was to determine the conditions for the formation of single-phase lithium-containing bismuth titanate with the pyrochlore structure and to study properties of the obtained compounds. The solid solutions $Bi_{2-y}Li_xTi_2O_{7-\delta}$ (y = 0.4; 0.6; 0.8; $x = 0.1 – 1$) have been studied. The homogeneity regions of Li-containing bismuth titanate with the pyrochlore structure have been established as $Bi_{1.6}Ti_2Li_xO_{7-\delta}$ at $0.1 \le x \le 0.6$; $Bi_{1.4}Ti_2Li_xO_{7-\delta}$ at $0.1 \le x \le 0.8$; $Bi_{1.2}Ti_2Li_xO_{7-\delta}$ at $0.3 \le x \le 0.4$ by XRD and SEM methods. Single-phase products have been characterized by DSC and ICP-AES. Rietveld analysis was carried out based on X-rays powder diffraction data using FullProf software package. The NMR ^{6}Li (MAS) signals for compositions $Bi_{1.6}Ti_2Li_xO_{7-\delta}$ (x = 0.4–0.6) recorded at a frequency of 58.87 MHz in the temperature range 25–100 ºC, represent singlet line at 0.23 ppm with a line width at half-maximum ~ 82 Hz. Constant parameters of the NMR spectra for the different composition and temperature show that the Li^+ ion doped in the same position (Bi) of $Bi_{2-y}Li_xTi_2O_{7-\delta}$. The any hops of lithium ions are absent at temperature 30–100ºC. The study of electrical properties was carried out by two-probe method and impedance spectroscopy. The dependence of the conductivity on lithium and bismuth concentration has been revealed. The phase angle and impedance module frequency dispersion indicates pronounced polarization phenomena in the compounds at T>450 ° C.

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The work is supported by RFBR grants 15-03-09173 and 14-03-31175 mol_a

DIFFUSION OF TL-204 ISOTOPE AND IONIC CONDUCTIVITY IN CHALCOGENIDE GLASSES MEMBRANE TLI-AG_2S-AS_2S_3 FOR THALLIUM SENSORS.

Krotov S.A., Ermolenko Yu.E., Kalyagin D.S., Vlasov Yu.G.

Institut of Chemistry, St. Petersburg State University, St. Petersburg 199034, Russia
Saint Petersburg, Russia
Postgraduate student
krotilla@gmail.com

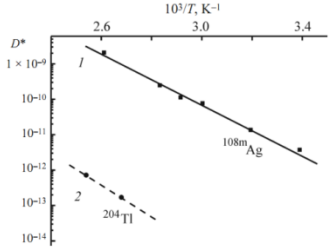
Ecological problems and numerous tasks of technological processes require rapid determination of various toxic metals, such as mercury, lead, cadmium and thallium. The most promising for in particular ecological monitoring are potentiometric, voltammetric and optical sensors.

The goal of our study was to synthesize and make a comprehensive analysis of the transport and analytical characteristics of chalcogenide glasses in the Ag2S– As2S3–TlI system to determine the extent and mechanism of the ionic transport.

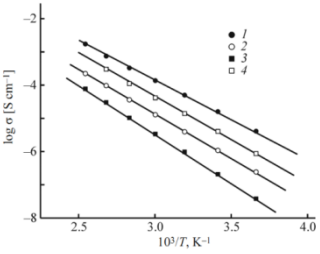
A study of the transport characteristics (electrical conductivity and diffusion of the 108mAg and 204-Tl radioactive) of chalcogenide glasses in the Ag2S–As2S3–TlI system demonstrated that the total electrical conductivity grows by nearly two orders of magnitude on making the silver sulfide concentration in a glass two times higher.

The ionic component of the conductivity was calculated for glass samples of composition 20 mol % Ag2S–53 mol % As2S3–27 mol % TlI from diffusion data to be approximately 20% of the overall conductivity.

The glasses under study were used to develop new chemical sensors for Tl ions in solutions and it was found that the best analytical characteristics are exhibited by sensors with membranes having higher silver ions conductivity.



Picture 1. (1) Dependence of the diffusion coefficient D* (^{108m}Ag) for the glass of composition 27 mol % TlI on temperature T and (2) data on diffusion coefficients D* (^{204}Tl) at temperatures of 100 and 120°C.



Picture 2. Dependence of the total electrical conductivity σ of various chalcogenide glasses compositions on temperature T. (1) 20 mol % TlI, (2) 23 mol % TlI, (3) 27 mol % TlI, (4) 40 mol % TlI.

DESIGN OF NEW CATALYSTS OF ETHANOL DECOMPOSITION BASED ON FRAME COMPLEX CESIUM-ZIRCONIUM PHOSPHATES

Krylova A.S., Chuklina S.G., Koleva L.D., Pylinina A.I.

Peoples' Friendship University of Russia
Moscow, Russia
Student
askrylova25@yandex.ru

The aim of this work was to study the effects of solid cesium-zirconium modifications by copper ions and different temperature pre-treatments. Results were measured by pyridine absorption tests and ethanol transformations.

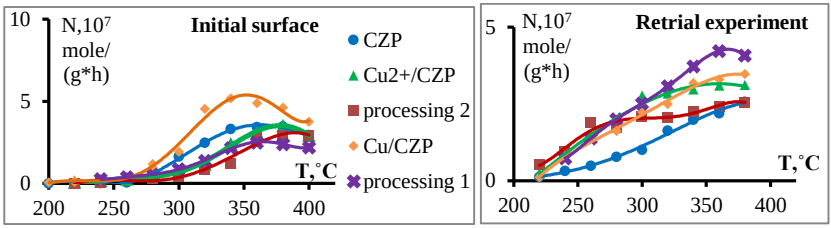


Fig.1. Yield of acetaldehyde on copper-containing samples

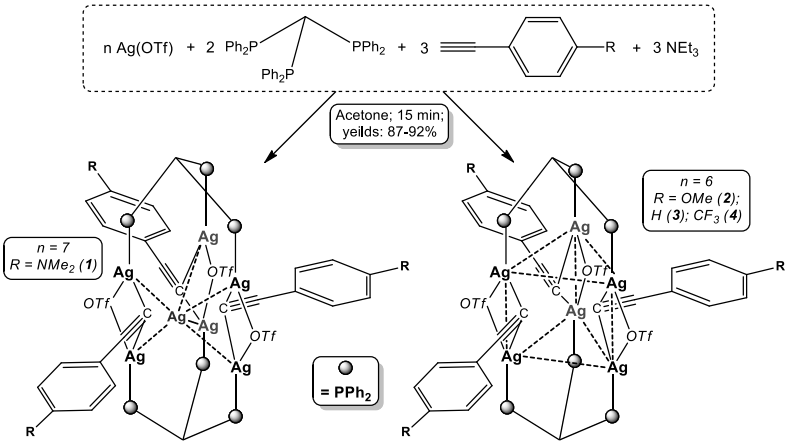
This study is focused on the activity of copper-containing samples based on cesium-zirconium phosphate with copper content 5 wt. %. Several experiments were done with various temperature pre-treatments. Catalytic experiments were performed on a flow-type setup with the chromatographic analysis of substances in the temperature range 250 - 400^{0}C. Figures show that previously reduced copper-containing sample has demonstrated the highest activity. The reaction impacts in different ways on the further formation of active surface sites. The last catalytic experiment has shown that unreduced copper sample has the lowest catalytic activity. At the same time, all other samples have higher activity with respect to reactions` environment. Catalyst`s properties depend significantly on a use of a copper content. Pre-treatment at T=-195^{0}C of a calcined copper-containing sample produces additional surface sites with high bond strength of alcohol with surface. Such sites increase the activity up to 1.5-4 times. It has been investigated that the acidity of the catalysts depends on pretreatments conditions. Variations of acidity were determined by studying the adsorption of pyridine. It was shown that surface of a copper-containing samples contains two different types of a sites with various bond strength between pyridine and surface. It is important to mention that such cites disappear after catalysis.

LUMINESCENT ALKYNYL-PHOSPHINE SILVER(I) CLUSTERS

Krytchankou I.S.[1,2], *Koshevoy I.O.*[1,3], *Tunik S.P.*[1]

[1]Saint-Petersburg State University,
[2]Vitebsk State Medical University,
[3]University of Eastern Finland
Vitebsk, Belarus
Postgraduate student
ilya.kritchenkov@gmail.com

The reaction of Ag(OTf) (OTf^- = $CF_3SO_3^-$) with 1,1,1-tris(diphenylphosphino)methane (tppm) and the corresponding alkyne in the presence of NEt_3 (***Scheme 1***) results in formation of polynuclear Ag(I) clusters with general formula $[Ag_7(C_2C_6H_4\text{-}4\text{-}R)_3(OTf)_3(tppm)_2](OTf)$ (R = NMe_2 (**1**)) and $[Ag_6(C_2C_6H_4\text{-}4\text{-}R)_3(OTf)_3(tppm)_2]$ (R = OMe (**2**), H (**3**), CF_3 (**4**)). The structural motif of the complexes studied consists of Ag_6 or Ag_7 metal core, supported by two phosphine ligands and stabilized by coordination of the alkynyl fragments together with OTf^- anions. The solid state structures of the complexes **3** and **4** were determined by single crystal XRD analysis. The structures in solution were elucidated by ^1H, ^{31}P and ^1H-^1H COSY NMR spectroscopy and ESI mass-spectrometry. The clusters **1–4** exhibit phosphorescence in solid state with quantum yield up to 9% and cover a wide range of the visible spectrum, i.e. from 719 (**1**) to 453 nm (**4**).



Scheme 1. Synthesis of complexes **1–4**

Acknowledgements. This research has been supported by SPbSU research grant 0.37.169.2014, RFBR grants 13-03-00970 and 13-03-32077. The work was carried out using equipment of the SPbSU Research Park.

HF-CONTAINING OXIDE THIN FILMS OBTAINING FROM CARBOXYLATES SOLUTIONS

Kuimov A.N.[1], *Kharchenko A.V.*[1].

[1]Lomonosov Moscow State University,
Moscow, Russia
Student
alexkuimov@gmail.com

Oxide thin film coatings HfO_2 and $La_2Hf_2O_7$ are promising materials for use in electrical, optical and catalytic applications. One of the promising methods for their preparation is a method of chemical deposition from solution of precursors. Such solutions in the carboxylic acids are stable at high concentrations and capable of proper wetting the oxide and metal surfaces. The composition of carboxylates can be varied, the formation of polyoxometalate complexes is possible. For such zirconium compounds we prove, that the formation of the oxide phase occurs at a relatively low temperature, which makes these compounds promising precursor for the obtaining of oxide films. In the literature, there is not enough information about hafnium polyoxometalates. With this in mind, the study of hafnium carboxylates remains relevant applied and fundamental task.

The aim of this work was obtaining thin oxide films from hafnium carboxylates solutions. We had the following objectives: search and synthesis of precursors for carboxylates, synthesis of carboxylates by various methods, the study of their structure, chemical properties and thermal stability, as well as the deposition of films on a metal substrate carboxylates and study oxide formation during annealing.

In this paper we selected two approaches to synthesis of carboxylates. The first method consists in the interaction of hafnium acetylacetonate with carboxylic acids, and the second method – from hafnium oxocloride.

In all cases, were prepared carboxylates having the general formula $HfO_x(OH)_y(RCOO)_z \cdot {}_nH2O$, where x, y, z, n are dependent on the conditions of synthesis: reagent ratio, pH, solvent. The resulting compounds were studied by elemental, thermal analysis and IR spectroscopy.

As the most suitable precursor of oxide film, we selected solution of hafnium propionate complex in propionic acid. By XRD analysis we confirmed the formation of phase HfO_2 and $La_2Hf_2O_7$. It was shown that the films $La_2Hf_2O_7$ on textured metal substrate of Ni-W alloy acquire its texture, which is then able to transmit to the layer $YBa_2Cu_3O_{7-x}$. This effect can be used in technology of creating the second-generation superconducting tapes.

SUCCESSIVE IONIC LAYER DEPOSITION (SILD) AND INVESTIGATION OF $M_xFeO_y \cdot nH_2O$ (M – Ag, Cu, Co, Ni, Zn, Mn, Bi, Ce, La) NANOCOMPOSITES

Kuklo L.I.

Saint Petersburg State University
lenkuklo@mail.ru

Nowadays, the synthesis of nanolayers of inorganic solid substances on the surface of the block and particulate substrates is known to be one of the most promising ways to obtain new materials, such as membranes, catalysts, adsorbents, superionic conductors, as well as various types of so-called multi-functional materials. Special attention is paid to the methodical techniques which allow to synthesize nanolayers by a "layer-by-layer" methods, for example SILD, since in this case it is possible to precisely control the thickness and composition of layers.

In the present work nanolayers of $M_xFeO_y \cdot nH_2O$ (M - Ag, Cu, Co, Ni, Zn, Mn, Bi, Ce, La etc.). was first obtained. Aqueous solutions of salts of the respective metals were used as the reagents in the syntheses, and the substrates were monocrystalline silicon wafer and fused quartz. The study of synthesized layers was done by SEM, EDX, FTIR and UV-Vis spectroscopies, and XRD.

When selecting the optimal conditions of synthesis pH, concentration and composition of the reagent solutions, and the processing times as well as the number of cycles were varied. As a result of this research there were found conditions under which nanolayers $M_xFeO_y \cdot nH_2O$ form with thick linearly increasing with the number of cycles. To explain the experimental results scheme of successive chemical reactions on the surface of the substrate have been constructed.

Acknowledgements
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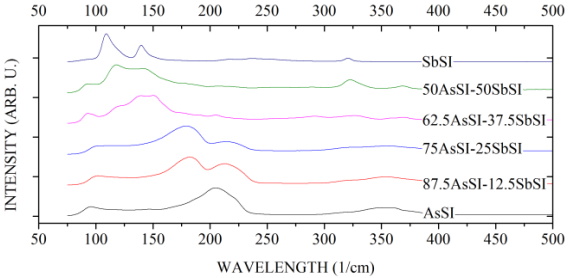
RAMAN SPECTRA OF THE ASSI-SBSI CHALCOGENIDE GLASSES

Kurushkin M.V.[1], *Semencha A.V.*[1], *Tverjanovich A.S.*[2], *Mikhailov M.D.*[3]

[1]Saint Petersburg State Polytechnic University,
[2]Saint Petersburg State University,
[3]Research and Technological Institute of Optical Materials Science
Saint Petersburg, Russia
Post-graduate
mkurushkin@spbstu.ru

Chalcogenide glasses based on the As-S-I system are of considerable interest in optoelectronics due to their outstanding physicochemical properties. In our previous research we have shown that introduction of small amounts of Sb (about 3 mol. %) into As-S-I system yields chalcogenide glasses with even enhanced characteristics. Yet, not much is known regarding the structure of the glasses of the quaternary As-Sb-S-I system. Several attempts have been made to investigate the structure of As-Sb-S-I glasses by Raman spectroscopy and mixed structural units like $As(Sb)S_{3/2}$ have been proposed. Unfortunately, in the abovementioned works the As-Sb-S-I system has mainly been observed along As_2S_3-SbSI section where the concentration of every component is variable as As and Sb are competing for I. Therefore, no satisfactory information about the influence of substitution of As with Sb is provided. In the present work we have studied the Raman spectra of the As-Sb-S-I system along the AsSI-SbSI section (Pic. 1).



Picture 1. Raman spectra of the AsSI-SbSI chalcogenide glasses

The possible equilibrium in the system based on the spectra analysis has been deduced and is described by the following equation: $3SbSI + 2AsI_3 = 3SbI_3 + As_2S_3$, the free Gibbs energy temperature dependence has been calculated (-130 kJ/mol at 750K) and has shown that the suggested process is thermodynamically allowed.

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SYNTHESIS OF STABLE COLLOIDAL WATER SOLUTION OF CDS@ZNS NANOPARTICLES

Kuznetsova Yu.V., Rempel S.V., Rempel A.A.

Institute of Solid State Chemistry, Ural Branch of the Russain Academy of Sciences
Ekaterinburg, Russia
PhD Student
jukuznetsova@mail.ru

At present, the synthesis of nanoparticles based on a hybrid semiconductor sulfides having promising optical and photocatalytic properties is relevant for fundamental science and practice [1]. Most techniques for producing nanoparticles use toxic precursors, which limits their utility in biological and medical applications. Because of this an additional steps are needed to transfer nanoparticles to aqueous solutions compatible with biological objects. To avoid this complicated step the chemical condensation technique was used to obtain a stable aqueous colloidal solution of cadmium sulfide (CdS) nanoparticles with the disodium salt of ethylenediaminetetraacetic acid $C_{10}H_{14}N_2O_8Na_2$ as a stabilizer [2]. In present work in order to enhance absorption and fluorescence properties, the creating core@shell structure CdS@ZnS by means of depositing of thin layer of zinc sulfide nanoparticles on stable colloidal CdS nanoparticles was carried out.

The hydrodynamic size and zeta-potential of CdS and CdS@ZnS nanoparticles were determined directly in solution using Dynamic Light Scattering (DLS) with a Zetasizer Nano ZS instrument (Malvern Instruments Ltd.). The samples obtained were characterized by UV-visible and luminescence spectroscopy in the region from 190 to 900 nm.

The data obtained show that the coating of fluorescent CdS nanoparticles by ZnS shell allows increasing a band gap value and luminescence intensity, and a change of emission contribution from different types of defects in comparison with a solution consisting of CdS nanoparticles only. The increase of the zeta potential of CdS@ZnS nanoparticle indicates the possibility of using zinc sulfide as stabilization factor.

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Acknowledgements

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THE INFLUENCE OF SIZE AND ZETA-POTENTIAL OF SILVER SULFIDE NANOPARTICLES IN AQUEOUS SOLUTION ON INTERACTION WITH CELL CULTURES

Kuznetsova Yu.V., Sadovnikov S.I., Rempel S.V.

Institute of Solid State Chemistry, Ural Branch of the Russain Academy of Sciences
Ekaterinburg, Russia
PhD Student
jukuznetsova@mail.ru

At present quantum dots (QDs) based on silver sulfide (Ag_2S) nanoparticles are used for cell culture imaging and in vivo study [1, 2]. One problem limited the use of quantum dots in biological imaging is an interaction of nanoparticles with living matter. This has been studied little, so further research is needed to develop nondestructive nanoparticle to biomolecule conjugation techniques. In this study, silver sulfide Ag_2S nanoparticles were prepared by chemical condensation directly in an aqueous solution in one cycle, which eliminated the need for solubilization of the synthesized nanoparticles [3].

The objective of this work was to study an interaction of Ag_2S nanoparticles with red blood cells depending on a size and zeta-potential of nanoparticles. The hydrodynamic size and zeta-potential of Ag_2S nanoparticles were determined directly in solution using Dynamic Light Scattering (DLS) with help of Zetasizer Nano ZS instrument (Malvern Instruments Ltd.).

The data obtained show that a conjugation of red blood cells with aqueous solution of Ag_2S nanoparticles having the size about 60 nm and zeta-potential about minus 47 mV leads to a coagulation of blood. The use of the solution of Ag_2S nanoparticles having the size about 20 nm and zeta-potential about plus 35 mV allows observing the red blood cells surrounded by Ag_2S nanoparticles.

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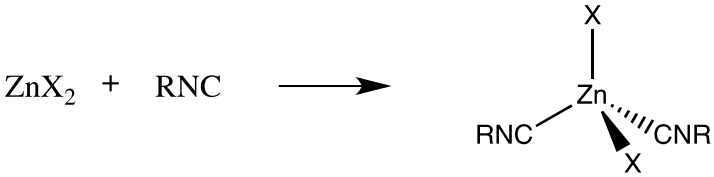
COMPLEXES OF ZN WITH ISOCYANIDE LIGANDS: PREPARATION AND STRUCTURAL STUDIES

Leonid V. Lavnevich, Mikhail A. Kinzhalov
Institute of chemistry, Saint-Petersburg State University
leonidlavn@gmail.com

While isocyanide complexes of 3d metals such as copper, nickel and manganese are well-studied, corresponding complexes of zinc relatively are nearly unknown. Examples known from the literature are represented by $[ZnBr_2(Bu^tNC)_2]$ obtained from either $ZnBr_2$ and Bu^tNC (Ref. 1) or $[ZnBr_2(S_2CNBu^n{}_2)_2]$ with Bu^tNC (Ref. 2) and by $[ZnI_2(Pr^iNC)_2]$ obtained from $[ZnI_2(S_2CNBu^n{}_2)_2]$ with Pr^iNC (Ref. 2).

In pursuit of our studies on chemistry of isocyanides (Ref. 3), we report herein on preparation and characterization of new isocyanide complexes of zinc $ZnX_2(RNC)_2$ (X=Cl, Br, I; R=Bu^t, Cy, Xyl).



X=Cl, Br, I
R=Bu^t, Cy, Xyl

All obtained compounds were characterized by ^1H, and $^{13}C\{^1H\}$ NMR and IR spectroscopies, ESI^+ MS and elemental analyzes (CHN), and by X-ray diffraction for all prepared compounds.

Acknowledgements. The authors thank Saint Petersburg State University (НИР 12.38.225.2014) and Russian Foundation for Basic Research (grant 14-03-31204 мол_а). The authors also are grateful to the Center for Magnetic Resonance, Center for X-ray Diffraction Studies, and Center for Chemical Analysis and Materials Research of Saint Petersburg State University.

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PHASE FORMATION AT REACTIONARY SYNTHESIS OF MAX-PHASE Ti_2AlN

Luginina M. A., Kovalev D. Yu., Sychev A. E.

Institute of Structural Macrokinetics and Materials Science Russian Academy of Sciences,
Chernogolovka, Russia
Ph.D. student
luginina@ism.ac.ru

Phase Ti_2AlN is a compound belonging to a new class of refractory materials, which have a layered structure and a unique combination of properties of the metal and ceramic, which can be described in the general formula $M_{N+1}AX_N$ (N = 1, 2 or 3), where M is a transition metal, A is an A-group (mostly IIIA and VIA) element, and X is either C or N. Such materials are called MAX phases have properties which combine the features of metal and ceramics. Synthesis of Ti_2AlN is carried out by hot isostatic pressing (HIP) [1], by the *spark plasma sintering* (SPS) [2] and by using self-propagating high-temperature synthesis (SHS) [3]. Regardless of the method of synthesis the presence of nitride (TiN and AlN) and intermetallic phases is always detected in the composition of the final product, and thus the minimizing of impurity content in the materials based on the MAX-phases is an important task. It is crucially important to obtain single-phase material Ti_2AlN, when it is used as a precursor for the synthesis of MXen phase Ti2N also. The aim of this work is to find compositions of mixtures, methods of their pre-processing and optimal time-depending temperature cycles for synthesis of the Ti_2AlN phase with the minimal content of impurity phases.

Synthesis of Ti_2AlN was conducted by reactionary sintering of powder mixtures containing AlN, Ti and TiN phases. Mixtures were processed in a planetary mill to determine the influence of mechanical activation modes to the composition of the final product. Sintering was carried out at temperatures 1100^0C, 1300^0C and 1500^0C by two ways: in argon atmosphere at pressure of 0.3 MPa and in vacuum condition. The duration of process was varied from 15 to 180 minutes. Diffractometer ARL`XTRA is used for X-ray diffraction analysis. Investigation of the mechanism of phase-formation directly during sintering was carried out by using high-temperature box equipment for the HTK2000 diffractometer. Preliminary programming such process parameters as the speeds of heating and cooling, isothermal exposure times in combination with XRD pattern recording were used for control of the modes of sintering.

As a result, the data revealed that the optimum composition of the starting mixture, which provides maximum quantity of Ti_2AlN product in the sintering process, is the reactionary mixture of Ti + AlN in molar ratio of 2:1. It was

found that isothermal annealing in argon at 1300^0C temperature for 2 hours provides the yield over 98% of Ti_2AlN. The XRD pattern of the material synthesized under these conditions demonstrates the minimum content of impurity phase TiN (Fig. 1). Reducing the exposure time and temperature leads to increasing of contamination by impurity phases, the main of which is TiN. Increasing the temperature and duration of annealing does not change the ratio of the phases in the final product. It was shown that pre-treatment of mixtures by the mechanical activation leads to substantial increase of content of TiN in the material. The study of phase formation sequence showed that the first phase, emerging from the interaction of the mixture components is the phase $TiN_{0.3}$, which has a hexagonal structure. Further there is formation of phases with a cubic structure - TiN and Ti_3AlN (Fig. 2).

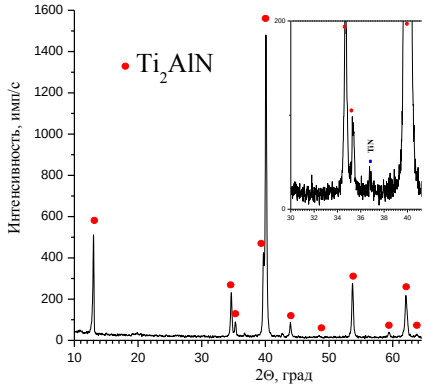

Fig. 1 The XRD pattern of the material obtained by sintering a mixture of 2Ti + AlN 1300^0C for 2 hours in argon.

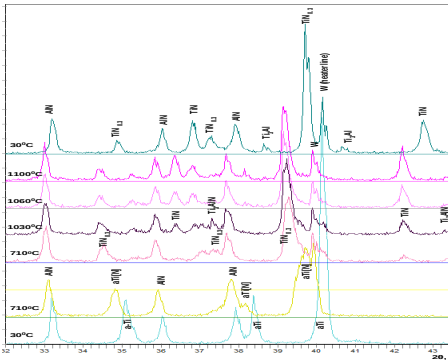

Fig.2 High-temperature XRD of process of the heating mixture 2Ti-AlN in vacuum 1100^0C 60 min.

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This work was supported by the Russian Foundation for Basic Research (RFBR) under Grant № 15-08-02331 A.

CALORIMETRIC STUDY OF TETRAPHENYLANTIMONY BENZOATE $Ph_4SbOC(O)Ph$

Lyakaev D.V.[1], *Markin A.V.*[1], *Letyanina I.A.*[1,2], *Smirnova N.N.*[1]

[1]Lobachevsky Nizhny Novgorod State University (NNSU)
Nizhny Novgorod, Russia
[2]Saint Petersburg State University Saint Petersburg, Russia
Student
lyakaev94@mail.ru

Organic derivatives of pentavalent antimony, their synthesis and investigation of their properties, are of considerable interest in view of the fact they find an application in different fields of practice, e.g. as reagents and catalysts in fine organic synthesis, pharmaceutical composition, biocides and fungicides.

For the first time, in the present research the temperature dependence of heat capacity of tetraphenylantimony benzoate $Ph_4SbOC(O)Ph$ was measured by precision adiabatic vacuum calorimetry and differential scanning calorimetry over the temperature range from 6 to 450 K. It was revealed that compound under study exists in crystalline and liquid states. The standard thermodynamic characteristics of fusion have been determined and analyzed. The thermal stability was studied by TG – analysis (TG 209 *F1 Iris*, Netzsch Geratebau*).*

The experimental results were used to calculate the standard (p° = 0.1 MPa) thermodynamic functions (heat capacity C_p°, enthalpy $H^\circ(T) - H^\circ(0)$, entropy $S^\circ(T)$, and Gibbs function $G^\circ(T) - H^\circ(0)$) of tetraphenylantimony benzoate in crystalline and liquid states from $T \to 0$ to 450 K.

The low-temperature (T < 50 K) heat capacity dependence was analyzed on the basis of Debye's heat capacity theory of solids and its multifractal model, so the characteristic temperature and the fractal dimension were determined, and chain-layered structure topology was established.

Some thermodynamic properties of tetraphenylantimony benzoate were compared with similar data of other organic derivatives of antimony(V) studied earlier.

Acknowledgements

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SORBENTS BASED ON CRWON-ETHERS IN THE PROCESSES OF SEPARATION OF RARE EARTH IONS

Maksimovskikh A.I., Fedorova O.V., Rusinov G.L., Charushin V.N.

Postovsky Institute of Organic Synthesis Ural Branch of Academy of Science
Postgraduate student
Ray.2056@mail.ru

On Earth, contains a lot of rare-earth elements, but their use is limited because of the difficult separation and purification. Now the demand for these materials is growing, as they are used in electronics, in nuclear reactors, metal, glass, ceramic industry, etc.

Also, rare earth elements occur in large quantities in acidic solutions used in the production of fertilizers. It becomes a matter of allocating appropriate rare earth ions of these solutions, since the alkalization to a pH value of about unity, begin to precipitate rare earth fluorides, and phosphates, which increases the consumption of hydrofluoric and phosphoric acids.

On the other hand, macrocyclic polyethers draw attention to themselves through their property to selectively interact with cations of suitable size to the cavity of the macrocycle. Based on this property, and is still essentially created new methods of analysis, the selective extraction of different substances.

In this paper was used as a substrate superfine silica and silica mixed with titanium oxide, which when deposited crown ether structure latter distorted altering the sorption properties of the material.

The factors affecting the sorption selectivity and REE crown ether-containing composites. It is shown that in the transition from crown ethers to their composites based on oxides SiO2, TiO2, an increase of efficiency and selectivity of sorption lanthanides. The largest distribution ratios recorded for ytterbium. Also indicated quantitative recovery of lanthanum ions in the sorption-crown ether-containing composites.

Demonstrated that in the presence of NaNO3 adsorption efficiency composite crown ether-SiO2-TiO2 from hydrochloric acid solutions is significantly increased. For example, the values of adsorption of La^{3+} 3 M hydrochloric acid solution increases from 1.36 mg / g to 17.9 mg / g.

THE STRUCTURE AND PROPERTIES OF ALKALI NIOBOPHOSPHATE GLASSES AS A MATERIAL FOR CREATION OF HIGH-CONTRAST PHASE ELEMENTS BY MEANS OF LASER RECORDING

Markov V.A.[1,2], *Sokolov I.A.* [1,2], *Manshina A.A.*[3], *Olshin P.K.*[3]

[1] Saint Petersburg State Politichnical University,
[2]LLC "AtomTiazhMash",
[3] Saint Petersburg State University
Saint Petersburg, Russia
Post-graduate
Viktor.A.Markov@gmail.com

Treatment of glassy materials with laser radiation can form planar optical structures for micro and optoelectronics. Laser radiation provokes reorganization of the structure and changes in physical and chemical properties due to the formation of structural defects and mechanical stress. Unlike traditional methods, laser-induced creation of optical structures with low-power laser radiation with ultrashort pulses does not destroy the structure of the glass but modifies it. In the case of niobophosphate glasses with high content of alkali metal oxides modification occurs due to the diffusion of high-mobility alkali metal ions. Femtosecond laser radiation can form three-dimensional optical structures in the volume of the glass . Vitreous phosphoric anhydride structure consists of $PO_{4/2}$ tetrahedral units. The introduction of alkali metal oxides into the phosphate glass leads to the rupture of bridging bonds which affects the length of the chains and the properties of the glass. Niobium in the structure of the phosphate glass forms octahedra $NbO_{6/2}$ which are connected through corners with other octahedra NbO_6 or PO_4 tetrahedra [1]. Depending on the ratio of components NbO_6 may be surrounded by different structural units which generally can be written as: $(PO_4)_x \cdot (NbO_6)_{(6-x)}$ $(1 \leq x \leq 5)$.
Density, microhardness, conductivity at various temperatures and the glass transition temperature for the samples of the niobophosphate glasses has been determined. Laser recording of high-contrast optical structures has been performed on the samples. X-ray analysis of the crystallized samples has been carried out, the Raman spectra have been recorded.

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SYNTHESIS, MAGNETIC AND CATALYTIC PROPERTIES OF NICKEL POLYOL NANOPARTICLES

Martinez Rodriguez N., Suslonov V.V., Osmolowskaya O.M., Osmolowsky M.G.
Saint Petersburg State University,
Saint Petersburg, Russia
Student
nicolasmaro@mail.ru

Recently metal nanoparticles attract attention due to their unique properties and potential use in such areas as nanoelectronics and optoelectronics, catalysis, magnetic devices for information storage, and medicine. The polyol synthesis is the most promising method of obtaining such nanoparticles due to two factors: first, the procedure was carry out in non-aqueous medium and the solvent (ethylene glycol) works as protective and reducing agent; second, the nanoparticles morphology can be vary by using the chelating agents (HA) and growth inhibitors. In this work the influence of different ratios of phosphonic acid on NPs morphology and growth mechanism was studied. The nanoparticles were prepared in an inert atmosphere according to a modified polyol route, using nickel acetate as precursor and borohydride as additional reducing agent. Samples with different nickel/HA ratio both with and without borohydride were obtained. The XRD and SEM data indicated the presence of two phases: nickel nanoparticles and organic matrix. According to the TG and DSC results the temperature of thermal treatment was determined. This procedure was performed for all samples with the aim of removing the organic matrix. Magnetic measurements show that the obtained particles in the absence of additional reducing agent have a multidomain structure and they knit together. On the other hand, the particles obtained in the presence of additional reducing agent show an individual behavior and an enhancement of crystal structure. Catalytic properties were also studied using a model hydrogenation reaction of 4-nitrophenol catalyzed by nickel nanoparticles [1]. According to the kinetic measurement of phenols concentrations it was concluded that the individual nanoparticles demonstrate the best catalytic properties.

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Scientific researches were performed at the Centre of X-ray Diffraction Studies and Innovative Technologies of Composite Nanomaterials of St. Petersburg State University.

SMTP IN PHYSICO-CHEMICAL PROPERTIES OF VO_2 RODS

Mashkovcev D.N., Petukhova Yu.V., Osmolowskaya O.M., Osmolowsky M.G.

Saint Petersburg State University
Saint Petersburg, Russia
Student
mashkovtcev.dn@gmail.com

VO_2 is a perspective material for optical switchers and IR sensors, "smart" covers for glasses, electrical switchers and elements of energy-independent memory because it undergoes a semiconductor-to-metal phase transition (SMPT) at 68°C for a bulk material resulting in abrupt change of magnetic, electrical and optical properties. Also vanadium dioxide can be used as an electrode material for Li-ions batteries.

Different areas of VO_2 application require definite transition temperature. As for "smart" covers for glasses the SMPT is necessary to be near room temperature. It is well known that characteristics of SMPT depend on VO_2 morphology, which can be controlled by variation of synthesis conditions.

VO_2 rods with 80 nm thick and 1 μm length were obtained via application of original approach in hydrothermal conditions. The morphology of powders was analyzed by XRD, SEM and SSA estimation. The characteristics of the SMPT were studied by a number of physical methods: impedance spectroscopy, vibration sample magnetometry, TGA and DSC, IR spectroscopy.

At present there is no unified theory about an initiating factor of the SMPT. Therefore, the transition must be observed from several different aspects: functional properties, structural changes and thermal effects. In our case the abrupt change in magnetic and electrical characteristics was demonstrated near 10°C; the crystalline structure and IR-transmittance changed near room temperature; the thermal effects of transition was observed at about 40°C. So it is shown that the SMPT temperatures found by five independent methods do not coincide with each other and constitute a quite wide interval. Thus, a SMPT study considering only by one method does not allow to make the adequate analysis of phase transition peculiarities.

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Scientific researches were performed at the Centre of X-ray Diffraction Studies, Centre for Geo-Environmental Research and Modelling (GEOMODEL), Innovate Technologies of Composite Nanomaterials, Center of Thermal Analysis and Calorimetry and Center of Chemical Analysis and Materials Research of St. Petersburg State University.

PRIMARY PHOTOCHEMICAL PROCESSES OF HEXACHLOROPLATINATE(IV) IN ACETONITRILE SOLUTIONS

Matveeva S.G.
Voevodsky Institute of Chemical Kinetics and Combustion,
Novosibirsk, Russia
svetlana.matveeva@kinetics.nsc.ru

Nowadays, practical needs of various technological applications gave a new stimulus for the photochemistry of platinum metal complexes. Firstly, in recent years a novel method for preparing pure nanoparticles of gold, platinum and other metals was demonstrated. This method applies high-intensity laser irradiation of a solution of metallic ions or a mixed solution of several different types of ions with certain mixing ratios. Metallic nanoparticles offer a set of advantages for catalytic, optical and electronic applications. Therefore, there is a pressing interest in the facile, low cost, and environmentally friendly synthesis of metallic nanoparticles. Secondly, the fundamental problem of photocatalysis is expansion of semiconductor absorbance spectrum to the visible spectral region. One of the solutions of this problem is the doping of the semiconductor (TiO_2, CdS) surface with the nanoscale metallic platinum. It is carried out by photoreduction of hexachloroplatinate. A proper description of such systems requires the knowledge of both the heterogeneous chemistry and the photochemistry of complexes formed by metal atoms in solution. $PtCl_6^{2-}$ complex is typically used for the described applications.

Photochemistry of $PtCl_6^{2-}$ is solvent-dependent. Photoaquation with the formation of $Pt^{IV}Cl_5(H_2O)^-$ complex occurs in aqueous solutions, but the mechanism includes redox stages. In alcohol solutions the electron transfer from the solvent molecule to the light excited complex results in photoruduction with the formation of Pt(II) complexes. As for acetonitrile solutions, in the only work available in the literature [1], the conclusion was made about photosolvation with the formation of $Pt^{IV}Cl_5(CH_3CN)^-$, but the primary process was assumed to be the homolytic cleavage of the Pt-Cl bond with the escape of a chlorine atom into the solvent volume:

$$PtCl_6^{2-} \xrightarrow{h\nu} Pt^{III}Cl_5^{2-} + Cl^{\bullet} \qquad (1)$$

In this work, photochemistry of $PtCl_6^{2-}$ in CH_3CN was studied by means of nanosecond laser flash photolysis with the excitation by 4th harmonics of the YAG laser (266 nm, 5-6 ns). Two successive Pt^{III} intermediates (Fig. 1) were registered and identified as $Pt^{III}Cl_5^{2-}$ and $Pt^{III}Cl_4^-$ complexes based on quantum chemical calculations [2]. In the experiments with the addition of free Cl^- ions (up to 0.4 M) we did not observe the appearance of the $Cl_2^{\bullet-}$ radical anion. Therefore, the mechanism based on the primary process (1) should be ruled out.

The alternative primary mechanism explaining the formation of Pt(III) intermediates is the electron transfer from acetonitrile molecule to light the excited complex, similar to the case of alcohol solutions:

$$(PtCl_6^{2-}) \xrightarrow[CH_3CN]{h\nu} Pt^{III}Cl_5^{2-} + {}^{\bullet}CH_2CN + HCl \quad (2)$$

In this case, to obtain the solvated Pt(IV) complex as the reaction product, the chain mechanism of photosolvation should occur. The following mechanism of the chain photosolvation was proposed:

$$Pt^{III}Cl_5^{2-} \rightarrow Pt^{III}Cl_4^{-} + Cl^{-} \quad (3)$$

$$Pt^{III}Cl_4^{-} + PtCl_6^{2-} + CH_3CN \rightarrow Pt^{IV}Cl_5(CH_3CN)^{-} + Pt^{III}Cl_5^{2-} \quad (4)$$

$$2\,Pt^{III}Cl_4^{-} \rightarrow Pt(II) + Pt(IV) \quad (5)$$

Mechanism (2-5) explains the photosolvation of $PtCl_6^{2-}$ via the formation of two successive Pt(III) intermediates. To support the chain character of the process, the quantum yield of photosolvation caused by laser irradiation at 266 nm was measured at different conditions. The quantum yield was found to be linear with the initial $PtCl_6^{2-}$ concentration and with the reciprocal square root of the incident light intensity. These two facts give evidence of the chain mechanism of photoaquation.

Finally, the mechanism of $PtCl_6^{2-}$ photosolvation in acetonitrile is established by means of laser flash photolysis.

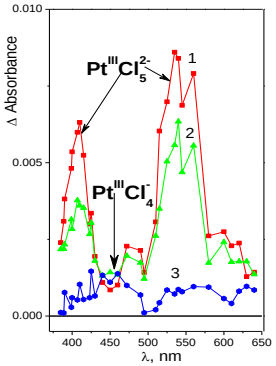

Figure 1. Intermediate absorption spectra obtained by laser flash photolysis (266 nm) of

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Acknowledgements. The financial support of the Russian Foundation of Basic Research (grant # 14-03-00692-a) is gratefully acknowledged.

PROTONATION AND HYDRATION OF LAYERED PEROVSKITE-LIKE TITANATES $A_2Ln_2Ti_3O_{10}$ IN AQUEOUS MEDIUM

Mechtaeva E.V.[1], *Rodionov I.A.*[1]

[1]Saint Petersburg State University,
Saint Petersburg, Russia
Postgraduate Student
mechtaeva.lisa@gmail.com

Layered perovskite-type oxides are crystalline compounds, which consist of perovskite layers alternating with layers having a different structure. The layered structure, as well as the ability of ion exchange and intercalation of molecules into the interlayer space, may cause high photocatalytic activity and ion conductivity. These compounds are used in Li-ion batteries and widely studied as photocatalysts e.g. for water splitting reactions. Therefore, detailed investigation of the properties of layered perovskite-type oxides, particularly their behavior in aqueous solutions with different pH, is of great importance.

Layered oxides with general formula $A_2Ln_2Ti_3O_{10}$ (A = Na, K; Ln = La, Nd) were synthesized with solid-state method under optimal conditions, which were developed in our laboratory. For all substances obtained, the possibility of ion exchange of the interlayer cation A^+ for H^+ and water intercalation into the interlayer space was examined. These processes lead to the change of both composition and structure of oxides under investigation, i.e. they have considerable influence on the properties. Therefore, the pH values at which ion exchange processes begin and occur with high rate were also determined. For this aim, we used the method of continuous potentiometric titration of $A_2Ln_2Ti_3O_{10}$ suspensions in aqueous AOH solution with hydrochloric acid. The characteristic bend on the titration curve indicates the occurrence of the ion exchange process in the appropriate pH range. It has been found that this process begins in an alkaline solution (pH=10) and at pH=7 an exchange degree of 70% is achieved. The inverse substitution of H^+ for A^+ almost doesn't occur under applied experimental conditions.

The phase composition, the amount of intercalated water, the morphology of the layered oxide particles and the degree of substitution of alkali metal for proton were controlled by powder XRD, SEM, TGA and emission spectroscopy (ICP).

Acknowledgements
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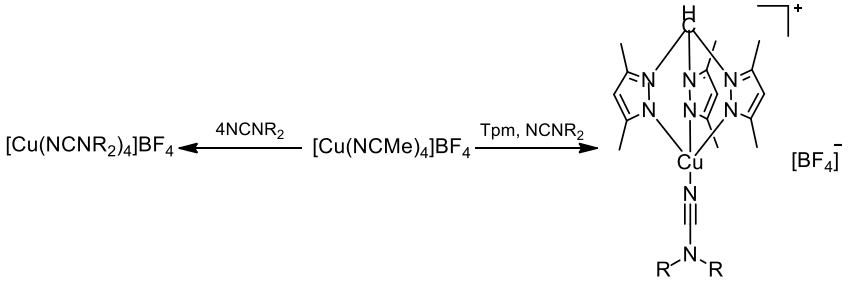
NOVEL DIALKYlCYANAMIDE COMPLEXES OF COPPER(I): PREPARATION AND STRUCTURAL STUDY

Melekhova A.A, Smirnov A.S., Bokach N.A.

Saint Petersburg State University
Saint Petersburg, Russia
Postgraduate student
annet222@mail.ru

Dialkylcyanamide complexes are known for a wide variety of transition and main-group metals, but the cyanamide copper(I) chemistry is almost unexplored and there are only a few reports describing synthesis and structure of (cyanamide)Cu(I) compounds: $[Cu(dmcn_2)(DPEphos)]BF_4$ (DPEphos = bis[2-(diphenylphosphino)phenyl]ether, dmcn = dimethylcyanamide) and $[Cu_2(dppm)_n(dmcn)_m]X$ (n = 2,3; m =1–3; X = BF_4, Cl, NO_3, ClO_4).[1,2] Moreover, no data on reactivity of cyanamide substrates at copper centers have so far been reported.



Scheme 1

In pursuit of this work, we have prepared a series of homoleptic complexes $[Cu(NCNR_2)_4][BF_4]$ (R = Me, Et, C_5H_{10}) and several monosubstituted complexes of formula $[Cu(Tpm)(NCNR_2)][BF_4]$ (Tpm = tris(3,5-dimethylpyrazolyl)methane; R = Me, Et, C_5H_{10}).

All complexes were characterized by elemental analysis (CHN), high resolution ESI^+-MS, ^1H, ^{13}C NMR and IR spectroscopic techniques, and also by single-crystal X-ray diffraction for three of them.

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MECHANISM OF FORMATION OF COPPER(II) CHLOROCOMPLEXES IN SOLUTION

Mereshchenko A.S. [1], *Olshin P.K.* [1], *Karabaeva K.E.* [2], *Panov M.S.* [1], *Skripkin M.Yu.* [1], *Tveryanovich Yu.S.* [1], *Tarnovsky A.N.* [2]

[1]Saint Petersburg State University,
[2]Bowling Green State University
Saint Petersburg, Russia
Postdoctoral fellow
andereym@chem.spbu.ru

The photochemistry of $CuCl_4^{2-}$ complex in acetonitrile and dichloromethane was studied by means of UV-vis time-resolved transient absorption spectroscopy upon 420-nm excitation into LMCT state in a wide time domain (20 ps – 8 μs) in conjunction with DFT calculations. The main photoreaction channel is ionic dissociation with formation of the copper(II) trichlorocomplex, $CuCl_3^-$, and a chloride-ion. In acetonitrile, the $CuCl_3^-$ complex rapidly reacts with the acetonitrile molecule to form $[CuCl_3CH_3CN]^-$ complex in less than 20 ps. In dichloromethane, the copper(II) trichlorocomplex complex does not form solvatocomplex exciting in a $CuCl_3^-$ form. The copper(II) trichlorocomplex complex rapidly recombine with the chloride ion to reform parent $CuCl_4^{2-}$ complex. The bimolecualar rate constants of the recombination reaction, k_q, are equal to $9.0 \cdot 10^7$ and $5.3 \cdot 10^8$ $s^{-1}M^{-1}$ in acetonitrile and dichloromethane, respectively. In acetonitrile, the recombination reaction is ligand exchange process, which described by the associative interchange mechanism with the formation of the intermediate pentacoordinated complex, $[CuCl_4CH_3CN]^{2-}$. In dichloromethane, recombination reaction is simple one-step addition reaction. In both solvents, recombination reaction is controlled by potential energy barrier, 30.5 and 25.0 kJ mol^{-1} in acetonitrile and dichloromethane, respectively.

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OXYGEN NONSTOICHIOMETRY AND DEFECT STRUCTURE IN $SrFe_{1-x}Mo_xO_{3-\delta}$

Merkulov O.V.[1], *Naumovich E.N.*[2], *Markov A.A.*[1], *Patrakeev M.V.*[1], *Bouwmeester H.J.M.*[3], *Leonidov I.A.*[1], *Kozhevnikov V.L.*[1]

[1]Institute of Solid State Chemistry, UB RAS,
[2]Institute of Power Engineering, Thermal Processes Department, Poland,
[3]University of Twente, Department of Science and Technology, The Netherland
Ekaterinburg, Russia
PhD Student
Merkulov@ihim.uran.ru

In recent years, iron-molybdenum perovskite-like oxides are considered as candidate materials for cathodes and anodes in SOFCs with hydrocarbon feed as well as electrodes in symmetrical SOFCs [1]. It is now widely recognized that oxygen stoichiometry, concentration and equilibrium of ion and electron defects formed in response to changes of temperature and oxygen partial pressure in the environment either control or strongly influence the properties of oxide solids.

The synthesis of the oxide series $SrFe_{1-x}Mo_xO_{3-\delta}$, where x = 0, 0.07, 0.15, and 0.25, was carried out with the using of a self-propagating combustion of organo-metallic precursors. The obtained powders were sintered in air at 1200°C. The oxygen content is measured by means of a coulometric titration technique at oxygen partial pressure varying from 10^{-20} to 0.5 atm within temperature range 800–950°C. The experimental data give evidence to the increase in concentration of *n*–type charge carriers with molybdenum content in $SrFe_{1-x}Mo_xO_{3-\delta}$. The thermodynamic modeling of the obtained non-stoichiometry data was performed based on red-ox reactions of iron and molybdenum cations, charge disproportionation of Fe^{3+} cations and electron exchange between iron and molybdenum sites. It is shown that partial replacement of iron for molybdenum is accompanied with strong decrease in concentration of Fe^{4+} cations, and the appearing electron *n*–type carriers are preferably localized on molybdenum cations. The results of atomistic simulations are indicative of strong bonding of molybdenum cations with surrounding oxygen anions. As a result, oxygen anions in molybdenum coordination are excluded from exchange with gas phase oxygen.

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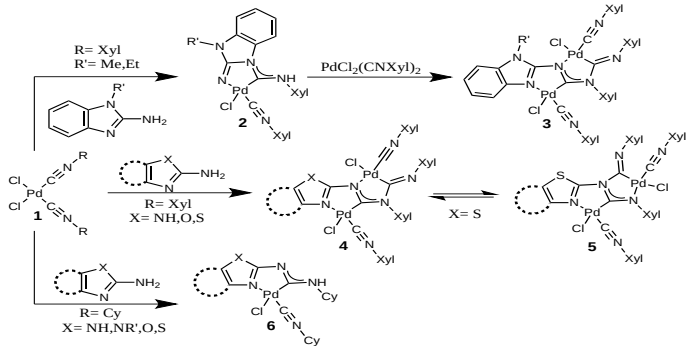
Acknowledgements

This work was partially funded by the Russian Foundation for Basic Research (grant №13-03-00931) and Polish Strategic Program NCBiR, project OZE. The authors are also grateful to the Ural Branch of RAS for support of this study through the regional programs (grants №12-Y-3-1005 and №12-3-2-002 Arctic).

REACTIONS OF PALLADIUM(II) ISOCYANIDES COMPLEXES WITH α-AMINOAZAHETEROCYLES

Mikherdov A.S., Kinzhalov M.A., Luzyanin K.V., Boyarskiy V.P.
Saint Petersburg State University,
Saint Petersburg, Russia
Student
asm93@yandex.ru

Coordination of isocyanides to the metal center leads to dramatical change in their reactivity. It makes possible the addition to triple bond CN the weak nucleophiles that usually don't react with free isocyanides. In our research group it was previously found that addition of palladium(II) isocyanides complexes to α-aminoazaheterocyles leads to carbene complexes which themselves are nucleophiles and able to attack another isocyanide complex with the formation of binuclear complexes[1].



In this research we have shown that the reaction may lead to different types of mononuclear (**2**, **6**) or binuclear (**3**, **4**) complexes depending on a substituent in isocyanide and a structure of α-aminoazaheterocyle. There is an equilibrium between products **4** and **5** at coupling of complex **1** (R = Xyl) with sulfur-containing nucleophiles (X = S). It means the reaction proceeds via splitting of the C-N bond in the diamino carbene fragment. This is the first example of reversible formation of diamino carbene.

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THE POLYOL SYNTHESIS OF COPPER NANOPARTICLES AND THEIR ANTIBACTERIAL ACTIVITY

Mingabudinova L.R., Osmolowskaya O.M., Prikhod'ko I.V., Osmolowsky M.G.

Saint Petersburg State University,
Saint Petersburg, Russia
Student
Leila.Mingabudinova@gmail.com

The bacteria caused by dangerous infectious affects for us every day. Despite improved sanitation, cases of disease remain very high. In order to solve this problem a number of methods are used. The most common ones, such as wet cleaning and use of a special antibacterial alloys are not efficient enough. One of the modern approaches is the use of silver, but it is expensive. As alternatively it is possible to use copper nanoparticles (NPs), which are cheaper.

Polyol synthesis is one of the most commonly used methods to obtain metal NPs because the synthesis carry out in nonaqueous medium and the NPs surface is protect from oxidation. In a typical procedure ethylene glycol is used as the solvent and a reducing agent for the metal ions. The high viscosity and the chelating properties of ethylene glycol are ideal for controlling nucleation and growth of nanoparticles as well as for stabilizing the particle surface and avoiding agglomeration.

The particle size is controlled by varying the synthesis parameters such as concentration and synthesis duration. According to XRD data we obtain the copper nanoparticle with high crystallinity. SEM and SSA data are shown that nanoparticles are monodisperse and has the form of spherical plates. The nanoparticle sizes varied from 40 to 300 nm

It is known that copper has antibacterial properties. A number of our experiments to prove efficiency of the obtained copper nanoparticles against microorganisms such as infusorians were performed. We also found a range of working NPs concentrations. Further experiments are planned with the bacteria E. Coli that is promising for the use of copper nanoparticles for protection from harmful effect of various pathogens.

Acknowledgements

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NEW SORBENT FOR PROTEOMICS BASED ON ALUMINUM OXIDE, OBTAINED BY MICROWAVE TREATMENT

Mitrofanov A.A.
Saint Petersburg State University
Saint Petersburg, Russia
Student
mitrofanov_a@icloud.com

In recent years high-selective methods of release of organic and bioorganic compounds from biological samples and objects of environment actively developing [1]. Sorption methods where using high-porous nanodimensional sorbents achieve a wide popularity. Search of approaches to receiving such objects is carried out still [2].

As a part of ongoing project the method of synthesis of nanodimensional of aluminum oxide was developed and optimized by the synthesis from water solutions of aluminum nitrate and urea induced by microwave treatment.

The structure and morphology of the received samples were studied by methods of laser diffraction, the X-ray phase analysis, the scanning electronic microscopy (SEM), thermogravimetric analysis a differential calorimetry and low-temperature adsorption of nitrogen (BET).

For determination of a specific surface, the method of low-temperature adsorption of nitrogen was used. The specific surface calculated on it matters about 450 m^2/g. By method of the X-ray phase analysis it was established that the sizes of crystallites don't exceed 10 nanometers that will be coordinated with the values of the average size of particles (6-7 nanometers) calculated from a specific surface. With the help of the SEM method the developed surface morphology is proved.

Sorption of insulin-glargine on the received porous material was studied at different temperatures, thermodynamic parameters of process of sorption are calculated. Sizes of change of an enthalpy and entropy of equilibrium sorption-desorption of insulin on the synthesized aluminum oxide are 130 kJ/mol and 530 J/mol·K respectively.

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Research Centre for X-ray Diffraction Studies
Centre of Innovative Technologies of Composite Nanomaterials
Resource center for Geo-Environmental Research and Modeling (GEOMODEL)

NOVEL PEROXO METHOD OF PREPARATION OF COMPOSITE SILICA-TITANIA SPHERES

Morozov R.S.[1], *Krivtsov I.V.*[1,2], *Avdin V.V.*[1], *Garcia J.R.*[2]
[1] South Ural State University, Chelyabinsk, Russia;
[2] University of Oviedo, Oviedo, Spain
Chelyabinsk,Russia
Post graduate student
yanatulskoi@mail.ru

Spherical particles containing titanium dioxide have a wide range of applications in the fields of heterogeneous oxidative catalysis, photocatalysis, chromatography materials. Research in this area permanently involves preparation of new composite materials based on TiO2. Formation of the composites is aimed to enhance surface area, surface acidity, distribution of active sites and to suppress TiO2 crystallization under thermal treatment. We have developed a new way of synthesis of nanoscale silica-titania composite spheres using titanium peroxo complex, which has recently been applied to prepare SiO2/TiO2 photocatalysts[1] .

The essence of the proposed peroxo-mediated technique is the precipitation of aqueous peroxo titanate complex and tetraethylortosilicate (TEOS) in the alkaline water-alcohol solution. The size of the spherical particles is easily manipulated by the choice of the solvent and varies in the range of 100-500 nm. The porous characteristics of the silica-titania composites are controlled by the post-synthetic treatment. The as-prepared and thermally treated composites are non-porous and have low specific surface area, about 10 m^2g^{-1}. The post-synthetic hydrothermal treatment favors increasing their specific surface area more than 10 times, while retaining spherical morphology and narrow pore-size distribution.

Formation of highly homogeneous silica-titania composites, in terms of Si-O-Ti bonds presence, was verified by XPS, FTIR, DR UV spectroscopy and TEM observations. The obtained material is of great interest for various applications such as heterogeneous catalysis and adsorption.

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LUMINESCENT SILICA NANOPARTICLES FOR SENSING

Mukhametshina A.R.[1,2], *Mustafina A.R.*[1], *Gorbatchuk V.V.*[2]

[1] A.E. Arbuzov Institute of Organic and Physical Chemistry
[2] Kazan Federal University
Kazan, Russia
Postgraduate student
alsu_mukhamet@mail.ru

Today promising direction of nanotechnology is creation of smart colloidal systems, which can change their properties in the presence of substrates. Luminescent lanthanide-doped silica nanoparticles are of great interest to researchers and can be used in biochemical analyses as biomarkers and biosensors.

The present work introduces the easy modification of the water-in-oil microemulsion procedure aimed at the doping of the Tb(III) complexes within core or shell zones of the silica nanoparticles (SNs), which are designated as "core-shell", "shell", and "core". The dye molecules, chelating ligands and copper ions were used as the quenchers of Tb(III)-centered luminescence. Two possible quenching mechanisms (dynamic and static mechanisms) of Tb(III) luminescence were shown, where quenching depends on distribution of Tb(III) complexes in silica matrix. The luminescence of "core" SNs remains unchanged under the binding of the quenchers at the silica/water interface. The quenching through dynamic mechanism is more significant for "core-shell" and "shell" SNs. Both "core-shell" and "shell" SNs have enough percentage of the Tb(III) complexes located close to the interface for efficient quenching through the energy transfer. The quenching through the ion or ligand exchange is most efficient for "core-shell" SNs due to the greatest percentage of the Tb(III) complexes at the silica/water interface, which correlates with the used synthetic procedure. The highlighted regularities introduce the applicability of "core-shell" SNs used as silica beads for phosphatidylcholine bilayers in sensing their permeability toward the quenching ions.

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GOLD NANOWIRE-BASED CHEMIRESISTORS

Muratova I.S.[1], *Mourzina Y.G.*[2], *Offenhäusser A.*[2], *Mikhelson K.N.*[1]

[1]Saint Petersburg State University, Saint Petersburg, Russia
[2]Forschungszentrum Jülich, Jülich, Germany
PhD student
muro4ka15@mail.ru

Ultrathin metal nanowires (NWs) with diameter < 10 nm are of interest for various applications, in particular due to high spatial resolution of measurements, high surface area and sensitivity when NWs are used in sensor arrays. This work was focused on the techniques to assemble gold NWs on sensor chips and on the study of the gold NW sensors as chemiresistors.

Two techniques were explored: (i) applying pre-synthesized NWs to electrodes using a microfluidic channel (MFC), and (ii) a direct synthesis technique (DST) when NWs were synthesized directly on the electrodes.

The sensor chips were prepared on a silicon wafer using e-beam lithography. Each chip contained a number of gold electrodes with spacing of 400, 600, 800 nm, and 1 μm. Next, ultrathin gold NWs (Fig. 1) were deposited on chips using either MFC or DST technique. The latter one ensured much better contact and adhesion of NWs to the electrodes, as compared with MFC technique. PMMA insulation was applied leaving open only NWs as sensing elements (Fig. 2).

The resistivity of ultrathin NWs is dependent on adsorption of species on the NW surface, and this is the origin of the chemiresistor response. Therefore, current-voltage measurements were performed in aqueous solutions of halogenides: NaF, NaCl, NaBr, NaI and pyridine over concentration range 10^{-5}–10^{-3} M. Fluoride showed only negligible adsorption, therefore 10^{-3} M NaF has been used as a background electrolyte in further measurements. The sensors also showed response to dopamine hydrochloride (DA) in phosphate buffer solution, pH 7. The response is linear vs. log of the DA concentration over the range 10^{-8} - 10^{-5} M so that the sensor appears promising for biomedical applications.

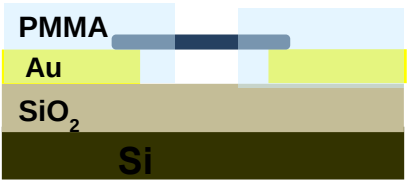


Fig 2. Electrode scheme

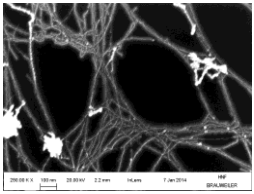


Fig 1. SEM microphotographs of Au NWs.

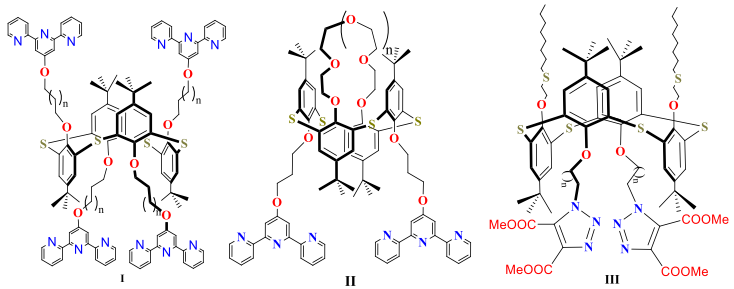
Financial support from the St.Petersburg State University (grant 12.38.235.2014) is greatly acknowledged.

MULTIFUNCTIONAL THIACALIX[4]ARENE DERIVATIVES BEARING METAL-BINDING FRAGMENTS FOR DESIGN OF HIGHLY LUMINESCENT SYSTEMS

Muravev A.A.[1], *Galieva F.B.*[2], *Soloveva S.E.*[1], *Antipin I.S.*[1,2], *Konovalov A.I.*[1]

[1]Arbuzov Institute of Organic and Physical Chemistry,
[2]Kazan (Volga Region) Federal University, Butlerov Institute of Chemistry
Kazan, Russia
Research Fellow
antonm@iopc.ru

The design of supramolecular fluorescent systems is of top-priority directions in the development of high-performance chemosensors that are able to perform specific functions in response to environmental parameters (pH, temperature, ions, voltage). Calixarenes are the scaffolds that may provide high selectivity for metal ion binding and include various recognition units that are specifically preorganized [1, 2].



I II III

This work focuses on the synthesis of lower-rim substituted thiacalixarenes containing crown-ether, as well as heterocyclic (triazole, terpyridine) fragments, and study of fluorescence with lanthanide ions. It was shown that lanthanide luminescence is greatly affected by the nature of metal-binding unit (I), aggregation of calixarene molecule (concentration dependence) through the metal-organic framework (I, II) or micellization mechanism (III), and the presence of other metal ions (II).

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ELECTROCRYSTALLIZATION OF DENDRITIC ZINC DEPOSITS UNDER PULSATING AND CONSTANT POTENTIAL

Nikitin V.S., Ostanina T.N.

Ural Federal University
Yekaterinburg, Russia
Post Graduate
nikitin-viachieslav@mail.ru

Electrolytic zinc powders due to its high purity and dendritic structure are used in manufacturing of catalysts, zinc-rich composite materials, electrodes of electrochemical power sources. Electrolytic method of producing powdered metals allows to regulate size and structure of particles by changing the parameters of electrolysis (i.e. the concentration of solution, polarization regime). In the present research the influence of parameters of pulsating potential (PP) electrolysis on the process of dendritic zinc deposits' electrocrystallization in zincate electrolytes (0.3 and 0.6 mol/dm^3 of ZnO and 4 mol/dm^3 of NaOH) was studied. PP regime was represented by alternating pulses of constant potential and pauses, during which the electrode was under initial equilibrium potential. Durations of pause and polarization pulse were varied as 10, 20, and 30 s. The amplitude of the potential in solutions with the zinc ions concentration of 0.3 and 0.6 mol/dm^3, respectively was –0,38 and –0,46 V relative to the unpolarized zinc electrode. During pauses the anodic currents were registered, which occurrence is explained by the shift of equilibrium potential of small curvature radius dendrite tops to the negative area compared to the equilibrium potential of the smooth electrode. It is determined that the growth rate and morphology of dendritic zinc deposits are significantly influenced by the ratio of pulse to pause durations $k = t_{imp} / t_p$. With enhancement of k ratio from 1/3 to 3/1 there is an increase of as cathodic currents during pulses as anodic currents during pauses, thus the density of deposits decreases and approaches to the density of those obtained under constant potential. Microstructure of deposits obtained in 10 minutes under PP electrolysis ($k = 1$) in a solution with concentration of zinc ions 0.3 mol/dm^3, is of plain dendrites with massive accrete branches formed by distinct hexagons. Particles obtained under the potentiostatic mode, have branched nanoscale structure that corresponds to lattice of hexagonal type.

The research is (partly) carried out using facilities of the Shared Access Center "Composition of Compounds" of IHTE UB RAS.

NANODISPERSED CATALYST OBTAINED FROM POLYMER COMPLEXES OF TRANSITION METALS WITH SALEN-TYPE LIGANDS.

Novozhilova M.V.[1], Peixia Yang, Gorislov G.G.[1], Kuznetsov N.A.[1], Levin O.V.[1]

[1]Saint Petersburg State University,
[2]Harbin Institute of Technology, Harbin, China,
Saint Petersburg, Russia
Ph.D. student
marya20154@mail.ru

Fuel cells have been one of the most expected technologies to solve many economic and ecologic problems of hydrocarbon economy. However, at present, we could speak only about perspectives of this technology, due to the high cost of energy produced by fuel cells. The lifetime of a fuel cell is limited by poisoning of catalysts during storage and operation. The particles of platinum are usually used for these cells as a catalyst, but it might be promising to replace them with their cheaper analogues, such as transition metals. A catalyst based on cheap Ni compounds could be used for direct alcohol, alkaline or direct borohydride fuel cells. These types of cells are considered as the most promising types for mass production. Many methods to produce fuel cell catalysts exist nowadays, but most of them have some disadvantages: a high size of catalyst particles, an irregular structure or a complicated synthesis route.

We propose a method to produce fuel cell electrodes, in which the catalyst could be kept in an inactive, stable state for a long time as a polymer film of metal complexes with a Schiff base ligand on the substrate layer. Deposition of such complexes is simple and described for a variety of substrates. We have developed several methods of obtaining an active catalyst from these polymers: alkaline hydrolysis and thermal decomposition. It was demonstrated that the catalyst prepared by any of these methods consists of nanosized particles with a necessary spacing between particles which are already fixed on the substrate surface. The polymeric structure of the Schiff base complexes ensures enough distance between the nucleation centers during hydroxide formation, so no agglomeration of nanoparticles is observed. Nanoscale particles have catalytic activity for some reactions such as oxidation of alcohols and electroreduction of oxygen. The activity of the catalyst for oxidation of alcohol does not depend on the method of preparation of the catalyst, but – on the ligand structure; while the reaction of electroreduction of oxygen proceeds better over a catalyst obtained in a thermal way.

Acknowledgements

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INVESTIGATION OF MOBILITY OF ALKALINE IONS IN LAYERED PEROVSKITE-LIKE OXIDES $ALnTiO_4$ (A = Li, Na; Ln = La, Nd)

Petrov A.A.

Saint Petersburg State University
Saint Petersburg, Russia
Student
basolon@gmail.com

Investigation of mobility of alkaline ions in layered perovskite-like oxides $ALnTiO_4$ (A = Li, Na; Ln = La, Nd). The compounds $ALnTiO_4$ (A = Li, Na; Ln = La, Nd) have completely ordered structure and consist of perovskite slabs interleaved with alkaline cations.

$NaLnTiO_4$ (Ln = La, Nd) were prepared by high-temperature solid-state reaction method. $NaLnTiO_4$ were obtained with reaction in melt of $LiNO_3$. All the compounds were characterized using X-ray diffraction technique.

Conductivity of $ALnTiO_4$ was measured by complex impedance spectroscopy between 1 Hz and 100 MHz in the temperature range of 250 – 650°C. Measurements were carried out in nitrogen atmosphere.

It was found that conductivity of $NaLaTiO_4$ is $2{,}39 \cdot 10^{-6}$ S/cm at 300°C and reaches up to $6{,}31 \cdot 10^{-3}$ S/cm at 600°C whereas conductivity of $NaNdTiO_4$ is $4{,}65 \cdot 10^{-7}$ S/cm at 300°C and $3{,}40 \cdot 10^{-5}$ at 600°C. Calculated values of activation energy of the conductivity process are 1,15 eV for $NaLaTiO_4$ and 0,62 eV for $NaNdTiO_4$.

The calculations were made with CASTEP module of software package Materials Studio. Basis set was limited with cut-off value of 400 eV. The calculated charges were determined according to Mulliken scheme. Diffusion coefficients of interlayered cations were calculated by means of classical molecular dynamics. UFF model was used for parameterization of the force filed, wherein charges defined in DFT calculations were used.

It was determined that atoms of lanthanide, oxygen and titanium make minor oscillations around equilibrium states, whereas sodium atoms are mobile in the layers perpendicular to *c* axis between perovskite slabs. The mobility of sodium ions in $NaLaTiO_4$ was higher, than in $NaNdTiO_4$.

Acknowledgements

The research was carried out provided by Resource Centres "Computer Centre of SPbU" (http://cc.spbu.ru), "Centre for X-ray Diffraction Studies" (http://xrd.spbu.ru), and "Centre for Thermogravimetric and Calorimetric Research" (http://thermo.spbu.ru).

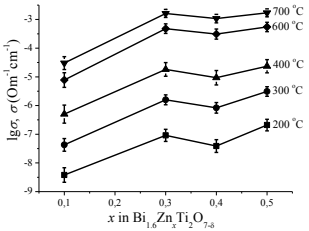
SYNTHESIS AND PROPERTIES OF ZINC-DOPED BISMUTH TITANATE WITH PYROCHLORE TYPE CRYSTAL STRUCTURE

Piskaykina M. M.
Ukhta State Technical University
Ukhta, Russia
Post-graduate student
PiskaykinaMM@yandex.ru

The 3d -metal doped of the $Bi_2Ti_2O_7$ allows to obtain compounds with the pyrochlore structure, which are stable in a wide temperature range, although the $Bi_2Ti_2O_7$ itself is stable in a narrow temperature range $t \leq 612$ °C [1, 2], what prospects for its use as a high temperature capacitor is limited [3] that is limited prospects to use it as a high temperature capacitor [3].

In the present paper zinc-doped bismuth titanate with the pyrochlore-type structure (synthesized by the method of combustion of nitrate-organic precursors) has been prepared for the first time and a range of single phase stability for $Bi_{1.6}Ti_2Zn_xO_{7-\delta}$ ($0.1 \leq x \leq 0.5$) has been defined. The melting temperature with the following decomposition of the compound has been determined ($t \sim 1235$ °C for $Bi_{1.6}Ti_2Zn_{0.1}O_{7-\delta}$) by the differential scanning calorimetry (DSC) method. The distribution of the zinc atoms on bismuth cation sites not less than one-half of their number has been determined by comparison of pycnometric and x-ray densities.

The total conductivity of $Bi_{1.6}Ti_2Zn_xO_{7-\delta}$ ($0.1 \leq x \leq 0.5$) with the pyrochlore-type structure has been investigated. The temperature dependence of the conductivity obeys the Arrhenius law with the activation energy $E_a \sim 1.10$ eV. In the temperature range 160-760 ° C the conductivity of the zinc-doped sample grows up when zinc content increased to x = 0.3. We assume it may be associated with an increase of the mobile oxygen atoms (O`) number.



Picture 1. The concentration dependence of the conductivity $Bi_{1.6}Ti_2Zn_xO_{7-\delta}$ (1 kHz).

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THE MORPHOLOGY, MAGNETIC AND ELECTRICAL PROPERTIES OF CROMIUM DOPED VO_2

Petukhova Yu.V., Sarnovsky-Gonsalez A.D., Osmolowskaya O.M., Osmolowsky M.G.
Saint Petersburg State University
Saint Petersburg, Russia
Student
yulia.petukh.ova@yandex.ru

Bulk vanadium dioxide undergoes a semiconductor-to-metal phase transition (SMPT) at 340 K resulting in abrupt change of magnetic, electrical and optical properties. Due to this fact, VO_2 becomes a perspective material for optical switchers and IR sensors, «smart» covers for glasses, electrical switchers and elements of energy-independent memory. What is more, vanadium dioxide has a rutile structure so that the different ions are able to intercalate easily into the lattice. Therefore, in recent years this material can be used as an electrode material for Li-ions batteries.

It is known that characteristics of SMPT depend on VO_2 morphology. As we showed before the temperature of the transition can be lowered by doping [1]. But there is one more way to regulate morphology of the product obtained. The introduction of a chelating agent leads to change in growth mechanism and thereby influences on particles shape and size. So a hydrothermal synthesis of size controlled Cr-doped VO_2 particles in presence and in absence of the chelating agent is reported. The morphology of powders obtained was analyzed by XRD, SEM and SSA estimation. Its electrical properties were studied by impedance spectroscopy. The temperature dependence of magnetization was measured by VSM.

It is shown that the particles shape changes from ribbons and microplates obtained before with large amounts of dopant [1] to carambola-like and sponge-like spheres with the chelating agent and smooth hollow spheres without one. The SMPT in samples synthesized become less expressed and the temperature of the transition lowers to 200 K with the chelating agent and 150 K without one compared to the bulk material.

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Scientific researches were performed at the Centre of X-ray Diffraction Studies, Centre for Geo-Environmental Research and Modelling (GEOMODEL) and Innovate Technologies of Composite Nanomaterials of St. Petersburg State University.

DEVELOPMENT OF SOFC UNIT CELL WITH THIN-FILM SOLID PROTON ELECTROLYTE

Plekhanov M.S[1,2], *Kuzmin A.V.* [1,2], *Stroeva A.Y.*,

[1]Institute of High-Temperature Electrochemistry of the Ural Branch of the Russian Academy of Science
[2]Ural Federal University
Yekaterinburg, Russia
Student
plexanovmax@mail.ru

At present alternative sources of energy are developed actively and one of perspective directions in this area is the development of solid oxide fuel cells (SOFC). SOFCs have the advantages compared to conventional energy sources, such as the environmental friendliness, a wide range of used fuel and others. SOFCs have a high coefficient of efficiency (~ 70%) due to direct conversion of chemical energy into electrical energy. Classic SOFCs are operating at high temperatures (800-1000°C) in order to avoid ohmic losses at an electrolyte. It significantly reduces the usability and increases the cost of the SOFC. Proton oxide electrolytes have sufficient conductivity at a low temperatures thanks to the relatively low activation energy. The use of thin-film technology allows to increase the conductivity by reducing the thickness of the electrolyte, and this has a positive effect on the polarization resistance of the electrode. Thus, the creation of SOFCs with a thin film proton electrolyte can significantly reduce their operating temperatures without loss of performance.

The present work is devoted to the development of basic technology for the creation of the SOFC unit cell with thin film proton electrolyte based on $LaScO_3$. Oxides with p-type conductivity based on lanthanum-strontium manganite have been investigated as cathode materials, and metall-ceramic composite materials on the base of the electrolyte with iron, nickel and copper have been used as an anodes. As a part of the research were carried out the study of the chemical interactions between the electrode and electrolyte and between the individual components of the composite anodes. The dependences of the linear expansion of the electrodes and the electrolyte in SOFC operating conditions were obtained. Regularities of the deposition of films from alcohol solutions of salts on porous electrode substrates were examined during changing parameters such as the concentration of oxides and thickener, heat treatment temperature, methods of film deposition and the number of layers. Continuous, gas-tight coatings have been obtained.

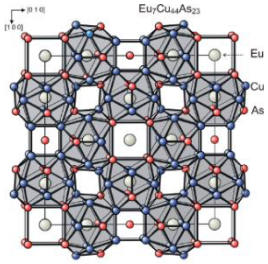
Acknowledgements: This work was supported by RFBR grant №14-29-04013. The facilities of the shared access center "Composition of Compounds" IHTE UB RAS were used in this work.

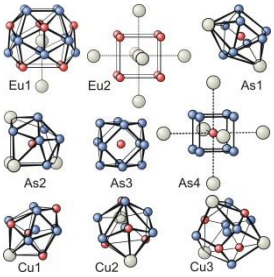
NEW SOLID SOLUTIONS WITHIN THE $Eu_7Cu_{44}As_{23}$ STRUCTURE TYPE AND THEIR MAGNETIC PROPERTIES

Plokhikh I., Charkin D., Shevelkov A., Verchenko V., Kazakov S., Ignat'ev. I.

Lomonosov Moscow State University
Moscow, Russia
Student
ig.plohih@yandex.ru

The systems alkaline earth – coinage metal – pnictogen host many attractive and peculiar ternary compounds. In heavier pnictides and also in phosphides, europium adopts the oxidation state +2 and behaves as a structural and electronic analog of alkaline earth metals, forming isostructural compounds. The semi-filled 4*f* level of Eu^{2+} gives rise to pronounced, sometimes outstanding, magnetic phenomena. Our recent studies resulted in two ternary arsenides, $Eu_7Cu_{44}As_{23}$ and $Sr_7Cu_{44}As_{23}$. Their crystal structure represents a new filled version of the $BaHg_{11}$ motif with occupied cubic voids. In the present study, we investigated the crystal chemical of the structure type *via* searches of both new representatives and solid solutions based on the $Eu_7Cu_{44}As_{23}$ prototype.





The synthesis was performed *via* solid-state routes, starting from elements, in evacuated silica tube. The synthesis temperatures vary with the compositions. Complete solid solutions was found in the $Eu_{7-x}Sr_xCu_{44}As_{23}$ and $Eu_7Cu_{44}As_{23-x}Sb_x$ systems, ending in a new compound $Eu_7Cu_{44}Sb_{23}$. The variation of the cubic lattice parameter *vs.* composition is linear in agreement with Vegard's rule starting from 16.6707(2) Å ($Eu_7Cu_{44}As_{23}$) to 16.7467(2) Å ($Sr_7Cu_{44}As_{23}$) and 17.436(5) Å ($Eu_7Cu_{44}Sb_{23}$). Antimony occupies sequentially As3 As4, As1 and As2 sites. Other solid solutions are restricted and are observed in series $Eu_{7-x}(Ca,Ce,Na)_xCu_{44}As_{23}$ ($x < 1$) and $Eu_7Cu_{44-y}Ni_yAs_{23}$ ($y < 10$). In both cases, site preference is observed (for Eu1 and Cu3, respectively). While $Eu_7Cu_{44}As_{23}$ exhibits ferromagnetic ordering below 17.5 K, the Eu → Ce as well as As → Sb substitutions lead to a slight decrease of the Curie point contrary to Cu → Ni where a notice increase of this temperature is observed.

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COLLOIDAL DISPERSIONS OF TANTALUM TRISULFIDE

Poltarak P.A.[1,2], *Artemkina S.B.*[1,2], *Fedorov V.E*[1,2]

[1]Novosibirsk State University,
[2]Nikolaev Institute of Inorganic Chemistry SB RAS
Novosibirsk, Russia
Student
poltarak_pa@mail.ru

Currently, considerable interest is paid to research nanomaterials and particularly methods of their preparation. One interesting approach is the dispersion method, which is based on the fragmentation of liquid or solid samples in an inert medium. Examples of dispersion methods are mechanical grinding, micromechanical cleavage ("scotch-tape" method), ultrasonication. In our work, we used the latter method for preparation of colloidal dispersions TaS_3.

Tantalum trisulfide is a quasi-one-dimensional compound [1]. Its structure is built from chains of tantalum atoms which are in trigonal-prismatic environment of sulfur atoms. Under certain conditions, crystalline TaS_3 undergoes a Peierls transition, leading to the formation of charge density waves. As a result, the temperature dependence of the electrical conductivity and thermal conductivity are dramatically changed [2]. Tantalum trisulfide crystallizes in the form of long thin needles, which are not manufacturable. Therefore, in order to use the interesting properties of TaS_3 one must learn to convert it into structures with controlled shape and size, in particular, to obtain thin films of material. A promising method in this field is to obtain a colloidal dispersion of TaS_3 with ultrasound. The advantage of ultrasonication is that its implementation does not require expensive reagents and devices.

In this work we studied the ability of tantalum trisulfide to form colloidal dispersions in various organic media under the influence of ultrasound. Optimal dispergation time and suitable dispersion media have been selected. For the prepared dispersions the kinetic stability, the particle size and shapes, as well as the spectroscopic characteristics have been studied. For films prepared from the dispersions, the crystal structure and spectroscopic characteristics were confirmed.

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Acknowledgements

The study was financially supported by Russian Scientific Foundation (Grant RSCF No. 14-13-00674).

SYNTHESIS OF IRON AND MAGNETITE NANOPATICLES IN THE PORES OF MESOPOROUS SILICA MCM-41 AND INVESTIGATION OF MAGNETIC PROPERTIES OF THE RESULTING COMPOSITES.

Ponomareva A. N.

Saint-Petersburg State University
Saint-Petersburg, Russia
postgraduate student
ponomareva2710@gmail.com

The creation of functional materials based on new composite nanomaterials with desired physical, chemical and structural parameters is one of the most important issues of modern science. Nanocomposite materials can be obtained by synthesis of nanoparticles in the pores of a solid matrix. Magnetic microcarriers containing superparamagnetic nanoparticles of iron or iron oxides are particularly interesting. If we get an array of magnetic particles in ordered solid matrices, such material will be used as a magnetic sorbent, particles for drug delivery, in a number of methods of diagnosis and therapy; for example, in magnetic resonance imaging, as well as magnetic recording media.

The aim of this work is to develop methods for the synthesis of iron and magnetite nanoparticles in the pores of mesoporous silica MCM-41 and investigation of the dependence of magnetic properties of nanocomposites MCM-41/Fe and MCM-41/Fe_3O_4 on the silica pore radius.

During the study we synthesized mesoporous silica MCM-41 41 with different pore diameters (from 3.3 to 5.1 nm). The resulting silica was investigated by SAXS and the specific surface area and specific pore volume were measured.

Iron and magnetite nanoparticles were synthesized by vacuum impregnation to obtain magnetic material in the pores of silica MCM-41. The nanocomposite materials (MCM-41/Fe and MCM-41/Fe_3O_4) were investigated by SEM and Mössbauer spectroscopy. The measurements of magnetic properties of the nanocomposites were also carried out.

The analysis of magnetic properties showed that the synthesized iron and magnetite nanoparticles are superparamagnetic. The dependence of magnetic properties of nanocomposites MCM-41/Fe and MCM-41/Fe_3O_4 on the pore radius of silica MCM-41 was also studied. It was found that the saturation magnetization of the obtained materials increases with the increase of the diameter of the pores mesoporous matrix MCM-41.

SORPTION COMPLEXES OF REE IN THE WEAKLY BASIC ANIONITE

Ponomareva M.A., Cheremisina O.V.
National mineral resources university (University of mine)
Saint Petersburg, Russia
Assistant of the Department of General and Physical Chemistry
mashulka-05@mail.ru

In this paper we studied the sorption of cerium, yttrium and erbium in the form of anionic complexes with Trilon B on a weakly basic anion D-403. Anionite D-403 is a polystyrene chelate anion exchange resin with active functional groups in the form of a tertiary nitrogen atom with hydroxy group in the β, γ, δ positions that reduce the inductive effect of the lone electron pair.

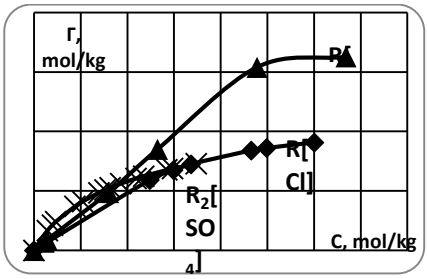
Anion exchange resin was converted to nitrate, chloride or sulfate form before the experiment. The sorption value of EDTA rare-earth ions was determined under statistical conditions with a solution capacity of 20 cm^3, a sorbent capacity of 4 cm^3, and a temperature of 298 K by alternating concentrations at pH 3. The content of cerium, yttrium and erbium was determined spectrophotometric method and X-ray spectroscopy on an X-ray fluorescence spectrometer.

Sorption value (Γ, mol/kg) was calculated using formula:

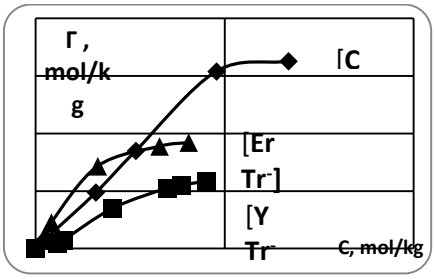
$$\Gamma = \frac{(C_0 - C_\infty) \cdot V \cdot \rho}{m}$$

where C_0 and C_∞ are the initial and equilibrium concentrations of REE ions in solutions, respectively, in mol/kg; V is the solution capacity (20 cm^3); ρ is density (1,05 g/cm3); m is the mass of dry anionite ($2{,}92 \cdot 10^{-3}$ kg).

Sorption isotherms of cerium on the anion exchanger converted into various forms are shown in Figure 1. The sorption isotherms of cerium, yttrium and erbium on the anion exchanger in the nitrate form shown in Figure 2.



Picture 1. Sorption isotherms of cerium on the anion exchanger D-403 in the nitrate, chloride and sulfate form at pH 3



Picture 2. Sorption isotherms cerium, yttrium and erbium on the anion D-403 in nitrate form at pH 3

For our thermodynamic evaluation of the sorption isotherm of rare-earth complexes, we used the proposed method of linearizing the equation of the law of active mass,

modified for ionic exchange reactions and assuming an ideal dense phase in which coefficients are equal to 1.
For the ion exchange reaction of yttrium complexes with Trilon B:

$$R[NO_3] + LnTr^- \leftrightarrow R[LnTr] + NO_3^-$$

The value of the ionic exchange constant *K* was expressed using the law of active mass:

$$K = \frac{\Gamma_{LnTr^-} \cdot a_{NO_3^-}}{\Gamma_{NO_3^-} \cdot a_{LnTr^-}} = \frac{\Gamma_{CeTr^-} \cdot [NO_3^-] \cdot \gamma_{NO_3^-}}{\Gamma_{NO_3^-} \cdot [LnTr^-] \cdot \gamma_{LnTr^-}}$$

After mathematical transformation is a linear form of the law of active mass has the form:

$$\frac{1}{\Gamma_{LnTr^-}} = \frac{1}{\Gamma_\infty} + \frac{[NO_3^-] \cdot \gamma^2_{\pm NaNO_3}}{K \cdot \Gamma_\infty \cdot [LnTr^-] \cdot \gamma^2_{\pm NaLnTr}}$$

Obtained thermodynamic and sorption characteristics are presented in Table 1.

Table 1. Thermodynamic and sorption characteristics of rare-earth complexes on anionite D-403

Form of D-403 and anione	Γ_∞, mol/kg	$\Gamma_{[LnTr^-]}$, mol/kg	K_{eq}	ΔG^0, kJ/mol
R[Cl], $CeTr^-$	1,01±0,03	0,090±0,004	0,03±0,01	+8,69±0,43
`$R_2[SO_4]$, $CeTr^-$	0,140±0,002	0,070±0,003	0,49±0,03	+1,77±0,08
$R[NO_3]$, $CeTr^-$	1,19±0,02	0,16±0,02	1,06±0,04	-0,152±0,008
$R[NO_3]$, YTr^-	0,17±0,02	0,058±0,003	6,93±0,28	-4,796±0,143
$R[NO_3]$, $ErTr^-$	0,27±0,02	0,092±0,005	10,06±0,50	-5,719±0,228

By the values of the Gibbs energy show sorption ability row of complex ions of REE: ErTr-, R[NO3] > YTr-, R[NO3] > CeTr-, R[NO3] > CeTr-, R2[SO4] > CeTr-, R[Cl]

SYNTHESIS AND OPTICAL PROPERTIES OF GLASS WITH CADMIUM SULFIDE NANOPARTICLES

Popov I.D.[1,2], *Kuznetsova Yu.V.*[1], *Vlasova S.G.*[2], *Rempel S.V.*[1,2], *Rempel A.A.*[1,2]

[1]Institute of Solid State Chemistry, Ural Branch of the RAS
[2]Ural Federal University named after the first President of Russia B.N. Eltsin
Ekaterinburg, Russia
Student
idpopov65@gmail.com

At present, the interest in synthesis of semiconductor nanoclusters and nanoparticles in amorphous matrixes is increased [1,2]. Design of energy structure and nonlinear optical properties of these materials can be used for study of fundamental aspects of quantum-size effect and can be perspective for practical application [3].

This work aims on synthesizing of a silicate glass with cadmium sulfide (CdS) nanoparticles, studying its optical properties and relations between properties and size of nanoparticles. New synthesis technique for cadmium-sulfide glasses was developed. It was found that zinc sulfide and cadmium oxide could replace CdS as a source of sulfur and cadmium ions. This way allowed decreasing of sulfur evaporation from a glass melt.

A number of glass samples with different optical properties were obtained by changing of annealing regimes. Characterization of samples was carried out by UV-visible and luminescence spectroscopy in the wavelength range from 190 to 900 nm. Bandgap energy value of samples ranges from 2.58 to 3.36 eV. This allows evaluating an average diameter of nanoparticles in glass samples, that varies from 3 to 8 nm, respectively.

Taking into account the data obtained allows encouraging the targeted synthesis of CdS nanoparticles in the silicate glass.

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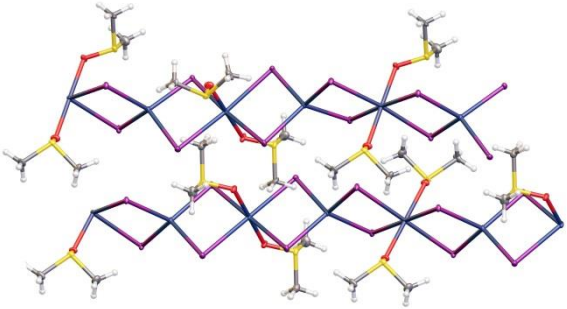
THE SOLUBILITY OF CADMIUM IODIDE IN BINARY ORGANIC AND WATER-ORGANIC SOLVENTS

Pushikhina O.S., *Bogachev N.A.*, *Skripkin M.Yu.*

Saint Petersburg State University
Saint Petersburg, Russia
Student
pushikhina_chem@mail.ru

This work continues the study of the solution-solid phase equilibrium research in systems with competing solvation. The results obtained before enabled to have allowed to trace the influence of the solvent on the isotherm-isobaric solubility diagrams form and on the properties of the resulting equilibrated solid phase, composition and structure in water-organic systems, including CdI_2-H_2O-DMSO. The main question of the study was and still remains somewhat unsolved is what are the main regularities what governs the solubility of salts including CdI_2 in individual and binary solvents.

In this communication the results of study of the solution-solid equilibrium in ternary systems CdI_2-DMSO-X, where X = H_2O, DX, DMA, DMF will be presented. Namely, solubility of the salt, composition and structure of an equilibrium solid phase were defined. The average composition of the coordinating sphere of cadmium ions in the liquid phase was determined by IR spectroscopy of saturated solutions in whole range of solvents ratio, and the dependence of the found data of these characteristics on the nature of the solvent and primarily on its donor properties was derived.



Picture 1. One of the structures of the equilibrated solid phase in water-organic system

Acknowledgements
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This work was financially supported by RFFR, the projects № 14-03-01003 and 15-03-05139.

INVESTIGATION OF CHARGE SEPARATED STATES AND ITS DYNAMICS IN SUBSTITUTED PORPHYRIN-FULLERENE DYADS

Pyshniak M.G. , Povolotskiy A.V., Mereshchenko A.S., Tver'yanovich Y.S., Prolubnikov P.I. , Konev A.S., Khlebnikov A.F., Levin O.V.

Saint Petersburg State University
Saint Petersburg, Russia
Student
mari-maya@bk.ru

Nowadays porphyrin-fullerenes become one of the most popular objects of modern nanoscience, nanotechnology and organic optoelectronics. They are often referred to as promising materials for artificial photosynthesis and for construction of organic photovoltaic devices [1]. The electron transfer from porphyrin to the fullerene leads to the formation of the charge separated state (CS) and represents the key process in the transformation of solar energy [2]. In the present work the photochemistry of series of covalently linked axially symmetric porphyrin-fullerene dyads with a rigid pyrrolo[3,4-*c*]pyrrolic linker was studied by means of time-resolved photoluminescence and transient absorption spectroscopy. From the data obtained it might be concluded that the major relaxation pathways of the singlet electronic excited state are fluorescence into the ground state and intersystem crossing into the porphyrin-localized triplet excited state. Also, the relatively long-lived triplet charge separated state, which is probably originated from the porphyrin-localized triplet excited state, was revealed. Moreover, it was demonstrated that the choice of the substituents in the porphyrin fragment is essential to achieve long lifetime of the CS state in a dyads. Thus, the introduction of *p*-Br substituent prevents the formation of the CS state or reduces its lifetime beyond nanosecond range, while introduction of *p*-MeO group to *meso*-phenyl ring increases the lifetime of the CS state, being up to 4 μs for a species with *meso*-(*p*-$MeOC_6H_4$) substituents.

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Acknowledgements
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CATIONITES POLYCONDENSATION TYPE

Rakhimova L.S., Berdieva M.I, Normirzaev D., Tursunov T.T., Nazirova R.A.

Tashkent chemical-technological institute
Tashkent, Uzbekistan
Senior scientific employee
latofat.2011@mail.ru

Ion exchange resins due to the valuable of property finds widely apply in many fields of science and industry. Nowadays operating ion exchange resins imported to Uzbekistan from CIS, which considerably affected to the cost of price for ready product. Main possibility decision this problem is creation competitive products by modification exist or developing technologies synthesizing of a new ion exchange resins. Intelligent use cheaper, available local substance and secondary raw materials, allows organizing manufacture ionits and it can solve the problem of raw - material base and provide balance of work enterprises by using ion exchange resins.

For creation manufacture of ion exchange resins in Uzbekistan available huge raw - material base - chemical, agricultural, cotton cleaning and other industries. It is known that polymer materials, which obtaining on the bases of furfural are highly thermostable and inert in relation to severe atmosphere. Necessary also noticed that, furfural less toxic than formaldehyde, which often use to obtaining different polymers [1].

In this aspect, big actuality presents using in the capacity of raw material for obtaining ionits – waste of chemical manufactures, for example manufacture of Shurtan gas-chemical complex. Polycondensation of furfural with distillation residue in the presence acidic catalyst obtained polymer with reticulate structure. Then this polymer exposed to process sulfonation with concentrated sulfuric acid. Obtained cationite has static exchange capacity by 0,1 N solution of NaCl – 2,5 mg-eqv/g, by 0,1 N solution of NaOH -4-4,5 mg-eqv/g.

For obtaining thermal,- chemical,- and mechanic stable ionits by us in the capacity of polymer matrix for initiating ionogen group was used product polycondensation diphenyloxide and furfural. Exchange capacity obtained cationite by 0,1 N solution of NaCl – 1,85-2,0 mg-eqv/g, by 0,1 N solution of NaOH -5,7-6,0 mg-eqv/g.

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SPECTROPHOTOMETRIC STUDY OF BASIC AND COORDINATION PROPERTIES OF BROMO-SUBSTITUTED TETRAPHENYLPORPHYRINS

Razumov M.I., Domanina E.N., Dao The Nam, Pukhovskaya S.G.

Ivanovo State University of Chemistry and Technology, Russia, 153000, Ivanovo, Sheremetev av., 7
Email:mandl@bk.ru

Porphyrins in nature perform various biological functions: oxygen transfer and keeping, conversion of light energy into chemical, electrons transfer, catalysis of redox reactions as metal complexes, etc. Previously the direct relationship between coordination properties of porphyrin toward metal salts and nature of porphyrin macrocycle substituents was established. It is also known that there is specific interconnection between coordination and basic properties of porphyrins: protonation of ligands competes with coordination process.

Basic properties of tetraphenylporphyrin (H_2TPP) derivatives containing electron-acceptor substituents (-Br) in *o*- (**I**) and *m*- (**II**) positions of benzene fragment and kinetics of copper complex formation in proton-donor solvent – acidic acid were studied in the present work.

Introduction of Br atoms, showing induction (-I) and slight conjugating +C effects toward benzene fragment, in *o*-positions of H_2TPP phenyl rings weakens basic properties of molecule greater than introduction if *m*-position. It is probably caused by greater influence of hither Br atom on reaction center. Basicity constants were determined by spectrophotometric titration of compounds (**I**) and (**II**) in acetonitrile – perchloric acid system, $\lg K_b$ (**I**) = 8.11 and $\lg K_b$ (**II**) = 8.90. Determination of coordinates of inflection point on titration curve allows to distinguish two areas in electronic absorption spectrum which are probably the first and the second stages of protonation, ie the stages of mono- and dicationic porphyrins (**I**) and (**II**) formation.

Thus, the constants of protonated porphyrins dissociation are in good agreement with classical submissions about nature of substituents introduced even through phenyl "buffer".

Obtained data are matched with results of kinetic measurements of copper complexes with the ligands formation. The rate of complexation of copper acetate with *meta*-substituted H_2TPP is about three times higher ($k^{298}_v = 0.78\ l^{0.5} \cdot mol^{-0.5} \cdot s^{-1}$) than with *ortho*-substituted one ($k^{298}_v = 0.27\ l^{0.5} \cdot mol^{-0.5} \cdot s^{-1}$) with slight difference in the activation energies.

Acknowledgements
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THE STUDY OF IMMISCIBILITY PHENOMENON IN WATER-DIOXANE SYSTEMS CONTAINING SALTS OF TRANSITION METALS

Razzhivin A.V., Bogachev N.A., Skripkin M.Yu.

Saint Petersburg State University
Saint Petersburg, Russia
Student
alexander.razzhivin.95@gmail.com

The investigation of competing solvation in liquid water-organic saline systems was the object of study for the last several decades. The determination of the features of the manner that the properties of the solvents affect on macro properties of all the multicomponent systems is the key to create new techniques of directed liquid-phase synthesis. During the study of the d-elements containing systems in the laboratory of Solution Chemistry, SPbSU, the phenomenon of immiscibility in ternary systems such as $CoCl_2$ – DX – H_2O, $CoBr_2$ – DX – H_2O, $CdSO_4$ – DX – H_2O in definite range of concentration of the solvents was found.

Both determination of the dependence of composition of the formed phases on concentration and properties of the dissolved substance and solvents and the determination of the same dependence for the degree of immiscibility have become the aims of that work. Solubility of the salts in each phase, composition and structure of equilibrium solid phase were determined with methods of chemical analysis. The IR spectroscopy of saturated solutions was used to identify the structure of the solvate shell of ions of metals.

The results of the research allowed to trace the influence of the nature of the saline component on properties of the immiscible ternary system and to find out the regularity of those change.

Acknowledgements

We acknowledge the support of resource centers "Optical methods of material study" and "Diffraction substance analysis method» of St. Petersburg State University Science Park in our research.

This work was financially supported by RFFR, the projects № 14-03-01003 and 15-03-05139.

STABILITY AND ACTIVITY OF Mo-MODIFIED Ni-Cu CATALYST FOR BIO-OIL HYDROTREATMENT

Rekhtina M.A.[1,2], *Bykova M.V.*[1,2], *Yakovlev V.A.*[2]
[1]Novosibirsk State University
[2] Boreskov Institute of Catalysis SB RAS
Novosibirsk, Russia
Master student
rekhti na@catalysis.ru

Nowadays the humanity becomes more and more interested in the use of renewable energy resources, such as biomass, as an alternative for fossil fuel reserves (coal, oil and natural gas) due to their gradual depletion. There are many different types of biomass processing, one of them is flash pyrolysis giving a liquid product − so called bio-oil (pyrolysis oil, PO). Bio-oil is positioned as a perspective feedstock for the production of engine fuels, but it has high viscosity, high acidity (pH=2-3), polarity, and also low stability upon storage. Such PO properties result from the high oxygen content and the presence of highly reactive components in its composition. Catalytic hydrotreatment of bio-oil allows one to reduce its oxygen content and gives products more suitable for further application. Previously it was shown that Ni-Cu catalysts possess high activity in bio-oil upgrading, but corrosion resistance of these catalytic systems was low. It was noted that addition of Mo helps to stabilize Ni-Cu catalysts in acidic medium, but optimal amount of Mo has not been determined yet.

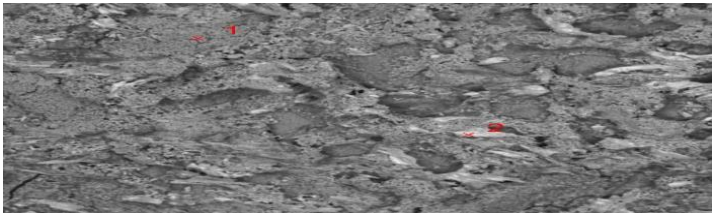
In the present work a series of Ni-based catalysts with different amount of Mo were prepared by a sol-gel technique. Then the samples were tested in hydrotreatment of guaiacol (GUA, model compound of PO), besides their stability to corrosion was examined by the glacial acetic acid treatment at severe conditions. A wide range of physicochemical methods was employed for the catalysts characterization: X-Ray fluorescence, XRD, XPS, HRTEM, BET, CO chemisorption, TPR.

The catalysts stability to corrosion was shown to increase with Mo content: mass loss of the most stable system was 1.8% in comparison with 30.9% observed for the non-modified catalyst, which could be explained by the formation of Ni-Mo alloys. Catalysts testing in GUA hydrotreatment has shown that Mo addition results in the change of product selectivities. Notably the catalysts selectivity towards cyclohexane formation (target product of GUA hydrotreatment) grew with Mo content. According to the catalysts characterization by physicochemical methods, the effects observed could be explained by the change of active component nature: electronic effects between Mo^0 and Ni^0, and the presence of coordinatively unsaturated species Mo^{x+} (x = 4, 5) on the catalysts surface, which most likely are profitable for an activation of O-containing organic substrates.

ELECTROCHEMICAL DISSOLUTION OF COPPER COLLECTOR CONTAINING HIGH CONCENTRATIONS OF PRECIOUS METALS

Rusalev R.E. Shigin E.S. Ergashev N.U.
National University of Science and Technology "MISIS"
Moscow, Russia
Rusalev Rostislav
rusalevrostislav@gmail.com

The specific feature of secondary metallurgy of precious metals is a great variety of physical forms and chemical formulations of waste, which contain Nobel metals.
Generic aspects of secondary resources which contain precious metals are a very extensive nomenclature, wide interval changes of the content of extracting elements, and a wide variety of material composition of related components such as metallic and nonmetallic salts, compact metallic and non-metallic materials with uniform and local distribution of recoverable elements.
The timeliness of the topic is linked with the increasing consumption of precious metals in industry every year. Since the development of scientific and technological progress in the field of electronics and electronics creates a demand for precious metals as their physical properties and electrical conductivity are better than their substitutes – semiconductors.
A huge amount of municipal solid waste which contains precious metals becomes more attractive than the primary raw material of the same metal, with the appropriate technology for the processing and extraction of precious metals.
The research is devoted to the electrochemical dissolution of copper collector, which contains Nobel metals with high concentrations. These metals were recovered from e-waste on pyro metallurgical step.
The quantitative and qualitative chemical analyses were made of the passivation of the anode film which showed at picture 1.



Picture 1. Solt anode film

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MODIFICATION OF THE PbS FILM BY ITS EXPOSURE TO SOLUTIONS OF STANNUM (II) SALTS CONTAINING DIFFERENT ADDITIVES

Saryeva R.Kh., Maskaeva L.N.

Ural Federal University named after the first President of Russia B.N. Yeltsin
Yekaterinburg, Russia
Student
Ragneta@rambler.ru

Lead sulfide is a narrow-gap semiconductor (ΔE_g=0.41eV) which can be used as sensitive elements of photodetectors in the infrared spectrum range of 1.0-3.5 mkm.

Synthesis of the substitution solid solutions for the PbS-SnS system is an important issue for expansion of a circle of semiconductive compounds with a variable spectral range. A method of ionic exchange at the "PbS_{solid} - $SnCl_2$ water solution" interphase boundary can be very perspective as a synthesis technique of the $Pb_{1-x}Sn_xS$ substitution solid solutions.

Therefore the present work is dedicated to studying the possibility of obtaining the $Pb_{1-x}Sn_xS$ solid solutions enriched in stannum.

The key-point of the ion-exchange synthesis consists in following. The basic material of PbS in a shape of thin films with the thickness of ~600 nm was applied on a preliminary defatted surface of a glass-ceramics substrate by the chemical precipitation from aqueous reacting mixtures containing the $Pb(C_2H_3O_2)_2$ lead acetate, the $Na_3C_6H_5O_7$ sodium citrate, the NH_4OH ammonia, the Nh_4I ammonium iodide, and the N_2H_4Cs thiocarbomide. After that, the synthesized PbS layers were exposed to the lead (II) chloride aqueous solution during 1-9 hours at 368 K. The reaction system containing ligands for lead (ammonium acetate or sodium hydroxide), apart from stannum salt, was of interest for the experimental research because the ligands form sufficiently strong complex compounds with the Pb^{2+} ions.

The experimental results revealed that after the films exposure to the solutions of lead (II) chloride containing ammonium acetate or sodium hydroxide the following basic elements: O, S, Sn and Pb were found in their layers.

The presence of lead in the prepared PbS layers after the contact with the $SnCl_2$ salt aqueous solutions indicates its inclusion into initial films. It was established that, under otherwise equal conditions (temperature and contact duration of the base film with the $SnCl_2$ solution) the maximal content of lead in the PbS films reached the value of 28.8 at.% and 27.1 at.% in the presence of ammonium acetate and sodium hydroxide, respectively. One can conclude that the presence of complexants in the $SnCl_2$ aqueous solution do not affect the composition of the semiconductive layer.

DEFECT STRUCTURE AND RELATED PROPERTIES OF $YBaCo_2O_{6-\delta}$.

Sednev A.L., Tsvetkov D.S.

Ural Federal University,
Ekaterinburg, Russia
Student
sovsem_ne_master@mail.ru

Double perovskite $YBaCo_2O_{6-\delta}$ is a potential cathode material for solid oxide fuel cells (SOFCs). Recently, it has received great attention due to high mixed ionic–electronic conductivity, fast oxygen transport and small thermal expansion coefficient close to that of $Zr_{0.9}Y_{0.1}O_2$ (YSZ). However, the defect structure of the $YBaCo_2O_{6-\delta}$ has not been studied so far as well as its oxygen nonstoichiometry, total conductivity and Seebeck coefficient.

Powder sample of $YBaCo_2O_{6-\delta}$ was prepared using glycerol–nitrate technique. Metallic Co, preliminary annealed Y_2O_3 and $BaCO_3$ were used as starting materials. All the materials used had purity 99.99%. The final calcination was carried out at 1100°C for 48 h. Phase composition of the as synthesized powder sample was controlled by X-ray diffraction by means of DRON-6 diffractometer using CuKα radiation.

Oxygen nonstoichiometry of the double perovskite $YBaCo_2O_{6-\delta}$ was measured as a function of oxygen partial pressure (pO_2) and temperature (T) using two independent techniques: thermogravimetry and solid state coulometric titration. The absolute oxygen content in the sample of $YBaCo_2O_{6-\delta}$ slowly (~100° C/h) cooled in air from 1100°C to room temperature was found to come to value $6-\delta = 5.512$. Oxygen content in $YBaCo_2O_{6-\delta}$ as a function of T varied in air atmosphere in a rather narrow range (5.51 - 5.10) as compared to similar double perovskites like, for example $GdBaCo_2O_{6-\delta}$.

Total conductivity and Seebeck coefficient of $YBaCo_2O_{6-\delta}$ were measured by four probe dc-method in the ranges of T and $pO2$ 900 - 1050°C and 10^{-3} – 0.21 atm, respectively. A significant drop in the total conductivity of $YBaCo_2O_{6-\delta}$ was found below the certain value of $pO2$ at given T suggesting the thermodynamic stability limit of this double perovskite with respect to pO_2 decrease. It was shown that both total conductivity and Seebeck coefficient of $YBaCo_2O_{6-\delta}$ are almost independent of pO_2 within the range of its thermodynamic stability due to weak pO_2 dependence of the oxygen content. Positive value of Seebeck coefficient as well as decrease of the conductivity of $YBaCo_2O_{6-\delta}$ suggests electron holes as dominating charge carriers. The experimental results obtained were discussed on the basis of the proposed defect structure model of $YBaCo_2O_{6-\delta}$.

HOMOATOMIC POLYHEDRAL EXTENSION OF $[B_9H_9]^{2-}$ ANION

Selivanov N.A.[12], *Bykov A.Yu.*[2], *Zhizhin K.Yu.*[2], *Kuznetsov N.T.*[2]

[1]HCC RAS, [2]IGIC RAS,
Moskow, Russia
Student
GooVee@yandex.ru

$[B_9H_9]^{2-}$ anion holds exceptional position among *closo*-borate anions. Presence of three low-coordinated apical boron atoms in $[B_9H_9]^{2-}$ define its unique ability in reactions of rearrangement and polyhedral extension [1, 2] and decreasing [3, 4]. As it is known heteroatomic polyhedral extension of $[B_9H_9]^{2-}$ results in formation of $[MB_9H_9L_n]$. However, the homoatomic polyhedral extension reactions are obscure to the date. We managed to fit conditions for $[B_9H_9]^{2-}$ transformation to $[B_{10}H_{10}]^{2-}$ and $[B_{12}H_{12}]^{2-}$.

In case of $[B_9H_9]^{2-}$ boiling inexcess of triethylamine borane complex it was totally converted to $[B_{10}H_{10}]^{2-}$ (50 $\%_{mol}$) and $[B_{12}H_{12}]^{2-}$ (50 $\%_{mol}$). In $^{11}B\{^1H\}$ NMR spectrum of reaction mixture there are peaks from triethylamine borane complex (13 ppm), $[B_{10}H_{10}]^{2-}$ anion (0 ppm and 28 ppm) and $[B_{12}H_{12}]^{2-}$ anion (15 ppm).

Since $[B_{10}H_{10}]^{2-}$ may interact with triethylamine borane complex yielding $[B_{12}H_{12}]^{2-}$ this method is nonselective to $[B_{10}H_{10}]^{2-}$. Carrying out of the reaction in inert solvent (toluene) with stoichiometric quantity of triethylamine borane complex result in considerable increasing of selectivity. In this case $[B_{10}H_{10}]^{2-}$ is quadruple as large as $[B_{12}H_{12}]^{2-}$. The detachment of this mixture presents few problems and accomplishes by fractional recrystallization that possible because of considerable differences in TFF$[B_nH_n]^{2-}$ (n = 9, 10, 12) salts solubility.

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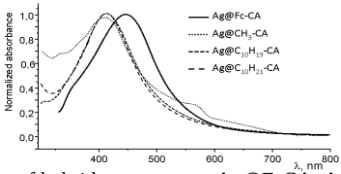
RESORCINARENES AS STABILIZERS OF SILVER NANOPARTICLES

Sergeeva T.Yu.[1,2], *Mukhitova R.K.*[2], *Nizameev I.R.*[2], *Kadirov M.K.*[2], *Ziganshina A.Yu.*[2], *Konovalov A.I.*[2]

[1]Kazan Federal University,
[2] A.E. Arbuzov Institute of Organic and Physical Chemistry, Kazan Scientific Center, Russian Academy of Sciences
Kazan, Russia
Student
tatyana_sergeeva93@mail.ru

Macrocyclic compounds have contributed to the progress in the synthesis of MNPs and their composites. They were applied as reducing agents, stabilizers and also as supporting matrix, controlling the shape and size of MNPs. We have used amphiphilic derivatives of resorcinarenes with decyle ($C_{10}H_{19}$-CA), decynyl ($C_{10}H_{21}$-CA), methyl (CH_3-CA) and ferrocene (Fc-CA) groups at the lower rim as stabilizers in the synthesis of the monodisperse silver nanoparticles (AgNPs). The resorcinarenes prevent the aggregation of AgNPs and control the size and shape of the silver nanoparticles.

AgNP were characterized by the data of UV-vis and IR spectroscopies, static and dynamic light scattering (SLS and DLS), atomic force microscopy (AFM), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) and thermogravimetry(TG).



Picture 1. UV-Vis spectra of hybrid nanosystems Ag@FcCA, Ag@CH_3CA, Ag@$C_{10}H_{19}$CA, Ag@$C_{10}H_{21}$CA.

Catalytic properties of the hybride nanosystems Ag@CA were studied in the common used reaction of reduction of p-nitrophenol with sodium borohydride in water. The highest catalytic activity is observed for Ag@$C_{10}H_{19}$-CA. The lowest activity is detected for Ag@Fc-CA.

Acknowledgements
This work was supported by the Russian Foundation for Basic Research (grant 15-03-04999).

PHASE EQUILIBRIA IN THE TERNARY SYSTEM Co-Mo-Ni AT 1375 K

Shaipov R.Kh.

Lomonosov Moscow State University, Chemical department, Moscow, Russia
postgraduate student
shaipov-ramil@mail.ru

Alloys based on cobalt and nickel are widely used for the manufacture of heat-resistance and wear-resistant materials. Such materials often include molybdenum, which provides solid solution hardening and forms carbides. Creation of new heat-resistance materials and prediction of changes in their properties during the exploitation is based on the information about the phase diagrams of multicomponent systems.

The aim of this work is the construction of the isothermal section of the phase diagram of the ternary system Co-Mo-Ni at 1375 K.

For determination of the phase, equilibria in the Co-Mo-Ni system 16 alloys were investigated. The alloys were synthesized in an arc furnace in an argon atmosphere. These alloys were homogenized in resistance tube furnaces at 1375 ± 5 K for 800 h. The concentration of the elements in the alloys and the concentration of the elements in the phases of the alloys were studied using electron-probe microanalysis in a "LEO EVO 50 XVP" instrument equipped with an "Inca Energy 450" energy dispersive analyzer (Oxford Instruments). The microstructure of specimens was examined using scanning electron microscopy in a "LEO EVO 50 XVP" instrument. X-ray phase analysis was carried out using the powder method in a "STOE STADI P" and in a "DRON-4" diffractometer.

In this system at 1375 K there are five phases: β (*Im*-3*m*, № 229, W), γ (*Fm*-3*m*, № 225, Cu), ε-Co (*P*6$_3$/*mmc*, № 194, Mg), μ (*R*-3*mh*, № 166, W_6Fe_7) и δ ($P2_12_12_1$, № 19, $Mo_3(Mo_{0,8}Ni_{0,2})_5Ni_6$). In the Co-Mo-Ni system at 1375 K two three-phase equilibria have experimentally established: β+δ+μ, γ+δ+μ (Figure 1). The existence of three-phase equilibrium γ+ε+μ has been suggested.

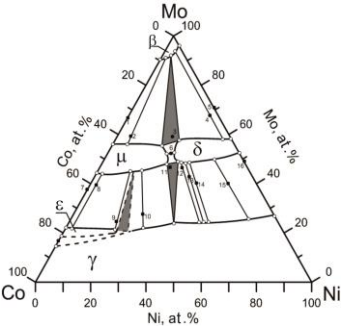


Figure 1. Isothermal section of the phase diagram of Co-Mo-Ni system at 1375 K.

Acknowledgements

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APPLICABILITY OF POLYELECTROLYTE COATED TERBIUM COMPLEXES-BASED NANOPARTICLES AS SENSORS

Shamsutdinova N.A.[1], *Mustafina A.R.*[1], *Amirov R.R.*[2]

[1]A.E. Arbuzov Institute of Organic and Physical Chemistry
[2]Kazan Federal University
Kazan, Russia
Postgraduate student
nataliyashams@gmail.com

Luminescent nanoparticles have attracted great attention due to their applicability in sensing and imaging. Core-shell morphology of luminescent nanoparticles is of great impact in their sensing function and biocompatibility. Our previous report introduces rather simple and convenient synthetic route of getting luminescent aqueous colloids based on lanthanide complexes [1]. The basis of the this approach is the reprecipitation of luminescent complexes from organic to aqueous solutions followed by a stabilization of the obtained colloids through an adsorption of polyelectrolytes onto hard templates.

The present work is aimed to highlight an origin of sensing function of polyelectrolyte-coated colloids based on Tb(III) complexes with calix[4]resorcinarene cavitand bearing four 1,3-diketone groups at the upper rim. The Tb(III)-centered luminescence of the colloids remains unchanged at pH 3-9 due to the retarded degradation of the complex-based colloids in weak acidic and alkaline media, although the Tb(III) complexes are highly pH-dependent. Both colloidal and luminescent properties of the colloids are stable within one month at least, which reveals stability of complex-based hard templates and soft polyelectrolyte deposition. The chelating substrates (catechol, tetracycline and fluoroquinolone derivatives) induce quick and reproducible luminescent response resulted from a ternary complex formation at the interface of the complex-based colloids without any detectable changes of their colloidal properties. The heterogeneity of the Tb(III) complexes affects the ternary complex formation, which is the reason for more selective luminescent response of the colloids on the tetracycline and fluoroquinolone antibiotics.

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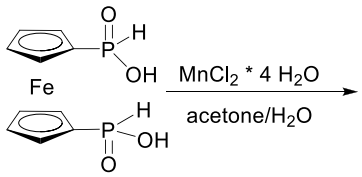
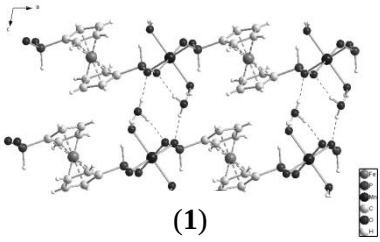
REVERSIBLE WATER-INDUCED CRYSTAL-TO-CRYSTAL TRANSFORMATION OF 2D POLY(MANGANESE 1,1'-FERROCENEDIYL-BIS(H-PHOSPHINATE)).

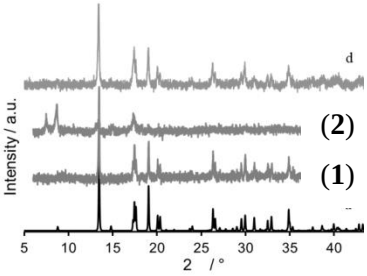
Ruslan Shekurov[1], Vasili Miluykov[1], Olga Kataeva[1], Oleg Sinyashin[1], Tatyana Gerasimova[1], Sergey Katsyuba[1], Valeri Kovalenko[1], Yulia Krupskaya[2], Vladislav Kataev[2], Bernd Büchner[2], Irena Senkovska[3] and Stefan Kaskel[3].

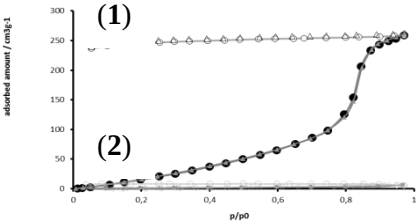
[1]A.E.Arbuzov Institute of organic and physical chemistry Russian academy of sciences, Arbuzov Str. 8, 420088 Kazan, Russia,
[2]IFW Dresden; Helmholtzstr. 20, 01087 Dresden, Germany,
[3]Department of Inorganic Chemistry, Dresden University of Technology, Bergstr. 66, 01062 Dresden, Germany
shekurovruslan@gmail.com

We have synthesized first example of porous coordination polymer $[Mn(H_2O)_2(Fc(PHOO)_2)\cdot 2H_2O]n$ (**1**) based on phosphinic acid, which demonstrates reversible crystal-to-crystal transformation and is able to form two different stable forms controlled by specific guest. The dehydrated compound $[Mn(Fc(PHOO)_2)]$ (**2**) can selectively adsorb H_2O molecules (17% on weight) over other adsorbtives such as methanol, ethanol, acetone, and tetrahydrofuran at 298K. The network is also not accessible for nitrogen and hydrogen at 77K. The structural transformations is also reflected in magnetic properties of the coordination polymer. The data reveal weak antiferromagnetic interaction between Mn spins.









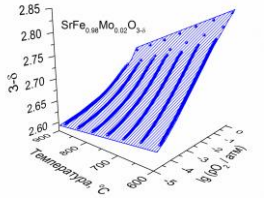
Acknowledgements
This work was financially supported by the grant of President of the Russian Federation (MK-5149.2014.3).

DEVELOPMENT OF FUNDAMENTAL BASES FOR OBTAINING OF NEW ELECTRODE MATERIALS WITH CONTROLLED CHARACTERISTICS FOR MICROTUBULAR SOLID OXIDE FUEL CELLS

Shoynkhorova T.B.

Novosibirsk State University
Novosibirsk , Russia
Student
shoynkhorova@gmail.com

Tyurhe strontium ferrite $SrFeO_{3-d}$ is known to exhibit fast oxygen ion transport and appreciable electron conductivity at moderately high temperatures. These properties combination is attractive for the use of $SrFeO_{3-d}$ as a base for development of SOFC electrodes and oxygen separating membranes. Depending on the nonstoichiometry value, d, the ferrite may crystallize with several modifications that differ in the distribution of oxygen vacancies over crystalline lattice. Generally, the ordering is regarded as undesirable because it leads to the removal of the vacancies from oxygen transfer and to deterioration of transport characteristics. The stabilization of this favorable structural state within wider limits of temperature can be achieved by B-site doping. It is known that molybdenum tends to have higher oxidation state than iron. Therefore, this substitution should increase the oxygen content in $SrFeO_{3-d}$ and the average coordination of iron by oxygen, and, consequently, one can await some decrease in the average size of the vacancy ordered domains, i.e., enhanced nano-structuring in the doped ferrite. For targeted regulation of properties of electrode materials (anode and cathode) for SOFC based on oxides with a perovskite structure ABO_{3-d} and double perovskite $A_2B_2O_{5+d}$, we proposed as dopants - ferroactive high -charged cations Nb, Ta, Mo, W. To determine the regions of stability of electrode materials, study their thermodynamic properties, we propose a new and original method for obtaining the phase diagrams of the "3-d-lg pO2-T" based on continuous registration of the first isothermal dependence "pO2 - t» at quasi-equilibrium separating oxygen from the sample MIEC oxide.



Phase diagram “3-d – lgpO2 – T” $SrFe_{0.98}Mo_{0.02}O_{3-d}$

PHASE TRANSFORMATIONS DURING $HLnTiO_4$ (Ln = La, Nd) THERMOLYSIS AND PHOTOCATALYTIC ACTIVITY OF OBTAINED COMPOUNDS

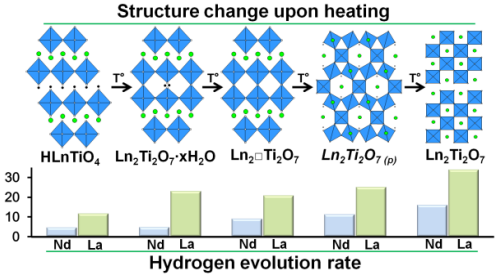
Silyukov O.I.[1], Abdulaeva *L.D.*[1], Burovikhina *A.A.*[1], Rodionov *I.A.*[1]

[1]Saint Petersburg State University,
Saint Petersburg, Russia
Engeneer-scientist
olegsilyukov@yandex.ru

Layered perovskite-like oxides are solid crystalline substances formed by two-dimensional nanosized perovskite slabs interleaved with cations or cationic structural units. Until present time perovskite-like compounds are actively studied as materials with wide range of important physical and chemical properties.

In the present work the phase transitions during the thermolysis process of protonated $HLnTiO_4$ (Ln = La, Nd) related to the Ruddlesden-Popper perovskite-type phases were studied. Photocatalytic activity of initial, intermediate and final compounds was measured.

$HLnTiO_4$ compounds were found to form partially hydrated $Ln_2Ti_2O_7 \cdot xH_2O$ during thermal dehydration as well as defect oxides $Ln_2\square Ti_2O_7$ as final products. Further heating of defect $Ln_2\square Ti_2O_7$ substances leads to the pyrochlore-type oxides $Ln_2Ti_2O_{7\,(p)}$, with subsequent transformation to stable layered 110-type perovskites $Ln_2Ti_2O_7$. The occurring structure transformations lead to an increase of photocatalytic activity in the order of $HLnTiO_4$ < $Ln_2Ti_2O_7 \cdot yH_2O$ < $Ln_2\square Ti_2O_7$ < $Ln_2Ti_2O_{7\,(p)}$ < $Ln_2Ti_2O_7$ in the reaction of hydrogen evolution from aqueous isopropanol solution.



Picture 1. Hydrogen evolution upon structure change

Acknowledgements

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THE ELECTROCHEMICAL BEHAVIOR OF METHIONINE ON THE GRAPHITE ELECTRODE MODIFIED GOLD NANOPARTICLES

Skirdin K.V., Perevezentstva D.O.

Tomsk Polytechnic University
Tomsk, Russia
Student
kvs21@tpu.ru

Methionine (Met) is an essential amino acid, that involved in the biosynthesis of epinephrine, choline, creatinine. Its deficiency leads to metabolic disorders. The determination of Met in the blood is the means of monitoring the biological state of the body [1]. Therefore, at the present time the development of the efficient methods for determination of Met is an actual problem. The purpose of this work is to investigate the electrochemical behaviour of Met in aqueous solution at a graphite electrode modified gold nanoparticles (AuNP-GCE) by cyclic voltammetry.

Gold sols were prepared by chemical reduction using sodium citrate and sodium borohydride, in the absence of high-molecular stabilizers according to the procedure described in [1] with a different molar ratio of reactants. The characteristics of sols were determined using transmission electron microscopy, stripping voltammetry with a graphite electrode (GE). The surface modification of GE by gold nanoparticles was carried by electrochemical deposition from 10 ml gold sol at E = -1 V, t = 300 s. The cyclic voltammograms of Met were recorded in 0.1 M NaOH, 0.1 M phosphate buffer pH 6,86, 0.1 M NaCl, 0.1 M $NaNO_3$ under the following conditions: ranges from -1 V to +1 V, scan rate of 100 mV/s. Met shows no electrochemical activity on GE under a concentration of $2 \cdot 10^{-12}$ mol/l and on AuNP-GCE at a concentration of $1 \cdot 10^{-13}$ mol/l in 0.1 M NaCl, 0.1 M phosphate buffer pH 6,86. While Met shows electrochemical activity on AuNP-GCE at a concentration of $1 \cdot 10^{-13}$ mol/l in 0.1 M NaOH, 0.1 M $NaNO_3$. The “inverse” cathodic peak of Met observed on the cathodic branch of cyclic voltammogram at E_c = 0.05 V at AuNP-GCE in 0.1 M NaOH. The “inverse” cathodic peak of Met observed on the cathodic branch of cyclic voltammogram at E_c = 0.05 V at AuNP-GCE in 0.1 M $NaNO_3$.

Thus, conditions are determined in which the Met at a concentration of $1 \cdot 10^{-13}$ mol /l has the electrochemical activity: potential ranges from -1 V to +1 V, scan rate of 100 mV/s, supporting electrolytes NaOH, $NaNO_3$, ratio of reagents used to prepare the nanoparticles $HAuCl_4$:$Na_3C_6H_5O_7$:$NaBH_4$= 1:15:5.

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LASER-INDUCED DEPOSITION OF NANOSTRUCTURED COPPER TRACKS FROM SOLUTIONS CONTAINING OXIDISING ADDITIVES

Smikhovskaia A.A[1], *Tumkin I.I*[1], *Kochemirovsky V.A*[1]

[1]Saint Petersburg State University,
Saint Petersburg, Russia
Student
Smihovskaya@yandex.ru

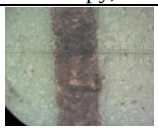
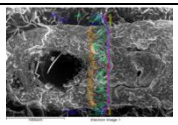
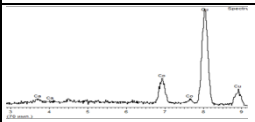
Laser-induced chemical liquid-phase deposition (LCLD) of metals from electrolyte solutions is based on local irradiation of a dielectric substrate/solution interface with a focused laser beam.

This work is dedicated to a study of different additives influence on laser deposition of copper from solutions. The main goal was to raise the speed of the copper tracks deposition process, to decrease their electrical resistance and to make solid solutions or intermetallic particles on copper tracks basis. To perform the deposition, we used a diode-pumped solid state laser in the continuous radiation mode with a power ranging from 250 to 1200 mW at a wavelength of 532 nm. Copper tracks deposition was conducted on sitall surface (glassceramic material composed of 60,5% SiO_2, 13,5% Al_2O_3, 8,5% CaO, 7,5% MgO, 10% TiO_2). The deposition was performed from solutions containing various additives (Table 1).

Table 1. Compositions of solutions for laser-induced copper deposition

Component		Concentration, M
Main components	$CuCl_2$	0,01
	NaOH	0,1
	$C_5H_{12}O_5$	0,075
	$KNaC_4H_4O_6{\cdot}4H_2O$	0,033
Additives	Metal chlorides (Fe, Co (II), Ni, Zn)	10^{-4}, $3{\cdot}10^{-4}$, 10^{-3}, $3{\cdot}10^{-3}$, 0,01

Dependence of tracks width on laser radiation power was studied. The samples were researched using scaning electron microscopy (SEM) and Energy-dispersive X-ray spectroscopy (EDX) methods

Parameters	Optical microscopy, 20X	SEM	EDX
Additive-$CoCl_2$ Concentretion-10^{-3}M Laser power-1000 mW			

Acknowledgements

We acknowledge the Russian Fund for Basic Research (grants 15-03-05139) and Saint Petersburg State University for a research grants (2015–2017, 12.38.219.2015).

The authors highly appreciate the Interdisciplinary Resource Center for Nanotechnology St. Petersburg State University

THE IRON (III) OXIDE PROCESSING FROM THE PYRITE CINDERS

Smorokov A.A.[1],

[1]National Research Tomsk Polytechnic University
Tomsk, Russia
Student
wolfraum@yandex.ru

The sulfuric acid waste processing, especially the pyrite cinders, can afford to get the high-purity iron compounds.

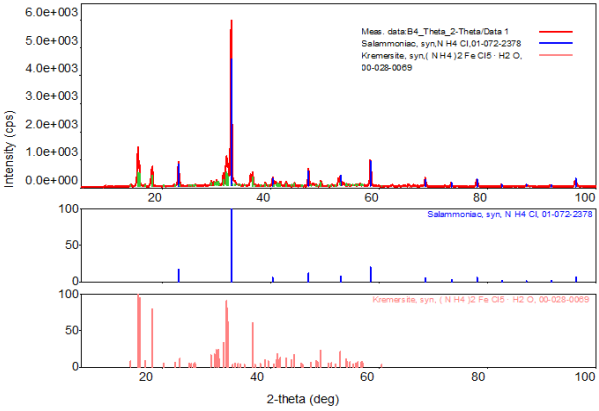
The pyrite cinders contain, in general, from the iron oxides admixed with the nonferrous metals.

The processing scheme of the cinders is offerd by ammonium chloride. Previously iron is calcined at high temperatures into trivalent oxidation state. After then, the product is chlorinated by ammonium chloride while stirring at 300 °C until the gaseous products of reaction stop to evolve. It means the chlorammonium compound of iron $(NH_4)_2FeCl_5$ generate admixed with the NH_4FeCl_3.

The chlorinated product is heated for the sublimation of the chlorammonium compound of iron, which going to be desublimated.

The desublimated product is heated at 350 °C for the free ammonium chloride sublimation and for the destruction of the chlorammonium compounds of iron to iron chloride (III). It has been discovered that iron chloride include aluminium – 0.2%, copper – 0.04% and zinc – 0.06%. Iron concentration is 33.4%. Iron chloride (III) is steamed at 500 °C until the stopping of the gase evolution. It generates iron oxide (III). The iron concentration is approximatly 68%. There was found a little bit aluminium .

Picture 1. Result of the x-ray analysis of the desublimation produkt



PROPERTIES OF THE LAYERED OXIDE $Rb_2La_2Ti_3O_{10}$ – A POTENTIAL PHOTOCATALYST FOR HYDROGEN PRODUCTION

Sokolova I.P., Rodionov I.A.

Saint Petersburg State University,
Saint Petersburg, Russia
Student
jpsokol@mail.ru

Nowadays, the production of such environmentally friendly fuel as hydrogen from water just using sunlight and a photocatalyst draw much attention of researchers around the world. Layered titanates $A_2Ln_2Ti_3O_{10}$ (A = Li, Na, K, Rb, Cs; Ln = La, Nd) with perovskite-like structure are attractive photocatalysts for water splitting. The increase of photocatalytic activity in the order Li-Na-K is likely to be connected with the intercalation of water into the interlayer space [1]. Therefore, $Rb_2La_2Ti_3O_{10}$ became an object of this research as potentially the most effective photocatalyst in this series.

$Rb_2La_2Ti_3O_{10}$ was synthesized by the solid-phase method and characterized by the methods of XRD, TGA, SEM, BET and UV-Vis spectroscopy. The mechanism and kinetics of $Rb_2La_2Ti_3O_{10}$ formation was analyzed to optimize the synthesis conditions. Photocatalytic activity in the reaction of hydrogen evolution was measured using a self-made reactor connected to a GC.

$Rb_2La_2Ti_3O_{10}$ was found to undergo both hydration and protonation processes under contact with water resulting in a final composition of $HRbLa_2Ti_3O_{10}\cdot 0.7H_2O$. The measured band gap energy of $Rb_2La_2Ti_3O_{10}$ (3.57eV) is close to the band gap of the isostructural compound $K_2La_2Ti_3O_{10}$. The average particle size was 100-150 nm and the specific surface area measurement gave a result of 2.14 m^2/g. Both values are comparable with those for the corresponding isostructural analogs.

The hydrogen evolution rate over $Rb_2La_2Ti_3O_{10}$ from aqueous isopropanol solution under UV-light equals to 996 mkl/h, which considerably exceeded the value for such well-known photocatalysts as TiO_2 and $K_2La_2Ti_3O_{10}$, measured under the same conditions. Probably it is due to the possibility of water decomposition in the interlayer space of the oxide.

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Acknowledgements

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INFLUENCE OF pH ON REDUCTION OF Au(III) WITH HYDROGEN CATALYZED BY GOLD NANOPARTICLES

Roman D. Solovov, Mikhail S. Pyrov, Evgeny V. Abkhalimov and Boris G. Ershov

IPCE RAC, Institution of Russian Academy of Sciences Frumkin Institute of Physical Chemistry and Electrochemistry of the Russian Academy of Sciences, Russia
Postgraduate Student
roman_solovov@mail.ru

Now a huge number of techniques of preparation of gold nanoparticles having different size distributions are known. Generally, these methods were very well investigated and described. The used reducing agents in these techniques can be any substances with high reducing potential: sodium borohydride, sodium aluminum hydride, sodium citrate, etc. However, these reducing agents have some disadvantages. The main disadvantage is the undesirable reaction products increasing the ionic strength of the solution or even causing aggregation and sedimentation of the sol. In this regard, we have chosen the «chemically pure» reducing agent – hydrogen – and have studied the influence of some parameters on catalytic reduction Au(III) to Au(0).

In our work the usable as catalysts-seed and high stable during a long time gold nanoparticles have been obtained by photochemical method in the aqueous medium. The obtaining gold sol was monodispersed and had an average crystallite diameter (4.6 ± 0.8) nm. The hydrodynamic diameter and absolute value of the zeta-potential were (6.1 ± 1.6) nm and 78.3 mV respectively.

The catalytic reduction Au(III) with hydrogen on the surface of the seed nanoparticles Au(0) carried out at various pH. The constancy of the pH was maintained by different buffer systems. The formation of new layers of reduced gold on seed nanoparticles was accompanied by an increasing in the absorption of the plasmon resonance of gold. Henry's law constant has allowed us in the start of the process to consider the zero order of the reaction on product Au(0). Thus, constants were measured catalytic reduction at different pH. It has been found that the dependence of rate constant from pH was linear. The same character of dependence from pH have got the standard hydrogen electrode. Similarity of behavior allows to observe nanoparticles of gold as microelectrode [1].

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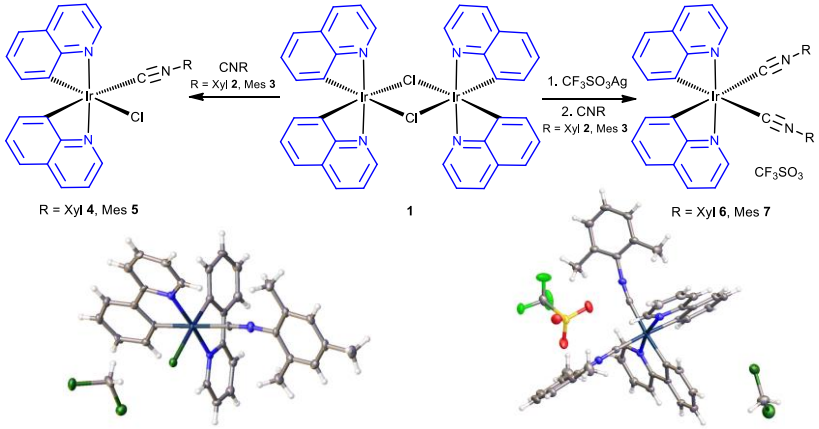
NEW ISOCYANIDE COMPLEXES OF IRIDIUM

Vera D. Somova, Mikhail A. Kinzhalov, Konstantin V. Luzyanin
Institute of chemistry, Saint-Petersburg State University
Saint Petersburg, Russia
Student
vsuns@yandex.ru

In pursuit of our studies of metal-isocyanide complexes, we have prepared new iridium(III)-isocyanide species of a general formula $[(ppy)_2IrCl(\underline{C}NR)]$ and $[(ppy)_2Ir(\underline{C}NR)_2](CF_3SO_3)$ (ppy = 2-phenylpyridine-C^2,N'). Indeed, complexes $[(ppy)_2IrCl(CNR)]$ (R = Xyl, Mes; isolated yields 82–87%), were prepared starting from the binuclear complex $[(ppy)_2Ir(\mu\text{-}Cl)]_2$ upon reaction with one equiv of appropriate isocyanide. Corresponding *bis*(isocyanide) complexes $[(ppy)_2Ir(CNR)_2](CF_3SO_3)$ (R = Xyl, Mes; isolated yields 76–79%), were generated from $[(ppy)_2Ir(\mu\text{-}Cl)]_2$ upon removal of chlorides with CF_3SO_3Ag and further action of two equivs of respective isocyanide (R = Xyl, Mes).



All obtained compounds were full characterized by ^1H, and $^{13}C\{^1H\}$ NMR and IR spectroscopies, ESI^+ MS and elemental analyzes (CHN), and by X-ray diffraction.

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THE STUDY OF POTASSIUM AND AMMONIUM DOUBLE SULFATE PRODUCING PROCESS AND ITS PROPERTIES

Stefantsova O.G, Rupcheva V.A., Poilov V.Z.
Perm National Research Polytechnic University,
Perm, Russia
Postgraduate Student
olgatnv07@rambler.ru

The production of complex fertilizers is promising trend in the technology of mineral fertilizers. The potassium and ammonium double sulfate (KNH_4SO_4) could be used as potassium nitrogen sulfate fertilizer. The absence of chloride and nitrate ions in its composition which could accumulate in plants fruitage and negatively affect on their growth and development is a main advantage of this compound. Also there is a possibility to use this sulfate fertilizer for the plants which are not tolerate to chlorine excess. In addition it could be used for different soils and for large number plants cultures.

The potassium and ammonium double sulfate was obtain by two steps process according to the following reactions [1, 2]:

$$KCl + H_2SO_4 = KHSO_4 + HCl \quad (1)$$

$$KHSO_4 + NH_3 = KNH_4SO_4 \quad (2)$$

The potassium chloride, concentrated sulfuric acid and ammonia were used as a raw material for KNH_4SO_4 production. In the first step potassium chloride reacted with sulfuric acid with isolation of hydrogen chloride in the gas phase and further formation of acid potassium sulfate suspension. Obtained acid potassium sulfate was neutralized by ammonia gas with potassium and ammonium double sulfate production. The gaseous hydrogen chloride was absorbed by water in order to obtain hydrochloric acid with concentration 28-32%. It was found by using X-ray phase analysis that the product which is obtained in described process is a potassium and ammonium double sulfate with crystal lattice of arcanite. The properties of potassium and ammonium double sulfate were investigated in comparison with the other fertilizers which are already known, such as potassium sulfate (K_2SO_4), potassium chloride (KCl) and carbamide ($(NH_2)_2CO$), in order to evaluate the possibility of its using as a fertilizer. The solubility and dissolution rate are basic properties which could be investigated in evaluation of fertilizers use.

Hygroscopicity is a main property which determinates fertilizer storage conditions and its transportation. All the above properties were studied at temperature 25°C. The results of the research are shown in table 1.

Table 1. The comparison of potassium and ammonium double sulfate properties with the properties of popular fertilizers

Fertilizer	KCl	K_2SO_4	$(NH_2)_2CO$	KNH_4SO_4

Solubility, g/100gH_2O	34,3	12,4	54,6	14,1
Dissolution rate, g/min	0,25	0,014	1	0,027
Hygroscopicity ,%	4,40	1,53	1,96	1,94

Based on the data which is presented in table 1, it is possible to say, that solubility of potassium and ammonium double sulfate is higher than the solubility of potassium sulfate, but lower than the solubility of potassium chloride and carbamide. The potassium and ammonium double sulfate could be used as a fertilizer when the value of solubility is 14.1 g/100g H_2O. The dissolution rate of KNH_4SO_4 is approximately twice higher than the dissolution rate of potassium sulfate, but it is several times lower than other fertilizers dissolution rate. There are several advantages of low dissolution rate of applied fertilizer such as: long stability in solid and higher resistance to wastewater.The potassium and ammonium double sulfate has small hygroscopicity, which is comparable with the hygroscopic of carbamide and potassium sulfate, therefore there is no necessityfor additional treatment.The production of potassium and ammonium double sulfate by described method is a non-waste production. Moreover there is a possibility to obtain marketable hydrochloric acid as a byproduct of this technology. Obtained potassium and ammonium double sulfate has avarage solubility in water, low dissolution rate and small hygroscopicity. These properties of investigated substance allow to use it as a complex potassium and nitrogen sulphate fertilizer.

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MACROPOROUS MOLECULARLY IMPRINTED POLYMER MONOLITHS FOR THE HPLC ANALYSIS OF MACROLIDE ANTIBIOTICS

Stepanova M.A.[1], *Vlakh E.G.*[1,2], *Tennikova T.B.*[1,2]

[1]Saint Petersburg State University, Institute of Chemistry, St. Petersburg, Russia
[2]Institute of Macromolecular Compounds Russian Academy of Sciences
St. Petersburg, Russia
Postdoc
maristepanova@gmail.com

The development of artificial receptors represents one of the actual directions of the modern biomedical chemistry. The simple and effective tool allowing the solvation of this task is the molecular imprinting represents. The approach is based on formation of a molecular fingerprint of the target compound (template) in the polymer matrix [1].

Erythromicin (ERY) is an antibiotic of the macrolide class. Macrolide antibiotics are the safest group of drugs with a broad spectrum of antimicrobial activity. Therefore, ERY is most widely used in human and veterinary medicine. The widespread administration of this drug in veterinary medicine represents a potential risk, because its residues may persist in the animal body and may result in the development of drug-resistant bacterial strains or allergies. The existing analytical techniques to determine the ERY are very laborious and difficult for sample preparation [2].

Molecularly imprinted polymer utilized as artificial receptor for ERY may be used for the highly selective separation and for the analysis of ERY and its analogues directly into biological substrates.

In this work, a series of new macroporous monolithic imprinted HPLC columns with different content of molecular prints of ERY were prepared by *in situ* thermo-initiated polymerization using 2-hydroxyethyl methacrylate as a functional monomer, ethylene glycol dimethacrylate as a cross-linker, 1-decanol–toluene as a porogenic solvent and 2,2'-azobisizobutironitrile as a initiator. The developed stationary phases were characterized by number of parameters such as average pore size, porosity, specific surface area, permeability. The surface morphology of polymers obtained were studied by scanning electron microscopy. The retention of ERY on the developed imprinted columns were compared with the standard non-imprinted sorbent and imprinting factors were calculated.

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COMPOSITE SELECTIVE SORBENTS FOR EXTRACTION OF CESIUM AND STRONTIUM RADIONUCLIDES FROM SEA WATER

E. A. Tokar'[1], *M. V. Tutov*[1,2], *A. M. Egorin*[2], *T. A. Sokolnitskaya*[1,2], *V. A. Avramenkoa*[1,2]

[1]Far Eastern Federal University,
[2] Institute of Chemistry, Far Eastern Branch of the Russian Academy of Sciences,
Student
d.edd@mail.ru

The report will be made to present the characteristics of new sorption materials for the extraction of cesium and strontium radionuclides from seawater. Sorbents' synthesis is immobilization of highly refined entities of barium silicate, which has a high selectivity to strontium ions [1, 2], in the volume of resorcinol-formaldehyde polymer (Fig. 1a). Will be shown a method for obtaining spherogranular sorbents (Fig. 2b) which can be used as a filter medium of charging columns. We got the series of samples with various contents of barium silicate (from 4.5 wt% to 28.2 wt%), examined their sorption-selective characteristics in the seawater. We have determined the optimal content of barium silicate in the composite sorbent, at which the value of the distribution coefficient of strontium-90 reaches the maximum value, and we also evaluated the efficacy of extraction of radionuclide of cesium-137 and strontium-90 composite sorbents from seawater Amur Bay (Primorsky Krai) under the dynamic conditions.

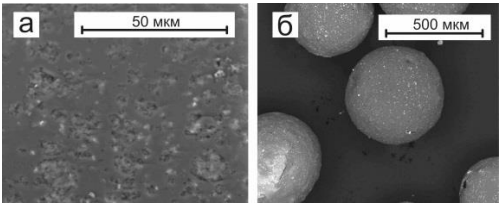

Fig. 1. SEM images of the surface of the sorption material at different magnifications

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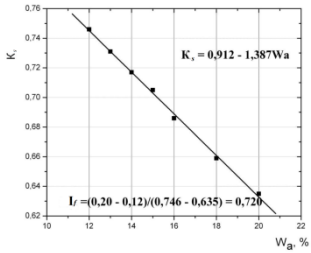
INFLUENCE OF PHYSICAL AND CHEMICAL CHARACTERISTICS AND FORMING CONDITIONS OF CLAY RAW MATERIALS IN TECHNOLOGY OF CLAYDITE.

Toropkov N.E.[1], *Kutugin V.A.*[1]

[1]National Research Tomsk Polytechnic University
Tomsk, Russia
Student
zerogooff@gmail.com

The article considers research of physical and chemical properties of clay raw materials for porous ability clay raw material in the production technology of expanded clay aggregate. Also is held dependence on the chemical composition of the clay pore formation in the granules of claydite gravel.
The aim of this work is to study the dependence of pressing conditions from intumescent ability of pellets.
Volumetric deformation of plastic ceramic materials are inherently different from the volume deformations of the solid. Plastic deformation of the ceramic material is accompanied by a change in volume of the phase composition, which can be quantified by the values of Ks, Kl and Kg. Studies have been conducted in order to obtain dependences of compaction pressure on the absolute moisture the mass and its ultimate shear stress on the moisture content, which determine the properties of molding clay mass.



Picture 1. The dependence of the volume fraction of the solid phase of the absolute moisture content

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INTERACTION OF VANADYL SULFATE AND LAYERED PEROVSKITE-LIKE OXIDE $HLATIO_4$ UNDER VARIOUS CONCENTRATIONS

Trofimova D.D. ,Abdulaeva L.D. , Silyukov O.I.

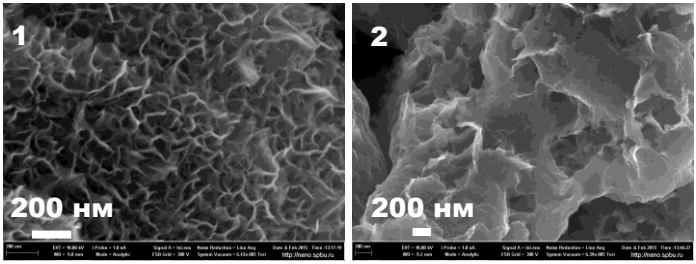
Saint Petersburg State University,
Saint Petersburg, Russia
Student
Dariya43010@yandex.ru

Layered perovskite-like oxides are widely studied class of compounds due to their structure and useful chemical properties, such as ion exchange and intercalation reactions. Also, there are perovskite-like compounds, which have a number of practically important properties: superconductivity, colossal magnetoresistance, catalytic and photocatalytic activity [1].

This work presents the results of interaction researches of $VOSO_4*3H_2O$ water solution with various concentrations and the protonic form of layered perovskite-like oxide $HLaTiO_4$, prepared from alkali form $NaLaTiO_4$ during the ion exchange in a hydrochloric acid solution.

Characterization by SEM, powder XRD, thermal analysis (TGA and STA) have been performed for the determination of the structure and content of synthesized oxides.

It was observed, that particles of initial protonic oxide transform into nanostructured agglomerates, which supposedly consist of the monolayers of vanadium containing phases. This process runs in varying degrees depending on initial concentration of vanadyl sulfate.



Picture 1. SEM of samples: 1. $HLaTiO_4$ + $VOSO_4$ (1:2), 2. $HLaTiO_4$ + $VOSO_4$ (1:10).

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HYDROTHERMAL SYNTHESIS OF TITANATES WITH ILMENITE STRUCTURE

Tsvetkova E.V.[1], *Golubeva O.Y.*[2], *Maslennikova T.P.* [2], *Ryabkov Y.I.*[1]

[1]Institute of Chemistry of Komi SC UB RAS,
Syktyvkar, Russia
[2] Grebenschikov Institute of Chemistry of Silicates RAS,
Saint Petersburg, Russia
Postgraduate Student
tskatya2010@yandex.ru

Materials based on transition metal oxides are widely used for the manufacture of gas sensors, catalysts and spintronic devices, dielectric resonators.

The present work is devoted to the preparation of $A_{1-x}Fe_xTiO_3$ (A = Ni, Co, Mn, Mg) titanates and their solid solutions by hydrothermal method, which has not been used for the synthesis of these compounds previously.

In our work we used metal nitrates $M(NO_3)_2*mH_2O$, titanium isopropoxide $Ti(i\text{-}OC_3H_7)_4$, ethanol C_2H_5OH, ammonium hydroxide NH_4OH and polyethylene glycol (PEG-15000) as starting materials to obtain titanates and their solid solutions.

Hydrothermal synthesis was carried out in steel autoclaves with a platinum crucible during 24-48 hours. The filling factor (k) was varied depending on the synthesis conditions: k = 0.80 at 250 °C and 10 MPa; k = 0.73 at 300 °C and 20 MPa; k = 0.60 at 350 °C, 24 h, 20 MPa.

The samples were tested by X-ray diffraction (DRON diffractometer, Cu Kα radiation, λ = 0.154178 nm) and electron microscopy (scanning electron microscope VEGA3 TESCAN).

Hydrothermal method allows to produce the monophasic manganese titanate solid solutions containing 5-20 mol.% Fe. The optimal synthesis conditions are as follow: 250 °C, 24 h, 10 MPa. It was established that submicron particles with an anisotropic form were predominant in the samples.

It was shown that the increase of temperature (from 250 ° C to 350 ° C) and synthesis time (from 24 to 48 hours) results in increase of the volume fraction of the ilmenite phase for cobalt and magnesium titanates (from 40 to 80 vol.%). According to the SEM results, the particles have an anisotropic shape (elongated and disc-shaped particles).

Acknowledgements
This work was supported by the Russian Foundation for Basic Research (grants 14-33-50730 and 13-3-00132).

SEMICONDUCTOR THIN FILMS OF In_2S_3 FOR SOLAR CELLS

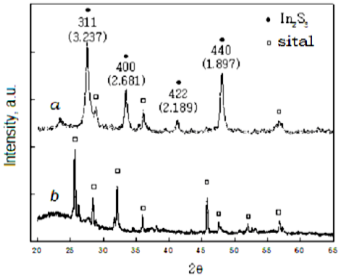
Tulenin S.S.[1], *Markov V.F.*

[1]Ural Federal University,
Yekaterinburg, Russia
Postgraduat student
stast1989@mail.ru

Nowadays solar energy is power field of non-traditional energy. Solar calls possess more and more high transformation coefficient (more then 21%). But main problem in this field is material of cells. We needs effective, safety to environment and inexpensive material which is cupper indium disulfide. But we well know that $CuInS_2$ or In_2S_3 are very difficult compound to preparation by means physical methods. Chemical bath deposition (CBD) method allow obtain two different thin films In_2S_3 and Cu_2S or InS and CuS us that together will give cupper indium disulfide. We described theoretical calculation of In_2S_3 thin films deposition in this article [1].

The indium precursor in the solution was indium nitrate $In(NO_3)_3$. The tartaric acid $C_4H_6O_6$ was used for complexation indium-ion which inhibited reaction of sulfide formation. Also the hydroxyl amine $NH_2OH{\cdot}HCl$ was used as stabilizing additional. A precursor of sulfide-ions was tioacetamide $CSCH_3NH_2$ that is unstable in an acid solution. A solution contained all components was than mixed and thermostatted at 353 K in Mo-glass beaker. After two hours deposition uniform orange films with good adherent were observed on sitall substrates. Thickness of obtained thin films was nearly 700 nm.

The XRD researches of the deposited In_2S_3 thin films have shown, that they crystallized in cubic structure (picture 1*a*). Diffraction peaks (311), (400), (422) and (440) observed on typical XRD pattern of the In_2S_3. Also it is given for comparison the XRD pattern of substrate (picture 1*b*).



Picture 1. XRD spectra of In_2S_3 thin film deposited at 353 K (*a*) and sital substrate (*b*)

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THE COMPLEX STUDY OF HYDRATION AND PROTONATION PROCESSES OF LAYERED TITANATES $A_2LN_2TI_3O_{10}$

Utkina T.D.[1]

[1]Saint Petersburg State University, Saint Petersburg, Russia
Graduate student
utkina.td7@gmail.com

Layered perovskite-like oxides $A_2Ln_2Ti_3O_{10}$ belong to Ruddlesden-Popper phases. There are crystalline compounds in which three-dimensional perovskite blocks are interleaved with layers of rock salt structure. These materials attract the attention of scientists because they demonstrate high ionic conductivity and photocatalytic activity, particularly in the reaction of water splitting with hydrogen production. Therefore, from a practical point of view, the study of oxides in aqueous solutions and humid atmosphere where the processes of hydration and ion exchange (protonation) are possible is relevant.

Alkaline forms of layered perovskite oxides are able to undergo protonation (substitution of alkali cations to protons) and hydratation (sorption of the water molecules on the surface of the oxide and introduction of water molecules into the interlayer space) when exposed to an aqueous solution or humid atmosphere. These processes can significantly influence the physico-chemical properties of oxides and their investigation should not be neglected.

Complex oxides $A_2Ln_2Ti_3O_{10}$ (A= Li, Na, K; Ln = La, Nd) were prepared by the ceramic method in the temperature range of 1100 – 1200^0C in air at the atmospheric pressure. Suspensions of the obtained compounds were prepared by adding the powdered samples to distilled water. These suspensions were kept under constant stirring for certain periods of time, then the samples were centrifuged and dried.

The phase composition and structural parameters of the raw materials and the obtained samples were monitored by XRD analysis. To determine the degree of protonation and the number of intercalated water thermogravimetric analysis (Netzsch TG 209 F1 Libra) was used. The thermal effects of dehydratation processes were determined by the DSC 204 F1 Phoenix.

As a result, the complex study of hydration and protonation processes was conducted. The composition of the hydrated and protonated forms was calculated. The thermal desorption and deintercalation effects were determined. It was found that the protonation is typical for all forms of layered oxides $A_2Ln_2Ti_3O_{10}$. In addition to the protonation process the intercalation of water molecules into the interlayer space was observed for $K_2Ln_2Ti_3O_{10}$. Thus, these materials exist in aqueous solution in the form of compounds with the general formula $H_xK_{2-x}Ln_2Ti_3O_{10}*yH_2O$ or $H_xA_{2-x}Ln_2Ti_3O_{10}$ (A = Li, Na).

This work was supported by the Russian Foundation for Basic Research (grants № 15-03-05981).

DSC INVESTIGATION OF HYDRATION PROCESS OF LAYERED OXIDES $K_2Ln_2Ti_3O_{10}$

Utkina T.D.

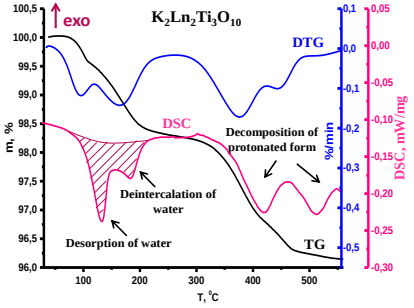
Saint Petersburg State University, Saint Petersburg, Russia
Graduate student
utkina.td7@gmail.com

$K_2Ln_2Ti_3O_{10}$ (Ln – an lanthanide) are crystalline compounds in which three-dimensional perovskite blocks are interleaved with layers of the rock salt structure. Complex oxides with perovskite-like crystal structures are an object of intense interest due to their unique properties, in particular catalytic properties in the photoinduced processes of water splitting and degradation of toxic organic compounds in water.

The hydration and ion-exchange processes of the layered titanates are normally examined on their contact with aqueous solution. Hydration includes the sorption of water molecules on the oxide surface and their intercalation into the interlayer space, where the alkali metal cations are located. These processes can significantly influence the physico-chemical properties of oxides and their investigation should not be neglected.

Complex oxides $K_2Ln_2Ti_3O_{10}$ (Ln = La, Nd) were prepared by the solid state synthesis at 1100^0C. Suspensions of the obtained compounds were prepared by adding the powdered samples to distilled water.

The composition of the obtained compounds $H_xK_{2-x}Ln_2Ti_3O_{10}*yH_2O$ was defined by thermogravimetry. The thermal effects of the dehydratation process consisting of the desorption and deintercalation of water were determined by the DSC 204 F1 Phoenix (pic. 1).



Picture 1. DSC obtained $K_2Ln_2Ti_3O_{10}$ after contact with water

As a result, the dehydration and deprotonation processes turned out to be endothermic. The heat of the desorption and deintercalation was calculated by software «NETZSCH Peak Separation 3».

This work was supported by the Russian Foundation for Basic Research (grants № 15-03-05981).

SELF-ASSEMBLING SYSTEMS BASED ON WATER-SOLUBLE Co(II) PHTHALOCYANINES

Filippova A.A., Voronina A.A., Vashurin A. S., Kuzmin I.A., Golubchikov O.A.

Ivanovo State University of Chemistry and Technology
Senior Reseacher
asvashurin@mail.ru

Supramolecular systems based on tetrapyrrolic macroheterocyclic compounds have a great potential to be used as electronics, pharmaceuticals and biological materials [1-2]. Substituted metallophthalocyanines have several centers of specific solvation and able to form molecular assemblies in crystals and solutions due to non-covalent interactions. Obtaining of polycentric catalytic supramolecular systems based on number of water-soluble metallophthalocyanines and organic bases is considered in present work. It is known that metallophthalocyanines form H-associates in solutions due to interactions between π-electronic systems of macrocycles [3-4]. The molecular structure was obtained by destruction of H-associates. J-aggregates were received based on monomeric phthalocyanines and DABCO. The structure of J-aggregates was confirmed by ^{1}H NMR and electron absorption spectroscopy methods. The influence of peripheral substitution nature and location of the functional group on stability of associates was identified. Thus, introduction of benzotriazole group in macrocycle periphery in combination with naphthoxy spacer bridge between the sulfonic group and the macrocycle leads to formation of stable supramolecular systems. Aggregation within a few days causes formation of blue precipitate that is sparingly soluble in water and ethanol but soluble in water-alkali solutions retaining the associated structure. Obtained structures were investigated the catalytic activity in homogeneous Merox process. It should be noted that stability of molecular associate is correlated with its catalytic activity.

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STRUCTURAL FEATURES OF SILVER-DOPED PHOSPHATE GLASSES IN ZONE OF FEMTOSECOND LASER-INDUCED MODIFICATION.

Vasileva A.A., Olshin P.K., Manshina A.A., Sokolov I.A.

Saint Petersburg State University
Saint Petersburg, Russia
Student
111nusha111@mail.ru

Nowadays there is a great requirement of materials with local change of some properties including optical properties for creating diminutive parts of different devices. One of the possible techniques for doing this is laser modification of glasses and silver-phosphate ones may be of interest. The results could be useful for creating of information storage and optical switches. The aim of this work is investigating of possible changes in structure made by laser irradiation which could cause changing of optical properties. First of all system included three binary Ag_2O-P_2O_5 glasses was synthesized by melt quenching technique. As raw materials $AgNO_3$ and H_3PO_4 were chosen. Then obtained samples were polished in transparent plates. Used containing of modification oxide (from 35 to 55 mol% of silver oxide) has a big influence on glass structure what was investigated by Raman spectroscopy. It was found that synthesized glasses contain mainly metaphosphate and pyrophosphate structural units. Then some structures by laser irradiation were obtained. The samples were irradiated by femtosecond Ti: Sapphire laser at 800nm that emits 120fs, 250kHz pulses with 60nJ energy. The sample was situated on 3D – translation stage. The laser beam was focused on the depth about 100mkm from the surface. Raman spectra for modified zone were considered in detail. There takes place changes of peaks intensities so we can make some conclusions about structure in modified zone. Also luminescence data were obtained for much complete conception of structure. Then it was found that laser modification causes formation of color centers and the influence of silver concentration to these processes was investigated.

OCTAHEDRAL RHENIUM CLUSTER COMPLEXES WITH S-DONOR APICAL LIGANDS

Volzhenin A.V.[1,2], *Brylev K.A.*[1,2]

[1]Novosibirsk State University,
[2]Nikolaev Institute of Inorganic Chemistry SB RAS
Novosibirsk, Russia
Student
volgenin123@mail.ru

At present, a large number of octahedral rhenium cluster complexes with the general formula $[\{Re_6Q_8\}L_6]^x$, where Q = S or Se as inner ligands; L – various organic or inorganic ions or molecules as apical ligands, is known. However, there aren´t any structurally characterized examples of soluble Re_6 complex with S-donor ligands L.

This work is devoted to the synthesis of the first hexarhenium cluster complexes with S-donor apical ligands.

It was found that boiling of aquahydroxo complexes $[\{Re_6Q_8\}(H_2O)_4OH)_2]\cdot 12H_2O$ in an aqueous solution of sodium sulfite leads to the formation of hexasubstituted sulfite complexes $[\{Re6Q_8\}(SO_3)_6]^{10-}$. Notably, the complexes have the highest charge (10–) reported so far for any transition metal cluster complex, and are the first soluble octahedral rhenium cluster complexes with a doubly charged apical ligand.

In addition, new cluster complexes with organic ligands were synthesized starting from $[\{Re_6Q_8\}(SO_3)_6]^{10-}$ by ligand exchange reactions. The obtained $[\{Re_6Q_8\}L_5(SO_3)]$ neutral clusters are promising precursors for preparing different mono-functional derivatives by substituting remained $SO3^{2-}$-ligand.

All the compounds obtained show red emission upon UV photoexcitation. As it was recently shown, photoluminescent hexarhenium cluster complexes can be immobilized into polymeric matrix forming a hybrid luminescent material and type of interaction with polymeric matrix is defined by apical ligand environment of cluster [1, 2]. Thus, the new complexes $[\{Re_6Q_8\}L_5(SO_3)]$ and their derivatives can be considered as alternative luminophores for creation of novel luminescent materials and study of their interaction with a polymeric matrix is the goal of our future study.

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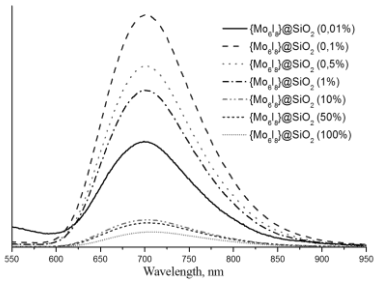
MATERIALS BASED ON SILICON DIOXIDE DOPED BY LUMINESCENT OCTAHEDRAL MOLYBDENUM CLUSTER COMPLEXES

Vorotnikov Y.A.[1,2], *Shestopalov M.A.*[1,2,3], *Brylev K.A.*[1,2], *Mironov Y.V.*[1,2]

[1] Novosibirsk State University
[2] Nikolaev Institute of Inorganic Chemistry SB RAS
[3] Institute of Clinical and Experimental Lymphology SB RAMS
Student
matashandu@gmail.com

Octahedral molybdenum cluster complexes with the general formula $[\{Mo_6X_8\}Y_6]^n$ (where X is an inner ligand (Cl, Br or I) and Y is an outer organic/inorganic ligand) exhibit photoluminescence in the visible and near-infrared regions with high emission quantum yields and lifetimes, and have excellent potential for singlet oxygen generation. Due to these properties molybdenum cluster complexes can find a number of applications in the fields of medicine and biology. Despite the great potential of molybdenum cluster complexes, they are not suitable for use in biological purposes, since they are often insoluble in water and can potentially react with physiological environments. Thus, they must be either coated with appropriate organic ligands or encapsulated into an organic or inorganic inert matrix. Silica is the most often used inorganic matrix for obtaining of luminescent materials intended for biological applications. Thus, molybdenum cluster complexes and silicon dioxide have been chosen for obtaining of luminescent materials.



Picture 1. Luminescence spectra of the powdered samples $\{Mo_6I_8\}@SiO_2$ with different concentrations of cluster complexes.

The Mo_6 cluster containing luminescent silica particles ($\{Mo_6X_8\}@SiO_2$) were synthesized by two different paths: Stöber and microemulsion methods. They were characterized by a number of physical and chemical methods. Inter alia, the luminescence properties of the obtained materials were studied (Picture 1). A dependence of the luminescence quantum yield on the concentration of encapsulated cluster complex was revealed.

Acknowledgements.
The work was supported by the Russian Science Foundation (project № 14-14-00192)

COMPOSITE MATERIALS FOR ENERGY CONVERTERS BASED ON POROUS SILICON WITH PLATINUM METALS CATALYST

Yashtulov N.A.[1,2], Zenchenko V.O.[1], Samoylov V.M.[3], Danilov E.A.[3]
[1]M.V. Lomonosov Moscow State University of Fine Chemical Technologies, Moscow, Russia,
[2]National Research University «Moscow Power Engineering Institute», Moscow, Russia,
[3]NRU «Graphite», Moscow, Russia,
e-mail: zenchenko-vitalij@yandex.ru

Today one of the most important goals for humanity is to provide themselves with energy [1-3]. Such task can be solved using chemical power sources, because they can operate using different fuels, such as hydrogen, methanol and others. The efficiency of the direct transformation of the chemical energy to the electric energy in the cells achieves 50-70%. The catalyst layer is important factor, which considerably influences the fuel cell performance and which is the basic production costs of fuel cells. In both the anode and cathode, the catalyst layer is the location of the half-cell reaction in fuel cell [1-3].

The aim of our study was the creation of new structural material, which had a higher catalytic parameters and lower cost. Porous silicon was effectively used as a functional support for nanocomposites formation which allows preventing catalyst agglomeration in current sources based on hydrogen-containing fuel oxidation. The application of bimetallic nanoparticles improve power source specific characteristics and increase the resistance to catalyst poisoning. The proposed novel method of synthesis in reverse micelles solution allows to obtain nanoparticles with controlled size and shape [1-2].

It was carried out a wide range of research in order to choose optimal conditions of synthesis of nanoparticles: the solubilization degree, platinum metals concentration and ratio in solution, porous silicon porosity degree, pores size and shape. Certification of composites was carried out by transmission and scanning electron microscopy atomic force microscopy and cyclic voltammetry methods.

It was found that the highest electrocatalytic activity have composites obtained from reverse micelle solutions with the solubilization degree of 1.5 based on silicon wafers with a porosity degree of 72%. According to the electron microscopy data, the nanoparticles were fixed not only on the surface but also in the volume of the porous silicon, the average size of nanoparticles was about 3 nm. The obtained nanocomposites on porous silicon containing platinum metal nanoparticles of different composition, size and shape, can be used as functional membrane-electrode materials for micro-power energy converters.

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INFLUENCE OF IODINE ADDITION ON STRUCTURE AND MORPHOLOGY OF PBSE THIN FILMS PREPARED BY THE CHEMICAL BATH DEPOSITION

V.M. Yurk[1], *L.N. Maskaeva*[12], *V.F. Markov*[12]

[1] The Ural Federal University
[2] Ural Institute of State Fire Fighting Service at RF Ministry for Emergencies
Ekaterinburg, Russia
Post-graduate student
v.jurk@yandex.ru

For improvement of functional properties layers of sulfide and selenide of lead are doped halogens [1-3]. Among halogens the iodine provides the highest signals of the photoresponse of chalcogenide thin films to IK-radiation. Also introduction to reaction mixture of an iodinated additive has strong impact on their microstructure keeping invariable phase structure [4].

In the present work the lead selenide thin films prepared by the chemical bath deposition technique were investigated. The growth kinetics of PbSe films depending on the content of ammonium iodide was studied. The thickness of a film decreases when the content of NH_4I increases and becomes 0,25 mol/l. The PbSe thin film is composed by from nanocrystalline grains with observed sizes ~ (1,0×0,1×0,1) mkm which has small packing density on a substrate, and chaotically locates on a surface.

The elemental analysis indicates that PbSe films includes oxygen. The line of oxygen is observed in PbSe layer EDX range, and its content reaches 61,37 ат. %. It is possible to conclude that as-deposited films are already enriched with oxygen. The oxygen containing in the phase PbSe allows to hope that formation of photosensitive structures on its basis is possible without the alloying additive in reaction mixture of ammonium iodide. Availability of oxygen as a part of a film suggests that the process proceeded according to the hydroxide scheme, that is through formation of a phase of lead hydroxide with the subsequent its selenization.

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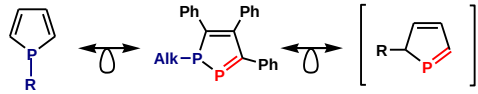
THE CHEMISTRY OF 1-ALKYL-1,2-DIPHOSPHOLES

Zagidullin A.A.[1], *Oshchepkova E.S.*[1], *Burganov T.I.*[1], *Zvereva E.E.*[1], *Miluykov V.A.*[1], *Katsyuba S.A*[1]., *Sinyashin O.G.*[1], *Hew-Hawkins E.*[2]

[1] *A.E. Arbuzov Institute of Organic and Physical Chemistry, Kazan, Russia*
[2] *Institute of Inorganic Chemistry, Leipzig University, Leipzig, Germany*
Kazan, Russia
Research assistant
zagidullin@iopc.ru

The pioneering work of the synthesis of monophosphole in the 1970s spurred the development in this novel area of chemistry that resulted in novel highly effective catalysts, materials for light-emitting diodes, nonlinear optics, conductive polymers and drugs.[1] Recently, we have found that it is possible to combine the thermal stability of 1*H*-phospholes and the high reactivity of 2*H*-phospholes in one molecule - 1-alkyl-1,2-diphospholes.[2]



1*H*-phosphole **1-alkyl-1,2-diphosphole** **2*H*-phosphole**

Cycloaddition reactions of 1-alkyl-1,2-diphospholes proceed under mild conditions with high regio- and stereoselectivity that open possibilities to construct new chiral polycyclic phosphines with chiral bridgehead phosphorus atoms for asymmetric catalysis.[3] At the same time, the simulations ([TD]-DFT) allowed a detailed interpretation of the experimental UV spectra of these compounds and revealed relationships between the chemical modification of 1,2-diphospholes and their light absorption properties.[4] Moreover, recent experimental work demonstrates the possibility of fine-tuning of the aromaticity as well as reactivity of 1-alkyl-1,2-diphospholes by choosing the appropriate substituents at the phosphorus atom. New 1,2-diphospholes containing electron-withdrawing groups are less stable but more reactive in cycloaddition reactions.[5] For this 'aromaticity' reason, 1,2-diphospholes with electron-donating substituents in the *para*-position of phenyl moieties were investigated as new building blocks for organophosphorus π-conjugated systems.[6]

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AU-M NANOCLASTERS AS CATALYTIC MATERIAL FOR ETHANOL CONVERSION INTO CHEMICALS

Zharova P.A.[1], *Chistyakov A.V.*[1,2], *Nikolaev S.A.*[3], *Kriventsov V.V.*[4], *Tsodikov M.V.*[1,2]

[1]Topchiev Institute of petrochemical synthesis RAS, Moscow, Russia
[2]Gubkin Russian State University of oil and gas, Moscow, Russia
[3]Lomonosov Moscow State University, Moscow, Russia
[4]Boreskov Institute of catalysis SB RAS, Novosibirsk, Russia
Moscow, Russia
Ph.D. student
zharova@ips.ac.ru

We present the results concerning with Au-M containing catalysts (M – Cu or Ni) creation based on γ-Al2O3 effective for ethanol conversion into olefins and linear alpha-alcohols.

A strong size effect of selectivity and activity was revealed for Au-M containing catalysts during ethanol conversion into olefins C4-C8. The influence of impregnated metals concentration on aim fraction yield was studied. The opportunity of olefins C4-C8 fraction yield increasing was found due to addition of glycerol with amount not exceeding 20 vol.%.

Conditions allow high selectivity conversion up to 85-92 % of ethanol into butanol-1, hexanol-1 and octanol-1 were found. Conversion rate of initial ethanol varied from 35 to 65 %. In the first time ever the reaction of β-alkylation of iso-propanol with ethanol over heterogeneous catalysts Au-M/Al2O3 was carried out. During combined conversion of ethanol with iso-propanol 3-methyl-2-butanol was obtained that is structural precursor of valuable monomer - isoprene.

Catalysts genesis was investigated with use of XAS, XPS, TEM and EDS. The peculiarities of the reaction mechanism are discussed considering the specific surface and electronic features of the synthesized catalysts.

Acknowledgements

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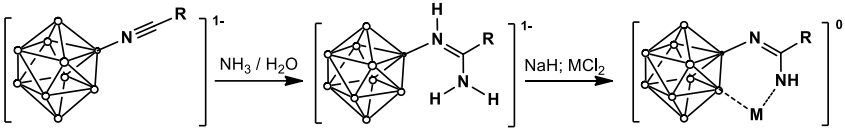
SYNTHESIS AND CHEMICAL PROPERTIES OF [2-$B_{10}H_9NH{=}C(NH_2)R]^-$ (R = Me, Et, ^{t}Bu, Ph) ANIONS

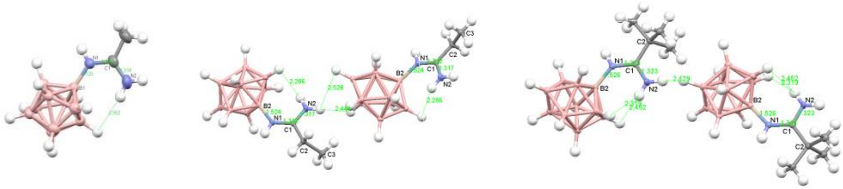
Zhdanov A.P., *Zhihin K.Yu.*
Institute of General and Inorganic Chemistry of N.S. Kurnakov RAS (IGIC RAS)
Moscow, Russia
Ph.D., Research Assistant
zhdanov@igic.ras.ru

We have found that nucleophilic addition of one molecule of ammonia to nitrilium derivatives of *closo*-decaborate anion lead to the unsubstituted amidines:



R = Me, Et, ^{t}Bu, Ph M = Zn, Co, Ni

This process is possible to carry out in aqueous solution, which greatly simplifies apparatus of the reaction and the isolation of the desired product. X-ray data and multinuclear NMR spectroscopy of the products indicate that amidine substituent is stabilized by an intramolecular hydrogen bond and a *Z*-configuration (Pic. 1). Also, increasing the steric effect of the R-substituent of nitrilium group promotes the formation of intermolecular hydrogen bonds and coordination substituted *closo*-decaborates in polymer chains (Pic. 1 *b* and *c*).



a *b* *c*

Picture 1. Crystal structure of $[2\text{-}B_{10}H_9\{Z\text{-}NH{=}C(NH_2)CH_3\}]^-$ (*a*), $[2\text{-}B_{10}H_9\{Z\text{-}NH{=}C(NH_2)C_2H_5\}]^-$ (*b*) and $[2\text{-}B_{10}H_9\{Z\text{-}NH{=}C(NH_2)C(CH_3)_3\}]^-$ (*c*) anions

Also we have studied the complexation reaction between the anhydrous metal halides and deprotonated amidine-substituent of closo-decaborate which are formed *in situ*. Preliminary data show that neutral complex compound generates in these processes.

Acknowledgements
Financial support by RFBR, grants 14-03-31789 mol_a, 13-03-00525 a.

Section 2.

Polymeric materials: methods of production and processing

POLYCONDENSATION TYPE ION-EXCHANGE POLYMERS

Abdutalipova N.M., Turobjonov S.M., Ismailova N.A.

Tashkent chemical and technological institute
Tashkent, Uzbekistan
The senior scientific employee - researcher
nellya85@list.ru

Ion-exchange polymers find wide practical application in various areas of a science and technics. The decision of problems of preservation of the environment, hydrometallurgy, medicine, complex processing of raw materials, edible and a pharmaceutical industry, creation of wasteless technologies is impossible without application of such materials. That is why it has increased requirements. The special attention is given to ion exchange kinetics, high selectivity, mechanical strength, chemical and thermal stability. The most known ion exchangers are polymerization type ion exchangers received on the basis of copolymers of styrene and divinyl benzene. Polycondensation type ion exchangers frequently remain underestimated since their production has a lot of complexities. Possibility of sewing agent quantity control in original stock of monomers at polyfunctional condensation and, the most important thing, suitability of formed copolymers to various polymeranalogous reactions open the big prospects. However existing methods of such sorbents synthesis have lacks: complexity of ion exchangers production with high physical and chemical properties, unavailability and toxicity of some initial monomers. Therefore, despite a considerable quantity of researches in the field of ion-exchange materials synthesis, search of accessible and comprehensible paths of new polycondensation type ion exchangers reception with the set properties remains actual. Insufficient efficiency of available ion exchangers in hydrometallurgy for sorption and division of ions of various metals has caused statement of the important scientifically-practical problem of creation of highly effective ion exchangers on the basis of the accessible monomers, containing relatives on reactivity functional groups and possessing a number of valuable physical and chemical properties.

Considering high interest to reproduced sources of raw materials we had been received ion exchangers on the basis of furfural. Furfural can be received from many vegetative raw materials: wood, an agriculture waste (a peel of various seeds, a shell of nuts, straw, corn cabbage stumps, etc.), a reed, etc. Besides, furfural is received as a by-product at the hydrolytic factories developing alcohol from a wood waste.

Use furfural as initial monomer opens opportunities of high-strength ion-exchange polymers synthesis with various functional groups by polymeranalogous reactions.

As mother substances for reception of anion exchanger we had been used styrene, furfural and polyethylenepolyamine (PEPA) in the presence of the zinc chloride as catalyst.

With the purpose of reception of anion exchanger with improved physical and chemical, sorption, complexing and kinetic characteristics we have been studied influence of various factors on process of polyfunctional condensation of styrene, furfural and PEPA. In this article were studyed influence of condensation temperature and quantity of the catalyst on exchange capacity of anion exchanger on 0,1 N solution of HCl are presented. Thus the ratio of initial substances remains invariable. Temperature varied in an interval 70-110°C, and quantity of the catalyst from 5 to 20 %. The yielded dependences have been constructed by means of program MathCad (figure1).

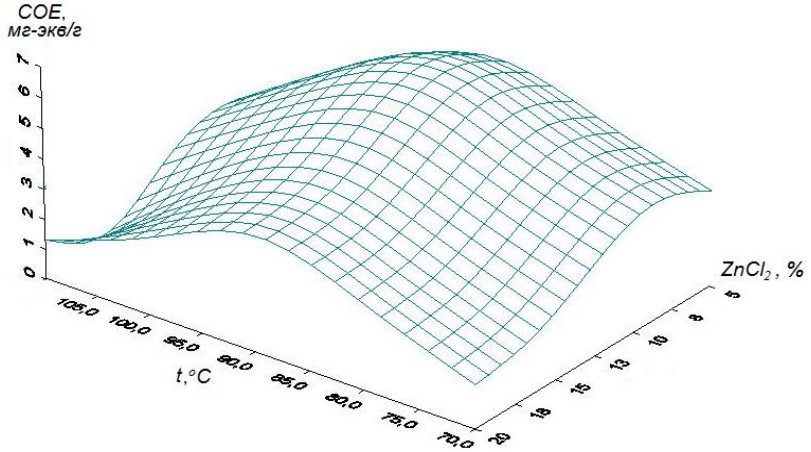


Figure1. Dependence of exchange capacity of anion exchanger «ANF» from temperature of polyfunctional condensation and quantity of the catalyst

Apparently from data of figure increase in quantity of the catalyst and increase in temperature of reaction considerably accelerates polyfunctional condensation process, however it result into reception of anion exchanger with high density of the crosslinking, having low swelling capacity and as consequence low exchange capacity. Optimum it is necessary to consider maintenance $ZnCl_2$ of 8-12 % at temperature of 85-95 °C. The most uniform current of reaction and as consequence reception of ion exchangers with the improved indexes is thus provided. Also it is necessary to notice, that the increase in maintenance $ZnCl_2$ above 12 % influences on the static exchange capacity more considerably, than its decrease below 8 %.

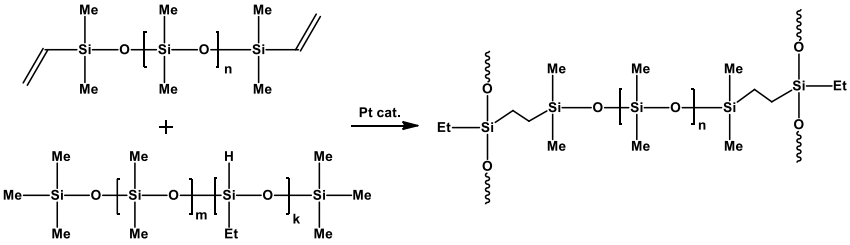
SYNTHESIS OF NEW ACYCLIC DIAMINOCARBENE COMPLEXES OF Pt(II), Pd(II) AND THEIR APPLICATION IN THE HYDROSILYLATION REACTION

Afanasenko A.M., *Boyarskaya D.V.*, *Chulkova T.G.*, *Boyarskaya I.A.*, *Islamova R.M.*

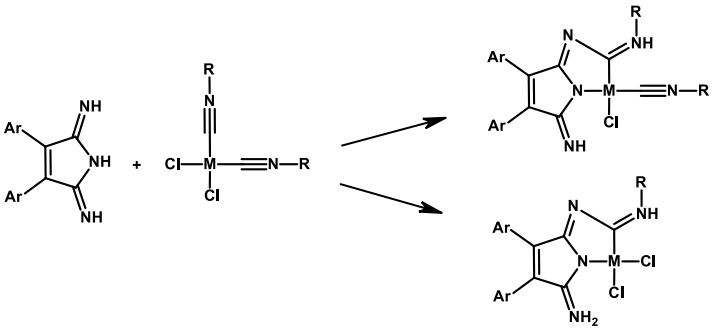
Institute of Chemistry, St. Petersburg State University, 198504 Peterhof, Universitetskii pr., 26, Russia
Student
chemistry28@mail.ru

The coupling between *N*-nucleophiles and isonitrile complexes of Pt(II) and Pd(II) represents an attractive approach for the synthesis of variety of complexes bearing carbene ligands, which may be used as catalysts for various reactions (e.g., cross-coupling reaction, hydroamination and hydrosilylation of unsaturated compounds) [1-4].

It is known that diaminocarbene platinum(II) complexes exhibit high activity in hydrosilylation reactions, hydroamination of alkenes and alkynes [4]. Well-defined silicones have been prepared by hydrosilylation of functional olefins with polymethylhydrosiloxanes predominantly in the presence of Pt-based catalysts to make a whole branch of materials for adhesives binders, ceramic and dielectric coating, encapsulates, membranes, sealants and a lot more. Also, the addition of polyfunctional silicon hydrides to poly(vinyl)organosiloxane leads to effective cure of silicon rubber [5].



We studied the reaction of 3,4-diarylpyrrole-2,5-diimines and *cis*-$[MCl_2(CNR)_2]$ (M = Pd, Pt; R = *i*-Pr, *t*-Bu, Cy, *m*-Xyl, 2-CH_3-6-Cl-C_6H_3, *p*-$(CH_3O)C_6H_4$, *o*-(*t*-BuCOO)C_6H_4, *o*-(4-NC-C_6H_4COO)C_6H_4) and found that the coupling proceeds with one isocyanide ligand to accomplish the carbene complexes depicted in scheme.



The obtained carbene metal species were characterized by X-ray crystallography, IR and ^{1}H, ^{13}C NMR spectroscopies, and also by ESI^{+} mass spectrometry and elemental analysis. Were investigated the photophysical properties of the compounds: absorption spectra and luminescence quantum yields and lifetimes of the excited state in solution.

We studied the reaction of hydrosilylation of vinyl polysiloxanes and hydrosiloxane oligomers in the presence of diaminocarbene complexes of Pt(II) and Pd(II). Were selected optimal process conditions, studied photophysical characteristics of obtained siloxane vulcanizates.

Acknowledgements:

The authors thank Saint Petersburg State University for a research grant (2013-2015) and Russian Fund for Basic Research (grant 13-03-12411). Physico-chemical studies were performed at the Educational Resource Center of the Institute of Chemistry, St. Petersburg State University and resource centers "Magnetic resonance methods of research", "X-ray diffraction methods of research", "Methods of analysis of the composition of matter", "Optical and laser methods of research material" St. Petersburg State University.

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POLYMETHYL METHACRYLATE PARTICLES WITH THE AMINATED SURFACE

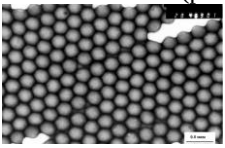
Baigildin V.A.[1,2], *Lavrov N.A.*[1], *Pankova G.A.*[2], *Shevchenko N.N.*[2]

[1]Saint Petersburg State Institute of Technology,
[2]Institute of Macromolecular Compounds RAS
Saint Petersburg, Russia
Postgraduate student
sir.vadim21-07@yandex.ru

Monodisperse polymer particles with surface functional groups have found use in biotechnology for binding biologically active compounds and for conducting biospecific processes in their surface layer [1]. These particles apply due to specific properties such as diameter, particle-size distribution, structures, and surface-layer properties (funcionality, degree of hydrophobicity, and surface-structure stability). At the present time there are methods of preparing polymer particles with surface sulfonic, chloromethyl, hydroxyl, and epoxy groups. But there is no simple method of preparing polymer particles with surface aminogroups.

Therefore, emulsifier-free copolymerization of methyl methacrylate (MMA), 2-aminoethyl methacrylate hydrochloride (AMH) and ethylene glycol dimethacrylate (EGDMA) as a cross-linked agent was explored to synthesize polymeric monodisperse particles. The cross-linker`s influence was investigated on conversion of MMA, shape and particle size distribution as well as surface characteristics of the particles formed. It is shown that the increasing EGDMA concentrations from 0 to 3 wt. % leads to increasing of rate the copolymerization. However, 4 and 5 wt. % EGDMA concentrations lead to decreasing of rate the copolymerization. The reason for decreasing of rate is likely to increasing of the viscosity within particles and limiting the diffusion of monomers in the growing polymer-monomer particles. Molecular weight of formed water-soluble oligomers decreases to 2 times by adding from 1 to 5 wt. % of cross-linked agent (3300 Da at 0 wt. % EGDMA, 1400 at 5 wt. % EGDMA, respectively).

The particle sizes are varied from 300 to 350 nm. The monodisperse spherical particles form only at 4 and 5 wt. % EGDMA (picture 1).



Picture 1. TEM image of cross-linked PMMA particles at 4 wt. % EGDMA.

The presence of functional groups on the surface determines the sign and the magnitude of ζ-potential. The positive charge is defined due to protonation of imidazoline groups of an initiator and aliphatic amino groups after the deprotonation of AMH amino groups. The negative charge is provided by carboxyl groups formed during the hydrolysis of an initiator terminal residues, as well as functioning MMA. It was shown that polymer particles are stability at wide pH-range and inversion of a ζ-potential takes place at alkaline region. This fact says that amino groups are much more than carboxyl groups on the particle surface.

The work is performed at financial support of RFBR (the project № 13-03-00741).

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DEVELOPMENT OF METHODS FOR THE MODIFICATION OF SULFUR DYES POLYMERS TO CREAT ARTIFICIAL STONES AND COLOURING AGENT

Bakytzhanuly B., Gabbasova S.M, Mamutova A.A., Rahmetullaeva R.K.

Al-Farabi Kazakh National University
Almaty, Kazakhstan
Student
b.bakytzhanuly@gmail.com

Creation of effective technological methods of multi-use valuable products production from sulfur is an important task which decision will have the significant environmental and economic benefits. Educing of sulfur-containing compounds from the oil, and further processing of sulfur with receiving of sulfur dyes, is the most promising and urgent task for the moment, implementation of transition from raw materials to finished target commodity products, the creation of the so-called cluster production.

For the first time three component synthesis of aniline with sulfur and styrene was conducted (one-pot synthesis). It is established that at the same time passes N-alkylation reaction of aniline and the polymerization of styrene. As a result of this interaction the dark brown pigment was obtained.

By interaction of aniline, sulfur and aniline hydrochloride were allocated 2 products: phenothiazine and 4,4-diaminodifenilsulfid. Conditions of formation of these products were established: ratio of reagents, temperature and duration of reaction. 4,4'-diaminodifenilsulfida formation proceeds at 180^{o}C for two

hours in a ratio of reactants aniline: aniline hydrochloride: sulfur 2.5:1:6, and at phenothiazine 195ºC for 6 hours at a ratio of 4:2:3.5.
Polyaniline (PANI) is synthesized in two ways: by reacting aniline with ammonium persulfate and ferric chloride (III). It is found that the highest yield of PANI of 81.6% at the oxidation of aniline ammonium persulfate with ferric chloride (III) - 52.49%. At interaction of the PANI and sulfur in the ratio 1: 3 at a temperature of 180 ° C the product of sulphuration of the PANI is received and its possibility of use as the painting pigment of artificial stones on the basis of a calcium carbonate, polyester resin is shown.

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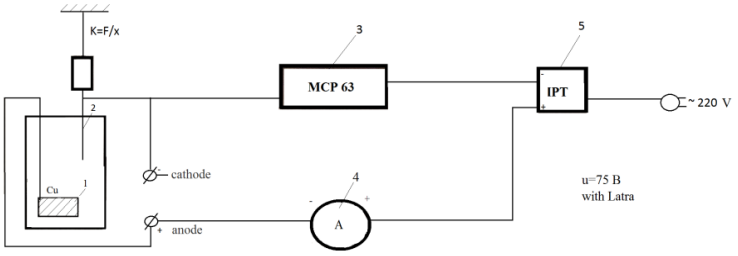
COPPER CONTAINING POLYMER SYSTEMS BASED ON WATER POLYFUNCTIONAL OLIGOBUTADIENS

Bazhenov I.A., Rodionova A.G., Mineeva N.S., Abramova A.V

Yaroslavl State Technical University
Supervisor: Solovyov M.E.
bazhenov.ilya@gmail.com

Metal-polymer composites - are new materials, which are dispersions of inorganic substances in the polymer. These materials combine the advantageous properties of organic and inorganic substances, and disclose the broad scope for various applications. A necessary condition for this is the occurrence of metal in the polymer chain by coordination and ionic crosslinking. As metals are iron, tin, lead, zinc and others. Metal-polymer composites are prepared by sputtering metal on the surface of the polymer or during its synthesis, or thermal decomposition, and other electrochemical techniques. For example, the sol-gel - the method allows to obtain materials with biologically active macromolecules. Metal-polymer systems are characterized by flexibility, elasticity, easy processability inherent polymers.
Undoubted interest for metallopolymers may be multifunctional oligobutadieny (PFOD). Promising methods for producing liquid rubber is modified hydroperoxide epoxidation and subsequent amination synthesized epoksioligobutadienov. Translation PFOD soluble in state is carried out by neutralization with organic or inorganic acids: boron, sorbic, citric, lactic and others. The resulting polymeric system used as katoforeznyh materials possessing bactericidal and corrosion resistance as well as reduced

goryuchestyue. Copper-containing polymer systems based on PFOD received an electrochemical method (see. Figure 1).



Position: 1 - anode; 2 - cathode; 3 – resistance box; 4 – amperemeter; 5 – power supply unit

Figure 1 - scheme of laboratory setup for a saturated aqueous solution of metal ions

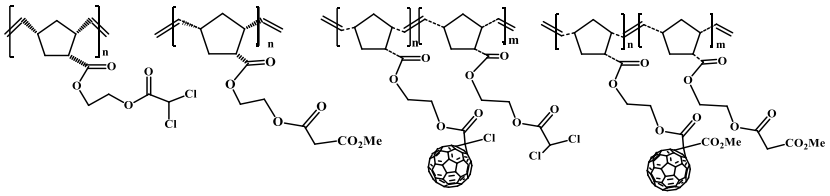
In operation, the systems investigated viscosity, particle size, pH, degree of saturation of copper ions as a function of time and the electrical parameters of the experiment. By chemical analysis and UV spectroscopy indicated the presence of copper ion polymer systems.
Thus, the polymer-based system PFOD may be of interest to the scientific and practical purposes: micro- and nano electronics and biomedical materials, as well as biocidal polymers.

THE STUDY PARAMETERS OF THE THERMAL STABILITY SYNTHESIZED OF NORBORNENES SERIES FULLERENE-CONTAINING POLYMERS

Biglova Yu.N., Mikheev V.V., Zagitov V.V.

Bashkir State University
Saint Petersburg State University
Ufa, Russia
Associate professor
bn.yulya@mail.ru

New norbornenes with the covalently bonded fullerene C_{60} have been prepared as monomers for ring-opening metathesis polymerization. Under the Grubbs catalyst these monomers smoothly enter homopolymerization as well as copolymerization reactions with the parent ‘non-fullerene’ monomers.



I II III IV

The thermal degradation of synthetic homo- (**I**, **II**) and copolymers (**III**, **IV**) of the norbornene series was studied. The temperature of intensive thermal degradation start (T_i), the final temperature of the mass loss (T_f) (calculated by the method of tangents), the temperature corresponding to the reduction of the weight of the polymer thermal destruction at 1% ($T_{1\%}$) and temperature of maximum rate of thermal degradation (T_{max}) are given in Table 1.

Table 1. Parameters of the thermal degradation of polymers norbornene series

Polymer	$T_{1\%}$, °C	T_i, °C	T_{max}, °C	T_f, °C	ΔH, kJ/g
I	118.7	236.9	368.7	437.9	3.65
III	275.9	376.4	395.6	413.8	7.48
II	99.7	262.9	366.0	511.2	8.42
IV	270.0	415.8	449.4	487.1	13.63

Presented in Table 1 parameters of thermal degradation of homo- and co-polymers of norbornene series demonstrate the following. In comparing the data for the homo- (**I**, **II**) and fullerene copolymers (**III**, **IV**), in the case of the latter has been a shift values ($T_{1\%}$, T_{max}, T_i) in the high temperature region. Thus the presence into macromolecule covalently bound fullerene increases the thermal stability of the polymer.

Acknowledgements

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RHEOLOGICAL AND THERMAL PROPERTIES OF HOMO- AND COPOLYMERS OF PROPYLENE

Bulatova G.G.[a,b], *Bezzametnov O.N.*[a,b], *Amirova L.M.*[a,b]

[a] Kazan National Research Technical University named after A.N.Tupolev - KAI (KNRTU-KAI)
[b] Kazan (Volga Region) Federal University (KFU)
Kazan, Russia
Student
GuliyaBulatova17.02@yandex.ru

Composite materials based on thermoplastic binders have a number of advantages compared to composites having a thermoset matrix: high impact strength and fracture toughness, low water absorption, and others. In a wide number of thermoplastic materials polypropylene and copolymers of ethylene and propylene are of especial interest due to their high performance and low cost. Therefore, the study and optimization of processing parameters for this class of polymers is actual.

The goal of this work was to study the rheological, thermal and thermomechanical characteristics of a number of commercially available homo- and copolymers of propylene and to reveal factors affecting these parameters.

The homopolymers (brand: PP1500J, RR1500N), random copolymers of propylene and ethylene (brand: PP4132V, PP4345S, PP4445S), block copolymers of propylene and ethylene (brand: PP7445LM, PP8300N, PP8300G, PP8348SM, PP8400G, PP9240M, PP9240K, RR9240N, PP9240P) were chosen as objects of study. Additionally, the polypropylenes with known molecular weight were used as standards for evaluation the molecular weight distribution (MWD).

Glass transition temperature, the melting point, pour point and the degradation of various brands of polypropylene were determined using differential scanning calorimeter DSC 204F1 Phoenix (Netzsch, Germany). The DSC method was also used to estimate the degree of crystallinity and the isothermal crystallization time. The ratios of ethylene and propylene groups were found from Fourier-Transform Infrared spectroscopy (FTIR) by TENSOR 27 (Bruker). Analysis of MWD for the selected number of homo- and copolymers of propylene was performed on Rheometer DHR-2 TAI and HAAKE RheoStress RS6000 supplied with special software. The rheological behavior of a selected number of polypropylenes in a wide range of temperatures and shear rates was studied. The influence of the content of ethylene groups on the rheological properties and thermal properties of the copolymers was revealed. The recommendations on the best modes of processing molding and extrusion were formulated.

PROTECTIVE IMPREGNATING COMPOSITIONS BASED ON BITUMEN MODIFIED WITH A C5 POLYMERIZED PETROLEUM RESIN

Chigorina E.A., Razinov A.L., Ryabenko V.S.

Federal State Unitary Enterprise "State Scientific Research Institute of Chemical Reagents and High Purity Chemical Substances" (FSUE "IREA")
echigorina@mail.ru

Nowadays, the problem of the protection of asphalt concrete pavement from the negative impact of natural and man-made factors is actual to increase their useful life. To solve the problem, one should consider impregnating compositions based on bitumen, since they improve performance properties and have a close affinity to the main component of pavement – bitumen [1]. It is well known that the use of polymerized petroleum resins (PPR) as modifiers allows to obtain new bituminous materials with improved properties and to recycle ethylene and propylene pyrolysis byproducts as well. For preparation of modified bitumens, useful in the prepataion of protective impregnating compositions, we selected C5 Hikorez © A-1100 PPR (with a softening point of 94-102 °C) that was not previously used for these purposes, as well as BND 60/90 and BV 50/70 bitumens. The modifications were made with 15% of PPR by introducing it into a "hot" bitumen and maintained for 90 minutes (the maximum level of the modifier was derived from experiments). The resulted modified bitumens were combined with solvents such as "Nefras" and applied to the asphalt concrete surface tested. The improvement of performance properties were confirmed by comparison of modified asphalt concrete pavements (with an applied protective compositions) with control samples ("bitumen+nefras" and a sample without any protection). The work is currently underway to modify bitumens with different factions of PPRs for to use the modified ones as main components of protective impregnating compositions. The applied research has been carried out with the financial support from the Ministry of Education and Science of Russian Fedration under the grant agreement №14.579.21.0025 on June 5, 2014. (Unique identifier for Applied Scientific Research (project) RFMEFI57914X0025)

Items	BND 60/90	BND 60/90 +15% PPR	BV 50/70	BV 50/70+15%PPR
Appearance	Dark brown resin			
Softening point (by the ring and ball	64	53	57	56

method), ºC				
Needle penetration 25 ºC, 0,1 mm	75	58	52	42

Table 1. A comparison of starting bitumens and the bitumens modified with 15% C5 Hikorez © A-1100 PPR

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MATERIALS BASED ON ORGANIC POLYMERS AND LUMINESCENT OCTAHEDRAL HALIDE MOLYBDENUM CLUSTER COMPLEXES

Chirtsova N. A.[1,2], *Shestopalov M. A.*[1,2,3], *Brylev K.A.*[1,2], *Edeleva M.B.*[1,4]

[1] Novosibirsk State University
[2]Nikolaev Institute of Inorganic Chemistry SB RAS
[3]Institute of Clinical and Experimental Lymphology SB RAMS
[4]Novosibirsk Institute of Organic Chemistry SB RAS
Novosibirsk, Russia
Student
n.a.chirtsova@gmail.com

Octahedral halide molybdenum cluster complexes $[\{Mo_6X_8\}L_6]$ have a cluster core $\{Mo_6X_8\}^{4+}$, which is an octahedron M_6, inscribed in a cube made of halogen atoms (X = Cl, Br, I) and each metal atom has a bond with apical ligand L. Compounds exhibit long-lived luminescence in the red region of the spectrum. One of the most interesting application is as agents for bioimaging. It means that materials have to be small, minimal toxic and have the notable lumenescence characteristics. We used $(Bu_4N)_2[\{Mo_6X_8\}(NO_3)_6]$ as precursors to obtain final materials. The luninescent properties and the effectiveness of singlet oxygen generation depending on the composition of the cluster core were studied for precursors. Cluster complex $(Bu_4N)_2[\{Mo_6I_8\}(NO_3)_6]$ (Fig. 1) can be immobilized into the polymeric matrix with preservation of high luminescent properties by an example of thiol-modified polystyrene (PS) $\{Mo_6I_8\}$@PS-SH [1]. Also nanospheres (average size is 700 nm) of $\{Mo_6X_8\}$@PS-COOH and $\{Mo_6X_8\}$@PS-Py (X = Cl , Br, I) were obtained by free radical copolymerization: of styrene and methacrylic acid or 4-vinylpyridine. The content of the cluster complex about 10% (weight relative to the monomer) inhibits radical polymerization. Photophysical parameters downturn for $\{Mo_6X_8\}$@PS-SH, $\{Mo_6X_8\}$@PS-COOH and $\{Mo_6X_8\}$@PS-Py

series. Materials don't have some effect on Hep-2 cells proliferation. To study an influence of different organic matrixes we made nanoparticles of more biocompatible polymers: PMMA (poly(methyl methacrylate)) and PLA (polylactic acid). Particles with average size about 100 nm were obtained and some of their properties were studied. Lumenescent characteristics for $\{Mo_6X_8\}$@PMMA and $\{Mo_6X_8\}$@PLA are higher than for $\{Mo_6X_8\}$@PS.

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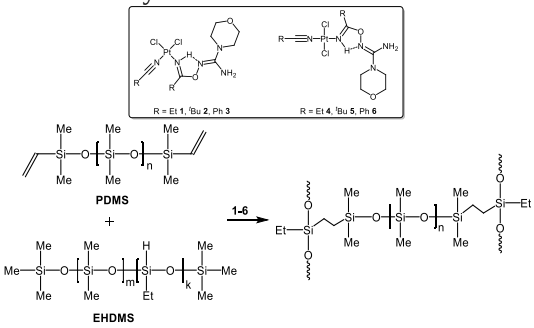
Pt(II)-MEDIATED NITRILE–HYDROXYGUANIDINE COUPLING GIVING NOVEL CATALYSTS FOR CURING POLYSILOXANES BY HYDROSILILATION

Demakova M.Ya., Bolotin D.S., Bokach N.A, Islamova R.M.

Saint Petersburg State University,
Postdoc
my-demakova@rambler.ru

Polysiloxanes (silicones) are the most popular representatives of silicon polymers. Development of new efficient catalysts for curing by hydrosilylation is an important task. In view of our general project on platinum chemistry and taking into account recent findings on hydrosilylations catalyzed by platinum species, we now examined platinum complexes **1**–**6** as catalysts for cross-linking of vinyl terminated poly(dimethylsiloxane) (PDMS) and trimethylsilyl terminated poly(dimethylsiloxane-*co*-ethylhydrosiloxane) (EHDMS) polymers. The curing was monitored by DSC method.



Picture 1. Platinum-catalyzed curing of silicone polymers by hydrosylilation

Complexes **1**–**6** do not require an inhibitor of the hydrosilylation, their activity is tunable by both temperature increase and catalysts concentration and variation of these parameters allows the selective generation of good quality polysiloxane resins. We investigated the thermal (dynamic thermogravimetry analysis in air or nitrogen atmosphere) and mechanical properties of the polysiloxanes.

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THERMOMECHANICAL PROPERTIES OF NEW NORBORNENE - CYCLOOCTENE MULTIBLOCK COPOLYMERS

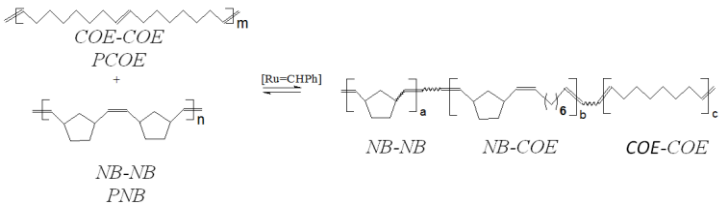
Denisova Yu.I., Gringolts M.L., Shandryuk G.A., Krentsel L.B., Litmanovich A.D., Kudryavtsev Y.V.

A.V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences
Moscow, Russia
denisova@ips.ac.ru

Continuing interest in studying structured block copolymer systems is associated with the possibility to obtain on their basis perspective composite materials that combine the properties of the individual components. Recent studies have shown that statistical multiblock copolymers have a pronounced ability to self-organization due to the block structure of their chains [1-4]. In perspective, a sufficiently simple way of synthesis makes them attractive to use but it should be an experimental study of polymer microstructure to predict the dependence chain structure - properties. Recently we have proposed a new approach to synthesis of norbornene – cyclooctene **mutliblock copolymers** via the interchain cross-metathesis between **polynorbornene (PNB) and p**oly(1-octenylene) **(PCOE)** [5]. Norbornene (NB) and cyclooctene (COE) are well-known objects in ring-opening metathesis polymerization (ROMP). Their homopolymers synthesized by ROMP are important commercial products. PNB, which is sold under the trademark Norsorex, has various special applications. PCOE, known as Vestenamer or polyoctenamer, possesses unusual properties for an elastomer. Synthesis of NB-COE copolymers by copolymerization is rather complicated because of the large difference in the

monomer reactivities. Our novel synthetic approach [5] enables obtaining NB-COE multiblock copolymers with various block lengths thus targeting their properties.

In this work, we studied some thermomechanical properties of the NB-COE mutliblock copolymers, which were synthesized by the cross-metathesis of PNB with PCOE in the presence of the 1st generation Grubbs' catalyst, $Cl_2(PCy_3)_2Ru=CHPh$ (Gr-1), according to the scheme below.



The reaction was performed in chloroform solution at room temperature and different PNB/PCOE and polymers/catalyst ratios to prepare a set of NB-COE multiblock copolymers with progressively decreasing average block lengths.

The synthesized copolymers were characterized by NMR spectroscopy, GPC, DSC, and DMA methods. The degree of crystallinity related to COE blocks was calculated from the DSC thermograms. It was demonstrated that this property depends on the average block lengths**.** The crystallinity of resulting copolymers is lost only when the average COE block length drops down to 2 units.

The glass transition temperature also depends on the average length of COE blocks, ranging from -44 to -32 ^oC for the copolymers compared to -79 ^oC for the PCOE homopolymer.

DMA analysis demonstrated the pronounced influence of NB and COE average block lengths on the elastic modulus and loss tangent.

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The work was supported by the RF President grant for young Russian scientists (MK-7525.2015.3)

MIXED MATRIX MEMBRANES BASED ON PVA FOR PERVAPORATION OF QUATERNARY ESTERIFICATION MIXTURE

Dmitrenko M.E., *Penkova A.V.*, *Polyakov E.S.*, *Sokolova M.P.*

Saint Petersburg State University
Saint Petersburg, Russia
PhD student
m.dmitrienko@spbu.ru

Pervaporation is one of the developing membrane technologies that can be used for various industrial. It is often used as a separated process, combining with one or more other separation technologies (distillation, adsorption, extraction and other processes). The potential of these hybrid processes is evaluated for various applications, especially for the synthesis of esters by esterification which requires the removal of one of the products of a reaction to shift the equilibrium in favor of the products, which can be easily achieved by pervaporation. Different types of membranes were used for separation of these mixtures but for effective realization of the hybrid process in the industry the membranes with high transport characteristics are required. One of the most promising ways of improving transport properties of membranes can be modification of polymers by nanoparticles. In the present research a low-hydroxylated fullerene is used as a modifier and a cross-linking agent for polyvinyl alcohol.

In this study, optimal conditions for the preparation and physico-chemical properties of PVA membranes modified by low-hydroxylated fullerenol $C_{60}(OH)_{12}$ were investigated. Various methods of cross-linking for composite membranes PVA-fullerenol were used. Structural and physico-chemical properties of the membranes were examined by scanning electron microscopy, spectroscopic methods, thermogravimetric analysis, differential scanning calorimetry and sorption experiments. The transport properties of hybrid membranes were studied under water treatment of chemical-equilibrium quaternary mixtures of *n*-propyl acetate - acetic acid – *n*-propanol – and water by pervaporation. It has been shown that the introduction of fullerenol to 5% in polyvinyl alcohol matrix changes the physico-chemical properties and leads to improved membrane transport characteristics.

Acknowledgments

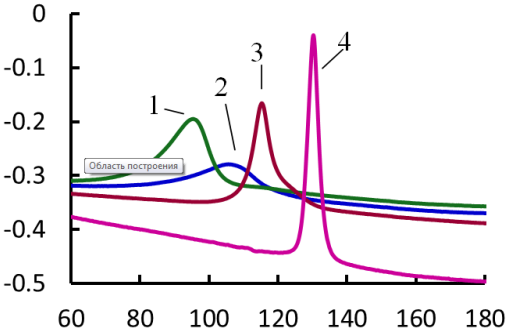
This work was supported by Fellowship of President of Russian Federation СП-1153.2015.1 (Penkova A.V.). The experimental work was facilitated by equipment from the Resource Center of X-ray diffraction studies, Center for chemical analysis and materials research, Resource Center of Thermal Analysis and Calorimetry, Resource Center for Nano technology and Centre for Physical Methods of Surface Investigation, at St. Petersburg State University.

Pt(II) NITRILE COMPLEXES AS CATALYSTS FOR POLYSILOXANES CURING

Dobrynin M.V., *Vlasov A.V.*, *Islamova R.M.*

Saint Petersburg State University,
Student
mdobrynin42@yandex.ru

Hydrosilylation is the main reaction for the production of such organosilicon compounds as organofunctional silanes and silicones. Nowadays polysiloxane rubber is used in such purposes as material for release coatings, elastomers, implants and optical lenses.[1] During our research we examined platinum nitrile catalysts with common formula $PtCl_2(NCR)_2$, where R=NMe_2, NC_5H_{10}, C_6H_5, $CH_2C_6H_5$ or NEt_2, on cross-linking of vinyl terminated poly(dimethylsiloxane) (PDMS) and trimethylsilyl terminated poly(dimethylsiloxane-*co*-ethylhydrosiloxane) (EHDMS) polymers. The curing was monitored by DSC method.



Picture 2. DSC curves of the PDMS and EHDMS curing process in presence of: 1 — trans-$PtCl_2(NC(CH_2C_6H_5)_2$, 2 — cis- $PtCl_2(NCNMe_2)_2$, 3 — trans- $PtCl_2(NCC_6H_5)_2$, 4 — trans-$PtCl_2(NCNC_5H_{10})_2$.

Complexes have different catalytic activity depending on ligands. Cis-trans isomerism also affects curing time. In addition compounds have improved thermal stability and mechanical properties according to dynamic thermogravimetry and dynamic mechanical analysis.

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We thank Russian Foundation for Basic Research (grant 14-03-00260-a) and FTP № 14.576.21.0028. V.A.V. is much obliged to Saint Petersburg State University for a postdoctoral fellowship 12.50.1188.2014. The authors also express their gratitude to Center of Thermal Analysis and Calorimetry, (Saint Petersburg State University) for physicochemical measurements.

OBTAINING NEW WATER SOLUBLE POLYMERS FROM WASTE OF CHEMICAL FIBERS

Dosbayeva A.M.,[1] Turebekova G.Z.,[2] Suliembek G.A.,[2] Sakibaeva S.A.[2]

[1]M.Auezov South Kazakhstan State University, Shymkent Kazakhstan
Postgradute
aidan2@mail.ru
[2]M.Auezov South Kazakhstan State University, Shymkent Kazakhstan
Candidate of technical science of Associate professor
g.ture@mail.ru

Insulating compounds are used for cooling, preservation of crude rubber mixture and improvement of technological properties in the mixing plant at the rubber compound manufacture. “Progress”, containing phosphate compounds which are toxic and are not resolved in the nature, is used in the quality of surfactants in the composition of insulating compounds. These surfactants are the most hazardous from all chemicals which contained in insulating compounds. Penetrating into a human body they are accumulated in cells and at the definite concentration may cause serious disorders. It can lead to the widespread allergy and serious problems up to affection in brains, liver, kidneys, lungs. We have carried out researches on the possibility of replacing these toxic components. In the insulating composition is proposed to replace the phosphate surfactants synthesized from waste fibers (TEAPAN and MEA PAN). TEAPAN (MEAPAN) is prepared by reacting the waste with a chemical fiber PAN triethanolamine (diethanolamine) in the presence of NaOH at a temperature of 95° C for 2,5 hour. Triethanolamine and diethanolamine modifiers are polymers obtained, whereby active functional groups are formed increases the surface activity of the synthesized polymers. Possess low foaming surfactants, good solubility in water and is therefore not require additives in insulating composition defoamers and stabilizers. The researches on possibility to use surfactants TEAPAN and MEAPAN in the base of insulating compounds have produces positive results.

Table 1 - Properties of insulating compositions

Name indicators		Number of recipes			
	IC-21	1	2	3	4
Foaming,mm[1]	17	6	6	6,9	7
Delamination resistance	178	101	95	92	91

from duplicate plates, N/m					
pH, through 0 day	8,7	10,0	10,9	10,5	10,5
6 day	8,1	10,9	10,8	10,3	10,4
10 day	7,8	9,8	10,8	10,3	10,2
14 day	7,1	9,8	10,6	10,2	10,2

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REVERSIBLE ADDITION–FRAGMENTATION CHAIN-TRANSFER (RAFT) COPOLYMERIZATION OF METHACRYLIC ACID AND BUTYL ACRYLATE

Dukova S.V., Zaitsev S.D.

Lobachevsky Nizhny Novgorod State University
Nizhny Novgorod, Russia
Student
kurakina_svetlan@mail.ru

Controlled synthesis of polymers with defined molecular weight characteristics and adjustable chain structure is a priority of modern polymer chemistry. In recent years, the researcher's attention has been attracted to Reversible addition–fragmentation chain transfer polymerization. This technique of polymerization can be applied to almost all monomers, polymerizable by a radical mechanism. That allows to implement a directed design of macromolecules, in particular block-copolymers and gradient copolymers. In this work we have presented an investigation of homopolymerization methacrylic acid by the reversible chain transfer mechanism, mediated by 2-cyano-2-propyl dodecyl trithiocarbonate, as chain transfer agent. It was found that polymerization had proceeded in the controlled manner, as indicated by a

narrow molecular weight distribution, the absence of the gel effect, and a linear increasing of the average molecular weight on the conversion. Besides, was carried out the copolymerization of methacrylic acid (20 mol. %) with butyl acrylate (80 mol. %) in the presence of two chain transfer agent - 2-cyano-2-propyl dodecyl trithiocarbonate and benzyl dithiobenzoate to high conversions, and classical radical copolymerization in the presence of the dodecyl mercaptan. Physico-mechanical properties of the synthesized copolymers were studied. It was found that the copolymers obtained by the reversible chain transfer polymerization have significantly better physico-mechanical properties than copolymers of the same composition, but received classical radical polymerization.

SURFACTANT POLYMERIZATION – A PATH TO PRODUCE NANOSTRUCTURED INTERPOLYELECTROLYTE COMPLEXES

Fetin P., Povshednaya M., Zorin I., Lezov A., Bilibin A.

Saint-Petersburg State University,
Saint Petersburg, Russia
Student
pitt90rock@mail.ru

The chemist's interest in systems with a self-organizing component has increased significantly in the last few decades. Polyelectrolyte-surfactant complexes (PeSC) are compounds formed from surfactant molecules and oppositely charged polyelectrolytes. Electrostatic and hydrophobic interactions are involved in PeSC formation. The binding of surfactants to polyelectrolytes of opposite charge has been reported to be a highly cooperative process at the surfactant concentration called critical aggregation concentration (CAC). If the surfactant molecule has a double carbon bond there is a possibility of PeSC modification by surfactant polymerization yielding interpolyelectrolyte complex (IPeC).

An original method of producing stable unimodal dispersion or precipitate of IPeC by polymerization of self-organizing polyelectrolyte - surfactant complexes (PeSC) is proposed in this work. We aimed to produce IPeC with the same gross formula by radical polymerization of two different PeSCs. The first PeSC was formed by an anionic polyelectrolyte of sodium poly-2-acrylamido-2-methil-1-propanesulfonate (PAMPS-Na) and a cationic surfactant 11-(acryloyloxy)undecyltrimethylammonium bromide (AUTAB). The second PeSC was composed of cationic polysoap PAUTAB and anionic monomer AMPS-Na. Unimodal dispersion of IPeC was produced from both PeSCs at complex concentration equal to 0.77mM. The polyelectrolyte molecular weights influence on hydrodynamic radius of IPeC dispersion was

investigated. A different liquid – crystalline phase of IPeC precipitate was produced from the first and the second PeSCs. A number of methods were employed to study properties of initial polyelectrolytes, PeSCs and IPeCs, among them are dynamic and static light scattering, small angle X-ray scattering, atomic-force microscopy, RAMAN-spectroscopy, exclusion chromatography, potentiometry with surfactant selective electrode, viscometry.

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DRUG RELEASE FROM FILM OF POLY(D,L-LACTIDE)

Fetin P.A.[1], *Nashchekina Yu.A.*[2], *Zorin I.M*[1], *Bilibin A.Yu.*[1]

[1]Saint-Petersburg State University,
[2]Institute of Cytology, Russian Academy of Sciences
Saint-Petersburg, Russia
Student
pitt90rock@mail.ru

Controlled drug release systems are smart medical devices that are used to support the concentration of a drug in a patient's blood at the therapeutic level for a long time. It is well established that most drugs have upper and lower concentration limits of efficiency. If the treatment takes place during one or two days or more, the efficiency concentration of the drug is achieved by multiple injections of it, which injures patients by exceeding the effective concentration limit after injections. Drug controlled release systems can solve this problem[1].

Acexamic acid (AA) is a wound-healing drug that promotes tissue regeneration. In this work, Poly(D,L-lactide) films filled with AA were produced and the acexamic release from a film was investigated. This composite system can be used as a material for burn treatment because of biological effects of AA and biodegradable and biocompatible properties of poly(D,L-lactide) matrix[2]. The films were produced by casting from the polymer and drug solution in THF. The kinetics of the AA release from the prepared films was monitored by conductometry and pH-metry. The release profile corresponds to the two-stage release model[3]. The first stage is a burst release caused by fast elution of AA that had formed its own crystalline phase in the film. The second stage is the release of AA that was dissolved in the poly(D,L-lactide) matrix. The high amount of AA causes a degrease of mechanical strength of films, but AA also acts as a softener for films that are

good for burn treatment. The solubility of AA is higher in more hydrophilic poly(D,L-lactides). The release rate increases with the degrease of the molecular weight of poly(D,L-lactide).
Thus, for burn treatment it is more suitable to use poly(D,L-lactide) films formed from hydrophilic polymers with low molecular weights.

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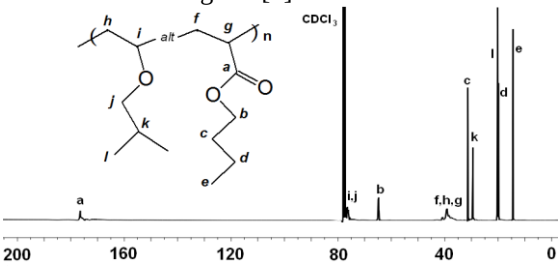
RADICAL COPOLYMERIZATION OF ALKOXY OLEFINS

Geraskina E.V., Matkivskaya Yu.O., Moikin A.A., Semenycheva L.L.

N.I. Lobachevsky Nizhny Novgorod State University
Nizhny Novgorod, Russia
Ph.D. student
geraskinaev@mail.ru

Creation of additive packages for the current generation of lubricants is impossible without the polymer components provide a constant viscous characteristics of oil at varying conditions of temperature and loads. Particular attention is given to copolymers, due to the possibility of obtaining a well-compatible multifunctional materials.
We have proposed synthesis of alternating copolymers in a compensatory approach. This method allowed the radical copolymerization of alkoxy olefins which is not prone to radical homopolymerization with alkyl (meth) acrylates. The copolymer was obtained at a high speed and with a quantitative yield for active component. Investigation of the structure of the copolymers by ^{13}C NMR-spectroscopy showed predominantly alternating character of the units distribution in the polymer chain (Picture 1). Data correlate well with the results of Mishima E. and Yamago S. [1].



Picture 1. ^{13}C NMR-spectrum of a copolymer (butyl acrylate-*alt*- iso-butyl vinyl ether)

The synthesized copolymers were tested as viscosity modifiers for lubricants. It was established that due to the different nature of units the copolymers have good compatibility with the mineral and synthetic oily bases and at a concentration of 5 wt.% can significantly increase the viscosity index of oils. It is important that due to alternating structure the copolymers exhibit good resistance to thermomechanical degradation.

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SILVER NANOCOMPOSITES BASED ON SYNTHETIC AND NATURAL POLYMERS POSSESSING POLYFUNCTIONAL BIOLOGICAL ACTIVITY

Zolotova Yu.I. [1], *Gogleva O.A.* [2], *Khripunov A.K.* [1], *Anan`eva E.P.* [3], *Andreev V.A.* [4], *Panarin E.F.* [1,5]

[1] Institute of Macromolecular Compounds, Russian Academy of Sciences
[2] St. Petersburg State Technological Institute (technical university)
[3] St. Petersburg State Chemical Pharmaceutical Academy
[4] Kirov Military Medical Academy
[5] St. Petersburg State Polytechnical University
incorporate@inbox.ru

Hydrophilic random copolymers of N-methacryloylamino glucose and N,N-dialkylaminoethyl methacrylate were synthesized by free radical copolymerization. The copolymers of varied composition and molecular mass $(10\text{-}100)\cdot 10^3$ were obtained. It was established that these copolymers synthesized are able to reduce the silver ions and possess own biological activity, namely immunomodulatory, antimicrobial, antitumoral ones [1, 2]. On basis of synthesized copolymers stable nanoparticles of Ag^0 with dimensions 2-15 nm were prepared. The reaction of nanoparticles formation runs without any additional reducing agents at room temperature and natural light. Ag^0 nanoparticles were used for preparation of composites based on bacterial cellulose of different morphology. Antimicrobial activity of these composites was investigated. Their possible areas of application are under consideration.

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PREPARATION OF POLYMER BRUSHES BY ATRP USING VARIOUS INITIATION PROCESSES OF METHACRYLATES BY A MULTICENTER POLYIMIDE MACROINITIATOR

Ivanov I.V., *Kashina A.V.*
Institute of macromolecular compounds RAS
Saint Petersburg, Russia
Ph.D. student
gangspil@gmail.com

In the past decade, an extensive development of controlled radical polymerization (CRP) methods resulted in the synthesis of numerous well-defined copolymers with complex architectures. Among these systems, regular graft-copolymers with narrow dispersed side chains (polymer brushes) are worth of emphasizing. Specifying the chemical structure, the main and side chains dimensions as well as the grafting density, it is possible to vary characteristics of macromolecules in a wide range. This opens up new opportunities for the creation of new materials with advanced properties. An important task is to develop an optimal method for the synthesis of graft-copolymers, allowing one to adjust the grafting density of side chains, their length and dispersity in a controlled fashion.

Atom transfer radical polymerization (ATRP) is one of the most successful CRP methods for the synthesis of polymers with predictable molecular weights (MW) and well-defined architectures.

However, normal ATRP methods have some limitations such as a high sensitivity of the catalyst used to traces of oxygen in the reaction mixture. In order to overcome the drawbacks of normal ATRP improved ATRP method, wherein activators generated by electron transfer (AGET ATRP), was recently developed.

In the present work, graft-copolymers with a polyimide (PI) main chain and polymethylmethacrylate (PMMA) or poly *tert*-butyl methacrylate (PtBMA) side chains were synthesized, using multicenter polyimide macroinitiator by both normal ATRP and AGET ATRP methods, and their results were compared. A well-controlled character of the processes studied under the determined optimal conditions was established.

The progress in ATRP provides an effective tool for the design and preparation of functional membranes. The homogeneous self-supporting films were formed

from solutions of synthesized polymer brushes. These films were tested as pervaporation membranes for the separation of water-alcohol mixtures.
Applicability of synthesized graft-copolymers with precisely adjustable structure parameters as material for high efficient pervaporation membrane was demonstrated.
Acknowledgements
The work was supported by the Russian Science Foundation (project № 14-13-00200).

RHEOLOGICAL PROPERTIES OF NETWORKS FORMED BY SURFACTANT CYLINDRICAL MICELLES AND POLYMER CHAINS

Ivanova A.A., *Shibaev A.V.*, *Philippova O.E.*

Moscow State University
Moscow, Russia
Student
ivanova@polly.phys.msu.ru

Surfactants are able to form enormously long cylindrical micelles in aqueous solutions in the presence of salts. These micelles can entangle with each other, forming transient networks that exhibit viscoelastic behavior. Due to viscoelastic properties such networks are very promising for use as thickening agents in fracturing fluids in oil recovery [1]. However, the surfactants are sensitive to external conditions such as high temperature. This fact makes their use in oil recovery difficult. Replacing a part of wormlike micelles with polymer chains is a promising way of getting the solutions with higher mechanical strength at elevated temperatures, while keeping responsiveness to hydrocarbons.
In the present work, we investigate the rheological properties of viscoelastic surfactant solutions (anionic surfactant potassium oleate) in the presence of polymer (hydrophobically modified polyacrylamide with high degree of blockiness). First, it was shown that the addition of a low polymer concentration (0.5 wt.%) results in the 5-fold increase of viscosity and storage modulus. Then, the rheological studies were performed on aqueous salt solutions of the surfactant and polymer in the presence of different concentrations of hydrocarbon. The decrease of viscosity upon addition of hydrocarbon, which is due to the disruption of wormlike micelles, is almost the same for both surfactant and surfactant/polymer systems. However, a higher concentration of hydrocarbon is necessary to disrupt a common polymer-micellar network than a pure micellar one.
Thus, the addition of a hydrophobically modified polymer to wormlike surfactant micelles retains their responsiveness to hydrocarbons, although a

slightly higher amout of hydrocarbon is necessary to disrupt a polymer-micellar network.

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MONODISPERSE COMPOSITE POLYMER PARTICLES WITH QUANTUM DOTS: SYNTHESIS AND SELF-ASSEMBLING

Iurasova D.I.[1], *Pankova G.A.*[1], *Shabsels B.M.*[1], *Ivan'kova E.M.*[1], *Zakharov V.V.*[2], *Veniaminov A.V.* [2], *Ukleev T.A.*[3], *Sel'kin A.V.*[3], *Shevchenko N.N.*[1]

[1] Institute of Macromolecular Compounds RAS
[2] Saint- Petersburg national Research University of Information Technologies, Mechanics and Optics
[3] Ioffe Institute
Saint Petersburg, Russia
Ph.D student, Junior Researcher
shevaldysheva@mail.ru

Polymerization methods leading to polymer colloids are well known and well developed for numerous polymer systems. In many instances, monodisperse polymer micro- or nanospheres can be obtained and the diameter of the polymer colloids can be tuned from the micrometer to the sub-100 nanometer scale. Therefore, many efforts have been focused on incorporating QDs into well-defined polymeric particles via monomer polymerization in a dispersed media. Monodisperse hybrid particles of a certain diameter can be used as the main structure-forming elements due to their availability and ability to self-assemble into three-dimensional ordered arrays with periodically modulated refractive index. Narrow particle size distribution of these hybrid "building blocks" makes it possible to control the period of distribution of quantum dots, which provide the realization of a "superluminescence" effect.
This study is focused on synthesis monodisperse hybrid core-shell particles with incorporated semiconductor luminescent nanocristals, hydrophobic quantum dots CdSe/ZnS, by heterophase polymerization methods. It was traced the influence of synthesis conditions (emulsifying mixture composition, cross-linked agent concentration, initiator nature, seed cores functionality, methacrylic acid concentration) on the composite particles and thin films

luminescence characteristics. It was shown the ability to self-assemble into the three-dimensional ordered structures exhibiting photonic crystal properties.

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ORGANOSILOXANE ADHESIVE SEALANTS WITH IMPROVED PHYSICOMECHANICAL PROPERTIES

Kabolova E.G.[1], *Chigorina E.A.*[2], *Chigorina T.M.*[1]

[1]North-Ossetian State University by the name of K.L. Khetagurov, Vladikavkaz, Russian Federation
[2]Federal State Unitary Enterprise "State Scientific Resrarch Institute of Chemical Reagents and High Purity Chemical Substances" FSUE "IREA"
Student
tchigorina@mail.ru

The development of contemporary science is impossible without creating polymer materials, which yield high and stable characteristics of goods during exploitation. Polyorganosiloxane compounds with improved physicomechanical properties are presented. The possibility of changing the properties of adhesive sealants by introducing them into the composition of new modifying additions, structureforming additions (QM-resins), curing accelerators, and coupling agents has been shown. The elaborated compounds can be recommended for sealing semiconductor devices and integral schemes.

The following silicon-organic rubbers were selectedas polydimethyloxane rubber SKTN-G. The derivatives of phenyltriorgan (phenyltriethoxy(methoxy)silane $PhSi(OR)_3$) served as sealing agents and served as the vulcanization accelerator. The component ratio of the vulcanized system was 1:1; which yielded a complete reaction process and, result compounds, with a wide spread spatial network. These compounds posses high physicomechanical properties, which was the problem and the aim of the present study.

The sealing agents in the system of silicon_organic compounds not only serve as curing agents, but are also chemical reagents in the structure_forming processes that occur by the polycondensation mechanism. Sample tests on determining the elongation during rupture (ε_r) and the conventional strength during stretching (σ_r) were performed according to the State Standard 270–75.

The values of the vitality and physicomechanical properties of the elaborated compounds based on SKTN-G (SilON) rubber are as follows: the maximal vitality value was 14 h, the conventional strength during rupture was 4.0–4.3 MPa, and the elongation during rupture was 130–140%. It is important to note

that at the same time the curing temperature of the sealant compounds decreased to 75°C.
In conclusion, it is necessary to note that the elaborated and researched compounds, which possess a high degree of purity, low internal stresses, and high electrical insulating properties, can be recommended for sealing radio-, electronic, and medical devices.

THE ANTIMONY AND BISMUTH-CONTAINING POLYMETHYLMETHECRYLATE

Kalisratova O.S., Gushchin A.V., Maleeva A.I., Andreev P.V.

Lobachevsky State University of Nizhni Novgorod
Nizhni Novgorod, Russia
Post graduate student
Olga.Kalistratova@yandex.ru

Metal-containing polymethylmethacrylate and polystyrene can be used as scintillators for the detectors. In this study the triphenylantimony dicrotonate and triphenylbismuth dicrotonate $Ph_3M(OC(O)CH=CHCH_3)_2$ (M = Sb,Bi) were used as a metal-containing compounds [1]. This compounds contain two double C═C bonds within the molecular fragment. Due to these bonds they can be used for polymerization filling of PS and PMMA. Triphenylbismuth dicrotonate is a very promising monomer for developing of metal-containing organic scintillators which recently attracted much attention in the field of high-energy physics. It was found that the participation of both acrylate groups in polymerization leads to cross-linking considerably decreasing the thermooxidative destruction of the resulting polymer [**2**].
Compounds are easily obtained by a one-step oxidative synthesis method:
$Ph_3M + ROOH + 2CH_3CH=CHCOOH \rightarrow Ph_3M(OC(O)CH=CHCH_3)_2 + ROH + H_2O$, where M = Sb, Bi; R = H, *t*-BuO.
Copolymerization of methyl methacrylate monomer and an organometallic compounds were carried out with two methods: peroxide initiated polymerization (60°C, benzoyl peroxide) and the photopolymerization (for dicrotonate triphenylbismuth; 25°C, visible light). The polymers were shown to decrease the thermo-oxidative destruction compared with pure PMMA obtained in the same conditions (TGA method). X-ray exposure study revealed an increase in absorption with increasing content of the organometallic compound. Light transmittance of the samples showed a slight decrease in transparency for antimony-containing polymers. The bismuth-containing polymethylmethacrylate samples were essentially coloured.
The polymerization of methyl methacrylate and styrene under the visible light with triphenylbismuth diacylates as an initiator is studied.

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This work was performed with the financial support or the Russian Foundation of Basic Research (№ 14-03-31625 mol_a).

OPTIMIZATION OF CURING PROCESS OF THERMAL RESISTANT RESINS BASED ON EPOXY OLIGOMERS AND COMBINED AMINE HARDENERS

Karamova A.I. [1,2], *Amirova L.M.* [1,2], *Khamidullin O.* [1,2]

[1] Kazan National Research Technical University named after A.N.Tupolev - KAI (KNRTU-KAI)
[2] Kazan (Volga Region) Federal University (KFU)
Kazan, Russia
Student
ais-karamova@mail.ru

To produce polymers with high thermal resistance it is reasonable to use aromatic amines as curing agents for epoxy resins. However, most of aromatic amines are solid crystalline compounds poorly compatible with epoxy resins. Therefore, the actual objective is to reduce the melting point and improve the compatibility of such systems. One of the possible ways to solve this task is to use mixtures of some aromatic amines with various other compounds. However, there is precious little information on this subject.

The goal of the research was to study the phase diagrams of binary systems based on aromatic amines and the study of the curing process of epoxy oligomers by eutectic mixtures.

4,4'-Diaminodiphenylmethane, 4,4'-diaminodiphenylsulfone, 4,4'-diaminodiphenyloxide, ortho-, para-, and meta-phenylenediamine were taken as objects of study. As epoxy oligomer were used following resins: NPPN-631. NPPN-638, ED-22.

Investigations were performed using differential scanning calorimeter DSC 204F1 Phoenix (Netzsch, Germany). Strength and viability of the compositions were determined with HAAKE RheoStress RS6000 rheometer. The degree of conversion of epoxy groups was found from infrared spectra using Fourier-Transform Infrared spectrometer (FTIR) TENSOR 27.

According to DSC data the compositions of eutectic mixtures and corresponding melting temperatures were identified. Then these eutectic mixtures were used for curing the epoxy oligomers. The possibility of reducing

the temperature and improving the processability of the epoxy oligomers curing with eutectic mixtures of aromatic amines were shown. The heat-resistant binders for composites are developed. The thermal physical properties of epoxy-amine polymers are studied.

NATURAL SORBENTS FOR THE REMOVAL OF THE IONS OF HEAVY METALS

Karibayeva Zh.K., Imangaliyeva A.N., Kenzhalina Zh.Zh., Seilkhanova G.A.

Al-Farabi Kazakh National University, Kazakhstan
Student
runia_i91@mail.ru

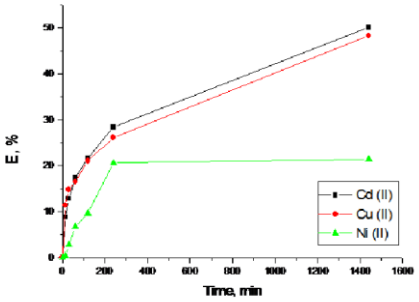
The problem of purification drinking water from heavy metal compounds continues to be relevant. Among the methods successfully used for this purpose, can be called sorption advanced treatment using natural materials. And recently, the possibility of replacing expensive non-traditional adsorbents, accessible and cheap materials such as artificial and natural origin [1-2].

This paper presents the results of a study the sorption of ions Cu (II), Ni (II) and Cd (II) from aqueous solutions of sorbents, which represent a waste of agricultural industries.

As the original objects used meal of milk thistle, walnut shells, as well as non-activated carbon obtained from the walnut shell. Sorbent section includes mechanical cleaning of raw materials and treatment of raw materials to 2.5-3 mm.

The concentration of heavy metal ions before and after sorption defined by atomic absorption on device brand «Shimadzu 6200". Determination of changes in the structure and surface morphology of the particles of natural sorbent conducted by SEM (Scanning Electron Microscopy). To determine the content of the components has been used X-ray quantitative phase analysis on computerized DRON-2. Samples meal, walnut shells and coal also studied by IR - spectroscopy. IR spectra recorded on a spectrophotometer Specord M80 (Carl Zeiss, Jena) as presstablets with KBr.

Theoriginal concentration of heavy metal ions was 14-30 mg / ml. The figure shows plots of the degree of heavy metal ions from aqueous solutions using coal from walnut shell.



Picture 1. The dependence of the degree of extraction of metal ions from time to unactivated carbon derived from walnut shell

On the basis of the degree of extraction of metal ions from time were calculated kinetic characteristics of the process under investigation. Established equilibrium constants of sorbent systems - a copper salt solution (II), cadmium (II) and nickel (II), calculated thermodynamic process characteristics which indicate their thermodynamic permission.

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CHROMATOGRAPHIC ANALYSIS OF STRUCTURAL ELEMENTS OF MOLECULAR POLYIMIDE BRUSHES WITH POLYMETHACRYLATE SIDE CHAINS

Kashina A.V., Litvinova L.S., Lezin I.P., Meleshko T.K., Vinogradova L.V., Yakimansky A.V.

Institute of Macromolecular Compounds, Russian Academy of Sciences,
Bolshoi pr. 31, 199004, Saint-Petersburg, Russia
kashina.anna@mail.ru

Intensive interest in branched polymers with complex architecture and controlled molecular characteristics has shown during the past decades due to their potential applications in solubilization, catalysis, modification of coatings, synthesis of engineered nanoparticles and others. Among them the molecular polymer brushes, in which narrow disperse side chains are regularly grafted to a main chain, have drawn increasing attention.

Adsorption chromatography at the critical conditions (ACCC) was used for the analysis of polymethylmethacrylate (PMMA) and poly(*tert*-butylmethacrylate) (PTBMA) side chains cleaved from polyimide (PI) regular PI-*graft*-PMMA and PI-*graft*-PTBMA molecular brushes synthesized via atom transfer radical polymerization (ATRP) of methacrylates by polyimide multicenter macroinitiators. PMMA and PTBMA side chains were cleaved by means of alkaline hydrolysis of the PI backbone, and, therefore, they had to contain one terminal COOH group, and might also have one OH group at the opposite chain end. It could not be excluded beforehand that cleaved chains also contain a certain amount of non-terminal methacrylic acid units if the alkaline hydrolysis of the PI backbone would be accompanied by a partial hydrolysis of ester groups of PMMA and PTBMA side chains. Therefore, a careful analysis of molecular-weight characteristics of side chains and distributions of functional groups in side chains was necessary in order to verify a controlled character of the ATRP process of the synthesis of polyimide brushes and to prove that middle units of cleaved side chains remain intact under the alkaline hydrolysis of the PI backbone. To this aim, mobile phases were composed in which either adsorption or exclusion regimes or ACCC are realized for 1) commercial PMMA and PTBMA homopolymers, containing neither COOH nor OH terminal functional groups, and 2) PMMA and PTBMA cleaved side chains with one or more polar terminal groups and possibly some middle COOH groups. It was shown that both PMMA and PTBMA cleaved side chains are functionally polydisperse (contain different sets of end functional groups), however, there are no carboxylic groups in their middle units.

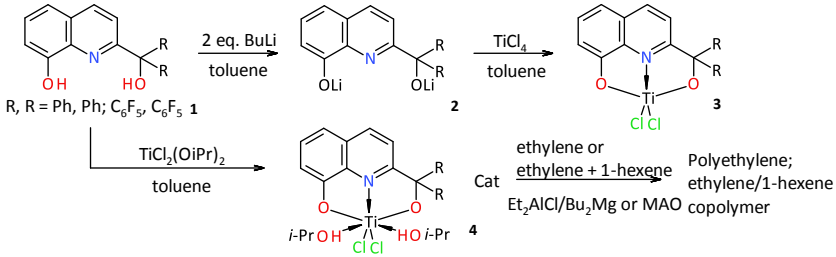
The work is supported by the Russian Science Foundation (grant 14-13-00200).

TITANIUM (+4) COORDINATION COMPOUNDS WITH 8-HYDROXYQUINOLINE DERIVATIVES AS CATALYSTS FOR HOMO- AND CO-POLYMERIZATION OF ETHYLENE AND 1-HEXENE

Kolosov N.A.[1], *Gagieva S.Ch.*[1], *Tuskaev V.A.*[1,2]

[1]Chemical Department, Moscow State University, Leninskie Gory 11, Moscow 119991, Russia
[2]Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, ul. Vavilova 28, Moscow 119991, Russia
Scientific researcher
kolosovna@mail.ru

Coordination compounds of titanium (+4) with 8-hydroxyquinoline derivatives have been synthesized (scheme 1). Composition and properties of the obtained complexes have been evaluated by NMR, IR spectroscopy, X-ray diffraction, and elemental analysis. Pre-catalyst **3** was obtained by treating dilithium derivative **2** with titanium (+4) tetrachloride. Interaction between ligand **1** and dichloro titanium (+4) isopropoxide leads to the compound **4**. It is interesting that isopropanol ligands remain in the coordination sphere of the metal.



Scheme 1. Synthesis of titanium (+4) complexes with 8-hydroxyquinoline derivatives; ethylene and 1-hexene homo- and co-polymerization catalyzed by obtained catalytic systems

Titanium complexes **3**, **4** were evaluated in their capacity as catalysts of the ethylene polymerization and ethylene/1-hexene copolymerization in the presence of cocatalysts - diethylaluminum chloride/dibutylmagnesium (Et_2AlCl/Bu_2Mg (3/1)) or methylaluminoxane (MAO). All obtained coordination compounds demonstrated high catalytic activities in ethylene polymerization reactions. Complex **4** showed maximum activity – 3940 kg PE*mol V^{-1}*atm^{-1}*h^{-1}. The same catalysts exhibited high efficiency in copolymerization reactions.

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DEVELOPMENT OF THE MONOMERS RECYCLING TECHNOLOGY IN PET PRODUCTION

Kondratev S.O., Vostrikov S.V., Nesterova T.N., Sagitova A.M., Gladyshev N.G.
Samara State Technical University,
Student
kso115@yandex.ru

The plastics recycling is the most actual direction of resource saving and environmental protection. Nowadays the polyethylene terephthalate (PET) waste makes up more than 30% of all plastic waste, 80% of which is recycled. The PET-waste formed both the result of raw materials into products processing and the result of completion of products use in the field of industrial and domestic consumption. Generally recognized that the chemical recycling of polymer is a promising method, corresponding to the principles of sustainable development, because it provides a return to starting raw materials (monomers). Closed-loop recycling occurs when a product can be received and reproduced infinitely as in the production of aluminum cans.

Global experience shows that effective way of the processing of any polymer is the environmentally safe and maximal complete recycling of the starting materials. The PET recycling technology provides 80% reducing of the carbon dioxide emission compared with the conventional production of polyester by the oil chain. Environmental Benefits from the closed-loop recycling of PET-plastic (data source: US EPA, 2006): energy savings 53 MBTUs/ton, avoided GHG emissions 0,42 (MTCE/ton of recovered material). In Russia, the PET-waste recycling by chemical way is not developed. Development and implementation of this technology will reduce the cost of PET production and solve the problem of utilization of non-conditional product and PET-waste.

In this article has been considered one of the possible way of chemical recycling of PET-bottles. The influence of temperature, contact time and reagent ratio to the conversion degree of polymer and process selectivity was examined. By special experiments were visualized processes occurring in the system at all stages of decomposition colorless and colorized PET-bottles. Chemical process of recycling allows to remove pollutants (e. g. dyestuff and bleach). It allowed us to find the relatively simple technical solutions for separating monomers from dyes. On the basis of this research is planned way in the development of technology, which, according to our estimates, will be able to compete with modern solutions in this area.

Acknowledgements
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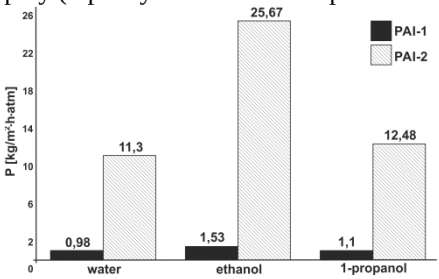
TRANSPORT PROPERTIES OF MEMBRANES WITH DIFFERENT POROSITY CHARACTERISTICS BASED ON POLYAMIDEIMIDE

Kremnev R.V.[1], *Zvereva I.A.*[1], *Sirotov V.V.*[1], *Kononova S.V.*[2], *Romashkova K.A.*[2]

[1]Saint Petersburg State University,
[2]Institute of macromolecular compounds RAS,
Saint Petersburg, Russia
postdoc
r.kremnev@gmail.com

Membrane separation technologies are widely used in biotechnology, pharmaceutical and food industries, as well as in wastewater treatment processes [1,2]. Great interest is using of polymers capable to form porous structures as separation membranes, particularly for processes of microfiltration (MF), ultrafiltration (UF) and nanofiltration (NF). It is known that the use of asymmetric microporous membranes for these processes is the most promising way, because in this case the membrane consists of a dense surface layer (skin layer) and an underlayer with large pores, and this type of structure can provide high strength and minimize mass transfer resistance. Polymer membranes with different porosity characteristics were obtained from poly (diphenylsulfonamide-N-phthalimide) (PAI).



Comparison of the flow rates of water, ethanol and propanol-1 through the membranes PAI-1 and PAI-2.

For membranes which differ with degree of tension in the stage of membrane drying, at the transition from PAI-1 to PAI-2 was determined increasing in the pore radius values on 30%, while flow value for ethanol grown more than 16 times.

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REVERSIBLE ADDITION–FRAGMENTATION CHAIN-TRANSFER (RAFT) COPOLYMERIZATION OF STYRENE AND ISOBORNYL ACRYLATE

Kulikov E.E., *Zaitsev S.D.*, *Zotova O.S.*

Lobachevsky Nizhny Novgorod State University
Nizhny Novgorod, Russia
Postgraduate Student
kulikoff.eug@ya.ru

The synthesis of narrow dispersity polymers with well-defined molecular weight characteristics provides a growing interest to controlled radical polymerization. This technique of polymerization allows synthesizing copolymers with various chain architecture, in particular, block-, gradient- and graft-copolymers. There're amphiphilic copolymers with narrow molecular weight distribution occupies a special place, it plays an important role in micro- and nanoelectronics and also drug delivery systems. In this paper we have presented an investigation of reversible addition–fragmentation chain-transfer (RAFT) polymerization of styrene (St) and isobornyl acrylate (*i*-BoA). It was found that (co)polymerization mediated by benzyl dithiobenzoate, as chain transfer agent, had proceeded in the controlled mode. It had been proved by linear increasing of the average molecular weight on the conversion, low polydispersity indexes, and the absence of the gel effect. Copolymerization of monomer mixtures with styrene content of 20 and 40 mol.% had allowed obtaining block-copolymers. Using macro-RAFT-agent we had implemented block-copolymerization. Further modification of synthesized poly(St–*b*–*i*-BoA) by acid hydrolysis of *i*-BoA's units to acrylic acid (AA) had been proved to obtain amphiphilic poly(St–*b*–AA).

BIMETALLIC/POLYMER NANOCOMPOSITES BASED ON PLATINUM METAL NANOPARTICLES FOR CHEMICAL POWER SOURCES

Lebedeva M.V.[1], *Yashtulov N.A.*[1,2], *Flid V.R.*[1]

[1]M.V. Lomonosov Moscow State University of Fine Chemical Technologies,
[2]National Research University "Moscow Power Engineering Institute",
Moscow, Russia
Ph-D student
lebedevamv221087@mail.ru

Among the various fuel cells, proton-exchange membrane fuel cells (PEMFCs) as energy conversion devices are promising future power systems with high power density, energy efficiency, and low operating temperature [1-5]. PEMFC are promising systems to deliver renewable energy because of their low environmental impact when supplied with hydrogen-containing fuels, such as methanol, ethanol, added to the capacity of producing high energy densities [1-5].

Nevertheless, a PEMFC operating with hydrogen (H_2) gas containing carbon monoxide (CO) from the reforming of fossil fuels shows low performance. This problem is caused by CO poisoning of the catalyst. The gas blocks the Pt surface because the bond strength of Pt–CO is greater than that of Pt–H, and thereby decreases the activity of the catalyst [5-8]. In order to improve the CO tolerance, many studies in recent years have reported details of new preparation methods and different compositions of Pt-based catalysts such as Pt–Ru, Pt–Pd, Pt–Sn and Pt–Mo [2,4,5]. In particular, the Pt–Ru system is an excellent anode electrocatalyst since it exhibits enhanced CO tolerance. For this reason synthesis of bimetallic nanoparticles (NPs) with controlled size, shape, and composition is key to the development of advanced nanocatalysts for chemical power sources (CPS).

The supporting materials with high surface area are vital to disperse catalyst particles and to reduce the catalyst loading under the condition of keeping high catalytic activity. Hence much efforts are in the underway in the development of various conducting supports for fuel cell applications. One of the main directions of formation of catalytically active, stable and inexpensive catalysts for the CPS is the development of nanostructured metals in polymer matrices [1-5]. Proton-exchange perfluorinated polymers with ionogenic sulfo-groups (-SO_3H) of the Nafion type are widely used as solid polymer membrane. Nafion is a polymer electrolyte that gives rise to efficient proton conduction when water content/structure and film thickness are optimized. Nafion® membranes modified by platinum-based mono- and bimetallic catalysts reduce the fuel crossover phenomenon and also allow a self-humidifying condition of the CPS,

leading to a high operation temperature with a consequently faster hydrogen-containing fuel oxidation kinetic [2,3,5].

The purpose of research is formation of high active and stable nano-membrane materials with bimetallic platinum metal nanoparticles (Pt-Ru, Pt-Pd) for CPS of new generation with high operating characteristics. By varying the synthesis conditions one can control the nanoparticles size, content and emerging properties. Synthesis of polymer nanocomposites was carried out by chemical reduction of platinum metal ions in water-organic solutions with ultrasonic treatment. By means of the electron microscopy, phase analysis, cyclic voltammetry, small-angle x-ray scattering methods it was performed the investigation of nanocomposite functional properties. Evaluation of the cyclic voltammetry results allows to conclude that the metal/polymer nanocomposites with bimetallic Pt-Pd and Pt-Ru nanoparticles have a higher catalytic activity than the nanocomposites with monometallic nanoparticles. The obtained metal/polymer electrodes containing nanoparticles of different composition, size and shape, can be used as a functional membrane-electrode materials for high-performance electrochemical fuel conversion of chemical energy sources.

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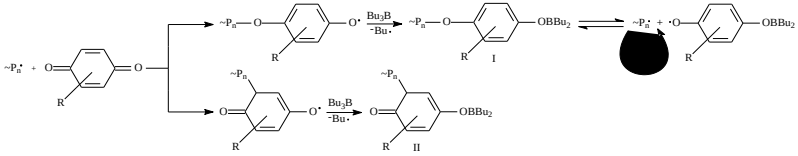
THE FEATURES OF POLYMERIZATION IN THE PRESENCE OF CATALYTIC SYSTEM TRI-*N*-BUTYLBORON – *P*-QUINONE

Ludin D.V.[1], *Kuznetsova Yu.L.*[1], *Zaitsev S.D.*[1]

[1]Lobachevsky State University
Nizhni Novgorod, Russia
Aspirant
dymass@rambler.ru

The catalytic systems based on tri-*n*-butylboron (TNBB) and *p*-quinones are effective mediators of the radical polymerization of many monomers [1, 2]. It is more efficient in the polymerization of styrene and acrylates (methyl acrylate (MA), *tert*-butyl acrylate) and less efficient in the polymerization of methyl methacrylate (MMA) and vinyl acetate (VA). It was shown that in the presence of such systems polymerization proceeds in the controlled manner according to the mechanism:



Formed adduct (I) is able to reinitiate (co)polymerization. It was shown that relative reactivity and the size of the substituents in *p*-quinone affect to the share of reversible inhibition. The polystyrene macro radicals are attached to the C=O bonds of quinone only. The addition of the propagating radical via the C=C bond of quinoid ring leads to the formation of the dead polymer; this situation facilitates widening of the molecular weight distribution of the final polymer. This way of addition can be realized for (meth)acrylate and VA radicals. The such adduct (II) is not able to reinitiation. The polyVA macro radicals react with quinones in this direction preferably. PolyMA and polyMMA propagating radicals are most sensitive to the characteristics of *p*-quinones. The activities of polystyrene-macroinitiators in the post-polymerization are distributed according to relative reactivities of quinones. There is more difficult regularity for the polyMMA-macroinitiators.

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STUDY ECOTOXICITY FIBER-FORMING POLYMERS OF DIFFERENT CHEMICAL NATURE

Nizamutdinova L.R., Yarmolenko A.S., Budina D.V.

Vyatka State University of Humanities
Kirov, Russia
Student
nizamutdinovalilija@mail.ru

In this work various samples of of textile fabrics for upholstery of different chemical nature: 2 samples of on the basis of lavsan with the addition of the nitrone and kapron and 6 samples on the basis of cotton, mixed lavsan, kapron and nitrone.

To determine the toxicity of aqueous extracts of textile fabrics in mortality and fertility change daphnia «Daphnia magna Straus» (Method of determining the toxicity of water and aqueous extracts from soils, sewage sludge, waste mortality and fertility change in Daphnia, FR.1.39.2007. 03222).

Table

The composition and the fiber-forming polymers toxicity

	Chemical composition	Toxicity (mortality),%		Fertility, the number of individuals
		acute, 4 day	chronic, 24 day	
Lavsan +	nitron	100	-	-
	caprone	100	-	-
Cotton + synthetic fibers	caprone	13	23	30
	caprone	0	20	26
	nitron	0	13	37
	nitron	0	0	35
	nitron	0	13	40
	lavsan	0	10	42

Research evidence that the samples on the basis of cotton with the addition of various synthetic fiber-forming polymers do not have an acute toxic effect. Chronic toxicity noted only for samples of textile fabrics based on cotton with the addition of kapron. In this case, there is less and fecundity of Daphnia compared to the nitrone and lavsan. Samples of synthetic polymers have acute toxicity.

Thus, our studies have shown that synthetic fiber-forming polymers exhibit ecotoxicity.

STABLE CONDUCTIVE POLYMER NANOCOMPOSION BASED ON POLYANILINE AND GRAPHENE

Omelchenko O.D., Gribkova O.L., Tameev A.R., Vannikov A.V.

A.N. Frumkin Institute of Physical Chemistry and Electrochemistry RAS
Moscow, Russia
Scientist
olgaomelchenk@yandex.ru

Polyaniline (PANI) is one of the most extensively studied conductive polymers due to the low cost of monomer, simplicity of polymer synthesis, environmental stability and high potential of the application. PANI can be used in sensors, batteries, light emitting and electrochromic devices, solar cells, etc Common procedure of PANI preparation in the inorganic acid leads to obtaining a product that is hardly soluble. In order to obtain water-processable material water-soluble polymers (mostly, polyacids) are used for aniline polymerization.

By variation of polyacid concentration in reaction medium, we determined the optimal condition for aniline polymerization in the presence of polysulfonic acid. The developed procedure leads to the preparation of PANI/polyacid dispersion that is stable without precipitation and remains the electrical properties of PANI films unchanged up to 2 years. The most stable dispersion is characterized by smaller objects as shown by TEM, UV-vis and EPR-spectroscopy.

To enhance performance of organic electronic devices the nanocomposites based on polyaniline and graphene were prepared, with graphene of different oxidation degree. Graphene with the low oxidation degree was found to provide the largest increase in conductivity up to 20 times doped into the nanocomposite at the concentration of 1 wt.%. Yet, if the material was used in solar cells as a buffer layer, the highest power conversion efficiency showed the device fabricated on nanocomposite of PANI with unoxidized graphene. The matter of the different performance of the nanocomposite is discussed basing on the results of AFM and FTIR-spectroscopy studies and including the different graphene distribution in the bulk of the nanocomposite film and the interactions between the nanocomposite components.

Acknowledgements
The Russian Foundation for Basic Research (grant No. 14-03-01137_a and 14-03-90413-Ukr_a) and Grant Council of the President of the Russian Federation (SP-2994.2015.1).

PH-SENSITIVE RAFT-AGENT

Polozov E. Yu., *Zaitsev S.D.*

N.I. Lobachevsky Nizhny Novgorod State University,
Nizhny Novgorod, Russia
Student
yegor.polozov@mail.ru

Reversible addition fragmentation chain (RAFT) polymerization is one of most convenient methods for synthesis of polymers with predetermined molecular weight characteristics and a fixed macromolecular structure. RAFT-polymerization can be used with a wide range of functional monomers and is easy to fulfill in laboratory conditions. However, there is a serious disadvantage, which reduces the usage of this method – you have to select a certain RAFT-agent for the used monomer or monomers. Dithioester and trithiocarbonate have proved their efficiency in polymerization of active monomers, such as methyl methacrylate, styrene and others. At the same time, the usage of these RAFT-agents in the polymerization of less activated monomers (vinyl acetate, N-vinylcarbazole) leads to inhibition/retardation and, in some cases, to stopping the process. That's why the synthesis of block-copolymers, which contain a block of MAM-units and a block of LAM-units is made difficult by RAFT polymerization. Recently, a new kind of RAFT-agents was reported in the literature, they were named "switchable" and demonstrated their efficiency at some monomers. In certain conditions they can be successfully used for polymerization of MAMs and LAMs. The target of this work is the study of possibilities of these RAFT-agents on the example of other monomers and a possible broadening of their application area. So we received polymers of polybuthylmethacrylate with low polydispersity and linear increase of the number average molecular weight with conversion.

STUDY OF PERVAPORATION SEPARATION OF A BINARY MIXTURE OF THF-WATER USING THE PVA-BASED MEMBRANES

Polyakov E.S[1]*., Penkova A.V.* [1]*, Dmitrenko M.E.*[1]*, Sokolova M.P.*[1]*, MikhailovaM.E.*[2] *Roizard D.*[3]

[1]St. Petersburg State University, Department of Chemical Thermodynamics & Kinetics, Universitetsky pr. 26, Peterhof, Saint Petersburg, 198504, Russia
[2]St. Petersburg State University, Department of Physics, Ul'janovskaja street 1, Peterhof, St. Petersburg, 198504, Russia
[3]Laboratoire Réactions et Génie des Procédés, CNRS, Université de Lorraine, ENSIC, 1 rue Granville, 54000 Nancy, France
St. Petersburg, Russia
Student
Polyakoves@bk.ru

Development of energy and resource saving environmentally friendly technologies is one of the major trends of innovative development of the chemical industry. In this connection the separation and purification of liquid mixtures needs, in particular by evaporation through polymeric membranes. One of such methods is pervaporation. Pervaporation is the membrane process, which is usually used for the separation of low molecular weight when application of distillation is impossible or requires a large energy consumption for the process.

The aim of this work was to develop the novel composite membranes with the selective layer based on polyvinyl alcohol and its composite with fullerenol. The relationship between characteristics of casting solutions and properties of nanocomposite membranes was studied. Hydrodynamic properties of PVA, fullerenol and PVA/$C_{60}(OH)_{12}$ composites in dilute solutions were studied by viscometry and Dynamic Light Scattering (DLS). The rise of the aggregates sizes with increase of fullerenol content in PVA/fullerenol composite solutions was found. The effect of low-hydroxylated fullerenol on the structure and morphology of PVA membranes were investigated by AFM, NMR, thermogravimetric analysis, differential scanning calorimetry and sorption experiments. The transport properties of the obtained diffusion and composite membranes were studied under the separation of a binary azeotropic mixture of tetrahydrofuran - water (94% by weight of THF) in pervaporation at different temperatures (30 ° C, 50 ° C, 60 ° C). The activation energy was calculated for the studied membrane on the base of transport characteristics. It was shown that the novel developed composite membranes have high transport characteristics and their efficiency increases with the rise of temperature.

Acknowledgments

The experimental work was facilitated by equipment from the Resource Center of X-ray diffraction studies, Center for chemical analysis and materials research, Resource Center of Thermal Analysis and Calorimetry, Resource Center for Nano technology and Centre for Physical Methods of Surface Investigation, at St. Petersburg State University.

MIXED MATRIX MEMBRANES WITH HYBRID STAR-SHAPED MACROMOLECULES FOR ORGANIC SEPARATION

Rostovtseva V.A., Polotskaya G.A., Pulyalina A.Yu.

Saint Petersburg State University
Saint Petersburg, Russia
Student
valfrank56@gmail.com

The development of novel materials is still the primary task due to their potential application in many industries. Assembly of inorganic particle with polymer matrix leads to changes in structure and physical parameters of materials. Mixed-matrix materials combine the benefits of both polymeric and inorganic materials due to the interface between the polymer matrix and agglomerated nanoparticle phase. By incorporating inorganic particles within the polymer matrix, the mixed-matrix materials inherit some of the characteristics of inorganic particles, especially their superior separation performance. At present the star-shaped macromolecules are a great interest because of its unique physico-chemical properties. The application of this materials in various spheres of industry including membrane separation process is growing rapidly. One of such membrane method is pervaporation: a process which is widely used for the purification, concentration and fractionation of liquids including azeotropic, close boiling-point and thermally unstable mixtures. In present work mixed matrix membranes were prepared by hybrid star-shaped macromolecules (HSM) in polymer matrix. As a branching center fullerene C_{60} molecule was used. This mixed matrix membranes were tested in pervaporation of organic mixtures.

Fig. 1. Hybrid star-shaped macromolecules

Scanning electron microscopy showed that HSM inclusion in polymer matrix leads to formation of domains in membranes and their amount increases with

the rise of HSP content. Mass transfer through the membranes was studied by sorption and pervaporation tests toward liquids under study. It was established that in pervaporation processes membranes permeate preferably small molecules of liquids and show high effectively in organic separation. The total flux through membrane increase with the rise of HSM content.

Acknowledgements

The work was supported by Russian Foundation for Basic Research (grant 15-03-02131).

THERMO-GRAVIMETRIC AND KINETIC STUDY OF COPOLYMERS OF POLYPROPYLENEGLYCOLMALEATE WITH ACRYLIC ACID

Sarsenbekova A.Zh.,[1] *Mukabylova A.O.*,[1] *Borsynbayev A.S.*,[1] *Sarsenbek A.Zh.*[1]

[1]Karaganda state university, 100026 Karaganda, Kazakhstan
PhD student
chem_akmaral@mail.ru

We presented the results of thermodynamic properties of copolymers of polypropyleneglycolmaleate with acrylic acid which were obtained by the using of thermo gravimetric analyses method (TGA) [1]. The differential scanning calorimeter DTA/DSC («Labsys Evolution» firm) was used during the research works. The experiments were carried out in differential regimen at the 303-773^{0}K temperature intervals with heating rate 10^{0}K/min within Al_2O_3 nitrogenic atmosphere. Copolymers of polypropyleneglycolmaleate (p-PGM) with acrylic (AA) acid with molar compositions 9,1:90,9; 87,0:13,0 were obtained by the reaction of copolymerization in solution of diethylene dioxide, ratio of monomeric mixture: solvent was 1:1 in the presence of initiator - benzoperoxide at the temperature 333^{0}K, according to the methodology described in the research [2]. During the research it was investigated that glass-transition temperature is about 357÷368^{0}K. Thermal interval of glass transition (ΔT_t) decreases with the increasing of the volume of polypropyleneglycolmaleate in copolymer composition. Temperature of the first stage beginning of the thermal decomposition (T_d) for all studied copolymers shifts to the region of higher temperature 427÷437^{0}K. The p-PGM:AA 9,1:90,9mol.% is the most resistant to heat and its meaning of activation energy is (E_a) ~25,85kJ/mol (*F.C.* method), ~27,77kJ/mol (S.W. method). So these parameters were determined on the basis of two models of *Freeman* and *Carroll* [3], Sharp and Wentworth [4] and the using of these models makes it possible to make a conclusion about the kinetic characteristics of thermal decomposition process, especially about the activation energy and pre-exponential factor.

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PVC MEMBRANES: STRUCTURAL, PHISICAL AND TRANSPORT PROPERTIES

Savon N.A., Penkova A.V., Dmitrenko M.E., Sokolova M.P.

Saint Petersburg State University,
Saint Petersburg, Russia
Student
savon-nadezhda@mail.ru

Nowadays membrane processes are widely used in science and industry. It requires the development of new high-performance membrane materials with improved physical-chemical and transport characteristics. One of the ways to get tailoring properties of polymeric membrane materials is their modification by inorganic and organic particles.

In this work, polyvinyl chloride (PVC) was chosen as a membrane material. This polymer has good chemical and physical properties, and low cost. The disadvantage of this polymer as a membrane material is low permeability.

In the present research the effect of the addition of organic (dioctyl phthalate, 2-nitrophenyl octyl ether) and inorganic (fullerene C_{60}) particles to the PVC matrix on the physical-chemical and transport properties of the membranes is investigated. Preparation of PVC-C_{60} composite was performed in two ways: the solid-phase synthesis and the solution method. To improve the transport properties the composite membranes were developed by creating a thin selective PVC layer on industrial porous supports. Structural and physical characteristics of diffusion membranes were studied by IR spectroscopy, SEM microscopy, thermogravimetric analysis and measuring their mechanical properties. The transport properties of membranes were investigated under separation of tetrahydrofuran - water mixture by pervaporation. It was shown that the addition of particles that have different nature to PVC matrix leads to the significant change of properties of the membrane due to changes in the structure and morphology.

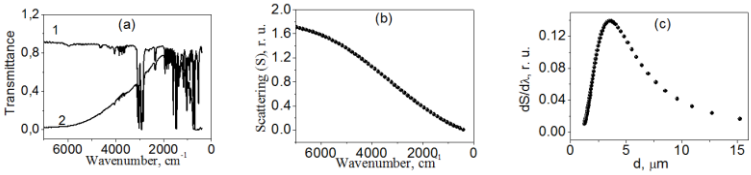
Acknowledgments
This work was supported by Fellowship of President of Russian Federation СП-1153.2015.1 (Penkova A.V.). The experimental work was facilitated by equipment from Resource Center of Thermal Analysis and Calorimetry, Resource Center for Nano technology, Resource Center of Innovative technologies of composite nanomaterials at St. Petersburg State University.

APPLICATION OF NEAR-, FAR-IR AND UV SPECTROSCOPY FOR STUDYING THE MORPHOLOGY OF POLYMER COMPOSITES AND POROUS MATERIALS

Sitnikova V.E.[1], *Khizhnyak S.D.*[2], *Pakhomov P.M.*[2]

[1]Tver State University,
Tver, Russia
Ph.D.-Student
kresenka@gmail.com

To fabricate polymeric material with definite properties various fillers are introduced into a polymer matrix. To characterize the particle size distribution in the polymeric materials a novel spectroscopic approach has been developed by authors. The procedure is based on the analysis of attenuation of an incident radiation due two effects, namely, absorption by polymeric matrix and scattering by filler particles. Effect of these two factors is shown an example of IR spectra of PET films – without filler (spectrum 1) and filled with 30% of TiO_2 (spectrum 2, Pic. 1a). Fig.1b demonstrates a result of subtraction of these spectra. Differentiation of the subtracted spectrum leads to obtaining the particle size distribution (Pic. 1c). Two types of polymeric materials – composites based on different matrices (PET, PS, PP, PVA) filled with various fillers – TiO_2, MMt, talcum, $CaCO_3$, CNF – and porous materials (track membranes based on PET, PP, PC (producing of United institute of nuclear researches, Dubna) and porous polyethylene films) are studied by FTIR, NIR, FIR and UV-vis spectroscopy. It is found that scattering is observed in all cases, if refractive indices of two components (matrix – filler) have some difference. The scattering depends mainly on difference of refractive indices and filler's concentration in the polymeric materials. The particle size distributions calculated from the spectra are in good agreement with the data obtained from the light and electron microscopy.



Picture 1: a – IR spectra of PET films, b – subtracted spectrum, c – particle size distribution

This work was supported by German-Russian Interdisciplinary Science Center (Project C-2014b-7)

The work is performed under financial support of the Ministry of Education and Science of the Russian Federation in the frame of realizing of the State task in the field of the scientific activity.

POLYANILINE/POLYACRYLAMIDE COMPOSITES AS ELECTRODE MATERIAL FOR SUPERCAPACITORS

Smirnov M.A.[1], *Bobrova N.V.*[1], *Sokolova M.P.*[2], *Kasatkin I.A.*[2], *Elyashevich G.K.*[1].
[1]Institute of Macromolecular Compounds, Russian Academy of Sciences,
[2]Saint Petersburg State University, Institute of Chemistry,
Saint-Petersburg, Russia
Research fellow
Smirnov_Michael@mail.ru

The composites containing the interconnecting polyaniline nanorods (PANI) inside the polyacrylamide (PAAm) hydrogel were prepared. PANI phase was formed by chemical oxidative polymerization of aniline in the solution of linear PAAm. After precipitation with methanol and drying the system looses solubility but acquires swelling ability in acidic water solutions. Degree of water uptake was 3-13 g/g depending on the synthesis conditions. It was established that the composite systems prepared by this method demonstrate the mixed type of conductivity (electronic and ionic charge transfer, both) due to the continuity of polyaniline phase inside the sample. The changes of composite structure during swelling/drying cycles were investigated by wide angle X-ray diffraction. It was found that swelling brings to decrease of the long-scale order in PANI molecules arrangement, and this process is reversible. The synthesized composites were tested as electrode materials for supercapacitor in galvanostatic charge/discharge experiments (Fig.1). Specific capacitance of the samples reaches 250 F/g at current density 1 A/g and retention ratio slightly increase during charge-discharge cycles. Cyclic votammograms proves that PANI/PAAm electrodes are characterized by the pseudo-capacitive behavior.

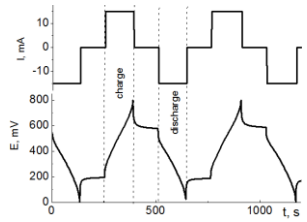


Fig 1. Galvanostatic charge-discharge cycling curves for PANI/PAAm composite

Acknowledgements
The work was supported by the Russian Foundation of Basic Research (Grant № 13-03-00219) and Research grant of Saint-Petersburg State University (Grant № 12.38.257.2014). The X-ray diffraction experiments were performed in the X-ray Diffraction Centre of Saint-Petersburg State University.

CORROSION PROTECTION OF CARBON STEEL WITH POLYANILINE: THE ROLE OF POLYMER STRUCTURE

Smirnov M.A.[1], *Sokolova M.P.*[2], *Dmitriev I.Yu.*[1], *Saprykina N.N.*[1], *Kasatkin I.A.*[2], *Elyashevich G.K.*[1].

[1]Institute of Macromolecular Compounds, Russian Academy of Sciences,
[2]Saint-Petersburg State University, Institute of Chemistry,
Saint-Petersburg, Russia
Research fellow
Smirnov_Michael@mail.ru

Protection of metals against corrosion still remains one of the most important problems for science and industry. Coatings based on conducting polymers such as polyaniline (PANI) and polypyrrol can be perspective electro-chemical inhibitors of metals corrosion. But mechanism of their activity is not completely understandable. The aim of this work is to find clarify the influence of crystalline structure and morphology of PANI on its anti-corrosion activity. The set of polymers were synthesized in the form of nano-particals by chemical oxidative polymerization of aniline with $(NH_4)_2S_2O_8$ as an oxidant in the presence HCl, H_2SO_4 or H_3PO_4 at 0 or 35°C. Crystalline structure has been investigated by X-ray diffraction. Degree of crystallinity and size of crystallites were measured. Anisotropy of the polymer particles was described by ratio of their length to diameter (l/D) which was calculated by statistical treatment of the scanning electron microphotographs. Polymer coatings on the surface of carbon steel plates were formed by casting from water dispersion of PANI and then dried. The samples as prepared were put into the corrosion active solution (3.5% NaCl) which initiates the formation of ferrous oxide-hydroxide layer on the boundary between polymer and metal. Being electro-chemically active, PANI is capable to influence on the structure of inorganic layer and thus to regulate its protective properties. The effect was investigated by polarization method. Composition of the layer was determined by X-ray phase analysis. It was found that PANI having degree of crystallinity >25% and l/D>3.5 promotes the formation of α-FeOOH (goethite) and Fe_3O_4 (magnetite) which is characterized by a high stability and, consequently, can slow down the rate of corrosion. Usage of the polymers with lower crystallinity and minor l/D leads to the formation of γ-FeOOH (lepidocrocite) which is less stable.

Acknowledgments
The work was supported by the Russian Foundation of Basic Research (Grant № 14-03-31411 mol_a) and research grant of Saint-Petersburg State University (Grant № 12.38.257.2014). The X-ray diffraction experiments were performed in the X-ray Diffraction Centre of Saint-Petersburg State University.

SYNTHESIS OF HIGH MOLECULAR MASS EPOXY POLYNORBORNENE

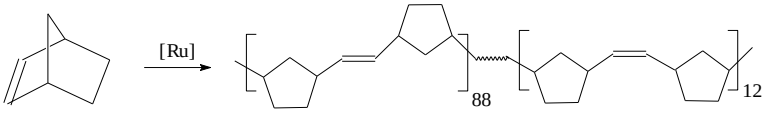
Tikhomirov V.A.[1,2], *Morontsev A.A.*[1,3], *Gringolts M.L.*[1], *Filatova M.P.*[1]

[1]A.V.Topchiev Institute of Petrochemical Synthesis, RAS
[2] D. Mendeleyev University of Chemical Technology of Russia
[3] Lomonosov Moscow University of Fine Chemical Technology
Moscow, Russia
Student
hasn200@mail.ru

Poly(cyclopentylenevinylene) or polynorbornene (PNB) obtained according to ring-opening metathesis polymerization (ROMP) of norbornene (NB) is well-known commercial product. PNB available under the trade mark Norsorex meets various specific applications. Several ways were used for improving of PNB gas permeability and adhesion properties, such as introduction of $SiMe_3$, $Si(OR)_3$ or epoxy groups in PNB side chain [1]. Only a few publications were devoted to epoxidation of double bonds in the main chain of PNB [2, 3]. Unfortunately they contain only poor data about properties of epoxy-polynorbornene (EPNB): nothing is known about its glass transition temperature, changing of PNB molecular mass during its epoxidation, adhesion, gas permeability etc.

The aim of our work was the synthesis of EPNB with rather high molecular mass which would be sufficient for preparing the polymer films needed for study of gas-permeability, adhesion and other properties.

The initial PNB was synthesized by ROMP of NB using Grubbs' catalyst of first generation ($Cl_2(PCy_3)_2Ru=CHPh$)(scheme 1).

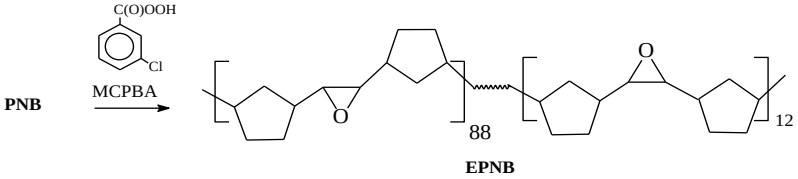


NB **PNB**

Scheme 1

The synthesized PNB was characterized by GPC, DSC, and NMR and contained predominantly trans double bonds (M_w = 1,9 x 10^5, M_w/M_n = 2.8, T_g = 39 °C, trans-88%).

The epoxidation of PNB was carried out by m-chloroperbenzoic acid (MCPBA) according Prilezchaev's reaction (scheme 2).



Scheme 2

EPNB obtained was characterized by NMR, IR, GPC and DSC. The cis/trans ratio of epoxy-group position was equal to those of double bonds in PNB. It was shown that as the degree of double bonds epoxidation increased the polymer molecular mass decreased. The influence of antioxidant and different type of solvents (chloroform, chlorobenzene and toluene) on the EPNB molecular mass was evaluated. In the presence of chloro-containing solvents M_w of PNB decreased from 1,9 x 10^5 down to 0,5 x 10^5. Usage of antioxidant 2,2'-methylenebis(6-tert-butyl-4-methylphenol) as well as epoxidation of PNB in toluene solution let us to obtain EPNB with rather high molecular mass Mw=(1,0-1,4)·10^5 (PDI=2,4-2,7, Tg=62ºC), up to 99% yield and 99,5-100% degree of C=C double bond epoxidation.

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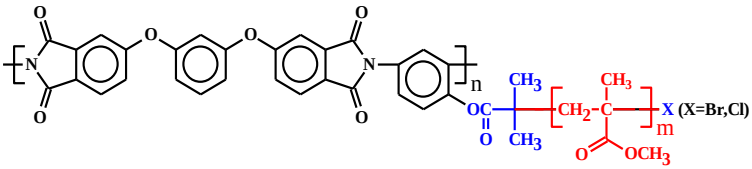
PREPARATION AND CHARACTERIZATION OF MEMBRANES BASED ON POLYIMIDE-POLYMETHYLMTHACRYLATE BRUSH

Tyan N.S., *Pulyalina A.Yu.*

Saint Petersburg State University,
Saint Petersburg, Russia
Student
tyan-nadezhda91@yandex.ru

Currently membrane methods of liquid and gas separation are extensively used due to the ability of high-purity substances obtaining even from azeotropic and unstable mixtures. Wide variety of membrane technology applications at limited assortment of commercial membranes promotes the development of novel membrane materials with improved transport properties. Polyimide membranes have high level of selective separation, thermal, chemical and

mechanical stability, however their permeability is very low. One of the way to increase the productivity of polyimide membrane - addition of bulk substitutes to polyimide chain. Graft co-polymerization is effective and often used method of polymer modification. Polymer brushes as novel type of graft copolymerization are becoming popular due to the ability of chemical configuration, density, architecture and thickness control. The objects of presence work - polymer membranes based on graft co-polymers polyimide-polymethylmethacrylate (PI-PMMA) - are the special group of polymer brushes whose transport properties had not been studied:



The aim of the presence work is preparation and research of novel membranes for organic dehydration by one of the most perspective membrane method - pervaporation. Thermogravimetry, scanning electron spectroscopy, sorption, pervaporation experiments and flotation method of density measurements were used for membrane characterization. For the evaluation of intrinsic properties of penetrant-membrane system, permeability and selectivity were calculated. It was found that membranes under study are thermal, mechanical and chemical stable. PI-PMMA membranes show high separation factor and high selective for water-organic separation.

Acknowledgements
The work was supported by Fellowship of President of Russian Federation.

INFLUENCE OF UNSATURATION PETROLEUM RESIN ON THE CONTENT OF EPOXY GROUPS

Ustimenko J.P.[1], *Slavgorodskaya O.I.*[1]

[1]National Research Tomsk Polytechnic University
Tomsk, Russia
Student
juliya08-11@mail.ru

Increasing of olefin production will make the implementation of novel technologies reasonable with growth of total efficiency of pyrolysis plants and reduce the cost of the main product. One of the most prospective areas of such technologies is liquid pyrolysis products processing technology improvement [1]. The polymerization of C_9 fraction is widely investigated process.

The goal of this work is to study the influence of unsaturation of the PR on the content of epoxy groups.

For preparation PR with different values of bromine number, which characterizes unsaturation, oxidation was carried out with peracetic acid [2, 3]. Different values of unsaturation achieved by adding different amounts of catalyst. H_2SO_4 was used as the catalyst (in an amount of 0.3, 0.5, 0.7 and 1% of organic phase). The dependence of epoxy number from the bromine number is shown in Figure 1.

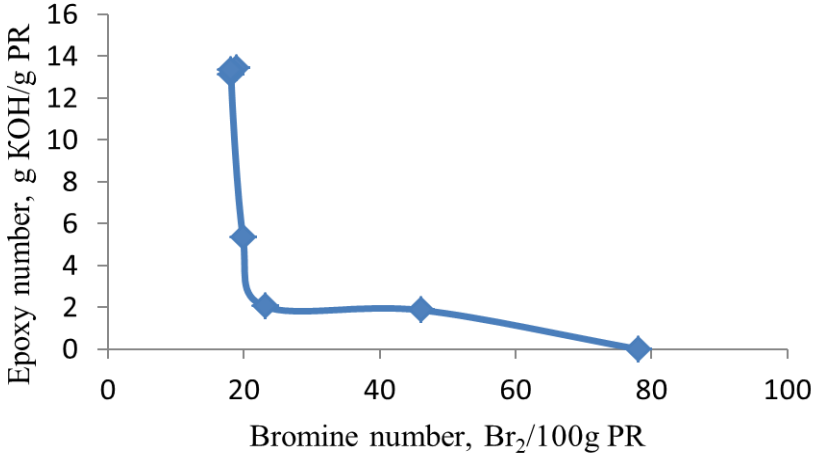


Figure 1. The dependence of epoxy number from the bromine number

With increasing unsaturation decreases epoxy number because by oxidation under these conditions prevail carboxylation reaction, which in turn is caused by the reaction rate constant carboxyl and epoxy groups formation [3].

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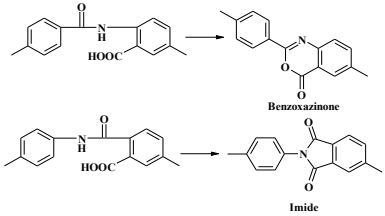
PREPARATION, THERMOCHEMICAL AND TRANSPORT PROPERTIES OF NOVEL MEMBRANES BASED ON POLYHETEROARYLENES

Veremeychik K.Yu., *Pulyalina A.Yu*, *Toikka A.M.*

Saint Petersburg State University
Saint Petersburg, Russia
Postgraduate Student
k.veremeychik@gmail.com

At present pervaporation is one of the most promising membrane technologies due to its energy saving, environmental and cost affectivity. The area of application involves biorefinery, petrochemical and food processing industries, where separation, purification and concentration of liquid mixtures are required. The main task of pervaporation is the actual choice of the membrane material. Polymers of heteroatomic structure are the perspective class for membrane fabrication because of their high mechanical, strength and heat resistance properties. Thus the aims of this work are the development of the membranes based on novel polyheteroarylenes obtained by solid phase synthesis of their precursors and the investigation of their physicochemical and transport characteristics.



Picture 1. Scheme of PBOZ and PBOI formation

Scanning electron microscopy and thermogravimetric analysis were carried out to investigate the structure of the membrane and its thermal stability. The mass transfer through the membrane was estimated by sorption and diffusion experiments.

The performance of the membranes was studied in pervaporation of commercially significant solutions including azeotropic mixtures. It was found that the membranes are extremely effective in purification of water-alcohol solutions and waste water.

Acknowledgements

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SYNTHESIS AND ELCTROCATALYTIC ACTIVITY OF POLYANILINE COMPOSITES WITH METAL CHLORIDES AND CARBON NANOTUBES

Visurkhanova Ya.A., Soboleva E.A., Izbastenova D.S., Ivanova N.M.

Institute of Organic Synthesis and Coal Chemistry of Kazakhstan Republic
Karaganda, Kazakhstan
Junior Researcher
yakhashovda@mail.ru

It is known that the introducing of carbon nanotubes (CNT) into polymers and polymer-metal composites may increase their conductive properties and possibly electrocatalytic activity when they applied to the electrode surface in electrochemical processes.

In this paper we investigate the influence of multi-walled CNT (series "Taunit") previously purified from the residual content of nickel catalyst and oxidized with a mixture of sulfuric and nitric acids on electrocatalytic activity of composites of polyaniline (PANI) doped with metal (Ni, Co, Cu) chlorides (with and without chemical reduction of metal cations) in electrohydrogenation of *p*-nitroaniline (*p*-NA).

By the experiments performed it was established that at an application of PANI+$NiCl_2$ composites with 10% MWCNTs (to aniline) for activation of Cu cathode the rate of hydrogenation of *p*-NA and its conversion to *p*-phenylene diamine are reduced in comparison with similar composites without MWCNT. According to X-ray analysis, as a part of these composites are no crystalline phases of $Ni(OH)_2$, which are formed in aqueous-alkaline medium of catholyte and define an electrocatalytic activity of PANI+$NiCl_2$ composites. In the phase constitution of PANI+1%MWCNT+$CoCl_2$ composites after electrohydrogenation of *p*-NA the crystalline phases of $Co(OH)_2$ were detected, but an intensification of the studied process was not observed.

The electrocatalytic activity of PANI+$CuCl_2$ composites with 1 and 10% MWCNTs is also decreased in comparison with the same composites without carbon nanotubes, that is due to the absence of crystalline phases of Cu^0 in these composites after hydrogenation of *p*-NA. At the same time, PANI+ MWCNT+$CuCl_2$ composites obtained with chemical reducing agents (sodium borohydride and hydrazine hydrate) are found more catalytic active in electrohydrogenation of *p*-NA, since the presence of oxidized-MWNT promotes a more complete chemical reduction of copper cations and formation of crystalline phases Cu^0 and its oxides in these composites before applying them to electrohydrogenation of *p*-NA.

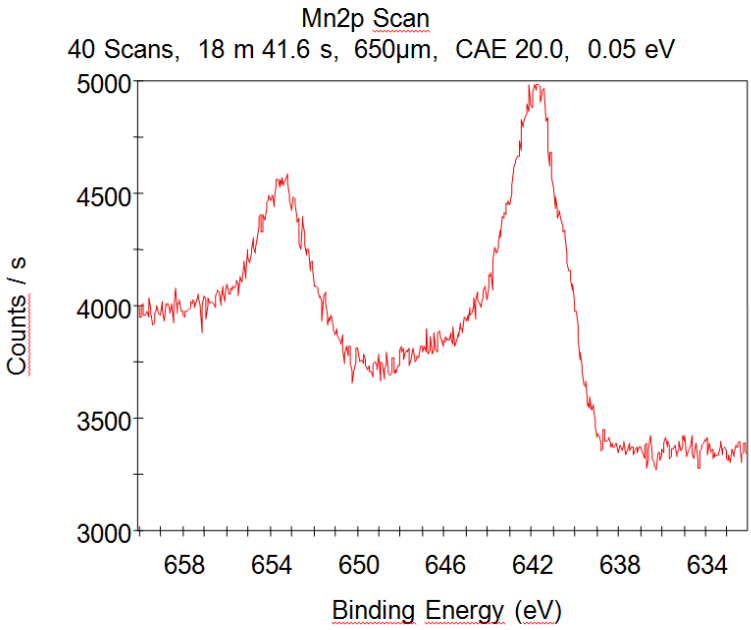
SYNTHESIS AND STUDY OF ELECTROCHEMICAL PROPERTIES OF POLY(3,4-ETHYLENEDIOXYTIOPHENE) / MANGANESE DIOXIDE

Volkov A. I., *Eliseeva S. N.*, *Kondratyev V. V.*

Institute of Chemistry of Saint-Petersburg State University,
198504, Petergof, Universitetskiy pr., 26, Russian Federation
Student
grulfex@gmail.com

In order to satisfy the fast growing demands on electronic devices of the 21st century it is necessary to develop new flexible materials for energy storage which would be altogether have such qualities as small size, high capacity, ability for fast charge-discharge process and low cost for mass production. To solve this task we used the method of dropwise of the composite material with even dimensional distribution of the particles of manganese oxide in the polymer matrix of poly(3,4-ethylenedioxythiophene)-polystyrene sulfonate (PEDOT:PSS). The composite films were synthesized from the three-compound mixture: PEDOT-PSS, 0.5% nafion in ethanol and 0.007-0.04M potassium permanganate.

The morphology of highly dispersed manganese oxide in the polymer matrix of PEDOT:PSS was characterized by the scanning electron microscopy method. XPS spectroscopy method was used for identification of the valence state of manganese. The XPS spectrum of the synthesized film is presented at Picture 1. The electrochemical properties of the composites were studied by such methods as cyclic voltammetry, galvanostatic charge-discharge curves and electrochemical impedance spectroscopy. Capacity parameters of the composites with different proportions of PEDOT:PSS and MnO_2 in the composite material were systematically studied and analyzed.



Picture 1. XPS spectrum of the composite film PEDOT:PSS/MnO_2

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Acknowledgements

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HYDROTHERMAL SYNTHESIS AND SURFACE FUNCTIONALIZATION OF ZrO_2-BASED NANOPARTICLES FOR OBTAINING A TRANSPARENT HIGH-INDEX POLYMER NANOCOMPOSITES

Zavialova A.Yu.[1], *Bugrov A.N.*[2]
[1]Saint Petersburg Electrotechnical University "LETI",
[2]Saint Petersburg State University
Saint Petersburg, Russia
Master student
alexander.n.bugrov@gmail.com

Zirconia nanoparticles are promising filler to obtain the transparent polymer-inorganic composites with a high refractive index (RI). Such composites are crucial for the manipulation or enhancement of light in optic devices (LCD, LED, holographic grating, etc.) Since the RI of a composite is determined by the volume fraction of components, its significant increase can be achieved only with a high content of ZrO_2. High loading degree of filler leads to agglomeration of zirconia nanoparticles in polymer bulk. In this regard, the purpose of this work was to study the effect of nanoparticles surface modification on the agglomeration process and distribution of nanosized ZrO_2 in polymethylmethacrylate (PMMA).

ZrO_2-based nanoparticles were prepared by dehydration of $ZrO(OH)_2$ and $ZrO(OH)_2$-LnOOH (Ln = Eu, Tb, Tm) mixtures under hydrothermal conditions. Oxyhydroxides and their mixtures prepared by precipitation from 0.5 M metal chloride solutions by 12M NH_4OH. Hydrothermal treatment was performed in a steel autoclave with a teflon vial at 250˚C for 4 hours.

According to XRD and SEM results, the formed ZrO_2 and ZrO_2-Ln_2O_3 nanoparticles have spherical shape and a narrow size distribution (10±2 and 20±3 nm, respectively). Surface hydroxyl groups of ZrO_2-based nanoparticles were used for the surface modification by vinyl compounds (2-hydroxyethyl methacrylate, diethoxy(methyl) vinylsilane, 3-(trimethoxysilyl)propyl methacrylate (TPM)). Modifiers containing vinyl group were attached to nanoparticles surface by condensation of the hydroxyl or hydrolyzed methyl groups with surface OH groups of zirconia. Dependence of the crosslinking density and character of interaction between nanoparticle surface and modifier on its concentration, time and temperature of the condensation reaction was determined. Thickness of vinyl compound layer and amount of modifier functional groups covalently bound to nanoparticle surface were also calculated. Zeta potentials and stability of the ZrO_2-based nanoparticles dispersions were measured by ELS and DLS methods.

It is found that the value of zeta potential varying in a range of 5÷40 mV depends on the composition and surface treatment. Results of DLS study shows that the toluene dispersion of the ZrO_2 nanoparticles modified by TPM is the most stable. It is proved that vinyl groups of modifiers are involved in the polymerization of MMA, forming covalent bonds with the polymer. This prevents agglomeration of ZrO_2 nanoparticles and contributes to their uniform distribution in PMMA.

^{1}H NMR STUDY OF COMPLEXATION REACTION OF THF WITH SEVERAL ORGANOALUMINIUM COMPOUNDS OPERATING AS ACTIVATORS OF IVB METALLOCENE COMPLEXES

Zharkov I.V., Bravaya N.M., Faingold E.E.

Institute of Problems of Chemical Physics Russian Academy of Sciences,
Chernogolovka, Moscow Region, Russia
igor.zharkov@phystech.edu

The metallocene-based catalytic systems are effective catalysts for homo- and copolymerization of olefins. The most common and effective activator is methylalumoxane (MAO). Recently we have shown that both isobutylalumoxanes and isobutylaluminium aryloxides also effectively activate metallocene precursors in homo- and copolymerization of olefins. So, these OACs, similarly to MAO, form cationic intermediates with transition metal species, therefore acting as Lewis acids. To achieve better understanding of how the OAC nature affects the properties of catalytic systems, it is important to compare Lewis acidity of OAC of different structures.

The work describes ^{1}H NMR study of complexation of isobutyl-based OAC with THF, followed by the comparison of their acceptor properties, based on evaluated complexation constants. The ^{1}H NMR spectra of binary OAC/THF mixtures at different Al/THF ratio (0.15 - 7) were quantitatively analyzed in order to determine the correlation between the Al/THF mole ratio and relative shifts of OCH_2 and CH_2 groups in THF ($\Delta\delta$ as shown on Fig.1)

The said correlation had been proved to include the initial linear area, where $\Delta\delta$ increases proportionally to Al/THF ratio, and saturation area, where $\Delta\delta$ rests at the same level ($\Delta\delta_\infty$). The dependencies, along with precise data on concentration of reagents, allowed determination of complexation constants. The relative chemical shift of CH_2 and CH_3 protons of isobutyl groups has been used for estimation of aluminum atom electronegativity in both pure OACs and their complexes with THF.

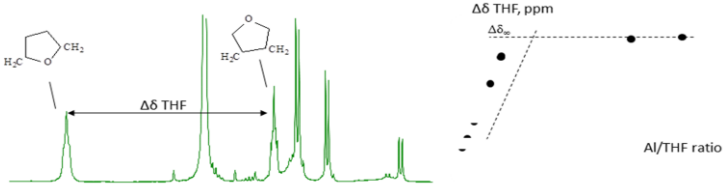


Figure 1. Left: ^{1}H NMR spectrum of THF/OAC mixture, with $\Delta\delta$ marked. Right: correlation between $\Delta\delta$ and Al/THF ratio with marked linear and saturation areas.

Acknowledgements

The work was supported by the Russian Foundation for Basic Research (projects № 13-03-01281-a, 15-03-02307-a).

CONTROLLED FREE-RADICAL COPOLYMERIZATION OF STYRENE AND ACRYLIC ACID BY REVERSIBLE ADDITION-FRAGMENTATION CHAIN TRANSFER

Zotova O.S., *Kulikov E.E.*

Lobachevsky Nizhny Novgorod State University
Nizhny Novgorod, Russia
Postgraduate Student
oksana_zotova@myrambler.ru

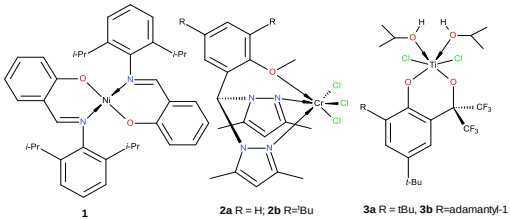
Now greatest interest for polymer chemistry is the development of new methods of control radical polymerization processes with a view to the controlled synthesis of polymers with narrow molar mass distribution with different structures. There are several methods, but the most effective, simple and universal technique of radical polymerization to synthesis polymers with predetermined molecular weight and narrow molar mass distribution, is controlled free-radical polymerization by reversible addition-fragmentation chain transfer (RAFT). The aim of my research is synthesis and study properties of copolymers acrylic acid and styrene with narrow molar mass distribution in presence RAFT agents – benzyl dithiobenzoate and its polymeric product with used monomers. It was shown that polymerisation acrylic acid with styrene in presence RAFT agents observed typical signs of controlled radical polymerization – lack of gel effect, the linear dependence of the average molecular weight from conversion, low polydispersity parameters. Copolymers styrene with acrylic acid have a gradient structure, when the proportion one of this monomers in a monomer feed was larger. Discovered case realization of the effect of the election solvatation - at copolymerization of styrene and acrylic acid in the presence of the polymer RAFT agent based on polyacrylic acid. Homogeneous composition distribution of copolymers had been proved. synthesized copolymers with different microstructures.

TANDEM CATALYTIC SYSTEMS BASED ON Ti (IV) COMPLEXES WITH 2-(HYDROXYMETHYL)-PHENOLE DERIVATIVE LIGANDS FOR BRANCHED POLYETHYLENE SYNTHESIS

Zubkevich S.V.[1], *Kurmaev D.A.*[1,2], *Gagieva S.Ch.*[1], *Tuskaev V.A.*[1,2], *Bulychev B.M.*[1]

[1] Moscow State University, Chemical Department, Leninskie Gory 11, Moscow 119991, Russia
[2] Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, ul.Vavilova 28, Moscow 119991, Russia
Moscow, Russia
Student
zubkevich.sergey@gmail.com

Low density linear polyethylene is the most demanded polyolefin, produced by copolymerization of ethylene with α-olefins or free radical ethylene polymerization. However, alternative approach exists, comprising simultaneous use of two catalytic systems *insitu*, one oligomerize ethylene, and second embeds formed higher α-olefins into growing polymer chain. The obvious advantages of tandem catalytic systems are: need in only one starting material and possibility to vary, in a wide range, properties of received polymer product by changing the ratio of catalysts or conditions of polymerization. In the present work phenoxyimine nickel (II) complex **1** [1] and heteroscorpionate chromium complexes **2** [2] were used as catalysts for ethylene oligomerisation. Choice of titanium (IV) complexes, stabilized with 2-(hydroxymethyl)-phenole derivative ligands (compounds **3a** and **3b**) was made depending on their ability to effectively catalyze ethylene copolymerization with propylene and higher α-olefins [3-4]**.** Tandem catalytic systems, containing of compounds 1 and 3, activated by mixture of diethylaluminium chloride and dibutylmagnesium, produce branched polyethylene with activity up to 2370 kg(PE)/mole(Ti)*h*atm and butene incorporation up to 5%. Research of tandem systems, containing compounds 3 and 2, continues (the latter oligomerize ethylene with predominant yield of hexene-1).



1 **2a** R = H; **2b** R=^{t}Bu **3a** R = tBu, **3b** R=adamantyl-1

Figure 1. Structures of coordination compounds, included in catalytic systems

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Section 3.

Bioorganic and medical chemistry

THE MUTUAL INTERFERENCE OF TWO SUBUNITS IN HETERODIMERIC RESTRICTION ENDONUCLEASE BspD6I

Abrosimova L.A.[1], *Migur A.Yu.*[1], *Gavshina A.V.*[1], *Zheleznaya L.A.*[2], *Pingoud A.*[3], *Oretskaya T.S.*[1], *Kubareva E.A.*[1]

[1]M.V. Lomonosov Moscow State University,
[2]Russian Academy of Sciences, Pushchino,
[3]Justus-Liebig-University, Giessen
Moscow, Russia
engineer
abrludmila@rambler.ru

Heterodimeric restriction endonuclease BspD6I (R.BspD6I) from thermophilic strain *Bacillus species* D6 consists of two subunits. The large subunit of R.BspD6I alone is able to cleave one strand in a double stranded DNA, so it is also called nicking endonuclease BspD6I (Nt.BspD6I). Nicking endonucleases have recently become a very important tool in biotechnology. The small subunit of R.BspD6I can cleave another strand only in the presence of the large subunit. Both subunits cleave DNA duplex outside the recognition sequence [1]. The binding of Nt.BspD6I with the product of hydrolysis, a DNA duplex with a single strand break, resulted in the inhibition of enzyme. Kinetic parameters of Nt.BspD6I interaction with DNA before and after catalysis were determined using thickness shear mode acoustic method. The modified DNA duplexes were used for further investigation of coordination between two subunits in R.BspD6I. Azobenzene residue was incorporated as the additional non-nucleoside insertion either in the “top” or in the “bottom” strand of DNA substrates. Azobenzene moiety in the cleavage site of Nt.BspD6I almost completely blocked its activity and correspondingly the activity of BspD6I small subunit. Azobenzene insertions in the other positions of DNA duplexes had an impact on the specificity of small subunit and in some cases led to the loss of its catalytic activity. The obtained data allow us to suggest which regions of DNA substrate have the most important role during the interaction with the large and the small subunits of R.BspD6I. The modified duplexes can be also used for directed change of restriction endonucleases’ properties that can find application in biotechnology.

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Acknowledgements

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IMPROVED CHEMICAL COLD PACK WITH PROLONGATION EFFECT IN SURGICAL PATHOLOGY

Alekseeva V.A., Sirotinkin N.V.
Saint Petersburg State Institute of Technology (Technical University)
Saint Petersburg, Russia
Postgraduate student
vilenaalekseeva@gmail.com

Improved chemical cold pack with prolongation effect is effective method of local cryotherapy. Local cryotherapy (LC) – is the effectiveness of curing the area of injure by cooling. Today the LC system is an integral part to prevent the inflammation in wounds before surgical treatment in case of emergency situation for the army, MES, athletes extremists. Thus, the solution of such problem as an attempt to transform system of cold pack is very relevant nowadays. Cold pack provides an endothermic reaction by mixing the components. The cold pack comprise a container having first and second compartments separated by a barrier which can be opened to mix the contents of the compartments. The first compartment contains a granular solid of an ammonium nitrate salt and the second compartment contains an aqueous solution. When the contents of the compartments are mixed, the granular components dissolve in the aqueous solution producing an endothermic reaction. The mechanism of dissociation ammonium nitrate in water mentioned before is used in commercial prototypes such us “Snegok”, “Appolo” etc. However, the main disadvantage of such devices is the absence of prolonged effect.

To solve the problem of prolongation, we suggested to use the water-soluble polymers, in particular the starch. The characteristic of the chemical cold pack is the minimum temperature (T_{min}), the time when the temperature is on it’s minimum and integral cooling time of the system (T_{max}). The result of laboratory studies was found that T_{min}, in normal condition, decreased to 8 degrees in comparison with system without the polymer. Same the time when the temperature is on it’s maximum T_{max} increased from 90 minute to 145 minute. The practical significance of the experiments is that the water-soluble polymer solution can increase cooling time of the cold pack and depth of cooling.

The data obtained allows to suppose that the reason of additional absorption of heat is the acid hydrolysis of starch to D-glucose in the system [1]. The decrease of the T_{min} and the increase of the cooling time is the result of the change in the conditions of dissociation NH_4NO_3, in particular in the solution of the polymer the value pH decreases from 7 to 4. With the decrease pH in the

solution with the polymer, likely, we can observe the two different reaction: the depolymerization of starch and the dissociation of ammonium nitrate solution.
In conclusion, it can be noted that we suggested the new mechanism of prolongation effect of chemical cold pack. It involves: the diffusion inhibition of dissociation of ammonium nitrate in the solution of starch; the separation of duration in to the time when the temperature is on it's minimum and the "heating time"; the starch depolymerization when the level of pH is lower than 7. In the future, we will plan to study the solution of different chemical nature.

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SYNTHESISAND PHYSICOCHEMICAL PROPERTIESOF GLUTAMIC ACID ALKYLIMIDAZOLIUM IONIC LIQUID; ITS EFFECT ON THE PHASE BEHAVIOR OF SOME AQUEOUS SALT SOLUTIONS

Alopina E.V., Pukinsky I.B., Safonova E.A., Smirnova N.A.

Institute of Chemistry, Saint Petersburg State University
Saint-Petersburg, Russia
Postdoc
alopina@mail.ru

During the last years amino acid ionic liquids (AAILs) have received much attention because of their potential for applications in chemistry, biology, medicine etc. For today ionic liquids are highly attractive alternatives to conventional organic solvents, in particular to those used for liquid extraction of the different classes of organic compounds (including proteins, enzymes, antibiotics, DNA), metal ions, nanoparticles, radioisotopes et al. [1-3]. Therefore, the synthesis of new AAILs and the studies of their physicochemical characteristics, phase behavior have a substantial interest for further applications.
The amino acid ionic liquid [BMIM][Glu]studied in our work is a combination of1-butyl-3-methylimidazolium cation and glutamic acid anion. It was synthesized using the modified Fukumoto method [4-5], and various characteristics were determined for the final product. In particular, its ^{1}H NMR, ^{13}C NMR spectra were measured. The volumetric Karl Fischer titration technique was used for determination of water content in the end product. The densities and refractive indices of aqueous solutions of [BMIM][Glu] in the

concentration range 0-70 wt % were measured at 298 K. The activity of water in dependence of the IL concentration was estimated at 298 K, the data being obtained by the method of vapor pressure osmometry (Osmometer K-7000, KNAUER, Germany);activity coefficients of [BMIM][Glu] in diluted aqueous solutions were determined.

The liquid-liquid equilibrium at 298.15 K was studied for ternary solutions [BMIM][Glu] + water + salt (K_2CO_3 or K_2HPO_4) by the isothermal titration method. The binodal curve data were correlated by the Merchuk equation [6]. The tie lines were obtained by using the data on the binodal curve and on the water concentrations in the coexisting liquid phases (by Karl Fischer titration).

The next step of the work will be the study of the distribution of various solutes (in particular, amino acids) between the liquid layers of heterogeneous aqueous-salt solutions containing [BMIM][Glu]. The results may be of interest viewing the tasks of extraction.

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NMR measurements were performed at the Magnetic Resonance Research Centre, and the osmometry data were obtained using the equipment of Chemistry Educational Centre of Research park of St. Petersburg State University.

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INFLUENCE OF CHLORIDES OF METALS AND TEMPERATURE ON VISCOUS PROPERTIES OF HYDROGELS WITH L-CYSTEINE AND SILVER NITRATE

Andrianova Y.V., Khizhnyak S.D., Pakhomov P.M.

Tver State University
Tver, Russia
Ph.d. student
nuri-chan-87@mail.ru

In the modern scientific world has been increasing interest in the study gels and gelation processes. Of particular interest are hydrogels based bioactive substances with a low content of the disperse phase (~ 0.01 M) in solution. In

this work the hydrogel prepared on the basis of aqueous solutions of L-cysteine, silver nitrate and different electrolytes, is a thixotropic system and has a supramolecular structure. The aim of this work: to synthesize the hydrogels based on silver-cysteine solution (CSS)with use of bioactive electrolytes andinvestigate process of self-organization and rheological properties in the considered systems at various temperature by methods of vibration viscometry and IR-spectroscopy.

For receiving hydrogel used as electrolytes aqueous solutions of the following salts of metals: (Al^{+3}, Co^{+2},Cu^{+2}, Mg^{+2}, Mn^{+2}, Na^{+}, Ni^{+2}).About presence and properties of the spatial gel-grid in this system can be detected by a change in viscosity. Thus studied dependence of viscosity on "time standing" of solution by method of vibration viscometry, and also defined how quickly the sample is destroyed by vibration. It is established that the increase in temperature accelerates process of maturing of CSS. Thus, measurement of viscosity during gelation with the studied chlorides of metals was carried out at two temperatures, 29 and 39°C.

These researches showed that the change in temperature significantly affects at value of viscosity of hydrogel and on the process of gelation, and with different electrolytes differently. According to the research were built graphs of the dependence of the change of viscosity on the time of gelation at a different temperature. Also by means IR spectroscopy were studied spectrums formed as a result of gelation precipitates.

Acknowledgement:

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SYNTHESIS AND THERMAL STABILITY GEMINAL ALKILPIPERIDINIUM OF SURFACE-ACTIVE SUBSTANCES

Andrianova E.V.[1], Rybakov E.V.[2], Voronchikhina L.I.[3]

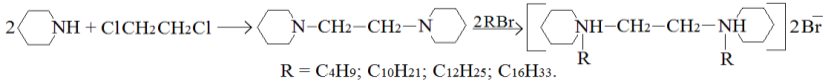
Tver State University
Tver, Russia
[1,2]Student
[1]dardinyuihongo@mail.ru, [2]4aferral@mail.ru

A new class of surface-active substances (SAS) known as gemini-SAS attracts attention and considerable interest with the theoretical and practical point of view. This is due to the specific properties of SAS, particularly low critical micelle concentration (CMC) in solutions of different ways of packing of the molecules in the process of self-organization, determines the morphology of

the aggregates formed. Shown the potential use of geminal SAS as a medium for chemical reactions. In addition, such SAS form vesicles and liquid crystal phases in a wide range of concentrations. This property is promising for practical use, such as for the production of mesoporous molecular sieves or template.

Basically investigated geminal alkyl-ammonium SAS with different length spacer alkylidene; information about similar SAS heterocyclic series is relatively small.

In this work we are synthesized geminal SAS of piperidine, representing cationic SAS, and their thermal stability is studied. The reaction products obtained by reacting 1,2-bispiperidinoetana with alkyl halides in abs. acetone; yields 70-80%. The composition and structure were confirmed by elemental analysis IR and NMR spectroscopy.



Synthesized gemini-SAS 10-2-10 (Pip); 12-2-12 (Pip); 16-2-16 (Pip) represent cationic SAS that is confirmed with qualitative reactions, and lower the surface tension of water, σ in the range 35-28 mN/m. Research of thermal stability was conducted in the range of temperatures 25-500ºC. The investigated compounds differ only by the length of the radical. Of the total consideration of «the curves of the loss of mass» and DTA bis-quaternary salts of piperidine follows that the nature of the processes occurring when heated similar; compounds decompose in two stages. In the molten state the compounds stable to 200°C, and at 450°C they lose almost 100% mass. It should be noted that the radical's length practically doesn't influence thermal stability of connections with an identical counter ion, which is consistent with the data for monomeric SAS.

PECULIARITIES OF OXIDATIVE ADDITION REACTIONS OF TRI(*M*-TOLYL)- AND TRI(*O*-TOLYL)ANTIMONY WITH 2-NITROBENZALDOXIME

Artemeva E.V, Makerova M.S, Sharutina O.K., Sharutin V.V.

South Ural State University,
Chelyabinsk, Russia,
Student
katriona-art@yandex.ru

We have studied the reactions of tri(*m*-tolyl)- and tri(*o*-tolyl)antimony with2-nitrobenzaldoxime in the presence of an oxidizing agent (hydrogen peroxide or *tert*-butyl hydroperoxide)at 1:1:1 and 1:2:1 molar ratio of the reactants. The solvents were diethyl ether, heptane, benzene. The molecular structures of the reaction products were investigated by means of X-ray diffraction analyses.

The interaction between tri(*m*-tolyl)antimony and 2-nitrobenzaldoxime in the presence of hydrogen peroxide or *tert*-butyl hydroperoxide, irrespective of the molar ratio of the reactants (1:2:1 or 1:1:1), leads to the formation of μ_2-oxo-*bis*[(2-nitrobenzaldoximato)tri(*m*-tolyl)antimony] as a main product.

$$2\ m\text{-}Tol_3Sb + 2\ HON{=}CHC_6H_4NO_2\text{-}2 + 2\ ROOH \rightarrow$$
$$\rightarrow [m\text{-}Tol_3Sb(ON{=}CHC_6H_4NO_2\text{-}2)]_2O + 2\ H_2O + ROH;$$
$$R = H,\ t\text{-}Bu.$$

But the reaction of tri(*o*-tolyl)antimony with 2-nitrobenzaldoxime in the presence of hydrogen peroxide or *tert*-butyl hydroperoxide at the molar ratio of 1:2:1 gives *bis*(2-nitrobenzaldoximato)tri(*o*-tolyl)antimony.

$$o\text{-}Tol_3Sb + 2\ HON{=}CHC_6H_4NO_2\text{-}2 + ROOH \rightarrow$$
$$\rightarrow o\text{-}Tol_3Sb(ON{=}CHC_6H_4NO_2{-}2)_2 + H_2O + ROH;$$
$$R = H,\ t\text{-}Bu.$$

At the molar ratio of 1:1:1 the mixture of products (tri(*o*-tolyl)antimony dioximate and dimeric tri(*o*-tolyl)antimony oxide) is formed. The antimony atoms of *bis*(2-nitrobenzaldoximato)tri(*o*-tolyl)antimony and μ_2-oxo-*bis*[(2-nitrobenzaldoximato)tri(*m*-tolyl)antimony] molecules have distorted square-pyramidal coordination with the oxygen atoms.

The reaction oftri(*m*-tolyl)antimony with the excess of *tert*-butyl hydroperoxide results in the formation of μ_2-oxo-*bis*[(*tert*-butylperoxy)tri(*m*-tolyl)antimony][*m*-$Tol_3SbOOBu\text{-}t]_2O$.

TEMPERATURE CONDITIONS OPTIMIZATION OF SYNTHESIS 4-PHENYL-4-METHYL-1,3-DIOXANE BY GAS CHROMATOGRAPHY WITH MASS SPECTROMETRY

Bektasov M.A.[1], *Mahabil G.M.*[1], *Kalugin S.N.* [1], *Elibaeva N.C.* [1], *Baimatova N.KH.* [1]
[1]Al-Farabi Kazakh National University
Almaty, Kazakhstan
Student
bektasovmarat@gmail.com

Prince reaction studies have shown that the nature of reaction products and their output depends from conditions of reaction such as temperature, time of reaction, nature of catalyst and concentration of the reactants and catalyst. The main method of 4-phenyl-4-methyl-1,3-dioxane synthesis was taken from book Weigand-Hilgetag "Methods of experiment in organic chemistry". Purity of final fraction of product was less than 50% by using that method.

The aim of the work was temperature conditions optimization of selective reaction oxymethylation methylstyrene by formalin with purity of product 4-

phenyl-4-methyl-1,3-dioxane at least 90% by gas chromatography with mass spectrometry. 4-phenyl-4-methyl-1,3-dioxane have a grown-stimulating properties at concentration 10^{-5}mg/L.

For checking optimized synthesis temperature was used gas chromatography with mass selective detector Agilent 6890N / 5973N, with capillary column J&W 122-7363 DB-WAXetr, length 60 m , diameter -250 μm, film thickness 0.50 μm.

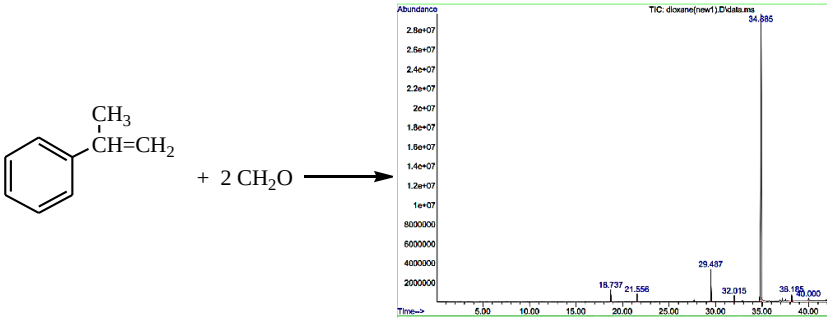


Figure 1. Reaction products chromatogram

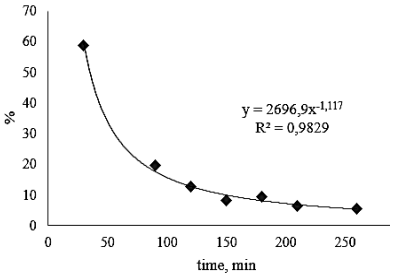


Figure 2. Conversion of α-methylstyrene

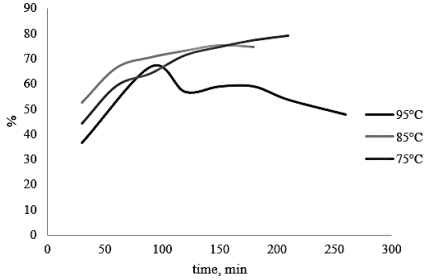


Figure 3. Dependence of 4-phenyl-4-methyl-1,3-dioxane output from temperature

Investigation of dependence of 4-phenyl-4-methyl-1,3-dioxane output from temperature and duration of the reaction was showed that the conversion of α-methylstyrene in the temperature range 75 – 95^{0}C after 90 minutes was 80% (Fig. 2).4-phenyl-4-methyl-1,3-dioxane output depends from temperature (Fig. 3).The optimalconditions for obtaining4-phenyl-4-methyl-1,3-dioxane are: the temperature 75 °C and time 210 minutes. Under these conditions, process of adverse reactions was slowed down.

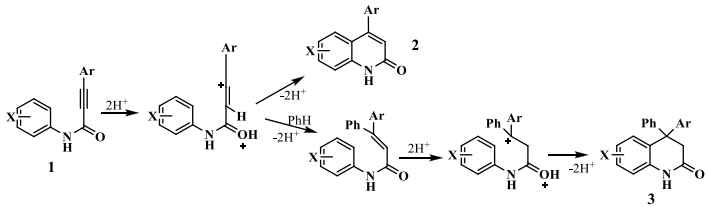
The work performed as a part of the grant funding of MES RK project in 1266/GF4 and 2290/GF4.

SINTHESISOF THEQUINOLIN-2(1*H*)-ONE DERIVATIVES FROMN-ARILAMIDES OF 3-PHENYLPROPYNOICACID

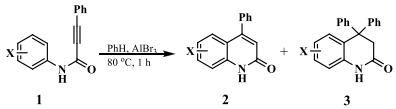
Belianskaia D.S., Gurskaya L.Y., Ryabukhin D.S.

Saint Petersburg State University,
Saint Petersburg, Russia
Student
belyanskaya.d@mail.ru

Substitutedquinolin-2(1*H*)-onesare of a great practical value. They posses antiviral, antibacterial, antiatherosclerotic and others biological activites. One of the synthetic approaches to quinolinones iselectrophilic cyclization of the N-arilamides of acethylenic acids promoted by different acids. Without external nucleophilesN-arilamides of the 3-phenylpropynoicacid**1**are smoothly cyclized into quinolin-2(1*H*)-ones**2** under theaction of CF_3SO_3H, FSO_3H, $AlCl_3$ or$AlBr_3$. With external π-nucleophile benzene, as it has been shown forN-phenylamide of the 3-phenylpropynoicacid, besides intramolecular cyclization product **2**,4,4'-diphenylquinolin-2(1*H*)-one**3**,as product of the consecutive benzene addition to the triple bond and intrarmolecular cyclization has been appeared.



To extend the scope of a vailable 4,4'-diphenylquinolin-2(1*H*)-one derivatives we examined interaction of different N-arilamides of phenylpropynoic acide with benzene in the presence of $AlBr_3$at 80 °C. It was found out, that ratio of compounds **2**:**3** strongly depends on electron properties of substituent X in N-aril ring of initial amides **1**.



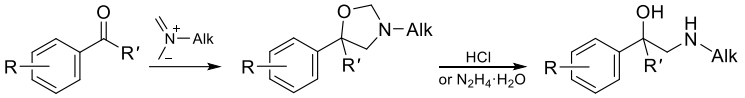
X (**1**)	X(**2**, **3**)	**2** : **3**, NMR
H	H	6 : 1
4-CH_3CO	6-CH_3CO	19 : 1
2-CH_3	8-CH_3	1 : 1
4-CH_3	6-CH_3	1 : 1
4-Cl	6-Cl	- : 1
4-F	6-F	- : 1
3-F	7-F	- : 1
3-F, 4-OCH_3	7-F, 6-OH	- : 1

This work was supported by SPbSU Grant for postdocs № 12.50.1558.2013.

CONVENIENT TWO-STEP SYNTHESIS OF 1-ARYL-2-AMINOETHANOLS VIA REACTIONS OF NONSTABILIZED AZOMETHINE YLIDES WITH AROMATIC ALDEHYDES AND KETONES

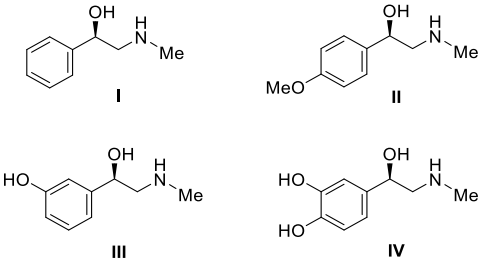
Buev E.M., Moshkin V.S., Sosnovskikh V.Ya.

Institute of Natural Sciences of Ural Federal University
Yekaterinburg, Russia
Student
eugene.soul@mail.ru



R = H, Br, NO_2, MeO, BnO, BzO (OH); R′ = H, Ph, CF_3, Bz, CO_2Et, $CONR_2$; Alk = Me, Bn

In the present work we would like to introduce a new method of the introduction of alkylaminomethyl moiety into the carbonyl compound, which has undeniable advantages over other known methods due to its simplicity and low cost of starting materials. This method includes two stages: first step is [3+2] cycloaddition of symmetric nonstabilized azomethine ylide to aromatic aldehyde or ketone to give 5-aryloxazolidines as intermediates; second step is a simple heating in an aliphatic alcohol with hydrochloric acid or treatment with hydrazine hydrate. Our technique allows to obtain1-aryl-2-aminoethanols in good yields,including such important compounds as alkaloids halostochine (**I**), and longimammine (**II**), as well as the drugs phenylephrine (**III**) and epinephrine (**IV**).



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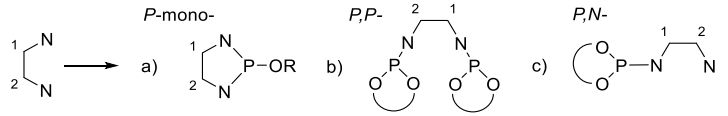
PD-CATALIZED ASYMMETRIC TRANSFORMATIONS INVOLVING NOVEL *P*-MONO, *P,P*- AND *P,N*-BIDENTATE LIGANDS WITH A C_1-SYMMETRIC 1,2-DIAMINE BACKBONE

Chuchelkin I.V.[1], *Zimarev V.S.*[1], *Vaganova J.A.*[1], *Gavrilov K.N.*[1]

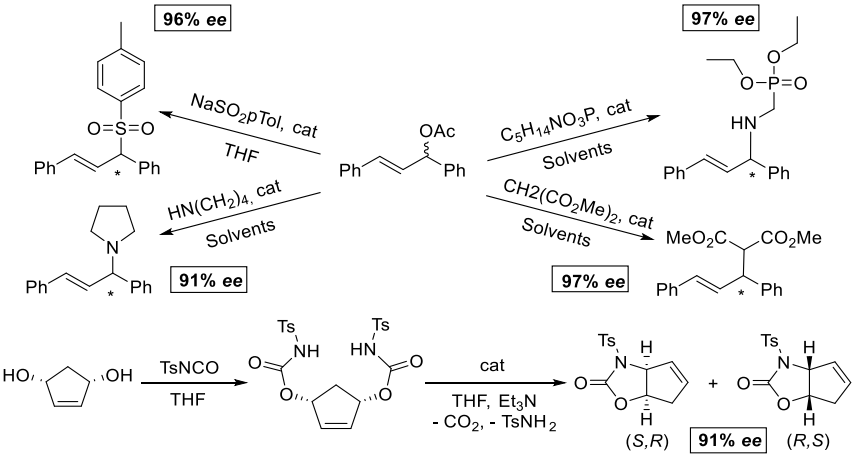
[1]Ryazan State University named for S. Yesenin
Ryazan, Russia
Scientific staff
doktor.che@gmail.com

Novel *P*-mono, *P,P*- and *P,N*-bidentate ligands have been readily synthesized from variety C_1-symmetric 1,2-diamines (**Scheme 1**). The structure and stereochemical features of all target compounds are determined based on ^{1}H, ^{13}C, ^{31}P, $^{1}H,^{1}H$ - COSY, $^{1}H,^{1}H$ - NOESY, $^{13}C,^{1}H$ - HSQC, $^{13}C,^{1}H$ - HMBC and $^{31}P,^{1}H$ - HSQC NMR spectroscopy, mass spectrometry, polarimetry and elemental analyses.



Scheme 1.

These ligands were tested as asymmetric inductors in the Pd-catalyzed enantioselective allylations of (*E*)-1,3-diphenylallylacetate and desymmetrization of N,Nr-ditosyl-*meso*-cyclopent-4-ene-1,3-diol biscarbamate (**Scheme 2**).



Scheme 2.

We acknowledge the financial support from the Russian Foundation for Basic Research, research Project No. 14-03-00396-a.

ADDITION OF C-NUCLEOPHILES TO NITRILIUM DERIVATIVES OF CLOSO-DECABORATE CLUSTERS

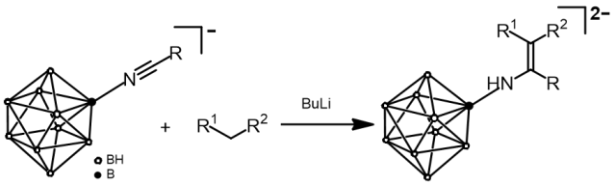
Daines E.A.[1], *Mindich A.L.*[1], *Bokach N.A.*[1], *Zhdanov A.P.*[2],*Zhizhin K.Yu.*[2]

[1]Saint Petersburg State University,
[2]Kurnakov Institute of General and Inorganic Chemistry RAS, Moscow
Saint Petersburg, Russia
Student
lena-daines@mail.ru

Boron neutron capture therapy (BNCT) of cancer is a noninvasive therapeutic modality for treating locally invasive malignant tumors. Advantages of BNCT include the potential ability to selectively deliver a radiation dose to the tumor with a much lower dose to surrounding normal tissues.

Thus the development of tumor-selective boron delivery agents is important synthetic problem in elaboration of BNCT.

The aim of present research was developing of new methods for synthesis of closo-decaborate cluster derivatives. Our work is based on evaluation the possibility of addition the various C-nucleophiles to nitrilium derivatives of closo-decaborate cluster.



Picture 1. The scheme of additionof C-nucleophiles to nitrilium derivatives of closo-decaborate clusters

Reactions of nitrilium derivatives of closo-decaborate[Ph_4P][$B_{10}H_9NCR$] (R = Me, Et, t-Bu, Ph) with different C-nucleophiles $R^1CH_2R^2$ (R^1 = R^2 = CN; R^1 = R^2 = COMe; R^1 = CN, R^2 = COPh; R^1 = CN, R^2 = C_6H_3-2,4-$(NO_2)_2$etc.) were carried out in the presence of BuLi as a base.

New developed method of functionalization of closo-decaborate cluster allows to synthesize various potential biological active compounds for ^{10}B-neutron capturing cancer therapy.

Acknowledgements: This work was financially supported by grants of Russian Foundation for Basic Research (№14-33-50679) and Saint-Petersburg State University (12.38.781.2013). Authors thank the Centre for Chemical Analysis and Materials Research, the Research Centre for X-ray Diffraction Studies and the Centre of Magnetic Resonance of Saint Petersburg State University, where the elemental analysis and the XRD and NMR studies were performed.

AMINOSALICYLIC ACIDS COCRYSTALS: THE STRUCTURAL FEATURES

Drozd K.V.[1],*Manin A.N.*[2]

[1]Ivanovo State University,
[2]G.A. Krestov Institute of solution Chemistry of the Russian academy of Science
Ivanovo, Russia
Student
ksdrozd@yandex.ru

A cocrystal is a multi-component molecular crystal that is built up of two or more organic compounds in stoichiometric ration which are connected by the hydrogen bonds and, in their pure form, are solid at ambient conditions. At present cocrystals are the most dynamically developing group of solid pharmaceutical substances. A cocrystal can have improved properties such as longer shelf life, improved dissolution rate and increased bioavailability without changing the chemical composition of the active pharmaceutical ingredient (API) [1].

The aim of this work was screening of new cocrystals with meta- and para-aminosalicylic acids (as APIs) and analysis of the amino group position (para- and meta-) on the ability to form new cocrystals. Para-aminosalicylic acid (4-AmSA) is a second-line drug used in the treatment of multidrug-resistant tuberculosis and is on the World Health Organization Model List of Essential Medicines. Meta-aminosalicylic acid (5-AmSA) is a nonsteroidal anti-inflammatory drug effective toward ulcerative colitis and Crohn's disease. We selected 12 compounds with amide function group or aromatic nitrogen as cocrystal formers (coformers) to form cocrystal via acid-amide or acid-pyridine supramolecular heterosynthons.

The screening procedure included 2 stages: cocrystals formation and its analysis. The first stage consisted of solvent-drop grinding and crystallization from solution (acetonitrile, acetone, methanol). Differential scanning calorimetry (DSC), hot-stage microscopy (HSM) and powder X-ray diffraction (PXRD) were used for cocrystal analysis. During of multistage screening we analyzed 24 binary systems: API – coformers. Thus, 4 new cocrystals with 4-AmSA were found in DSC experiments and their formation was proved by PXRD. New cocrystals with 5-AmSA were not found. So a slight modification of functional group location from meta- to para- influences over ability of aminosalicylic acids to form cocrystals.

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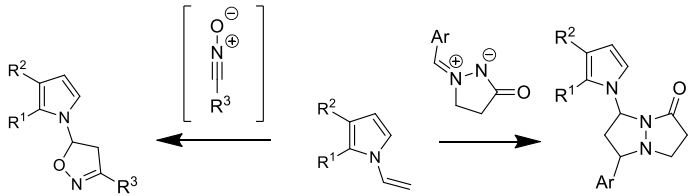
This work was supported by the Russian Scientific Foundation (№14-13-00640). We thank “the Upper Volga Region Centre of Physicochemical Research” for technical assistance with DSC and PXRD experiments.

THE INTERACTION OF NITRILE OXIDES AND AZOMETHTINE IMINES WITH *N*-VINYLPYRROLES

Efremova M.M., Molchanov A.P.

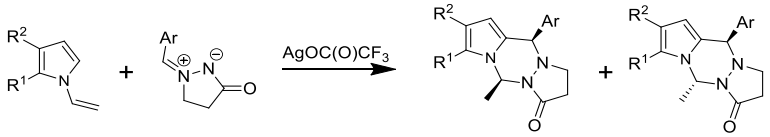
Saint Petersburg State University
Saint Petersburg, Russia
Graduate student
efremova-1264@mail.ru

The pyrrole ring is a major structural fragment of natural products, such as heme, chlorophyll and vitamin B12. Products containing a pyrrole fragment display a variety of pharmacological effects including cytotoxic, antiviral, antibiotic and oncolytic activities. One of the universal types of reactive pyrrole fragment carriers suitable for different purposes of organic synthesis are N-vinylpyrroles. In this study we demonstrated that1,3-dipolar cycloaddition of various nitrile oxides to substituted N-vinylpyrroles proceeds with high efficiency and selectivity with the formation of a single isomer of 5-pyrrolyl-substituted isoxazoline.The reaction of N-vinylpyrroles with cyclic azomethine imines occurs regioselectively affording 7-(pyrrol-1-yl)-substituted pyrazolo[1,2-a]pyrazolones as a mixture of two diastereomers.



Furthermore, we found that the addition of a catalyst to the N-vinylpyrrole - azomethine imine reaction system leads to a change in the mechanism of the process.

A formal (3+3)-cycloadditionis observed.



We gratefully acknowledge the financial support from Russian Scientific Fund for the research grant 14-13-00126. NMR, HRMS and XRD studies were performed at the

Saint Petersburg State University Center for Magnetic Resonance, Center for Chemical analysis and materials research and X-Ray Diffraction Center, respectively.

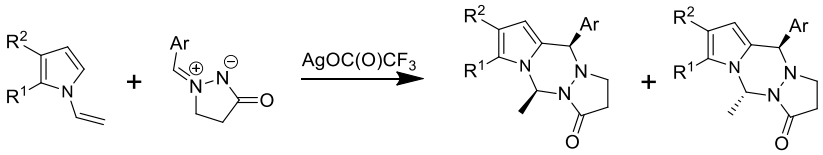
CATALYTIC (3+3)-CYCLOADDITION OF AZOMETHINE IMINES TO *N*-VINILPYRROLES

Efremova M.M., *Molchanov A.P.*

Saint Petersburg State University
Saint Petersburg, Russia
Graduate student
efremova-1264@mail.ru

Pyrroles have found wide application in the synthesis of analogues of natural compounds, and as pharmacophores and building blocks in the synthesis of pharmaceuticals. The pyrrole ring is a major structural fragment of natural products, such as heme, chlorophyll and vitamin B12.

Lewis Acids have been widely used as catalysts in 1,3-dipolar cycloaddition reactions. In the absence of a catalyst the reaction of N-vinylpyrroles with cyclic azomethine imines occurs regioselectively giving the products of 1,3-dipolar cycloaddition as a mixture of two diastereomers. We found that the addition of a catalyst to the N-vinylpyrrole - azomethine imine reaction system leads to a formal (3+3)-cycloaddition instead of (3+2)-dipolar cycloaddition.



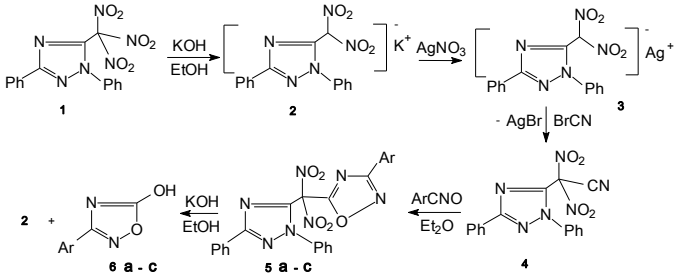
In the presence of silver trifluoroacetate the reactions proceed giving moderate yields, with the formation of a system of 8,9-dihydro-5H-pyrazolo[1,2-a]pyrrolo[1,2-d][1,2,4]triazin-7(11H)-one as a mixture of two diastereomers with *cis*-isomer predominance.

We gratefully acknowledge the financial support from Russian Scientific Fund for the research grant 14-13-00126. NMR, HRMS and XRD studies were performed at the Saint Petersburg State University Center for Magnetic Resonance, Center for Chemical analysis and materials research and X-Ray Diffraction Center, respectively.

THE SYNTHESIS OF 2-(1,3-DIPHENYL-1,2,4-TRIAZOL-5-YL)-2,2-DINITROACETONITRILE AND REACTIONS WITH A SUBSTITUTED N-OXIDE NITRILE

Elina V.V., Tyrkov A.G.
Astrakhan State University
Astrakhan, Russia
Student
fibi_cool@list.ru

A method of synthesis of 2-(1,3-diphenyl-1,2,4-triazol-5-yl)-2,2-dinitroatsetonitrile**4** and studied its reaction with N-oxides of substituted nitrile [1]. It was established that dinitroatsetonitrile **4** implements properties dipolarophile in reactions with active 1,3-dipoles - N-oxides of aromatic nitriles. The process proceeds via a mechanism of 1,3-dipolar cycloaddition, and terminates yield regiospecific cycloadducts **5a-c** (yield 65-70%) [2]. The structure of the compounds was established by IR, ^{1}H, ^{13}C NMR, electron spectroscopy, mass spectrometryand chemical transformations.



Ar = Ph (**5a**,**6a**); 3-$NO_2C_6H_4$ (**5b**,**6b**); 4-$MeOC_6H_4$ (**5c**,**6c**)

Interaction of the compounds with the **5a-c** and alcoholic solution with an excess alkali under mild conditions followed by cleavage of the 1,2,4-oxadiazole ring and leads to the K-salt 1,2,4-triazole **2**and substituted 5-hydroxy-1,2,4-oxadiazole **6a-c**. At the moment of compounds **5a-c** studied the biological activity profile.

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The work was supported by the Russian Ministry of Education, grant № 01201259085.

DESIGN AND SYNTHESIS OF CLICK CHEMISTRY PRECURSORS BASED ON AZIDO-CONTAINING DERIVATIVES OF CALIX[4]ARENE ANDCLICK-REACTIONS WITH SOME TERMINALALKYNES.

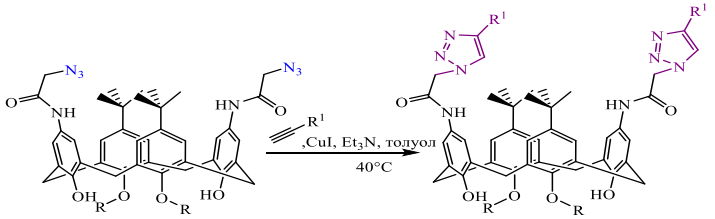
Fatyhova G.A.[1], *Burilov V.A.*[1], *Antipin I.S.*[1,2], *Konovalov A.I.*[2]

[1]Kazan Federal University
[2]A.E. Arbusov IOPC KSC RAS
Kazan, Russia
Student
E-mail:guselka777@mail.ru

Calixarenes are an essential part of supramolecular chemistry [1]. Their ability to form complexes such as "host-guest" was successfully used in selective extractants receptors and sensors[2], [3]. Application of calixarenes can be significantly enhanced by using click-reactions. Click reactions allow to connect required molecular units to the calixarene platform in very light conditions.The most used click reaction is azide-alkyne cycloaddition which is catalyzed by copper salts that can increase the reaction rate on the order and results in the selective formation of 1,4-isomers.

As a result of this work we have developed a methodology for the synthesis of calix[4]arenes containing azide groups at the upper rim connected via acetylamide fragments, and used this derivatives in click reactions with some terminal alkynes. The resulting compounds can act as polydentate ligands for transition metals and bind organic molecules.

We gratitude to the RSF grant No. 14-13-01151 for financial support.



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The work is performed according to the Russian Government Program of Competitive Growth of Kazan Federal University

SYNTHESIS OF TERPENYLPOLYFLUOROBENZOATES

Fedorov A.N., Gavrilova V.V., Shafeeva M.V., Kudryavtseva A.I.,
RudenokJ.S., TrishinYu.G.
Saint-Petersburg State Technological University of Plant Polymers
Saint-Petersburg, Russia
Postgraduate
where_shadows_bloom@inbox.ru

Terpenylpolyfluorobenzoates (TPFB) are substances, not subscribed in literature, with general formula $Ar^FC(O)OR$, where R is a terpene radical. Using computer prediction by PASS program [1] we found, that TPFB possess high potential physiologic activity. We used two methods for obtaining the substances: esterification of terpene alcohols with pentafluoro- and 2,3,4,5-tetrafluorobenzoic acids or their chloroanhydrites and addition of these acids to C=C bond of terpene hydrocarbons. Tendency of terpenes and terpenoids to isomerization imposes restrictions at these methods. Thus, esterification of terpene alcohols with polyfluorobenzoic acids affords corresponding TPFB only with menthol and isoborneol.

$$R{-}OH + Ar^FC(O)OH \underset{-\ H_2O}{\overset{H_2SO_4}{\rightleftharpoons}} Ar^FC(O)OR$$

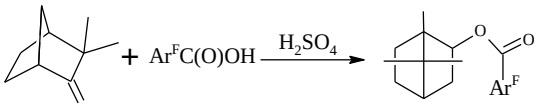
$Ar^F = C_6F_5, C_6F_4H$;
R-terpene radical

The obtaining of corresponding 2,3,4,5-tetrafluorobenzoates from terpene alcohols (menthol, α-terpineol, betulin) is also possible by using chloroanhydride of 2,3,4,5-tetrafluorobenzoic acid.

$$R{-}OH + Ar^FC(O)Cl \xrightarrow[-\ HCl]{Py} Ar^FC(O)OR$$

$Ar^F = C_6F_4H$;
R– terpene radical

Among terpene hydrocarbons (camphene, 3-carene, limonene) campheneis able to add $Ar^FC(O)OH$ to C=C bond with formation of corresponding TPFB.



$Ar^F = C_6F_5, C_6F_4H$

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Aknowledgements
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THE INFLUENCE OF BIOCOMPATIBLE COATINGS ON THE MAGNETIC PROPERTIES AND MRI RELAXIVITY OF MAGHEMITE NANOPARTICLES

Furasova A.D.[1], KozlovaM.A.[1]; OsmolowskayaO.M.[1]; KorzhikovV.A.[1,2]; DobrodumovA.V.[2]; OsmolowskyM.G[1].
[1]Saint Petersburg State University
[2]Institute of Macromolecular Compounds RAS
Saint Petersburg, Russia
Student
furasova@inbox.ru

At last few years the method of magnetic resonance imaging (MRI) has been widely introduced into clinical practice. The difference between healthy and unhealthy tissues on the MRI picture is based mainly on variations in relaxation times of water protons (T1 and T2). To increase the contrast of the image signal and, consequently, improve the precision of the analysis, the contrast agents were used. For T1 mode agents based on paramagnetic metal encapsulated in a chelating agent are now successfully applied. Nevertheless gadolinium ion is rather toxic and free gadolinium ion can replace some endogenous metal ions in vivo. Because of their biocompatibility and non-toxicity superparamagnetic iron oxide nanoparticles were offered as the contrast agents both forT1 and T2 mode.

In this study the maghemite (γ-Fe_2O_3) nanoparticles have been obtained via application of original approach by hydrothermal synthesis. The morphology of NPshave been determined by XRD, TEM, SSA and DLS. The magnetic properties of the nanoparticles have been measured using FC-ZFC technic by VSM. The adsorption of the coatings was conducted at 30°C for 30 minutes. As biocompatible coating the macromolecularcompounds of different types were studied: (1) BSA – model protein for biomedical research, (2) dextran used for this purpose at commercially available CA, and (3) oxidized poly-MAG which contains aldehyde groups for further biofunctionalization. At room temperature the samples show superparamagnetic behavior. The influence of the coating type on blocking temperatures and coercively (7 K) values were determined. It was found that r_1 and r_2 relaxivity of NPs were also depend on the coating type. So the variation of relaxivity is possible by changing the structure and composition of the coating. The relationship between these parameters requires further study.

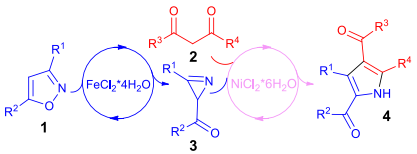
Acknowledgements
The work was financially supported by RFBR (grant № 13-03-00943). The authors express their gratitude to the Centre of X-ray Diffraction Studies, Center for optical and laser materials research and Innovative Technologies of Composite Nanomaterials (St. Petersburg State University).

ONE-POT 2,4-DICARBONYLPYRROLES SYNTHESIS FROM ISOXAZOLES AND 1,3-DICARBONYL COMPOUNDS UNDER Fe/NiMULTICATALYSIS

Galenko A.V.[1], *Galenko E.E.*[1], *Khlebnikov A.F.*[1]

[1]Saint Petersburg State University,
Universitetskii Ave., 26, Saint Petersburg, Russia, 192504
Postdoc
a.galenko@spbu.ru

Pyrroles, indoles and other fused pyrrole derivatives are widely present in natural compounds and pharmaceuticals. They are considered by medicinal chemists as privileged structures. Thus a plenty of synthetic methods have been developed to obtain pyrroles. The reaction of 2*H*-azirineswith 1,3-dicarbonyl compounds under transition metal catalysisis one of these methods. However highly strained 2*H*-azirines are not “easy to handle” substances, so finding of stable and readily available 2*H*-azirine precursors seems to be an attractive goal. 3-Aryl-5-methoxy/alkylamino-isoxazoles are known to isomerize to 3-aryl-2*H*-azirine-2-carboxylic acid derivatives at room temperature under $FeCl_2$ catalysis. We envisioned that the application of the multicatalysis concept would permit the transformation1→3+2→4 as a domino reaction (Scheme 1).



Scheme 1. One-pot 2,4-dicarbonylpyrrole synthesis from isoxazoles.

As a result of our work a simple procedure for the preparation of derivatives of 4-acylpyrrole-2-carboxylic acid, 4,5,6,7-tetrahydro-4-oxo-1*H*-indole-2-carboxylic acid, and pyrrole-2,4-dicarboxylic acid bydomino reaction of 5-alkoxy- or 5-aminoisoxazoles with 1,3-dicarbonyl compounds under Fe(II)/Ni(II) relay catalysis was developed. The approach was especially effective using symmetric1,3-diketones as starting materials. Esters and amides of acyl-acetic acids reacted regioselectively giving derivatives of pyrrole-2,4-dicarboxylic acid as the main products in moderate yields.

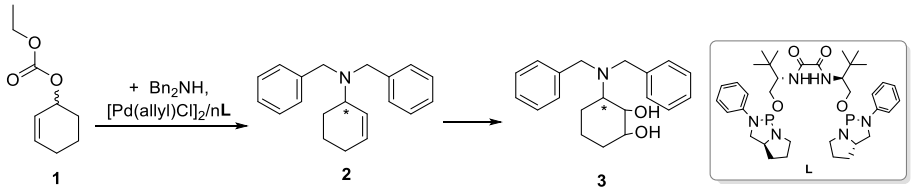
We gratefully acknowledge the financial support of the Russian Foundation for Basic Research (grant no. 14-03-00187) and Saint Petersburg State University (grant no. 12.50.1565.2013,12.38.239.2014, 12.38.217.2015). This research used resources of ‘Research resource center for Magnetic Resonance’ and‘Center for Chemical Analysis and Material Research’ of Saint Petersburg State University.

N,N-DIBENZYLCYCLOHEX-2-EN-1-AMINE AS ANINTERMEDIATE OF THE POTENT AND SELECTIVE KINASE INHIBITOR

Gavrilov V.K.[1], *Zheglov S.V.*[1], *Filippova T.V.*[1], *Gavrilov K.N.*[1]

[1]Ryazan State University named for S. Yesenin
Ryazan, Russia
Graduate
samurayb@yandex.ru

Cyclin-dependent kinases play an important role in cell cycle regulation. Various directions of implications CDAs have stimulated the search for pharmacological inhibitors. One of them – 2,6,9-trisubstituted purines[1].
Herein, we report successful use of diamidophosphite ligand **(L)** with asymmetric phosphorus atoms and an oxalamide framework in Pd-catalyzed enantioselective allylic amination **(Scheme1)**.



Scheme1.

In the interaction of cyclohex-2-en-1-yl ethyl carbonate **(1)** with dibenzylamine up to **97% *ee*** of the *N,N*-dibenzylcyclohex-2-en-1-amine **(2)** was achieved. This compound plays an important rolein the synthesis of aminodiol, which were not commercially available. The substituted purine in the final step can be prepared by reaction of the chloropurine with diol **(3).**

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CHEMICAL EQUILIBRIUM AND SOLUBILITY IN QUATERNARY REACTING SYSTEM ACETIC ACID – ETHANOL – ETHYL ACETATE - WATER UNDER POLYTHERMAL CONDITIONS

Alexandra Golikova[1], *Anna Sadaeva*[1], *Maria Toikka*[1] *and Maya Trofimova*[1]

[1] Department of Chemical Thermodynamics and Kinetics, Institute of Chemistry, Saint Petersburg State University, Russia
PhD student
al.golikova@gmail.com

The study of combined processes is of great interest for the development of science at the moment. Experimental data about phase equilibrium are necessary for the elaboration of methods of substance separation and purifying. The utilization of combined processes (phase and chemical equilibrium) in industry permits one to significantly increase the output of products, provide high selectivity, and to simplify technological schemes [1]. The investigation of such systems is also useful for the development of modern technologies which include "clean" energy from renewable sources. One representative of this type of energy is ***biodiesel***. The composition of vegetable oils, the main component in the preparation of biodiesel, is rather complicated, so the object of the study is to provide a fundamental model system. As a model, we have chosen the reaction mixture of ethanol and acetic acid.

The study of chemical equilibrium was performed by two different methods: the classical method of gas chromatography and a relatively new one in this field – the nuclear magnetic resonance method. The solubility was studied by cloud point techniques method.

This work presant thermodynamic research of a properties of a system with ethyl acetate synthesis reaction. A complete thermodynamic description of the considered system requires a study of double and triple subsystems.
The chemical equilibrium and solubility data for the system investigated was studied at 30˚C, 40˚C and 50˚C at atmospheric pressure. A complete topological structure of the liquid phase diagram has been obtained. The compositions of critical states were determined.[2]

These sets of new experimental data enable us to present the binodal surface and chemical equilibrium surface in a composition tetrahedron.

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COMPARISON OF THE ANTIOXIDANT PROPERTIES OF A SYRINGA VULGARIS CALLUS EXTRACT AND QUERCETIN IN VITRO ON RAT LIVER MITOCHONDRIA IN AN OXIDATIVE DAMAGE SYSTEM BASED ON TERT-BUTYL HYDROPEROXIDE

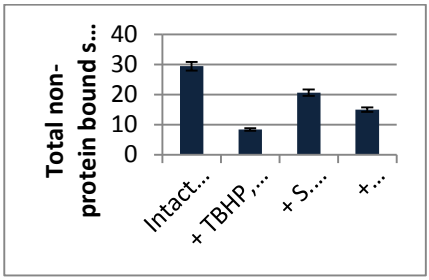
Gotina K.A., *Korik E.O.*

Belarussian State University
Minsk, Belarus
Student
hapi_kat@mail.ru

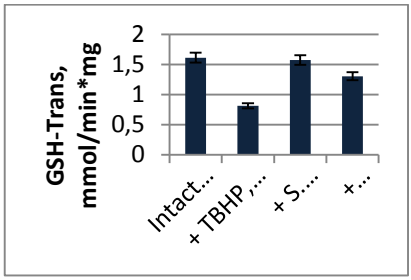
Many secondary plant metabolites have strong antioxidant properties and are used in pharmacology, cosmetics and food industry for various purposes. Antioxidants are potential therapeutic agents because most diseases are more or less connected with oxidative stress caused by the loss of balance between oxidants and antioxidants. This study aimed to determine the biological activity of a *Syringa vulgaris* callus extract, the main component of which is verbascoside, in vitro and compare it to a common antioxidant – quercetin.

The antioxidant properties of the two substances were compared based on their ability to restore the levels of total non-protein bound sulfhydryl groups and glutathione s-transferase activity in rat liver mitochondria when incubated with tert-butyl hydroperoxide – an oxidative agent.

In average for the studied parameters, in its optimal concentration, the callus extract was shown to be 30% more efficient as an antioxidant than quercetin, which makes it a potential protective agent against oxidative-stress related disorders. This study could provide a basis for further in vitro and in vivo studies and clinical trials to develop new therapeutic agents.



Picture 1 Total non-protein bound sulfhydryl groups in analyzed samples



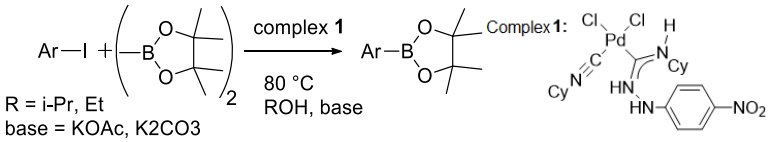
Picture 2 Activity of glutathione s-transferase in analyzed samples

SYNTHESIS OF ARYLBORONIC ACIDS USING ACYCLIC DIAMINOCARBENE COMPLEXES OF Pd(II).

Gozdanker Y.A., Timofeeva S. A., Boyarskiy V.P.
Saint Petersburg State University
Saint Petersburg, Russia
Student
south063@yandex.ru

Arylboronicacids are reagents for Suzuki reaction, which is the most important cross-coupling synthetic methodology to prepare diverse biaryls and heterobiaryls, ubiquitous motifs in pharmaceuticals, natural products, and organic chemistry. The typical preparation of arylboronic acids or esters involves the reaction including aryllithium compounds or Grignard reagents. However, the method is difficult to apply for substrates bearing some heterocycles or functional groups that are not compatible with organolithium reagents. In 1995, Miyaura pioneered the Pd-catalyzed borylation of aryl halides without the use of organometallic reagents. The report described the first synthesis of numerous arylboron derivatives bearing sensitive functional groups via cross-coupling of bis(pinacolato)diboron (B_2Pin_2) with arylhalides. Despite being mostly successful, the method has some drawbacks: using phosphine ligands and large amount of catalyst (as many as 3 mol%).

A catalytic system for C-C cross-coupling, based on diamino carbene complexes of Pd(II), has been earlier developed in our workgroup. It is free from such disadvantages. Furthermore, the reaction proceeds in comparably harmless solvents, EtOH and i-PrOH and with available bases (e.g. K_2CO_3). Here we have studied the usage of Pd(II)diaminocarbene complex (complex **1**) as a catalyst in the C-B coupling. We have showed that aryliodides reacted completely with 0.1 mol% of catalyst.



Acknowledgments: Physicochemical studies were performed at Center for Magnetic Resonance and Center for Chemical Analysis and Materials Research of St. Petersburg State University.The authors thank the Russian Foundation for Basic Research (grant №14-03-00297) and St. Petersburg State University (grants № 12.50.2525.2013 and 12.38.195.2014) for financial support of this work.

SYNTHESIS OF NOVEL C(2)-GLUCOSYLATED LUPANE AND URSANE TRITERPENOIDS BY EMPLOING A CLICK CHEMISTRY APPROACH

Gubaidullin R. R., Galimshina Z. R.,

NedopekinaD.A., Khalitova R.R., SpivakA.Yu.

Institute of Petrochemistry and Catalysis, Russian Academy of Sciences
Ufa, Russia
Post-graduate
ink@anrb.ru

Plant-derived pentacyclictriterpenoids of lupane and ursane families (betulin, betulinic and ursolic acids) constitute a very important class of biologically active compounds with a broad spectrum of biological and pharmacological activity. Particular interest in these compounds is due to their antitumor and antiviral properties. Pentacyclic terpenoids show low toxicity against animals even in high concentrations; however, the relatively weak potential of their biological activity and low solubility in water presents a serious hindrance to clinical use of these compounds. To increase the bioavailability of native pentacyclic triterpenoids we have developed an efficient approach for linking the hydrophilic sugar moieties with betulinic or ursolic acids at the C(2)-position in ring A. The new method of the synthesis of amphiphilic native triterpenoids derivatives based on the 1,3-dipolar cycloaddition («click-reaction») between azides and alkynes catalyzed by copper (I) salts. As starting compounds in 1,3-dipolar cycloaddition of triterpenoids and amphiphilic sugars are used hitherto unknown C(2)-propargyl derivatives of 3-oxolupanes **2**and 3-oxoursanes **4**. The compounds **2**and **4**obtained by a method developed by us.The methods involve reaction of propargyl bromide with potassium enoxy(triethyl)borates, generated in situ from 3-oxoterpenoids under the action of $KN(SiMe_3)_2$—Et_3B in 1,2-dimethoxyethane.

REDOX-ACTIVE MANGANESE(II) COMPLEXES WITH MANNICH BASES AS SOD MIMICS

Harbatsevich H.I., Faletrov Y.V., Loginova N.V., Koval'chuk T.V., Osipovich N.P., Azarko I.I., Polozov G.I.

Belarusian State University,
Minsk, Belarus
Postgraduate student
hleb.harbatsevich@gmail.com

The superoxide radical, a side product of the cell breath is one of the factors causing oxidative stress, tissue damage and development of various pathogenic physiologic conditions [1]. In this connection it is of topical interest to search for compounds decreasing the superoxide content in mammalian cells and behaving at the same time as low-molecular analogues of superoxide dismutase enzyme (SOD mimics), particularly Mn(II) complexes [2]. Among the compounds with such properties it is redox-active Mn(II) complexes with phenolic ligands that deserve particular attention [3]. We have synthesized novel bioactive complexes of Mn(II) with diphenolic derivatives of Mannich bases: 2-tetrahydro-1H-1-pyrrolylmethyl-4,6-di-*tert*-butyl-1,3-dihydroxybenzene, 2-piperidinomethyl-4,6-di-*tert*-butyl-1,3-dihydroxybenzene, 2-(1-azepanyl-methyl-4,6-di-*tert*-butyl-1,3-dihydroxybenzene), 2-morpholinomethyl-4,6-di-*tert*-butyl-1,3-dihydroxybenzene, 2-(4-methylpiperazinomethyl-4,6-di-*tert*-butyl-1,3-dihydroxybenzene. According to the data of elemental analysis the molar ratio Mn(II) : ligand = 1 : 2. The results of thermogravimetric analysis demonstrate that the complexes are thermally stable up to 70°C, and that water molecules are present in their coordination sphere. The molar conductivity values of acetonitrile solutions of the complexes testify that they are neutral. According to the data of spectral investigations, the coordination cores of the complexes are octahedral chromophores $[MnN_2O_4]$. Using the method of superoxide generation from alkaline DMSO solution [4], superoxide dismutase activity (IC_{50}) of the complexes synthesized was determined, which was equal to 19,2-50 $\mu mol \cdot cm^{-3}$. The results obtained give grounds to characterize Mn(II) complexes with Mannich bases as potential inhibitors of oxidation processes involving superoxide radicals.

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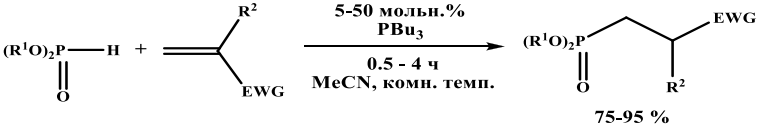
TERTIARY PHOSPHINES AS ORGANOCATALYSTS FOR THE PUDOVIK REACTION

Il'in A.V., Shamsutdinova F.G., FatkhutdinovA.R., Salin A.V.

Kazan (Volga region) Federal University,
Kazan, Russia
Post-graduate student
Antonilin.1989@mail.ru

The addition of hydrophosphoryl compounds to activated multiple bonds (the Pudovik reaction) is one of the most important methods in organophosphorus chemistry. Traditionally, the reaction is catalyzed by strong bases such as alkaline alkoxides, however basic reaction conditions promote a number of undesirable processes. The development of new convenient synthetic protocols for this reaction remains a great challenge. In contrast to the well-documented addition of hydrophosphoryl compounds to activated alkenes in the presence of tertiary amines, the phosphine-catalyzed Pudovik reaction is much less explored. Taking into account greater activity of tertiary phosphines in many catalytic reactions compared with amines, it seemed us reasonable to study catalytic activity of tertiary phosphines in the Pudovik reaction.

We found that phosphorylation of electron-deficient alkenes in the presence of PBu_3proceeded smoothly in acetonitrile at room temperature. In case of less nucleophilic triarylphosphines the formation of addition products was not observed. Low-polarity solvents inhibited the reaction. The reaction rate was strongly sensitive to the nature of both reactants. Less acidic diisopropyl phosphite required longer reaction time. Less electrophilic acrylamide and α-substituted derivatives were also less reactive. In these cases the reaction rate can be improved using increased concentration of the catalyst. Long chain alkyl groups in the phosphite were well tolerated in this transformation.



75-95 %

EWG = CO_2Me, CN, $CONH_2$; R^1= Me, Et, i-Pr, C_8H_{17}; R^2=H, Me, CH_2CO_2Me

Low basicity of tertiary phosphines argues for the mechanism, in which PBu_3 acts as a nucleophile, but not as a base. The initial attack of the phosphine to the activated alkene generates zwitterionic intermediate whose carbanionic center then deprotonates dialkyl phosphite.

In summary, a highly efficient protocol for the addition of dialkyl phosphites and alkyl *H*-phosphinates to electron-deficient alkenes was developed using PBu_3 as a catalyst. High operational simplicity, commercial availability of the catalyst and ease of its recovery make this protocol attractive for synthesis of useful organophosphorus compounds.

TOWARDS NEW RADIOCONTRAST MATERIALS BASED ON OCTAHEDRAL CHALCOGENIDE RHENIUM CLUSTER COMPLEXES

Ivanov A.A.[1,2], *Krasilnikova A.A.*[1,3], *Solovieva A.O.*[3], *Shestopalov M.A.*[1,2,3]

[1]Novosibirsk State University,
[2]Nikolaev Institute of Inorganic Chemistry,
[3]Scientific Institute of Clinical and Experimental Lymphology
Novosibirsk, Russia
Student
jiuc_13@mail.ru

Radiocontrast agents are used in medicine to improve visibility of inner body structures in X-ray imaging techniques. The most of radiocontrast agents are based on 1,3,5-triiodobenzene derivatives. Low toxicity and high solubility allowed these compounds to integrate into a medical field. However, their application has some drawbacks like cardiovascular, anaphylactic (allergic), painful effects, and probability of emergence contrast-induced nephropathy. We suppose that octahedral chalcogenide rhenium cluster complexes may become alternative radiocontrast materials. In these compounds a cluster core may potentially act as a radiocontrast component and ligand environment similar to substituent in 1,3,5-triiodobenzene radiocontrast agents may provide biocompatibility.

In this work, we present a first study of radiocontrast properties for rhenium complexes $Na_4[\{Re_6Q_8\}(CN)_6]$ (Q = S, Se, Te), as well as synthesis of new cluster complexes with functional organic ligands and investigation their properties. Thus, cluster complexes $[\{Re_6Q_8\}(PPh_2(CH_2)_2COOH)_6]Br_2$, $Na_2H_2[\{Re_6Se_8\}(L1)_6]$, $(Bu_4N)_2[\{Re_6Se_8\}(L2)_2I_4]$, $[\{Re_6Q_8\}(L2)_4Br_2]$ (Q = S, Se, L1 = 3,3'-[(3-amino-3-oxopropyl)phosphanediyl]dipropanoic acid, L2 = N-[1,3-dihydroxy-2-(hydroxomethyl)propan-2-yl]pyridine-4-cardoxamide) were obtained by reaction of octahedral chalcogenide rhenium cluster complexes $Cs_4[\{Re_6S_8\}X_6]$, $Cs_3[\{Re_6Se_8\}X_6]$ and $K_4[\{Re_6Se_8\}(OH)_6]$ (X = Cl, Br, I) with the organic ligands. All synthesized compounds were characterized byX-ray diffraction on the single crystal and powder, IR– and NMR–spectroscopy, and elemental analysis. Radiopacity, luminescence and biological (cytotoxicity, cellular uptake and excretion from the animal's body) properties were also studied.

Acknowledgements. The work was supported by the Russian Foundation for Basic Research (project № 14-03-92612) and Grant of President of the Russian Federation (MK 4054.2015.3).

THE ANALYSIS OF G4-OLIGONUCLEOTIDE STRUCTURES AND THEIR ABILITY TO INHIBIT TARGETS IN TUMOR THERAPY

Khristich A.N.[1], *Ogloblina A.M.*[2], *Yakubovskaya M.G.*[2]

[1]Lomonosov Moscow State University,
[2]N.N. Blokhin Russian Cancer Research Center,
Moscow, Russia
Student
khristich@gmail.com

Multitargeted therapy, which utilizes drugs that are able to simultaneously inhibit multiple signaling pathways activated in tumor cells, has emerged as a novel paradigm for anticancer treatment. The oligonucleotides capable of forming alternative nucleic acid secondary structures, called G4-quadruplexes (G4) are promising candidates for this role. There are many proteins and enzymes, which have an affinity to G4. This is due to the fact that DNA and RNA G4 form *in vivo* in the genomic DNA, retain within the mRNA, and play an important role in various biological processes.

The goal of our research is to investigate the relationship between structure and biologically significant properties of G4 oligonucleotides and to search for G4 oligonucleotide capable of inhibiting the activity of several proteins which become more active in tumor cells. The analysis of published data revealed some proteins that could be inhibited by G4: DNA metabolism enzymes (topoisomerase I [1] and telomerase [2]), protein tyrosine phosphatase (Shp2 [3]), a number of the transcription factors (Stat-3 [4], Sp1, nucleolin, NF-kB) and the vascular endothelial growth factor (VEGF). G4-oligonucleotides with the lowest K_d and IC_{50} values for the above proteins were selected. The primary structure and topological properties of the selected G4 were analyzed. New G4-oligonucleotides with averaged nucleotide sequences were created based on the data obtained. Next, we are planning to measure the IC_{50} values for the entire pool of selected G4 (24 sequences) and target proteins in order to identify the most promising oligonucleotides. For some of the target proteins IC_{50} values have already been obtained, and were found to have micro- and nanomolar levels.

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RECOMBINANT CATHEPSIN L FROM *TRIBOLIUM CASTANEUM*: ISOLATION AND PROPERTIES

Klimova M. A.[1], *Vorotnikova E. A.*[1], *Tereshchenkova V. F.*[1]
[1] Lomonosov Moscow State University
Student
mariaklimova92@gmail.com

This research is devoted to recombinant cathepsin LNP_001164001 from *Triboliumcastaneum*, its isolation and properties. The goal is a structure-functional characteristic of the recombinant cathepsin L, cysteine peptidase from papain family C1.The red flour beetle (*Triboliumcastaneum*) is a species of beetle in the family *Tenebrionidae* and a worldwide pest of stored products, particularly food grains. Analysisof *T.castaneum* larvae gut transcriptome revealed the presence of twenty-five cysteine peptidases from C1 family.The highest level of expression in the gut of this insect pest was for the major cathepsin LNP_001164001, which is considered as the major digestive enzyme of this insect. [1] The diet of *T. castaneum* larvae consists mainly of cereals. The major storage proteins in cereals are prolamins that cause celiac disease in susceptible people. Given that, we can assume, that cathepsin L NP_001164001can be used as part of combination enzyme therapy of coeliac disease. Native cathepsin L isolated from the insect gut is extremely unstable. Therefore, the recombinant protein may facilitate investigation of this enzyme. In this research recombinant *T. castaneum* cathepsin L was expressed in *Pichia pastoris* as an inactive proenzyme, therefore the autocatalytic processing of procathepsin L was studied in detail *in vitro*.

Procathepsin L is stable at slightly alkaline pH, and the proregion protects the protein from the denaturing effect of neutral to alkaline pH. Proenzyme activation step consists of proteolytic cleavages of the proregion, autocatalytic processing of procathepsin L occurs under acidic conditions. [2] Based on that, the optimal conditions for processing are determined. Mature enzyme is characterized according to activity profiles in buffers of different pH, mass spectrometry analysis, electrophoretic mobility under native and denaturation conditions, inhibitor sensitivity and substrate specificity. Furthermore, comparative analysis with other cysteine cathepsins will be conducted.

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We express our deepest sense of gratitude to Benevolensky S. V. and Klyachko E. V. from A. N. Bach Institute of Biochemistry Russian Academy of Sciences for providing all the necessary materials. The research is supported by RFBR grant № 14-04-91167-NSFC_a.

SYNTHESIS AND REACTIVITY OF NEW *CLOSO*-DECABORATE ANIONDERIVATIVES WITH BORON-OXYGENBONDS

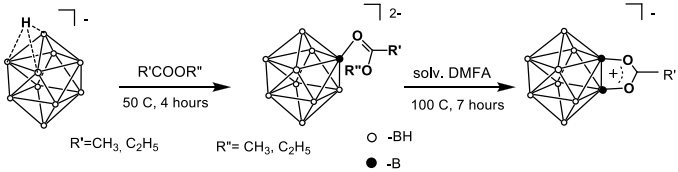
Klyukin I.N., ZhdanovA.P., Zhizhin K. Yu.
Kurnakov Institute of General andInorganic Chemistry
of the Russian Academy of SciencesIGIS RAS,
Moscow, Russia
Postgraduate Student
klukinil@gmail.com

To date, a great number of *closo*-borate anion derivatives with *exo*-polyhedral boron-oxygen bonds are well known. Among these compounds, oxonium derivatives of polyhedral boron hydrides are most studied.

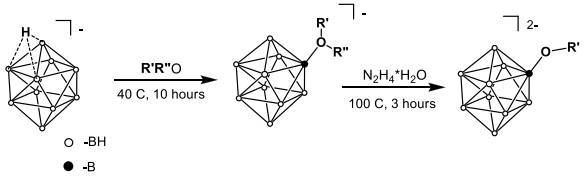
However, there are a few examples in which the boron is attached to the organic moiety by carbonyl oxygen atom. In a number of papers interactions of the *closo*-borate anions with carboxylic acids and their derivatives: esters, amides, acylchlorides were studied.

This work is devoted to the development of new methods for the synthesis of *closo*-decaborate anions with *exo*-polyhedral bonds B-O based on the reaction of anions $[B_{10}H_{10}]^{2-}$ with carboxylic acid derivatives and ethers.

The interaction between the anion $[B_{10}H_{11}]^{-}$ and carboxylic acids and esters has stepwise nature and depends on reaction temperature.



Also, we proposed a new method of the preparation of alkoxy-closo-decaborate $[B_{10}H_9OR]^{2-}$. This method of functionalization *closo*-decaborate anion involves two steps: obtaining oxonium derivatives of *closo*-decaborate anion and further cleavage of the CO bond.



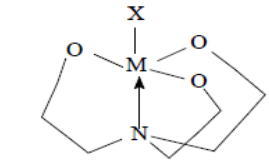
Acknowledgements. This work was supported by the Russian Foundation for Basic Research (project nos. 14-03-00864) the Presidential Grant Program “Leading Scientific Schools” (grant no. NSh 596.2014.3).

NEW COMPOUNDS BASED ON (2-HYDROXYETHYL)AMINE

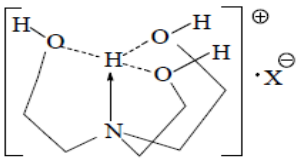
Kondratenko J.A.[1], *Kochina T.A.*[1,2]
[1]Institute of Silicate Chemistry RAS
[2]Saint Petersburg State University
Saint Petersburg, Russia
Postgraduate Student
kondratencko.iulia@yandex.ru

Synthesis of new biologically active compounds is a promising trend in contemporary chemistry. In 1963 Academician M.G. Voronkov showed that chelate tricyclic organosilicone esters of triehanolamine ("silatranes", figure 1 a) possess high biological activity which is determined by their unique atrane structure [1]. In the later years this discovery led to the synthesis of the new derivatives of triethanolamine (TEA): protatranes (triethanolammonium salts of protonic acids) and hydromatalatranes (figure 1 b, c).

For the purpose of obtaining new potentially biologically active compounds we synthesized protatranes by refluxing a mixture of triethanolamine with carbonic acids in methanol for 1 hour. It is known from literature that the biological activity of protatranes exceeds the activity of the original acids, so we chose carbonic acids with a variety of properties: antimicrobial, antifungal (benzoic, cinnamic acids), anti-inflammatory (salicylic acid), vitamin (nicotinic acid) [2]. The protatranes of dibasic (oxalic, malonic, succinic and malic acids) and tribasic (citric acid) carbonic acids were for the first time obtained. The yield of the all reactions exceeded 90 %. Protatranes are water-soluble liquids or fusible powders. It should be noted that liquid protatranes were obtained from carbonic acids with hydroxyl group (salicylic, malic and citric acids). The composition of these compounds was confirmed by the data of elemental analysis and their structure was established by X-ray diffraction analysis and IR spectroscopy. The obtained protatranes were further studied for antimicrobial and antifungal activities.



a)



b) c)

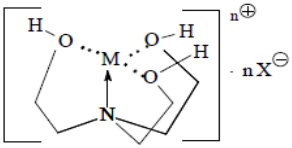


Figure 1. Structure of a) silatrane; b) protatrane; c) hydrometallatrane

Of particular interest are extremely hard-to-reach salts of tetrakis(2-hydroxyethyl)ammonium being ionic liquids. It is known from literature that activity of enzyme (horseradish peroxidase) in ionic liquid based on tetrakis(2-hydroxyethyl)ammonium triflouromethanesulfonate is extremely high [3]. Furthermore, the derivatives of tetrakis(2-hydroxyethyl)ammonium may be considered as precursors of a new class of compounds of hypervalent silicon. In order to prepare the tetrakis(2-hydroxyethyl)ammonium halide, we studied the reaction of triethanolamine with 2-chloroethanol in the presence of ethylene oxide. Tetrakis(2-hydroxyethyl)ammonium chloride was obtained with satisfactory yield by boiling methanol mixture of triethanolamine, 2-chloroethanol and ethylene oxide (the molar ratio: 1:1:0,35 respectively) in autoclave at 115 °C for 22 hours. The structure of the obtained compounds was investigated by X-ray diffraction analysis and IR spectroscopy. The reaction of tetrakis(2-hydroxyethyl)ammonium chloride with tetraethyl orthosilicate was for the first time carried out. The mixture of reactants with the solvent (dimethylsulfoxide or dimethilformamide) was heated up to 90 °C in two modes for 6 and 22 hours, and the precipitate that formed was washed with ether and dried in vacuum. The products of this reactions were investigated by X-ray diffraction analysis and IR spectroscopy.

The studies of X-ray diffraction analysis and IR spectroscopy were performed atthe Research Centre for X-ray Diffraction Studies and the elemental analysis was performed at theChemical Analysis and Materials Research Centre of Saint-Petersburg State University.

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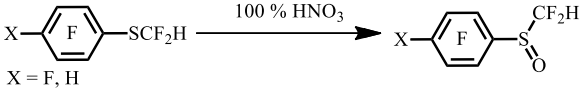
SYNTHESIS OF DIFLUOROMETHYL POLYFLUOROPHENYL SULFOXIDES AND STUDY OF THEIR INTERACTIONS WITH O-NUCLEOPHILES

Koscheev B. V.[1]

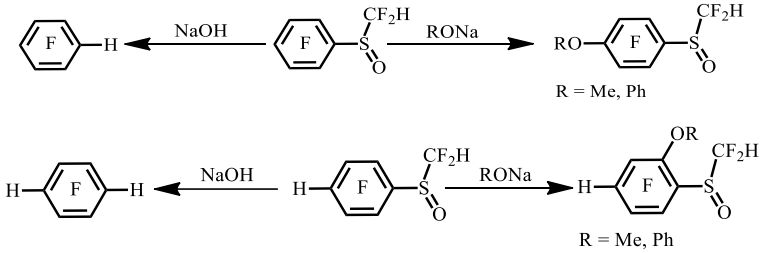
[1]Novosibirsk State University,
Novosibirsk, Russia
Student
kosheevb@mail.ru

Fluorine-containing alkyl aryl sulfoxides are used in the pharmaceutics as antitumor and antiseptic drugs[1] and agriculture as insecticides and fungicides[2]. In this connection, the development of methods for the synthesis and study of the reactivity of fluoro-containing alkyl aryl sulfoxides is an current topic.

Difluoromethyl polyfluorophenyl sulfides were reacted with 100% nitric acid to give difluoromethyl polyfluorophenyl sulfoxides.



Interactions of these sulfoxides with sodium methylate and sodium phenolate were studied. Difluoromethyl pentafluorophenyl sulfoxide gave *para*-methoxy and -phenoxy derivatives, whereas difluoromethyl 2,3,5,6-tetrafluorophenyl sulfoxide resulted in *ortho*-methoxy and -phenoxy derivatives. But interactions of these sulfoxides with sodium hydroxide gave pentafluorobenzene and 1,2,4,5-tetrafluorobenzene, respectively.



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THE STRONTIUM-82 MEDICAL GENERATOR RADIOISOTOPE: DEVELOPMENT OF THE NEW EFFECTIVE TARGETS FOR THE CYCLOTRON C-80

Krotov S.A.[1],*Ermolenko Y.E.*[1] , *Moroz F.V.*[2], *Orlov S.Y.*[2], *Molkanov P.L.*[2], *Filatova A.M.*[2], *Fedorov D.V.*[2], *Panteleev V.N.*[2]
[1]Saint-Petersburg State University,
[2]Petersburg Institute of Nuclear Physics
Saint Petersburg, Russia
Postgraduate student
krotilla@gmail.com

The last decades have seen an intensive development of nuclear physics methods, nuclear and other modern technologies in various directions related to the quality of human life and in particular the development of new medical technology. In this period, the use of the fundamental achievements of nuclear science has been the basis for the creation an entirely new field of modern medicine so-called nuclear medicine. Nuclear medicine technology aimed both at the diagnosis and at therapy of diseases is mainly based on the use of various types of radiation of radioactive nuclides.

The goal of our research is the development of new highly-effective targets for producing medical high purity radioisotopes on the cyclotron complex RIC-80 with a proton beam power up to of 80 MeV and an amperage of 200 μA and the implementation. The development is based on an innovative method involving a separation of radioisotopes, based on the difference of the isotope boiling points. One of the main targets is generating the isotope Sr-82, the parent isotope for Rb-82, which is used in positron emission tomography for the diagnosis of diseases of the cardiovascular system. This development is related to the direction Life Science in nuclear technology.

Target material RbCl was irradiated on the synchrocyclotron complex IRIS with a proton beam power up to of 1GeV and an amperage of 0.5 μA by the reaction ^{85,87}Rb (p, 4,6n) ^{82}Sr.The efficiency and relevance of innovative isotope separation method, the so-called «dry separation» was proved experimentally. The first amount of a mixture of Sr-82 and Sr-85 isotopes was obtained by dry separation with the subsequent optimization of the separation technique. It was found that the target material could be reused and there are no large quantities of liquid radioactive wastes.

The development of a new high-performance target apparatus for the cyclotron complex RIC-80 is the most promising solution to the problem of obtaining high-purity radionuclide for medical purposes.

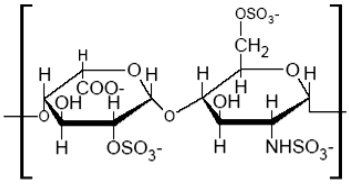
COMPLEXATION OF MACROMOLECULAR HEPARIN WITH ZINC CATION (II) AND AMINO ACID (PROLINE)

Kryukov T.V. , Skobin M.I.

Tver State University
Tver, Russia
Student
p528491@yandex.ru

The aim of this work was to study complexation of Zn (II) ions with high molecular weight heparin and amino acid (proline) in a molar ratio of 1: 1: 1 using pH titration (background electrolyte 0,15 M NaCl; temperature 37 ° C) and methods of mathematical modeling of chemical equilibria (algorithms New DALSFEK, AUTOEQUIL and HYPERQUAD 2008).

It was considered that the high molecular weight heparin forms monoligand and polyligand complexes with Zn (II) ions (caused by a number of factors: the conformation of the polymer chain, steric factors) monomer unit of heparin (Picture 1) in this case acts as tetradentate ligand.



Picture 1. Monomer disaccharide unit of heparin.

As a result, after processing of titration curves using methods of mathematical modeling of ternary systems: metal ions – heparin – amino acids were obtained equilibria models including the most likely possible forms. Equilibrium, forms and the corresponding stability constants are shown in the table below:

Equilibrium	lgβ
$Hep^{4-} + Pro^{-} + Zn^{2+} \leftrightarrow ZnHepPro^{3-}$	9.54 ± 0.29
$Hep^{4-} + H^{+} + Pro^{-} + Zn^{2+} \leftrightarrow ZnHepHPro^{2-}$	16.26 ± 0.31

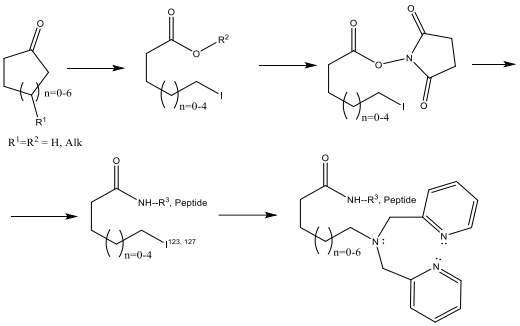
All efforts demonstrated in this paper are focused on complex ion-molecule equilibria, which involve Zn (II) ion, high molecular weight heparin , as well as amino acid (proline). Particular interest for us is the synthesis and structural identification of ternary metal complexes due to possibility of their use in medicine.

NEW SYNTHESES OF BIS(2-PYRIDYLMETHYL)AMINO ACID

Kulibaba E.V.[1], *LarkinaM.S.*[2], *Yusubov M.S.*[1,2]

National Research Tomsk Polytechnic University,
[2]Siberian state medical university
Tomsk, Russia
Kulibaba E.V.
katerina.kulibaba@mail.ru

One of the promising directions for applying ω-amino derivatives of aliphatic carboxylic acids is the chelation with ^{99m}Tc, which is widely used as a radiopharmaceutical for labeling biologically active substances, such as peptides, proteins, and derivatives of monosaccharides [1,2].The goal of this work is to develop a new method for preparing of ω-aminoaliphatic carboxylic acid based on ω-iodoaliphatic carboxylic acids. The resulting compound has an excellent solubility in water, which is one of the conditions for effective binding with ^{99m}Tc.



Bis-(2-pyridylmethyl)amino-6-caproic acid (Hpmca) is widely used as a precursor for the synthesis of radiopharmaceuticals; it is prepared by alkylation of 6-aminocaproic acid, 2-picoline action chloride or bromide [3,4], or reduction of the reaction products of ω-aminoaliphatic acid with heterocyclic aldehydes [5].

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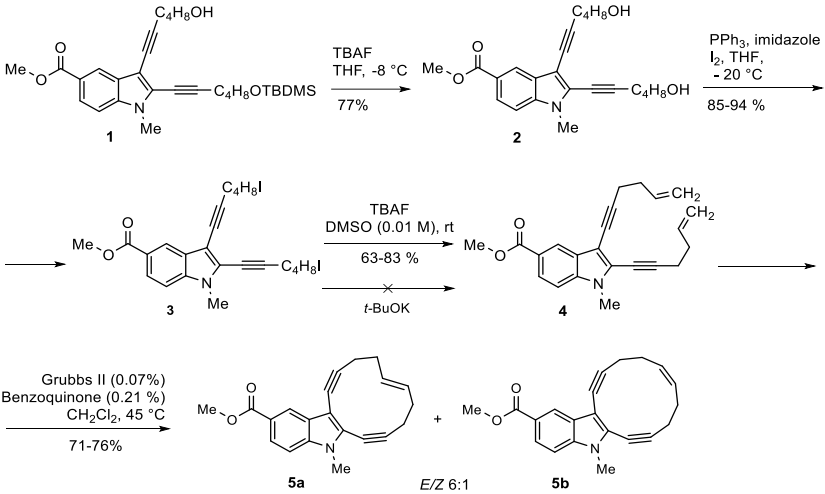
THE SYNTHESIS OF 12-MEMBERED MACROCYCLIC DIENDIYNE FUSED INDOLE CORE

KulyashovaA. E., DanilkinaN.A., Balova I. A.

[1]Saint Petersburg State University,
Saint Petersburg, Russia
PhD, Research Assistant
a.e.kulyashova@spbu.ru

Macrocyclic enediynes are strong antitumor natural agents. However just a few example of macrocyclic enediynes fused heterocyclic core have been known up to now.Here we report a new approach to the synthesis of indoleannulated 12-membered dienediynes through ring-closing olefin metathesis.



For recent references see:
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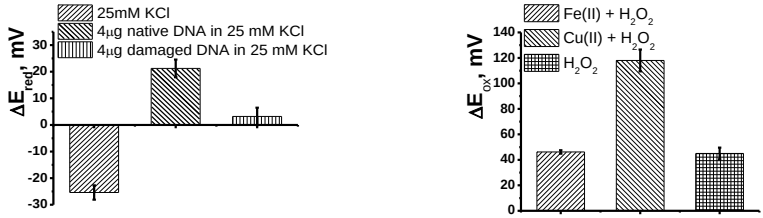
Acknowledgements:
The researches were carried out using the equipment of the resource centres of St. Petersburg State University: Centre of Magnetic Resonance, Center for Chemical Analysis and Materials Researchand Centre for X-ray Diffraction Studies. This study was supported by grants 12.38.195.2014, МК-3322.2014.3 (12.11.514.2014), НК 14-03-31761 (12.15.448.2014).

ELECTROCHEMICAL DNA SENSORS BASED ON ELECTROPOLYMERIZED REDOX-ACTIVE MATERIALS

Kuzin I.I., *Sysoeva A.V.*

Kazan Federal University
Kazan, Russia
Postgraduate Student
yzinkyra@mail.ru

New electrochemical DNA sensors based on electropolymerized redox-active materials for an oxidative DNA damage registration have been developed and characterized. Commercially available DNA from salmon sperm (Fluka) was used as biocomponent and glassy carbon electrode as electrochemical transducer. Modification procedure included electropolymerization step and immobilization of biological component (DNA). The characteristics of DNA sensor were recorded with cyclic voltammetry. Polymeric forms of Neutral red and Methylene Blue were generated in potentiodynamic mode from $5 \cdot 10^{-4}$ M monomer solutions. The selection of materials mentioned above was caused by intercalative activity of appropriate monomers partially retaining in DNA-polymer hybrid structure. DNA immobilization was performed by casting 2 □l of the DNA solution on the electrode surface followed by drying until film production. The DNA sensors were tested in detection of reactive oxygen species generated from hydrogen peroxide and two mixtures, Fe(II) + $H_2O_2$and Cu(II) + H_2O_2. The comparison of peaks referred to polymer-DNA composited on cyclic voltammograms made it possible to distinguish native and damaged DNA (Picture 1a). The contribution of reactive oxygen species (ROS) to DNA damage process was evaluated for different oxidizing agents (Picture 1b).



a b

Picture 1. a -The shifts of reduction peak potential of Poly(Neutral Red) for different coverings. b - The shifts of oxidation peak potential of Poly(Neutral Red) for different oxidizing agents.

Acknowledgements: This work was funded by the subsidy allocated to Kazan Federal University for the project part of the state assignment in the sphere of scientific activities (Project 14-75).

LIPOSOMAL NANOCONTAINERS FOR TARGETED CISPLATIN DELIVERY TO BRAIN TUMOR WITH OVEREXPRESSION OF VASCULAR ENDOTHELIAL GROWTH FACTOR

Kuznetsov I.I.[1,2], *Shein S.A.*[1], *Korchagina A.A.*[1], *Bychkov D.A.*[2], *Grinenko N.F.*[1], *Kabanov A.V.*[2,3], *Nukolova N.V.*[1,2], *Chekhonin V.P.*[1]

[1]Serbsky National Research Center for Social and Forensic Psychiatry
[2]Lomonosov Moscow State University
[3]University of North Carolina at Chapel Hill
Moscow, Russia
Student
kuznec505@gmail.com

Platinum derivatives are widely used for treatment of cancer, but they characterized by low solubility, high systemic toxicity and rapid elimination from the body. To increase the maximum tolerated dose of such drugs and improve pharmacokinetic characteristics, they can be encapsulated into nanocontainers. For selective delivery of drug to the specific tissue in the body these containers can be modified by different targeting groups, such as monoclonal antibodies (mAbs) to VEGF receptor type 2 (VEGFR2).

The goal of this work was to develop the stable VEGFR2-targeted liposomes, efficiently loaded with cisplatin (CDDP) and cis-diamindinitratplatin (II) (CDDP3). The synthesis involved three steps: 1) formation of lipid film from phosphatidylcholine, cholesterol, DSPE-PEG (2000), mal-DSPE-PEG (2000) and DPPG, 2) emulsification of the lipids in an aqueous solution of platinum salts and 3) conjugation with monoclonal antibodies to VEGFR2. Unbound monoclonal antibodies and free drug were eliminated by gel filtration chromatography using Sepharose CL-6B. Physicochemical characteristics of the loaded liposomes were studied by dynamic light scattering and X-ray fluorescence analysis. Activity of conjugated mAbs was determined by ELISA and immunocytochemical analyses. The cytotoxicity of obtained formulations was studied on glioma C6 cells using MTS-test. As a result we obtained the stable negatively charged targeted-liposomes. The maximum loading capacity of liposomes (LC) was 24±4 % for CDDP3, which is substantially exceed the loading of commercially available liposomal nanoparticles (Lipoplatin, LC=10%). Conjugated mAbs to VEGFR2 retained activity (up to 80% from initial affinity) and allowed to increase the cytotoxicity of the system compared to controls (untargeted liposomes and nonselective IgG-liposomes) as well as accumulation of targeted liposomes in the glioma C6 cells.

This work was supported by grant of RSF 14-15-00698, contract №182-MRA between non-profit organization for higher education "Skolkovo Institute of Science and Technology", MSU and MIT (USA).

CORRELATION AND MODELING OF THERMOCHEMICAL PROPERTIES OF THE SYSTEM WITH ESTER SYNTHESIS REACTION ON THE BASE OF UNIFAC AND NRTL MODELS

Letyanina I.A., Tsvetov N.S.,Toikka A.M.

Saint Petersburg State University,
Saint Petersburg, Russia
PostDoc
irina-letyanina@mail.ru

Esterification reaction is one of the most convenient methods to obtain esters which have important scientific and practical importance. For the synthesis and separation processes optimization various thermodynamic data and computation methods are needed. The multicomponent system with *n*-propyl acetate synthesis reaction (*n*-propanol + acetic acid +*n*-propyl acetate + water) is considered in this work. The purpose of our study was to determine experimentally the excess enthalpy of the mixing for binary sub-systems of the mentioned quaternary system at T = 313.15 K with following correlation and modeling by various approaches. In spite the applications of different models for the analysis of H^E data are discussed in literature the case of reacting systems needs additional consideration.

The measurements of the H^E values were carried out with the C80 calorimeter with membrane mixing cells manufactured by Setaram Instrumentation (France). The C80 calorimeter works on the Tian-Calvet heat flow principle. Principally, esterification reaction can occur in the mixtures during the calorimetric measurements and influence on results. But the approbated by us experimental technique allow to claim the negligible influence of the reaction.

For the preliminary correlation of experimental H^E data we used the traditional methods such as Redlich-Kister equation and its modified version. Then UNIFAC and NRTL models have been used to predict and to correlate the excess enthalpy data. The application of UNIFAC model for the prediction of H^Evalues leads to significant differences between experimental and calculated data (in the case of considered systems). Accordingly this approach needs improvement for thermochemical data consideration. Relatively good agreement has been archived between experimental and calculated H^E data by means of the NRTL model. The discussion of other opportunities for the modeling of H^E data will be also presented.

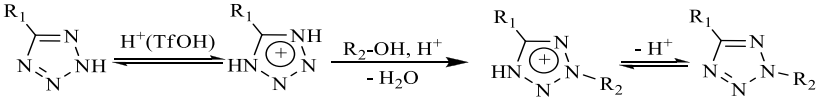
Acknowledgements

Irina Letyanina acknowledges St. Petersburg State University for a research grant (12.50.1564.2013). Alexander Toikka and Nikita Tsvetov are also grateful to Russian Foundation for Basic Research (grant 15-03-02131).The experimental study has been carried out using the equipment of the Center of Thermal Analysis and Calorimetry of St. Petersburg State University.

ELECTROPHILIC REACTION OF 5-SUBSTITUTED NH-TETRAZOLES WITH ALCOHOLS

Lisakova A.D.[1], *Ryabukhin D.S.*[2]
[1]St. Petersburg State Institute of Technology (Technical University)
[2]Saint Petersburg State University
Saint Petersburg, Russia
PhD student
goryachih.anna@gmail.com

Development of methods for the synthesis of substituted tetrazoles is an actual task of organic chemistry. To date, one of the main methods for the synthesis of N-substituted tetrazoles is alkylation of salts of tetrazoles by alkylhalogenides or alkylsulfates, leading to mixture of isomeres 1- and 2-substituted tetrazoles [1, 2]. Selective method for preparation of 2-alkyltetrazolium ions is the reaction of tetrazoles with stable carbocations, generated usually from alcohols in concentrated sulfuric acid [2]. However, this reaction can be used only in case of secondary or tertiary alcohols, among that mineral acids readily generate appropriate carbonium ions. Alkylation of tetrazoles by primary alcohols in H_2SO_4 does not observed. The generating of highreactive carbonium ions from primary alcohols may occurs only in superacids [3]. Ability of 5R-NH-tetrazoles to be alkylated by carbonium ions, generated from primary alcohols in superacids, does not has been previously described. We have investigated the reaction of 5-R-NH-tetrazoles with primary and secondary alcohols in Bronsted superacid CF_3SO_3H. In this medium the tetrazolium ions interact with the carbonium ions or O-protonated forms of primary alcohols.



R_1 = H, Me, Ph, 4-$NO_2C_6H_4$, 4-$MeOC_6H_4$, 2-ClC_6H_4, 2-MeC_6H_4, Bn
R_2 = Me, Et, iPr, tBu, Pr, Cy, Oct, 4-$NO_2C_6H_4CH_2$

Thus, for the first time regioselective alkylation of 5-substituted NH-tetrazoles with primary alcohols in superacid TfOH has been achieved.

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This project was supported by the Russian Foundation for Basic Research (grants no. 15-03-02936-a).

DNA/CATIONIC SURFACTANT INTERACTION AT THE AIR-LIQUID INTERFACE AS STUDIED BY DILATION RHEOLOGY

Lyadinskaya V. V.[1],*Noskov B.A.*[1], *Lin S.-Y.*[2]
[1]Saint Petersburg State University
[2]National Taiwan University of Science and Technology
Saint Petersburg, Russia
Postgraduate Student
lyadinskayavanda@gmail.com

Deoxyribonucleic acid (DNA) is a nucleic acid responsible for the storage of biological information. At the same time, DNA is a highly negatively charged biopolymer that strongly associates with any oppositely charged species. The interactions in mixed solutions of DNA with multivalent metal ions, cationic surfactants, polymers, proteins, lipids and nanoparticles are interesting not only because of their direct biological implications, but also of applications concerning separation, purification and transfection of DNA. As expected, the association depends strongly on the charge of a cationic agent (or the charge density in the case of macromolecules and nanoparticles), the solution temperature and ionic strength, the rigidity of DNA molecule and other factors.
The interactions of DNA with oppositely charged surfactants have received special attention recently. This is probably connected with the formation of the ordered hierarchical structures by the DNA/surfactant complexes in aqueous solution with unique functional properties. Although the bulk properties of DNA/surfactant solutions have been intensively studied, any information on the surface properties of these systems is extremely scarce until now.
In this work the method of dilation surface rheology was applied to mixed solutions of DNA and cationic surfactants. The concentration and kinetic dependencies of the dynamic surface tension and the dynamic surface elasticity were estimated by the oscillating barrier method in a wide range of surfactant concentrations and surface ages. The kinetic dependencies of the dynamic surface elasticity of mixed DNA/DTAB and DNA/CTAB solutions prove to be non-monotonic in a narrow surfactant concentration range. The local maximum of the dynamic surface elasticity shifts to the lower concentration range for more hydrophobic surfactant and can be connected with the conformation transition of the DNA/surfactant complex in the surface layer.
The application of the Brewster Angle Microscopy (BAM), Atomic Force Microscopy (AFM) and ellipsometry to DNA/surfactant solutions reveals different states of the adsorption layer.

The work was financially supported by the Russian Foundation of Basic Research (RFFI No.14-03-00670_a), the National Science Counsel of Taiwan (joint project RFFI-NSC No.12-03-92004-HHC_a) and St. Petersburg State University (project No. 12.38.241.2014).

THE RESEARCH OF STRUCTURE AND TOXICITY OF GLUTATION-BEARING SOLUTIONS OF COPPER SULPHATE

E. I. Lyalina, A. I. Fokina, A.S. Olkova
Vyatka State University of Humanities
Kirov, Russia
Postgraduate student
lyalina.ekaterina@inbox.ru

Glutathione – is a tripeptide which protects cells from toxic effect of heavy metals. The compounds of copper with the restored glutathione can possess new properties. During the reaction of formation of these connections by-products can appear. The purpose of the research – is to reveal the interrelation between the structure and the toxicity of water solutions of copper sulfate with various content of the restored glutathione. The objects of research – the copper (II) sulfate solutions with the concentration of ions of copper of 1 mg/dm3 with addition of the restored glutathione to a ratio of Cu:GSH 0:1, 1:1, 1:2, 1:4.

Viability of soil cyanobacteriae of Nostoc linckia 273 decreases, with the increase of duration of an exposition of the studied systems and with the increase of glutathione level in solution. With the increase of a glutatin level the copper accumulation by test object increases too.

Indicators of fertility and mortality of the lowest Crustacea of D. magna testify to tread effect of glutathione, and copper accumulation by organisms decreases in the presence of a tripeptide.

The nature of the formed complex connections and difficult composition of blend can be the reason of distinctions in accumulation and toxicity. The existence of complex connections of the structure corresponding to Cu:GSH ratio in initial blend [1] was established. It was defined that the oxygen dissolved in water also reacts with solution components with formation of active forms. And the maintenance of free ions of copper in solution decreases with increase of addition of glutathione.

The work is done with financial support of the grant of the Russian President of MK-3964.2015.5.

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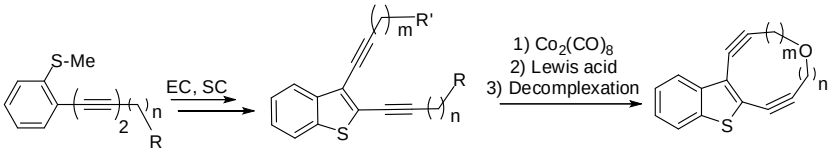
NICHOLAS REACTION AS A USEFUL TOOL FOR THE SYNTHESIS OF MACROCYCLIC ENEDIYNE SYSTEMS

Lyapunova A.G., Danilkina N.A., Balova I.A.

Saint Petersburg State University
Postdoc
a.lyapunova@spbu.ru

Enediyne antibiotics represent an important family of naturally occurring acetylenic anticancer molecules [1]. Antineoplastic activity of enediynes is determined by their ability to undergo Bergman cyclization (BC) [2]. In order to obtain highly active synthetic analogs of enediyne antibiotics, 10- (**1, 2**) and 11-membered (**3**) enediynes fused to a benzothiophene core were chosen as target compounds. Using the electrophilic cyclization (EC) and the Sonogashira coupling (SC) on initial steps allowed us to synthesize substrates for the macrocyclization by Nicholas reaction (NR) in good overall yields.



NR as a macrocylization step proceeded smoothly affording desired Co-protected macrocycles, which after the subsequent mild decomplexation were converted to desired oxaenediynes in good yields.
The activity of enediynes **1-3** in BC was estimated by Differential Scanning Calorimetry (DSC).

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Acknowledgements. This study was supported by Saint Petersburg State University(research project 12.38.195.2014 and 12.50.1187.2014), grant of President of the Russian Federation for young scientists (MK-3322.2014.3) and RFBR grant for young scientists (14-03-31761). The research was carried outusing equipment at the resource centres of Saint PetersburgState University: Centre of Magnetic Resonance, Centre forChemical Analysis and Materials Research, Centre for X-rayDiffraction Studies, and Thermogravimetric and Calorimetric Research Centre.

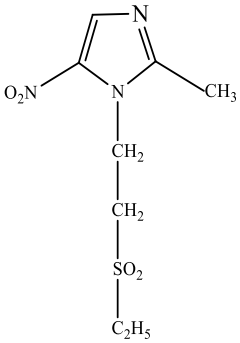
THE SYNTHESIS OF A PHARMACEUTICAL SUBSTANCE TINIDAZOLE

Lyapunova M.V., Belykh S.I., Malkov V.S.

Tomsk State University
Tomsk, Russia
Postgraduate Student
Lyapunova.mari@mail.ru

Tinidazole (picture 1) is a compound with antibacterial, antiprotozoal and antifungal topical activity. It is used against Trichomonas vaginalis, Entamoeba histolytica, Lamblia intestinalis and other bacteria [1]. The mechanism of action of this drug due to inhibition of synthesis DNA and its damage disease agents. Tinidazole is used for the prevention of postoperative anaerobic infections, for treatment aerobic-anaerobic infections. Thus it has a high degree of absorption. Its bioavailability is almost 100%.

For several years ago tinidazole received permission of the Office of the Food and Drug Administration (FDA) for use in a variety of diseases of the female reproductive system [2]. This work is devoted to the synthesis of tinidazole. The result was obtained intermediate substance. It was characterized by IR and NMR spectroscopy. Optimal conditions were selected for the oxidation of the substance to obtain tinidazole.



Picture 1. Tinidazole.

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MOLECULAR DYNAMICS STUDY OF ALLOSTERIC SIGNAL TRANSMISSION IN RIBOSOMAL TUNNEL

Makarov G.
Department of chemistry, Lomonosov Moscow State University
Moscow, Russia
Postgraduate student
ftorazyne@mail.ru

Ribosome is molecular machine that synthesize all cell proteins translating genetic information contained in messenger RNA. During this process functional centers of ribosome which are distant from each other by scores of angstroms acts strictly concordantly; so researchers conjecture that signal exchange between these centers pass allosterically by key role of ribosomal RNAs. Though allosteric phenomena in proteins are efficently investigated of about half of century, mechanisms of allosteric signal transmission in RNA macromolecules and ribonucleoprotein complexes are begun to study recently and they are not known yet. In this work we attempt to investigate transmission mechanism of allosteric signal linking two functionally important areas of *E. coli* ribosome: macrolide-binding site placed in ribosomal tunnel and peptidyltransferase center (PTC), that are distant from each other. It is known that peptide chains of some proteins being synthesized by ribosome are able to interact with ribosome tunnel walls in itself or in combination with low-molecular cofactors, inactivating PTC and thereby stopping translation. This phenomenon serves cell for regulation of protein synthesis, metabolism and antibiotic resistance. We performed simulation of ribosome large subunit core area by molecular dynamics method, that is able to describe dynamic aspects of biological macromolecules structure and functioning in solution. Obtained results allow us to make an assumption about mechanism of allosteric link mentioned above. 21 molecular dynamics simulations with length from 200 till 360 nanoseconds of *E. coli* ribosome large subunit core area were performed. While analyzing results of simulation A2058 and A2059 bases placed in macrolide-binding site approaching , G2061 and C2063 bases adjoining to PTC divergence, A2062 base wedging between them, stacking interaction formation between C2063 base and highly conserved U2585 base and, at last, aggregation of A2058-A2059-m^2A2503-G2061 and A2062-C2063-U2585 stacks together were discovered. When *in silico* mutations m^2A2503G or A2062U being introduced, conformation transition described was not observed in the former case due to non-canonical G2503-A2062 pair formastion, in the latter case due to unstable U2062 stacking interaction with G2061 and C2063. Conformation transition described leads in “freezing” of ribosome's peptidyltransferase center structure and, thus, can be an important element of protein synthesis regulation in translation level. Calculations were performed on Moscow State University supercomputer.This work was supported by grants from the Russian Foundation for Basic Researches (13-04-00986-a, 13-04-40211-H).

MOLECULAR DYNAMICS STUDY OF ALLOSTERIC SIGNAL TRANSMISSION BETWEEN E-SITE AND ELONGATION FACTOR G BINDING SITE

Makarova T.
Department of chemistry, Lomonosov Moscow State University
Moscow, Russia
Postgraduate student
perhlorat@mail.ru

Ribosome is molecular machine with complicated mechanisms of coordination of inner elements during elongation cycle. There are a lot of evidence of interaction and coordinated changes in remote bases and helices. One of such proposal allosteric correlation was investigated in this study via molecular dynamics simulation and conformational analysis.

Mutation C2394G in E-site of large ribosomal subunit is known to suppress GTPase activity of elongation factor G necessary for GTP-dependent translocation of subunits after peptidyltransferase reaction [1]. This mutation is established to prevent deacetylated tRNA CCA-end binding to E-site of large ribosome subunit forming hybride E/P-state. The GTP-binding site of elongation factor is remote from C2394 base of about 70 A; between this regions there are P- and A-sites of large subunit. Also, according to unique character of E-site for bacterial ribosomes and its engagement in crucial allosteric pathway, this may be important for design of new antibiotics for E-site.

9 molecular dynamics simulations with length from 600 till 1500 nanoseconds of *E. coli* ribosome large subunit core area were performed. Conformational torsion angles of nucleotides and aminoacids, energy of interbase interaction during trajectories were compared revealing crucial changes in structure of chosen fragment. Particularly, some bases in A- and P-site mentioned in literature as underwent conformational changes in allosteric pathways caused by remote mutations. Stacking between some of such nucleotides A2451-A2450-2064-2065 was revealed to undergo disruptions without tRNA in E-site. Also, serious conformational changes was found in SRL (sarcin-ricin loop, H95 of 23S rRNA) region in adjacent area of GTP-binding site of the elongation factor – bases 2660-2662. This is in correspondence with data about necessity of A2660 for GTPase activity of EF-G [2]. Also, interdependence of U2585 area and GTP-bonding site adjacent region, described in literature, was confirmed.Calculations were performed on Moscow State University "Lomonosov" supercomputer.

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PECULIARITIES OF OXIDATIVE ADDITION REACTIONS OF TRI(*M*-TOLYL)- AND TRI(*O*-TOLYL)ANTIMONY WITH 5-NITRO-2-FURFURALDOXIME

Makerova M.S., Artemeva E.V., Sharutina O.K., Sharutin V.V.
South Ural State University,
Chelyabinsk, Russia,
Master
marina.mms74@mail.ru

Our group pioneered in studying the reactions of tri(*o*-tolyl)- and tri(*m*-tolyl)antimony with 5-nitro-2-furfuraldoxime in the presence of an oxidizing agent (hydrogen peroxide or *tert*-butyl hydroperoxide)at 1:1:1 and 1:2:1 molar ratio of reactants. The solvents were diethyl ether, chloroform, heptane, THF, benzene.

The interaction between tri(*m*-tolyl)- and tri(*o*-tolyl)antimony and 5-nitro-2-furfuraldoxime in the presence of hydrogen peroxide or *tert*-butyl hydroperoxideat the molar ratio of the reactants 1:2:1 gives tri(*m*-tolyl)antimony and tri(*m*-tolyl)antimony dioximates.

$$Ar_3Sb + 2\ HON{=}CHC_4H_2ONO_2\text{-}5 + ROOH \rightarrow$$
$$\rightarrow Ar_3Sb(ON{=}CHC_4H_2ONO_2\text{-}5)_2 + H_2O + ROH;$$
Ar = *m*-Tol, *o*-Tol; R = H, t-Bu.

However, the reaction between tri(*m*-tolyl)antimony and 5-nitro-2-furfuraldoxime in the presence of *tert*-butyl hydroperoxideas well as the interaction betweentri(*o*-tolyl)antimony and 5-nitro-2-furfuraldoxime in the presence of hydrogen peroxide (at the molar ratio of 1:1:1) leads to the formation of μ_2-oxo-*bis*[(5-nitro-2-furfuraldoximato)tri(*o*-tolyl)antimony]and μ_2-oxo-*bis*[(5-nitro-2-furfuraldoximato)tri(*m*-tolyl)antimony].

$$2\ Ar_3Sb + 2\ HON{=}CHC_4H_2ONO_2\text{-}5 + 2\ ROOH \rightarrow$$
$$\rightarrow [Ar_3Sb(ON{=}CHC_4H_2ONO_2\text{-}5)]_2O + 2\ H_2O + ROH;$$
Ar = *m*-Tol, R = t-Bu; Ar =*o*-Tol,R = H.

The molecular structures of the reaction products were determined by means of X-ray diffraction analyses.

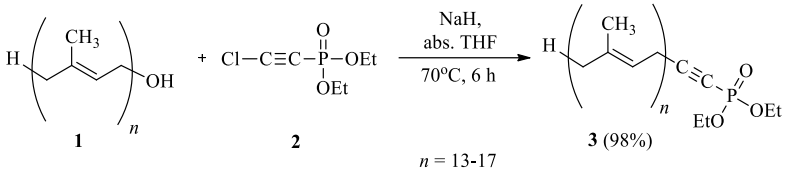
PHOSPHORYLATION OF POLYPRENOLS

Maksimova E.A.[1], *Ryabukhin D.S.*[2]

[1]Saint PetersburgState Forest Technical University,
[2]Saint Petersburg State University
Saint Petersburg, Russia
Student
katrisha.07@list.ru

Polyprenols are natural long-chain isoprenoid alcohols of with general formula H-$(C_5H_8)_n$-OH, where *n* – is number of isoprene units. They are present in all organism, from bacteria to human (who contains dolichol – 2,3-dihydro derivatives of polyprenols). Needles of conifer trees are one of the richest sources of polyprenols. But, despite amazing abilities of natural polyprenols, a new trend is their chemical modification, especially the introduction of phosphorus in their structure. Phosphates of polyprenols stimulate release of stem cells into the bloodstream, slow down the general aging of the body, supplant «the bad cholesterol», possess antioxidant activity, anti-inflammatory and antiviral effects. They can be used as a new class of immunomodulators for the treatment of atherosclerosis.

Our work is focused on synthesis of phosphorylated polyprenols and on research of their further modifications. A mixture of polyprenols **1**, containing 13-17 isoprene units, was phosphorylated using diethyl (chloroethynyl) phosphonate **2** and NaH in absolute THF. As a result we obtained a mixture of phosphorylated compounds **3** in yield of 98%.

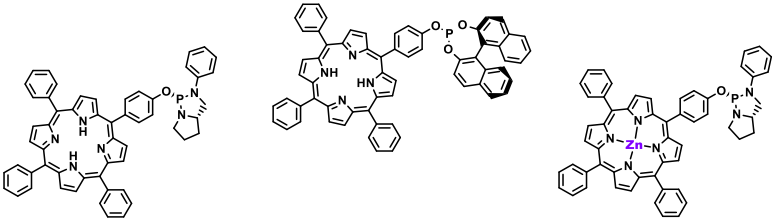


5-(4'-HYDROXYPHENYL)-10,15,20-TRIPHENYLPORPHINE-BASED CHIRAL PHOSPHITE-TYPE LIGANDS

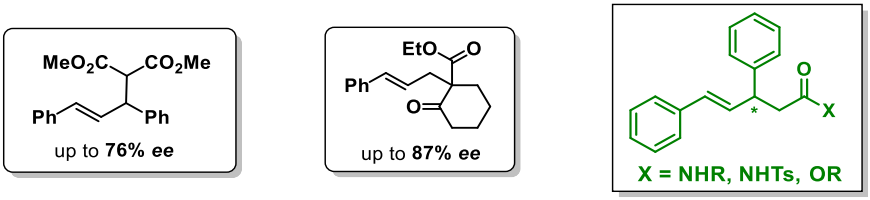
Marina G. Maksimova,[a] *Ivan M. Novikov*,[a] *Viktor V. Lugovskiy*,[a] *Konstantin N. Gavrilov*,[a] *Ilya A. Zamilatskov*,[b] *Igor S. Mikhel* [b]

[a]Department of Chemistry, Ryazan State University
[b]A. N. Frumkin Institute of Physical Chemistry and Electrochemistry RAS
Senior researcher
marinagmaximova@mail.ru

Novel *P*- and *P**-monodentate phosphite and diamidophosphite ligands have been readily synthesized from 5-(4'-hydroxyphenyl)-10,15,20-triphenylporphine and its Zn (II) complex. The structure and stereochemical features of all target compounds are determined based on ^{1}H, ^{13}C, ^{31}P, $^{1}H,^{1}H$ - COSY, $^{1}H,^{1}H$ - NOESY, $^{13}C,^{1}H$ - HSQC, $^{13}C,^{1}H$ - HMBC and $^{31}P,^{1}H$ - HSQC NMR spectroscopy, mass spectrometry, polarimetry and elemental analyses.



These ligands were preliminary tested as asymmetric inductors in the Pd-catalyzed enantioselective allylic substitution. In particular, in the allylic alkylation of (*E*)-1,3-diphenylallylacetate with dimethylmalonate and in the allylic alkylation of cinnamyl acetate with ethyl 2-oxocyclohexane-1-carboxylate up to 76% and 87% *ee* were achieved, respectively.



It should be noted that the product of alkylation with dimethyl malonate under mild conditions and without involvement of the *C**-stereocenter can be easily converted to esters and amides of natural chiral unsaturated carboxylic acids.

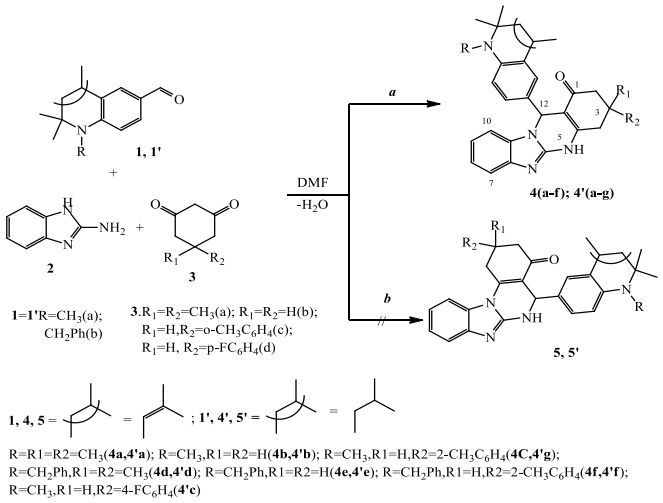
We acknowledge the financial support from the Russian Science Foundation (Grant No. 14-13-01383)

NEW BENZIMIDAZOQUINAZOLINONES CONTAINING HYDROQUINOLINE GROUP

Manahelohe G.M., Shikhaliev Kh.S., Potapov A.Y.

Voronezh State University, Department of Organic Chemistry, Voronezh; Russia
Ph.D Student
E-mail: gizachewm75@gmail.com

The method of synthesis of tetrahydrobenzimidazoquinazolinone cycle using a series of substituted benzaldehydes is extended to hydroquinoline carbaldehydes. A short time reflux of equimolar quantities of 1-alkylhydroquinoline-6 carbaldehydes **1a,b, 1'a,b**, 2-aminobenzimidazole **2** and cyclohexan-1,3-dione compounds **3a-d** in N,N-dimethylformamide gives exclusively 3-R^1-3-R^2-12-(1-alkylhydroquinolin-6-yl)-3,4,5,12-tetrahydrobenzimidazo[2,1-b]quinazolinones **4a-f, 4'a-g** (path **a**, scheme 1). In the ^{1}H-NMR spectra of synthesized compounds, the value for the NH group signals at δ 10.91-11.05 ppm is typical for dihydroazolopyrimidine systems. The singlet signals which resonate in the range δ 6.22-6.33 ppm are assignable for methine (CH-12) protons. In the alternative dihydro isomers **5, 5'** (path **b**) with the separated amino group and ethylene fragment the proton discussed resonates at a much higher field and there must be splitting of CH-proton by NH-group. Hence, the synthesized compounds have structure **4, 4'**. An attempt that was made to synthesis the desired products in different polar solvents (ethanol, 1,4-dioxane) resulted in longer reaction time and lower reaction yields.



Scheme 1. Synthesis of 12-(1-alkylhydroquinolin-6-yl)benzimidazoquinazolinones **4a-f, 4'a-g**

DETERMINATION OF CO-CRYSTAL SUBLIMATION ENTHALPY BY INERT GAS FLOW METHOD

A.N. Manin, *A.P. Voronin*

G.A. Krestov Institute of solution chemistry of the Russian academy of scienses,
"Physical Chemistry of Drugs" department, Ivanovo, Russia
alexnmanin@gmail.com
young scientist
alexnmanin@gmail.com

The pharmaceutical co-crystals offer a possible route for the modification of the physicochemical properties of drugs, such as solubility, physical and mechanical properties, thermodynamic stability etc., without changing the pharmacological activity. The key design tool used to select a suitable compound (a co-crystal former) for a given substance is the concept of supramolecular synthon. [1] Several types of supramolecular synthon are usually realized in two-component crystals and are characterized by intermolecular hydrogen bonds (H-bonds) of different types and strengths. The energy of these interactions was evaluated in a number of papers. [2] A lot less attention has been paid to the quantitative description of the intermolecular interactions of homo- and heterodimers with the neighbor molecules which play an important role in the successful co-crystal phase formation. The cumulative characteristic of the intermolecular (noncovalent) interactions in solids is the sublimation enthalpy ΔH_{sub}. Despite the active investigation of various physicochemical properties of co-crystals, no papers concerning co-crystal sublimation have been published until now.

The aim of our study is to provide an experimental validation of the transpiration method for co-crystal enthalpy of sublimation estimation. The present research work considers the co-crystal of hydroxybenzamides with benzoic acid derivatives. A presumable mechanism of the sublimation process was proposed with the heterodimer sublimating and eventually dissipating into separate molecules.The thermodynamic functions of sublimation for both components have been obtained by us earlier.

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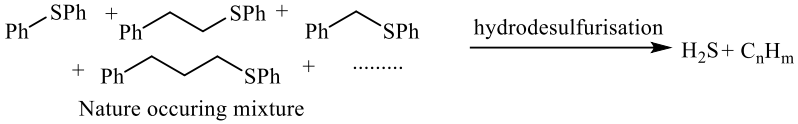
C-H ALKENYLATION OF THIOETHERS IN MIXTURES

Marianov A.N.[1], *Luzyanin K.V.*[1], *Ananikov V.P.*[1,2]

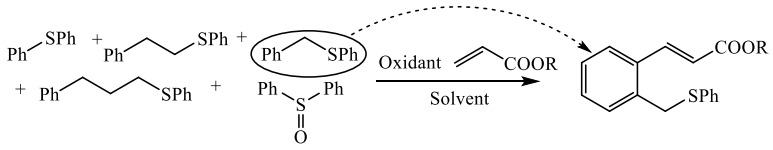
[1]Saint Petersburg State University,
[2]Zelinsky Institute of Organic Chemistry,
Saint Petersburg, Russia
Masters student
marjanov-alexei@yandex.ru

Crude oil is a major natural source of organosulfur compounds that are present there as a complex mixture. These organosulfur species are not directly used but are transformed into hydrogen sulfide via hydrodesulfurisation process (scheme 1) [1]. Required organosulfur derivatives are further re-constructed from hydrogen sulfide and appropriate organic reagents – this approach for their production is not sustainable.



Scheme 1: Processing of natural-occurring mixtures of sulfur-containing compounds.

In our studies, we found that under established conditions, a single component in a mixture of thioethers can be converted into corresponding *ortho*-substituted cinnamate (scheme 2). This methodology was verified for mixtures containing up to five organosulfur components; high selectivity was observed in all cases.



Scheme 2: Substrate-selective C-H alkenylation of the sole component.

In this report, data concerning selectivity of C–H olefination of thioethers in mixtures are discussed from the point of view of application of this approach for direct functionalization of thioethers present in crude oil.

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Acknowledgements: This work has been partially supported by the Saint Petersburg State University (research grant from Laboratory of Cluster Catalysis), and the Russian Fund for Basic Research (grant 14-03-01005).

HINDERED ROTATION AROUND C-N BOND IN TETRAALKOXYCARBONYL SUBSTITUTED AZIRIDINES: EXAMPLE OF ATROPISOMERISM OF A NEW KIND

Kirill.I Mikhailov, Ekaterina E. Galenko, Alexander S. Konev, Alexander. F. Khlebnikov
St. Petersburg State University
St. Petersburg, Russia
mikhaylovcyril@yandex.ru

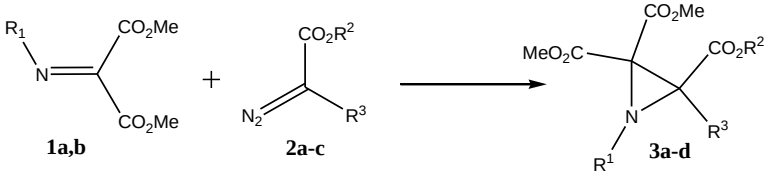
Atropisomerism in compounds designed for pharmaceutical applications can affect their biological activity [1]. As a vast amount of pharmaceuticals are nitrogen-containing compounds, it is quite important to be able to predict possible formation of atropisomers around C-N bond in potential drugs. According to quantum-chemical calculations performed in our group, N-substituted aziridines containing four substituents at the ring carbon atoms can form atropisomers due to the hindered rotation around C-N bond.

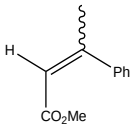
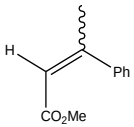
To experimentally verify this hypothesis we decided to synthesize N-alkenyl substituted aziridines **(3c,d)**, which contain vinyl proton as a good reference signal in ^{1}HNMR spectrum. However, the most evident route that employs typical procedure for the synthesis of bis-alkoxycarbonyl substituted aziridines *via* reaction of imine with corresponding diazo compound [2], failed in this case. To optimize the synthetic technique, we studied this reaction on model compounds: dimethyl 2-(phenylimino)malonate and ethyl 2-(phenylimino)acetate as the imine compounds and ethyl diazoacetate and dimethyl diazomalonate as the diazo counterparts. A number of parameters have been varied including catalyst type, catalyst load, and solvent. Under the reaction conditions of choice (equimolar amount of $AlCl_3$ as Lewis acid catalyst, chlorobenzene as a solvent, room temperature) 39% of aziridine **3a** was obtainedby reaction of dimethyl 2-(phenylimino)malonatewith ethyl diazoacetate. However, the reaction of dimethyl 2-(phenylimino)malonatewith dimethyl diazomalonate gave no aziridine **3b**. Neither aziridine **3a** was observed in the reaction of ethyl 2-(phenylimino)acetate with dimethyl diazomalonate. This means that the electronic effects are the most probable reason of inactivity of dimethyl diazomalonate in the reaction.

Taking thesefindings into account, a method implying different mechanism of aziridine formation was applied. Thus, we succeeded to obtain tetrasubstituted aziridine **3b** from dimethyl 2-(phenylimino)malonate and dimethyl diazomalonate in 39% yield by rhodium carbenoid reactionusing $Rh_2(OAc)_4$ as a catalyst. Under the same conditions the target N-alkenyl substituted aziridine **3c** was synthesized in 17% yield.

According to the NMR spectra, tetrasubstituted aziridines **3c** and **3d** showed hindered rotation around C-N bond, with compound **3d** existing as a mixture of

atropisomers. As far as we know, the atropisomerism around C-N bond in aziridines have not been described before.



R^1	R^2	R^3	Conditions	Yield (%)
Ph (**1a**)	Et (**2a**)	H (**2a**)	$AlCl_3$, PhCl, 25 °C, 2h	39 (**3a**)
Ph (**1a**)	Me (**2b**)	CO_2Me (**2b**)	$Rh_2(OAc)_4$, $PhCF_3$, 120 °C, 2h	39 (**3b**)
 (**1b**)	Me (**2b**)	CO_2Me (**2b**)	$Rh_2(OAc)_4$, $PhCF_3$, 120 °C, 2h	17 (**3c**)
 (**1b**)	Et (**2c**)	CO_2Et (**2c**)	$Rh_2(OAc)_4$, $PhCF_3$, 120 °C, 2h	<20 (**3d**)

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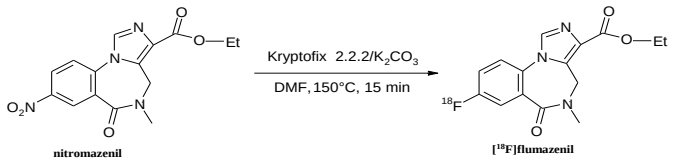
Acknowledgements:
We gratefully acknowledge the financial support of the Russian Foundation for Basic Research (Grant No. 14-03-00187) and Research resource center for Magnetic Resonance Saint Petersburg State University for the investigations.

NEW APPROACH TO PRODUCTION OF [^{18}F]FLUMAZENIL, RADIOPHARMACEUTICAL FOR BENZODIAZEPINE RECEPTORS IMAGING BY PET

Nasirzadeh M.[1], *Vaulina D.D.*[2], *Gomzina N.A.*[2]

[1]Saint Petersburg State University,
[2]N.P.Bechtereva Institute of the Human Brain, Russian Academy of Sciences,
Saint-Petersburg, Russia
Postgraduate student
morteza.lp@gmail.com

Positron emission tomography (PET) is an imaging modality that allows studying of physiological, biochemical and pharmacological functions at a molecular level *in vivo*. Fluorine-18 (^{18}F) is an attractive positron-emitter due to its low positron energy (0.64 Mev), maximum range in tissue (2.4 mm), useful half-life (110 min) and steric similarity to hydrogen atom (Van der Waals radius: 1.2 A° for H and 1.35 A° for F). Aromatic nucleophilic substitution is widely used to synthesize radiotracers based on ^{18}F. ^{18}F-labeling can be performed by nucleophilic displacement of nitro, trimethyl ammonium or other leaving groups in precursors on [^{18}F]fluorine. Radiolabeled flumazenil (FMZ) is an important radiopharmaceutical for the assessment of the central benzodiazepine receptor (cBZR) concentration by PET. These receptors play regulating role in many neurological and psychiatric disorders, such as epilepsy, panic disorder, dementia, acute stroke, alcoholism. Synthesis of [^{18}F]FMZ by nucleophilic substitution of nitro group in nitromazenil with [^{18}F]fluoride had been proposed in IHB RAS [1]. As [^{18}F]FMZ and its unlabeled precursor have no big difference in physic-chemically properties, semi-preparative HPLC is required to separate them. On the other hand, one of the main problems limiting the widely clinical use of [^{18}F]FMZ is its losses on semi-preparative HPLC purification step. Therefore, the aim of this study was to develop the SPE purification method avoiding time-consuming HPLC purification. This method involves derivatization of nitromazenil precursor and consequently purification of [^{18}F]FMZ via SPE, using commercially available cartridges. Preliminary studies carried out on nitromazenil and none-radioactive FMZ demonstrated that the precursor converted to less lipophilic species under strong bases (potassium methylate), whereas FMZ was more stable, that gives opportunity for their following separation.



Picture 1. Scheme of [^{18}F]flumazenil synthesis.

No carrier added [^{18}F]Fluoride was produced by H_2O[^{18}O] water target of PETtrace cyclotron (GE Healthcare, USA) and separated using anion change cartridge (QMA) in the presence of potassium carbonate and Kryptofix 2.2.2 as a phase transfer catalyst. [^{18}F]FMZ was prepared by nucleophilic substitution of a nitro-group in the nitromazenil (ABX, Germany, ~2 mg) with [^{18}F]fluoride in DMF as aprotic organic solvent (see Pic.1). After [^{18}F]fluorination potassium methoxide in methanol was added to the reaction vessel, which was heated (60°C). Cooled and diluted reaction mixture was passed through the reversed phase SPE cartridge and the activity trapped on cartridge was eluted by 10-15% ethanol/ acetic buffer. [^{18}F]FMZ recovery was about 50 % from the loaded activity. This is two times more than we had by HPLC (25%). The product obtained after SPE purification has high radiochemical purity, more than 97%, with high specific activity. The amount of nitromazenil was negligible ($\leq$1μg) and other chemicals impurities were under the limits set by the European Pharmacopoeia.

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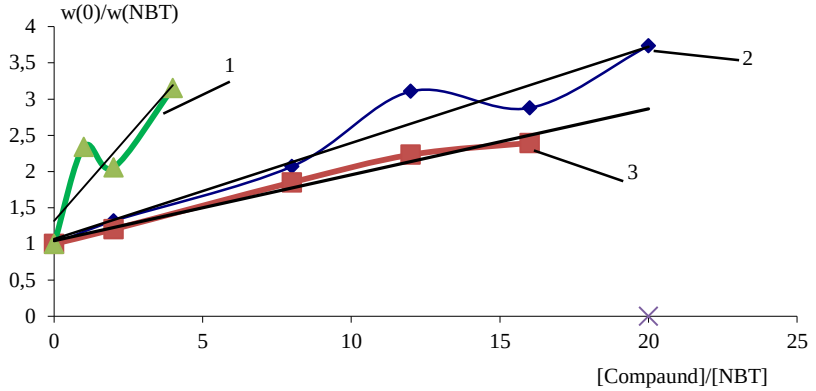
REACTIVE ABILITY OF ESCULETIN, ESCULIN AND CAFFEIC ACIDS WITH SUPEROXIDE ANION-RADICAL

V.V. Nikolaeva, I.G. Antropova, Phyo Myint Oo, K.I. Polyakova

D. Mendeleev University of Chemical Technology of Russia
Moscow, Russia
valli888@bk.ru

A growing interest toward natural compounds sensibly "fits" into the concept of a healthy lifestyle. It's no secret that the world ecology is in a critical condition. The human body is constantly under a harmful influence of free radicals. Toxic xenobiotics in food, water and air; ionizing and ultraviolet radiation stimulate the body to form bioradicals [1]. In the absence of the necessary amount of antioxidants and radioprotectors [2] in food and in the environment, a need arises for an additional source of antioxidants coming from natural compounds with a strong therapeutic effect. Abundance, accessibility, effectiveness, and an absence of heavy side-effects for a biological body demonstrate why natural compounds should be prioritized. The compounds under analysis are: Esculin (EscGl), Esculetin (Esc), and caffeic acid (Caf) that are widely presented in the plant kingdom. In order to model the reactions of the analyzed molecules with free radicals, a source of ionizing radiation was used - a RChM-γ- 20 unit (D. Mendeleev University of Chemical Technology of Russia). The power of absorbed dose Fricke dosimeter is 0,078 Gy/s,radiation is carried out in the range of doses of 0-220

Gy. As the negative impact of radical superoxide anion radical (SOAR) is represented. In this paper we used the method of determining the education diphormazane reaction with nitro blue tetrazolium (NBT) chloride at pH = 7.4. Under physiological conditions, the concentration SOAR maximum at given pH. The measurements were performed an SF-2000 spectrophotometer at λ = 542,5 nm.



Pic.1 Changes [**w**(0)]/[**w**(NBT)] of [**w**(compound)]/[**w**(NBT)]: 1-Caf, 2-EscGl, 3- Esc.

In work constants of interaction of active agents with SOAR in the model aerated conditions is defined. The constant of reaction of interaction of SOAR with the studied connections is described by the equation of the 2nd order.Experimental constants of interaction are equal: k [EscGl+ SOAR] =8,9×10^{3}l/(mole×s), k [Esc+ SOAR] =5,8×10^{3}l/(mole×s), k [Caf+ SOAR] =3,2×10^{4}l/(mole×s).

It is established that anti-radical activity decreases among Caf>EscGl>Esc. When comparing anti-radical activity of an eskuletin and eskulin in relation to SOAR it is experimentally established that Esc didn't show anti-radical activity in relation to SOAR.

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TANDEM HYDROARYLATION AND IONIC HYDROGENATION OF PHENYLPROPIOLIC ACID DERIVATIVES UNDER SUPERELECRTOPHILIC ACTIVATION CONDITIONS

Nilov D.I.

Saint Petersburg State University,
Saint Petersburg, Russia,
Postdoc
d.nilov@spbu.ru

An alternative synthetic approach for the synthesis of diaryl substituted derivatives of propionic acid is proposed. Thus, phenylpropiolic acid derivatives (esters, amides, and nitrile) under action of strong Lewis (AlX_3, X = Cl or Br) and Bronsted (TfOH) acids undergo hydroarylation followed by reduction to produce phenylpropionic acid derivatives. Some of preliminary results of experiments with methyl phenylpropiolate are summarized in table 1.

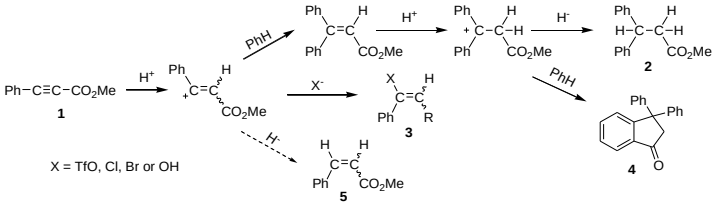

Table 1. Reaction of ester 1 under superelectrophilic conditions (C = 0,125 M. T = 20°C).

Exp #	Reaction Conditions: Acid (equiv)	Source of hydride ion	Arene or Solvent	Time, hrs	Reaction Products: Product	Ratio, %	Yield, %
1	$AlCl_3$ (5)	CyH	PhH	15	**2**	-	85
2	$AlCl_3$ (5)	AdH	PhH	15	**2**	98	86
					E,Z-3 (X=Cl)	2	2
3	$AlCl_3$ (5)	CyH	DCM	15	**E,Z-3** (X= Cl)	-	90
4	$AlBr_3$ (5)	CyH	PhH	15	**2**	-	90
5	$AlBr_3$ (5)	CyH	DCM	1	**E,Z-3**(X= Br)	-	82
6	$AlBr_3$ (5)	AdH	PhH	1	**2**	85	75
					E,Z-3(X= Br)	15	13
7	TfOH (75)	CyH	PhH	0.25	**4**	-	81
8	TfOH (75)	AdH	PhH	15	**4**	25	22
					2	75	66
9	TfOH (75)	CyH	--	15	**E,Z-3** (X= TfO)	-	82
10	Zeolite CBV-720	CyH	PhH	30	**2**	70	29
					E,Z-3 (X= OH)	30	12

This work is supported by grant for postdocs of Saint-Petersburg State University № 12.50.1187.2014 “Cationic Intermediates in Synthesis of Organic Compounds”.

DETERMINATION OF DNA BEND ANGLE INDUCED BY DNA METHYLTRANSFERASE SSOII

Norkin M.V, Ryazanova A.Yu.

Lomonosov Moscow State University
Student
norkin_1991@mail.ru

This research is devoted to the optimization of the current approach for the determination of DNA bend angles induced by DNA-binding proteins. The goal is a subsequent application of this method for any proteins from restriction-modification (RM) systems. DNA methyltransferase SsoII (M.SsoII) from SsoII RM system was taken as a model.

M.SsoII belongs to a special class of methyltransferases, which not only methylate DNA, but regulate gene transcription in RM systems [1]. There are two proteins in SsoII RM system, the DNA methyltransferase and the corresponding restriction endonuclease. They recognize the same sequence 5'-CCNGG-3'. Their genes are directed divergently and separated by an intergenic region (109 bp) which contains a regulatory site. M.SsoII consists of two domains, one of which binds to the regulatory site and thereby regulates transcription; and the other one is responsible for DNA methylation.

A lot of transcription regulators bend DNA. Given that, we can assume that M.SsoII can bend DNA as well. So, the determination of DNA bend angle, induced by protein at the regulatory site and methylation site, is an actual task, which helps to clarify functional features of the SsoII RM system in cell.

DNA bend angles induced by M.SsoII at the regulatory and the methylation sites are successfully determined, on the basis of the method suggested by S. Ferrari et al. [2] and the plasmid constructed by C. Zwieb et al. [3].

References

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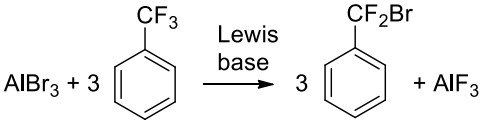
Acknowledgements The work was supported by RFBR-DFG grant N 14-04-91340.

DEVELOPMENT OF A CONVENIENT SYNTHETIC METHOD FOR 1-BROMO-1,1-DIFLUOROTOLUENE PREPARATION

Obrezkov F.A.[1], *Eliseenkov E.V.*, *Boyarskiy V.P.*
Institute of Chemistry, Saint Petersburg State University
Saint Petersburg, Russia
[1]Student
obrezkovchem@gmail.com

Synthesis of fluorinated organic compounds is one of the most important branches of modern laboratory and industrial organic synthesis.
Silicone compounds are actively used for this in recent years. For example: Ruppert reagent (CF_3SiMe_3) and its analogs, one of which is Me_3SiCF_2Ph.**[1]** Availability of this compound is extremely limited due to the absence of a convenient method for the synthesis of its precursor ($PhCF_2Br$). Therefore, the aim of our study was to develop a new method of this substance obtaining.
We used the transhalogenation reaction:



Scheme 1

There is only one method of obtaining the product described in the literature applying BBr_3.**[2]** However, a large amount of byproducts formed during the synthesis and the reaction proceeds with a low yield. We managed to solve the problem by applying $AlBr_3$ complexes with Lewis bases (required to increase the selectivity of the reaction).

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Acknowledgements:
Physicochemical studies were performed at Center for Magnetic Resonance, Center for Chemical Analysis and Materials Research, and Chemistry Educational Center of Saint Petersburg State University. The authors thank Russian Foundation for Basic Research (grant 14-03-00297a) and Saint Petersburg State University (НИР12.38.225.2014).

DESIGN AND STUDY OF OLIGONUCLEOTIDE MODEL CONTAININGG-QUADRUPLEX MOTIF, INTEGRATED INTO DNA DUPLEX

Anna M. Ogloblina[1], *Marianna Yakubovskaya*[1], *Nina Dolinnaya*[2]
[1] N.N. Blokhin Cancer Research Center RAMS
[2]Lomonosov Moscow State University, Chemical Department
Moscow, Russia
PhD student
globbi@mail.ru

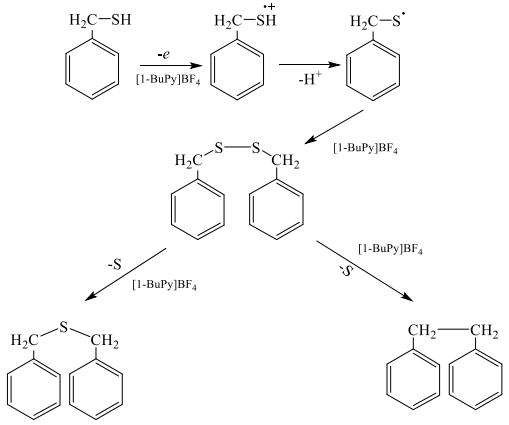
The G-quadruplexes (G4), the alternative DNA structures that arise in the result of rearrangement of B-form double-stranded DNA, can be formed by sequences that are widely distributed throughout the human genome. G4s were shown to may influence the key biological processes such as transcriptional regulation, DNA replication, telomere maintenance. On the other hand, the G-quadruplexes are the sites of genomic instability associated with numerous human diseases including cancer ones. At present, a lot of proteins have been identified that recognize and interact with G4. For studies of DNA quadruplex-protein interactions, the isolated G4 structures are typically used. Here we developed the new oligonucleotide model, which imitates the parallel intramolecular G4 in DNA duplex context. In order to obtain this model, the G4-motif ($d(GGGT)_4$) was flanked by the random sequences Then the oligonucleotide obtained was hybridized to the template oligomer that does not contain the site complementary to G4-forming sequence. Since the microsatellite repeat $d(GGGT)_4$ are folded in a parallel G4, its ends are removed in space and oriented in such a way that can easily fit in a DNA duplex without the aid of structured linker, as it takes place for antiparallel G4. The advantage of such models is that the non-canonical form (G4) is fixed in a duplex environment, as *in vivo* systems. The following synthetic oligonucleotides:
(1) 5'-d (GTTACTCGAGC-TT-GGGTGGGTGGGTGGG-TT ATATGGCTCAG), (2) 5'-d (GTTACTCGAGC-TT-GTGTGTGTGTGTGTG-TT-ATATGGCTCAG), (3) 5'-d (CTGAGCCATAT- TT-GCTCGAGTAAC), (4) 5'-d (CTGAGCCATAT-GCTCGAGTAAC), were applied to prepare several DNA duplexes (oligomers (3) and (4) were used as the complementary templates). Oligomer (2) with insertion $d(GT)_8$ served as a negative control. Using UV-melting at 260 and 295 nm, we have shown that the DNA duplex and G-quadruplex domains coexist in the equimolar mixtures (1) + (3) and (1) + (4). At the same time, in the mixtures (2)+(3) and (2)+(4), which contain a dinucleotide repeat $d(GT)_8$, G-quadruplex domain does not occur, although the duplex structure is formed.
Acknowledgements: The work was supported by RFBR-DFG grant N 14-04-91343.

ELECROCHEMICAL REACTIONS OF THIOLS IN IONIC LIQUIDS

Okhlobystina A.V., Okhlobystin A.O., Abdulaeva V.F., Berberova N.T.

Astrakhan Technical State University,
sanikohl@gmail.com

At present time chemistry of ionic liquids is developing in Russia. The electrochemical transformation of C_4H_9SH и $C_6H_5CH_2SH$ inionic liquid - [1-BuPy]BF_4 was researched. As are sultofelectrolysis $C_6H_5CH_2SH$ in [1-BuPy]BF_4 the corresponding disulfide, sulfide, dibenzyl and nanosulfurwere obtained.



The yield of disulfide is about80-90% in ionic liquid;this is better then in traditional aprotic solvents, and dependon electrolysis potential and reaction time. Further disulfide and sulfide can be oxidized to thiosulfinate in ionic liquid. Thiosulfinates are biologically active compounds which are usually used to obtain medicines with anti-neurotic,antiemetic and antiallergic activity.

Work is executed at financial support of the grant of the President №МК-2943.2015.3and grant of RFBR № 14-03-31930 mol_a.

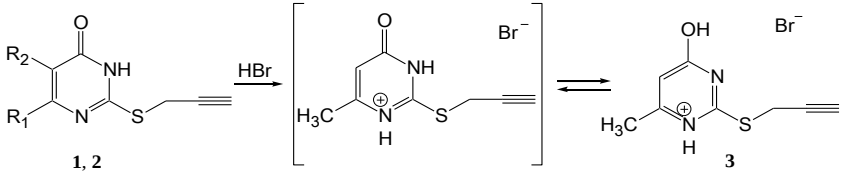
INVESTIGATION OF 2-PROPARGYLTHIO-4(3*H*)-PYRIMIDINONE HETEROCYCLIZATION DIRECTION USING ACIDS

Osheko K.Yu., Frolova T.V., Kim D.G., Sharutin V.V.

South Ural State University
Chelyabinsk, Russia
Student
osheko_kseniya@mail.ru

It is well known that 2-propargylthio-4(3*H*)-pyrimidinones can be cyclized in the presence of sulfuric acid with the formation of linearly annelated thiazolopyrimidinones [1-2] and in the halogen presence with the annelation of angular systems[1].

We have found byX-ray analysis that 2-propargylthio-6-methyl-4(3*H*)-pyrimidinone (**1**)reacts with hydrobromic acid to give the protonation product at the nitrogen atom $N_{(1)}$, 4-hydroxy-6-methyl-2-propargylthiopyrimidinium bromide (**3**). Notice that compound **3**isinthetautomeric form with protons at the oxygen atom and the nitrogen atom $N_{(1)}$. As a result the nitrogen atom $N_{(3)}$ can take part in the further heterocyclization reaction in acidic media.



1, **2** **3**

Scheme 1. R_1=CH_3, R_2=H; R_1=CH_3, R_2=C_2H_5

The distance between β-carbon of the propargyl group and the nitrogen atom $N_{(1)}$ in propargylsulfide **2** is less than with the nitrogen atom $N_{(3)}$ according to the X-ray analysis. In contrast, the distance between β-carbon of the propargyl group and the nitrogen atom $N_{(3)}$ in bromide **3** is less than with the nitrogen atom $N_{(1)}$. Thus the heterocyclization of S-unsaturated derivatives of 2-thiouracile goes with the participation of the trisubstituted nitrogen atom.

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SMALL NON-CODING 6S RNA AS A REGULATOR OF GENE EXPRESSION IN BACTERIA

Ovcharenko A.V.[1], *Burenina O.Y.*[1], *Hartmann R.K.*[2], *Kubareva E.A.*[1]

[1]Lomonosov Moscow State University, Russia
[2]Philipps-Universität Marburg, Germany
Moscow, Russia
Student
anna.v.ovcharenko@gmail.com

6S RNAs are widespread among all bacterial species and act as global inhibitors of transcription targeting RNA polymerase (RNAP). Direct interaction of 6S RNA with RNAP active site and further blocking of enzyme activity are provided by conservative secondary structure of the 6S RNA molecule, which mimics open conformation of DNA promoter [1]. It is considered that 6S RNAs pause transcription and store housekeeping RNAP under unfavorable or stress conditions, thus preventing overconsumption of nutrients and prolonging cell life. The aim of the present research was to investigate the influence of 6S RNAs from *Escherichia coli* and *Bacillus subtilis* on cell viability and gene expression under extreme growth conditions including basic, acidic, osmotic and oxidative stresses. For this purpose mutant *E. coli* and *B. subtilis* cell lines with deletions of 6S RNA genes were cultivated in parallel with wild type strains. Changes of 6S RNAs expression profiles during different stages of cell growth were analyzed by Northern blotting. Effects of 6S RNA knockouts in *B. subtilis* on cell growth were negligible although this bacterium encodes two different 6S RNAs expressing mostly in exponential (6S-2) as well as in stationary (6S-1) phase [2]. The most prominent phenotype was observed for 6S RNA-depleted *E. coli* strain in presence of H_2O_2. To elucidate putative proteins, which expression is regulated by this 6S RNA under oxidative stress, comparative proteomic analyses of mutant strains related to wild type cells was performed. Total protein extracts isolated from each strain were labeled by fluorescent dyes Cy5 and Cy2 and analyzed simultaneously by 2D gel electrophoresis. A set of different proteins affected by 6S RNA was identified finally by MALDI-spectrometry.

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This work has been supported by the joint DFG-RFBR program "International Research Training Groups" (grants GRK 1384, 14-04-91336) and Russian National Foundation 14-24-00061.

SYNTHESIS OF POLY(AMINO ACIDS) FOR THE PREPARATION OF NANOPARTICLES

Pogodaev A.A.[1], *Hubina A.V.*[1], *Vlakh E.G.*[1, 2]

[1]Saint Petersburg State University, Institute of Chemistry
[2] Institue of Macomolecular Compounds RAS
Saint-Petersburg, Russia
Student
alexandr.pogodaev@gmail.com

In last two decades *polymer nanoparticles* have attracted the high attention as perspective delivery vehicles for drugs, genes and vaccines due to the preservation for encapsulated substance and controlled release. One of the intensively developed approaches for the preparation of nanoparticles is the self-assembling of amphiphilic block-copolymers in water or water-organic media. Depending on applied conditions such approach allows the formation of several types of nanoparticles, namely polymer *micelles* or hollow spheres called also *polymersomes*. Contrary to micelles that are suitable for encapsulation of hydrophobic substances only, the polymersomes can be used as drug delivering system for both hydrophilic and hydrophobic compounds. Polymersomes comparatively to liposomes represent the bilayer systems consisted of an aqueous core surrounded by a bilayer polymer membrane. However, contrary to liposomes polymersomes are characterized with improved chemical and mechanical stability.

Application of amphiphilic block-copolymers based on poly(amino acids) for preparation of the self-assembling nanoparticles have several advantages over conventional synthetic polymers such as their biodegradability, ability to form stable, ordered structures as well as exhibit their own biological activity.

In the present research the series of polyglutamate-b-polyphenylalanine block-copolymers were synthesized using the polymerization of N-carboxyanhydrides. Chemical structures of monomers, homopolymers and block-copolymers were confirmed *via* NMR method. Molecular weight and polydispersity index of homo- and block-copolymers were determined by gel-permeation chromatography (GPC). The self-organization of amphiphilic poly(amino acids) were held in aqueous media with different pH. The dependence of average hydrodynamic diameter on the polymer concentration as well as morphology of nanoparticles obtained were evaluated by dynamic light scattering and transmission electron microscopy, respectively.

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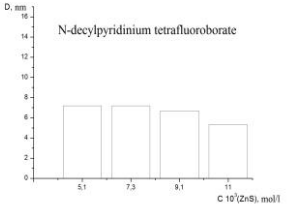
METHOD OF SYNTHESIZING NANOPARTICLES OF ZINC SULFIDE IN IONIC LIQUIDS

Presnyakov I.A., Zhuravlev O.E.
Tver State University
jamanger@gmail.com

Quantum dots - semiconductor nanocrystals with a size of 2-10 nm, composed of 103 - 105 atoms that are based on inorganic semiconductor materials of Si, InP, CdSe. Quantum dots may be used to produce various fluorescent materials as well as the basis for production of miniaturized LEDs, white light sources, single-electron transistors, nonlinear optical devices, photovoltaic and photosensitive devices. Colloidal synthesis method has several advantages: the ability to monitor the growth of nanoparticles, for example by varying the temperature parameters; possible to obtain nanoparticles in powder form; relatively low temperature synthesis; the method allows to synthesize nanoparticles having small spread of geometric parameters (dispersion medium size 5-10%). In this paper we synthesized nanoparticles of semiconductors (zinc sulfide and cadmium sulfide). Precursors for the synthesis of nanoparticles (solutions of salts of zinc and cadmium, as well as sodium sulfide) is administered concurrently with constant stirring in an ionic liquid comprising a mixture of organic solvents. Having a semiconductor nanoparticle sols was established by UV spectroscopy and dynamic light scattering. Synthesis medium held in ionic liquid N-decylpyridinium tetrafluoroborate in the presence of ethyl acetate and acetone. Particle size depending on the concentration of ZnS presented on picture 1. Dimensions of nanoparticles synthesized zinc sulfide is in the range 2-15 nm. The ionic liquid in this case also acts as a solvent for the role of nanoparticles and stabilizer. The stabilizing effect of IL due to the presence of domain structure which in turn is caused by various types of interactions (Coulomb interactions, hydrogen bonding, stacking interactions, and others.).



Picture 1 The dependence of the size of nanoparticles of zinc sulfide in the ZnS sols of concentration

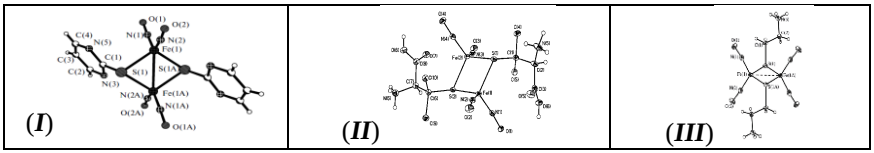
This work was financially supported by the Ministry of Education of the Russian Federation as part of the public works in the field of scientific activity.

THE REASON FOR THE DIFFERENCE OF "μ_2-S"STRUCTURAL TYPENITROSYL IRON COMPLEXES DECAY MECHANISMS

Syrtsova L.A., Sanina N.A.,Pokidova O.V., Psikha B.L., Shkondina N.I., Kotelnikov A.I., Aldoshin S.M.

The Institute of Problems of Chemical Physics of the RAS
Chernogolovka, Russia
Postgraduate Student
olesiapokidova@gmail.com

It was found by numerous studies of the recent years that nitrogen monoxide (NO) is an important agent in bioregulation of diverse physiological processes.This fact stimulate the interest to the synthesis and study of new compounds transported NO to biological targets at physiological pH values and serve a basis for the new generation of medicines. Thiolate nitrosyl iron complexes (NICs) $[Fe_2(SR)_2(NO)_4]$ are new class of quasinatural NO donors for pharmacological applications. They are hydrolyzed similarly to *S*-nitrosothiols and diazenium dialates to form NO in protic media.



Picture 1. Molecular structure NIC with 2-mercaptopyrimidinethiolyl (***I***)and the structures of NICs dications: with penicillamine(***II***)**,** and cysteamine(***III***) thiolic ligands**.**

Two decay mechanisms of NICs μ_2-S-type have been described. In one case (e.g., a complex $[Fe_2(\mu_2\text{-}SC_4H_3N_2)_2(NO)_4]$ (***I***), Picture 1), the irreversible and rapid hydrolysis of NICs with NO release, accompanied by the formation of products of the further NO transformation carried out. In other cases (for example, complexes$[Fe_2(\mu_2\text{-}SC_5H_{11}NO_2)_2(NO)_4]SO_4{\cdot}5H_2O$(***II***),[1]and$[Fe_2(\mu_2\text{-}S(CH_2)_2NH_3)_2(NO)_4]SO_4{\cdot}2.5H_2O$(***III***)**,**[2], Picture 1)hydrolysis does not occur, and there is a reversible dissociation of the NICs with the release to medium both NO and the thiolate ligands. We have established the reason for the difference of NICs decay mechanisms. It is associated with NICs redox potential. We present experimental evidence for this conclusion.

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Acknowledgments

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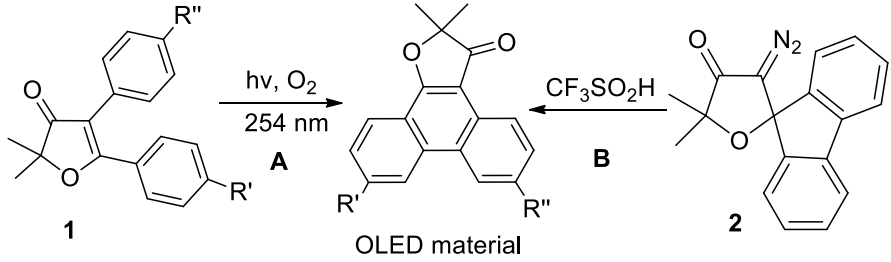
PHENANTHRO[9,10-B]FURAN-3(*2H*)-ONES AS A BLUE OLED PROMISING CANDIDATES

Semenok D.V., Medvedev Y.Y., Poloneeva D.Y., Pavlovsky V.V., Rodina L.L.

[1]Saint Petersburg State University
Saint Petersburg, Russia
Student
dashapolon@gmail.com

Extension of unbroken work time of blue OLED is one of the most actual problem today in the field of electroluminescent organic materials [1]. It has been shown recently, that the replacement of anthracene fragment in the well known OLED molecules onto phenanthrene unit leads to improve of their working characteristics [2]. The synthesis of a series of substituted phenanthro[9,10b]furan-3(*2H*)-ones was carried out in our research by photochemical oxidative cyclization reaction of 4,5-diaryl-3(*2H*)furanones **1**. The proposed approach (route **A**) is more effective than way **B** based on ring-enlargement reaction observed during acid-catalyzed decomposition of diazofuranones **2**. The practical utility of all synthesized compounds as OLED materials is planned to investigate. These studies would stimulate the synthesis of more complex and effective polycondensed systems.



R' =	SMe,	SOMe,	SO_2Me,	H,	H,	H,	H
R'' =	H,	H,	H,	SMe,	SOMe,	SO_2Me,	H

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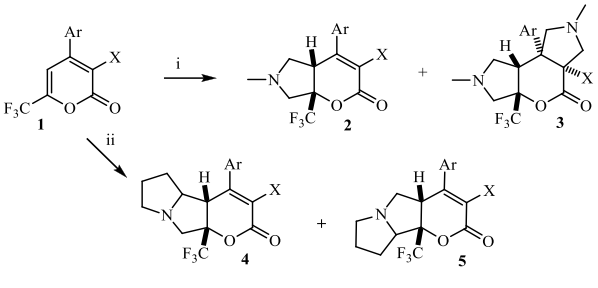
SYNTHESIS OF PYRROLIDINE DERIVATIVES VIA 1,3-DIPOLAR CYCLOADDITION OF AZOMETHINE YLIDES TO ACTIVATED 2-PYRONES

Popova N.V., Usachev S.A., Sosnovskih V.Ya.

Ural Federal University named after the first President of Russia B.N.Yeltsin

lostwind2008@gmail.com

Pyrrolidines are among the most frequently used aliphatic amines in organic chemistry. Moreover, this functional group can be found in many biologically active compounds, including nine FDA approved drugs. Not surprisingly, that substituted pyrrolidine analogues are valuable building blocks used in the design of new drug molecules, and the development of agrochemical compositions. That is why, development of effective methods of the synthesis of pyrrolidine moiety is so important.



Ar	X
Ph	CO_2Et
	CO_2Et
	CO_2Et
Ph	H
	H
	H

Reagents: *i*, N-methyl glycine, paraformaldehyde; *ii*, L-proline, paraformaldehyde.

Picture 1. Interaction of 4-aryl-6- (trifluoromethyl) -2H-pyran-2-ones **1** with azomethine ylide generated from proline and sarcosine

One of the most common approach to pyrrolidines is1,3-dipolar cycloaddition of azomethine ylides to an activated double bond. 2-Pyrones can be regarded as push-pull alkenes, however, no such reactions are described in the literature. Pyranopyrrolidines **2,3** and pyranopyrrolizines **4,5** were generated as the cycloaddition products via reaction of 4-aryl-6-trifluoromethyl-2-pyrones **1**with azomethine ylides generated *in situ* from sarcosine and proline respectively in medium to good yields.

AMINO ACIDS DERIVATIZATION WITH DMF-DMA

Pushkareva T.I., Zenkevich I.G.
St. Petersburg State University
St. Petersburg, Russia
Student
Tatyana-tyshkan@yandex.ru

The analysis of amino acids is an important task in gas chromatography. However, it is necessary to convert nonvolatile amino acid into volatile derivatives. One of the most popular methods of single-stage amino acid derivatization is their interaction with dimethylformamide dimethylacetal (**DMF-DMA**):

$R\text{-}CH(NH_2)CO_2H + (CH_3)_2NCH(OCH_3)_2 \rightarrow R\text{-}CH[N{=}CHN(CH_3)_2]CO_2CH_3$

Only one product (N-DMAM derivative) is formed in this reactionfor most of amino acids; the isolation of products from reaction mixtures is not required.

Reaction conditions: Most amino acids(1-2 mg)are dissolved at 80 °Cduring 1 h in excess of solvent-free DMF-DMA (50 μl) in sealed glass ampoules.

Conditions of GC analysis: Gas chromatograph ChromaTech Kristall5000.2 with FID, column BPX-1 (length 10 m, i.d. 0.53 mm, film thickness 2.65 μm), temperature programming from 70 to 200 °C, ramp 5 °C/min. Carrier gas (nitrogen) flow rate was 5.3 mL/min, linear velocity 43 cm/sec, split ratio6 : 1. Injector temperature was 220 °C, detector temperature 250 °C.

Mass spectrometric condition: Mass-spectrometer Shimadzu GC-2010 Plus, column RTX-5 MS (length 30 m, i.d. 0.32 mm, film thickness 0.25 μm) in the same temperature programming regime.

Table. Retention indices (RI) values of N-DMAM derivatives of amino acids and some aminesfor BPX-1 (GC) and RTX-5 (GC-MS) stationary phases

Compound	RI(GC)	RI(GC-MS)	Compound	RI(GC)	RI(GC-MS)
Ethanolamine	1064±2	1054±2	Leucine	1342±1	1380±2
Aniline	1366±1	1382±2	Aspartic acid	1460±1	1515±1
Benzylamine	1396±1	1406±2	Lysine	1961±1	1969±0
Alanine	1143±3	1175±2	Glutamic acid	1578±2	1637±1
Serine	1233	1280±1	Methionine	1581±2	1638±1
Proline	1332±1	1387±3	Phenylalanine	1692±0	1734±1
Valine	1265±2	1288±2	Arginine	1842±1	1909±2
Norleucine	1390±1	1426±3	Tyrosine	1905±20 1953±23	1987±4 2038± 5
Isoleucine	1344±1	1380±2	Tryptophan	- / 2327±43	2321±15 2374±17

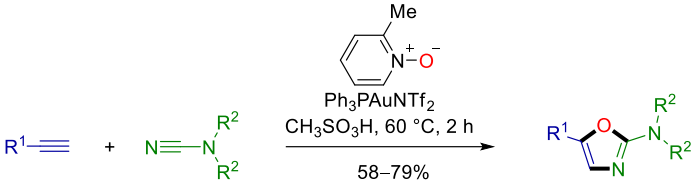
Mass spectra were obtained for all derivatives. The most intensive peaks in them belong to the ions $[(CH_3)_2N]^+$ $(m/z)^{100} = 44$, $[M - 59] = [M - CH_3OCO]^+$ and others. Proline (contains secondary NH-group) forms N-formyl derivative of its methyl ester.

α-OXO GOLD CARBENES IN THE SYNTHESIS OF SUBSTITUTED OXAZOL-2-AMINES

Rassadin V.A., Boyarskiy V.P., Kukushkin V.Yu.

Instituteof Chemistry, Saint Petersburg State University
Saint Petersburg, Russia
Postdoctoral Fellow
v.rassadin@spbu.ru

Homogeneous gold catalysis is among cutting edge projects of the modern organic chemistry. From many versatile aspects of gold catalysis the one leading to generation of highly reactive α-oxo gold carbenes should be noted. Respective gold species could be generated from a wide range of alkynes and pyridine oxides in the presence of a suitable gold salt. In general, obtained α-oxo gold carbene species could be trapped with various nucleophiles.



In the present contribution, we reporton a novel approach toward substituted oxazol-2-amines. The key step of this transformation includes generation of α-oxo gold carbene species followed by their trapping with different cyanamides. This method gives an access to substituted oxazol-2-amines functionalized at the nitrogen atom as well as heterocyclic ring formed in good yields.

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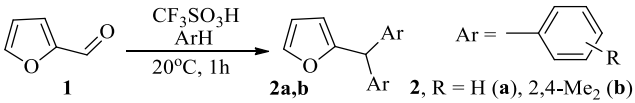
REACTIONS OF FORMYLFURANES WITH ARENES UNDER SUPERACIDIC CONDITIONS

Ryabukhin D.S.[1], *Tarakanov A.A.*[2]

[1]Saint Petersburg State University,
[2]Saint Petersburg State Forest Technical University
Saint Petersburg, Russia
Postdoc
rdms@bk.ru

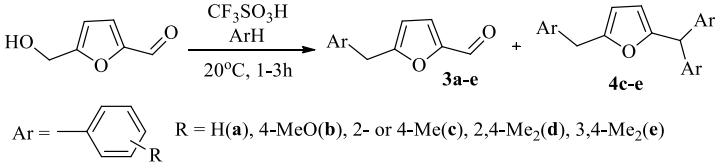
Selective dehydration of fructose and other saccharides will lead to 5-hydroxymethylfurfural (5-HMF) and furfural, that can replace key petroleum-based building blocks. The main derivatives obtained from 5-HMF may found their application not only as a nutritional supplements and as a fuel, but also as a drugs, additives and polymer materials.

This work includes superelectrophilic activation of furane derivatives with Brønsted and Lewis acids in presence of arenes. Reaction furfural **1** under CF_3SO_3H in presence of benzene gave a product **2a** only in trace amount, but use instead of benzene *m*-xylol led to a compound **2b** with yield 16% for 1h at 20°C.



1 **2a,b** **2**, R = H (**a**), 2,4-Me_2 (**b**)

5-HMF in reactions with benzene or anisole in CF_3SO_3H gives 5-benzylfurfural **3a** and 5-(4-methoxyphenyl)furfural**3b** corresponding. Reactions of 5-HMF with arenes containing donating group (Me, Me_2) leads to mixture of compounds **3c-d** and **4c-d**.



3a-e **4c-e**

R = H(**a**), 4-MeO(**b**), 2- or 4-Me(**c**), 2,4-Me_2(**d**), 3,4-Me_2(**e**)

This study was supported by the Russian Science Foundation (grant no. 14-13-00448)

SOLUBILITY AND CHEMICAL EQUILIBRIUM IN THE SYSTEM WITH ETHYLPROPIONATE SYNTHESIS REACTION UNDER POLYTHERMAL CONDITIONS

Sadaeva A.A.[1], *Golikova A.D.*[1], *Toikka M.A.*[1]

[1]Saint Petersburg State University, Institute of Chemistry, Department of Chemical Thermodynamics and Kinetics
Student
a.sadaeva@chem.spbu.ru

This work deals with considering of thermodynamics and some peculiarities of multicomponent heterogeneous systems with mass-transfer. The main task is thermodynamic analysis of the features of liquid-liquid (LL) phase diagrams of the systems with equilibrium and non-equilibrium chemical reaction in solution. The objects investigated are heterogeneous systems with ester synthesis reaction that were carried out both for basic and industrial purposes. The main trend of such purposes is the use of "clean" energy. One representative of this type of energy from renewable sources is biofuel. This product has several advantages over fossil energy sources: manufactured from renewable raw materials, non-toxic, biodegradable, its composition no contains sulfur, and this fuel has better lubricating properties [1, 2]. A recent and comprehensive review of the achievements in the field of production and application of biofuels is presented in a review article [3].

The object of investigation in this research is quaternary reacting system propionic acid - ethanol - ethyl propionate – water. The ternary and binary subsystems (propionic acid - ethyl propionate - water, ethanol - ethyl propionate - water, ethyl propionate - water) were studied.

Chemical equilibrium was studied at 20, 30 and 40 °C. The experimental data on chemical equilibrium in system investigated was obtained by gas chromatographic method analysis and NMR. To study the solubility was used cloud-point technique method. The experimental data on the solubility was obtained at a temperature of 20˚C. Someof these experimental data on the chemical equilibrium and solubility will be used to further complex research for the system with ethyl propionate synthesis reaction.

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FENAMATE CO-CRYSTALS WITH 4,4'-BIPYRIDINE: STRUCTURAL AND THERMODYNAMIC ASPECTS

SimaginaAA.[1], *Surov A.O.*[2]
[1]*Ivanovo State University of Chemistry and Technology, Ivanovo, Russia*
[2]*G.A. Krestov Institute of Solution Chemistry RAS, Ivanovo, Russia*
annsimagina@gmail.com

Cocrystal is a multicomponent system comprising two or more compounds crystalline under ambient conditions. Mixed pharmaceutical cocrystal includes active pharmaceutical ingredient (API) and associated molecule (coformer). However, in spite of great interest in the structure and preparation of co-crystals, relatively little data exist on their thermodynamic aspects, which are fundamental measures of their stability.

In this work we focus on the crystal structures, thermophysical properties and thermodynamic characteristics of the cocrystals formation of fenamates with 4,4′-bipyridine [BP]. Fenamates (N-phenylanthranilic [NPA], niflumic [NFA], flufenamic [FFA], tolfenamic [TFA] and mefenamic [MFA] acids) refer to the extensive class of nonsteroidal anti-inflammatory drugs, widely used as weak analgesics. Fenamates are famous for propensity to polymorphism, and many of them exhibit the so-called conformational polymorphism.

According to differential scanning calorimetry and powder X-ray diffraction fenamates were found to form cocrystals in 2:1 molar ratio. Furthermore, for all the systems single crystals were obtained and their crystal structures were determined by single-crystal X-ray diffraction method. Differential scanning calorimetry data suggest that the increase in the melting temperature of the co-crystals is accompanied by an increase in the melting temperature of the pure fenamates. It indicates that the intermolecular interactions, which are responsible for the thermal stability of the pure fenamates crystals, are partially conserved in the fenamate co-crystal. Solution enthalpies were measured by solution calorimetry method at 298.15 K, and then formation enthalpies were calculated. The enthalpies of formation for the co-crystals are small. The [FFA+BP] co-crystal shows the largest value which may be caused by additional interactions between the fenamate molecules in the crystal.

This work was supported by a Grant from the President of the Russian Federation no. МК-67.2014.3 and Russian Foundation for Basic Research (project № 14-03-31001).

SYNTHESIS AND STUDY OF THE BIOLOGICAL ACTIVITY OF PYRIDINE AZOMETHINES BENZO-15-CROWN-5 DERIVATIVES AND COPPER COMPLEXES

V.N. Glushko, N.Y. Sadovskaya, L.I. Blokhina

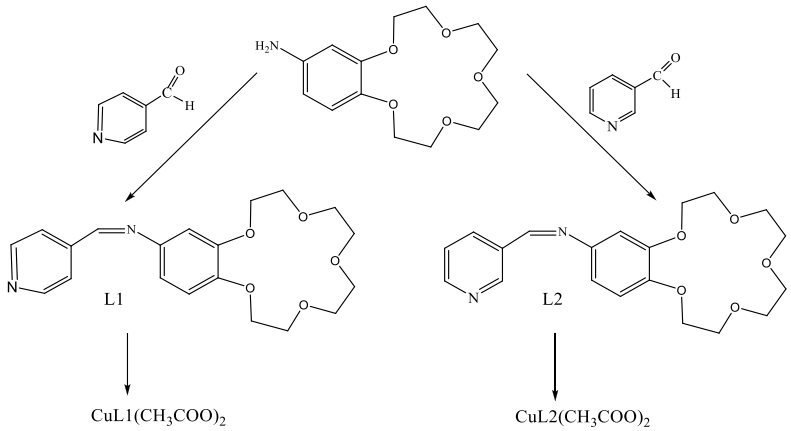
Federal State Unitary Enterprise «State Scientific Research Institute of Chemical Reagents and High Purity Chemical Substances» (FSUE «IREA»), Moscow, Russia.

Research associate, graduate student

sadovskaya-n@mail.ru

The great interest of the crown-containing azomethines caused the possibility of using as a highly selective sensors for metal cations, effective corrosion inhibitors, anti-oxidant additives for oils and fuels. Furthermore, imines and their complexes are biologically active compounds. Imines derivatives can be the part of a number of drugs and plant protection products.

We prepared azomethine derivatives benzo-15-crown-5 prepared by condensation the appropriate pyridinecarboxaldehyde and 4-aminobenzo-15-crown-5:



The evaluation of the antitumor activity of the compounds was obtained. The study was carried out on human tumor cell lines: HCT-116; LNCap; PC-3; A549; MCF-7; Mel Kor; Jurkat.

Analysis was carried out in FSUE IREA Shared Research Analytic Center.

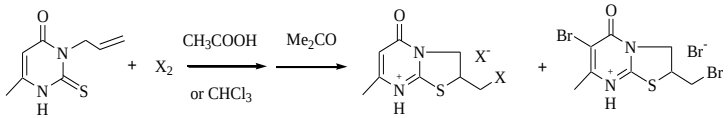
HETEROCYCLIZATION OF 3-ALLYL-6-METHYL-2-THIOURACIL UNDER THE ACTION OF HALOGENS

Saichik A.D., Frolova T.V., Kim D.G.

SouthUral State University,
Chelyabinsk, Russia
Master
saichiknastya-93@mail.ru

Thiazolo[3,2-*a*]pyrimidines have been well studied as immunomodulators, anticancer agents, analgesics, psychotropes, anti-inflammatory and anti-HIV-1 agents [1]. Thiazolo[3,2-*a*]pyrimidinesare formed by heterocyclization reaction of S- and N-substituted derivatives of 2-thiouracils [2].

We have studied the previously undescribed halogenation reaction of 3-allyl-6-methyl-2-thiouracil which is formed due to interaction between N-allylthiourea and acetoacetic easter in MeONa. The structure of 3-allyl-6-methyl-2-thiouracil has been determined by X-ray diffraction method [3]. It has been shown that compound **1** undergoes a heterocyclization reaction with excess of iodine in a chloroform solution with the formation of 2-iodomethyl-7-methyl-5-oxo-2,3,5,6-tetrahydrothiazolo[2,3-*b*]pyrimidinium iodide (**2a**) with the product yield 74%.



Scheme 1. Heterocyclization reaction of 3-allyl-6-methyl-2-thiouracil (1)

The interaction of compound **1** with the equimolar amount of bromine in glacial acetic acid is at once the bromocyclization reaction and the electrophilic substitution on the pyrimidine ring with the formation of the mixture of bromides (**2b**) and (**3**) at the ratio of 3:1.

The structures of the synthesized compounds are proved by the nucleic magnetic resonance method 1H NMR.

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DESIGN AND SYNTHESIS NEW ECDYSTERONE CONTAINED DRUG TO COMBAT ISCHEMIC STROKE

Sarychev G.A.[1], *Budanova U.A.*[1], *Sebyakin U.L.*[1]

[1]Lomonosov Moscow State University of High Chemical Technology (MITHT), Moscow, Russia
Student
sarychevgregor@gmail.com

Ischemic stroke is major problemof modern medicine. It's important to prevent brain injury, and also important to help patient to deal with neuropathological consequences.

In our laboratory we developed structure and synthesis scheme of new drug, contained ecdysterone derivative and peptide fragment (Fig. 1).

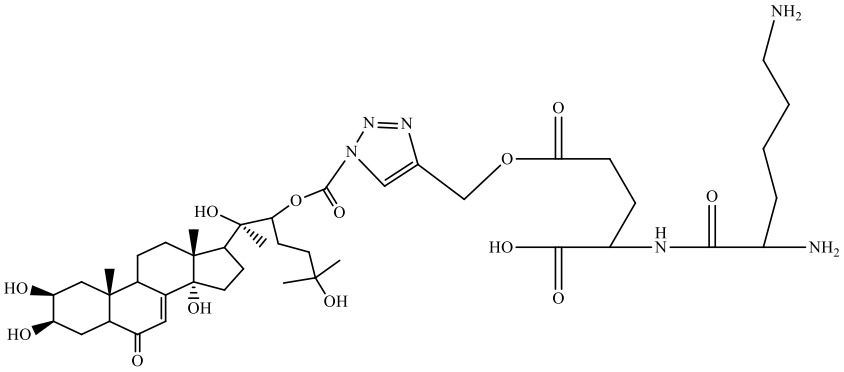


Figure 1.

Data review showed, ecdysterone is substance with strong adaptogenic activity, which increases nonspecific resistance of cells. But it's not soluble in water, that why we need to attach polar fragment such like dipeptide. This was obtained by block-synthesis with Lysine and Glutamic acid. Lysine is nature building block for a lot of proteins, and stimulatestissue regeneration. To connect steroid and peptide parts of molecule we used Azide-Alkyne Huisgen Cycloaddition with copper catalyst, this reaction is used to obtain product with high yield, and give durable triazol linker.

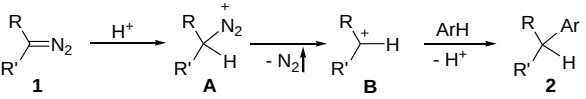
In future, we plan to investigate biological activity of obtained compound.

REACTIONS OF DIAZO-DIESTERS IN SUPERACIDS

Satymov E. T., *Medvedev Yu.Yu.*

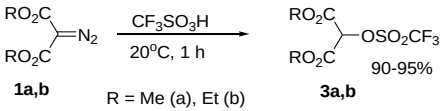
Saint Petersburg State University
Saint Petersburg, Russia
Student
set167@gmail.com

Protonation of diazo-compounds **1** in Bronsted superacids (CF_3SO_3H, FSO_3H) occurs on carbon atom of diazo-group, affording cations **A**. Elimination of nitrogen from these species gives cations **B**, which may interact with arenes, leading to compounds **2**.

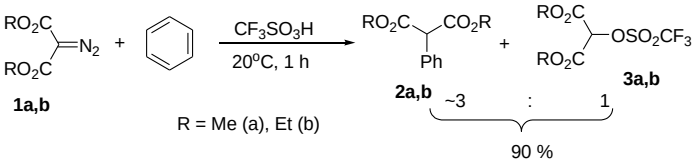


H^+ - Bronsted superacids (CF_3SO_3H, FSO_3H)
conjugated Bronsted-Lewis superacids (CF_3SO_3H-SbF_5, FSO_3H-SbF_5)

We have found that diazo-diesters **1a,b** in neat CF_3SO_3H at 20°C for 1 h gives quantutatively triflates **3a,b**.



Reactions of substrates **1a,b** with benzene in CF_3SO_3H result in formation of mixture of triflates **3a,b** and products of benzene alkylation **2a,b** with predominant part of the latters.



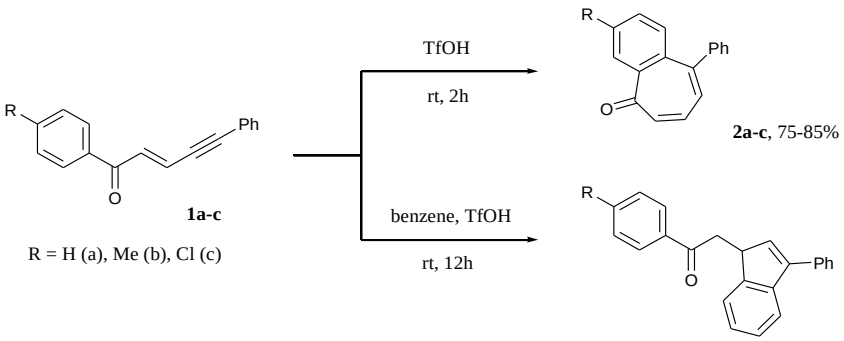
Thus, this transformation of diazo-diesters in superacids may be used as synthetic method for alkylationof arenes.

REACTIVITY OF CONJUGATED ENYNONES UNDER SUPERELECTROPHILIC ACTIVATION CONDITIONS

Saulnier S.A.[1], *Golovanov A.A.*[2]

[1] Saint Petersburg State University
[2] Togliatti State University
Saint Petersburg, Russia
Post Doc
saulnier.steve@gmail.com

Superelectrophilic activation takes place typically via the formation of dicationic species in superacidic media, or by coordination with strong Lewis acids. The high reactivity of these superelectrophiles has been widely used in synthetic transformations involving weak nucleophiles, especially Friedel-Crafts and related reactions with nonactivated or deactivated arenes [1]. Conjugated enynones should be particularly well suited to superelectrophilic activation due to their extended π-system. The reactivity of 1,5-diaryl substituted pent-2-en-3-yn-1-ones**1a-c** in trifluoromethanesulfonic acid (TfOH) is examinedwith and without benzene. Reactions without benzene give cyclisation products **2a-c** with high yields through intramolecular electrophilic aromatic substitution. With benzene, an intermolecular aromatic substitution on benzene proceeds first, followed by intramolecular cyclisation leading to compounds **3a-c**. This work shows that diaryl susbstitued pent-2-en-4-yn-1-ones are promising precursors in the synthesis of benzo[7]annulen**2** and chiral indene derivatives**3**.



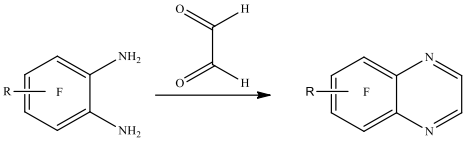
[1] Olah, G. A. and Klumpp, D. A. *Superelectrophiles and Their Chemistry*. Wiley-Interscience, Hoboken, New Jersey, 2008.

NEW FLUORINATED QUINOXALINES AND THEIR FUNCTIONALIZATION BY NUCLEOPHILIC SUBSTITUTION

Selikhova N.Yu.[1],*Makarov A.G.*[1,2], *Makarov A.Yu*[1,2], *Slizhov Yu.G.*[1], *Malkov V.S.*[1], *Zibarev A.V.*[1,2]

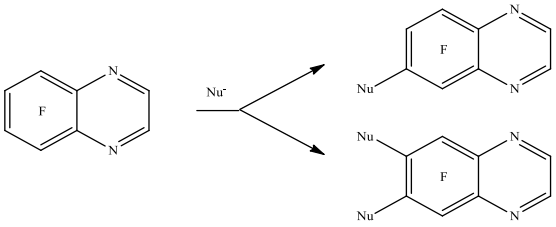
[1]Tomsk State University,
[2]N.N. Vorozhtsov Institute of Organic Chemistry of the Siberian Branch of Russian Academy of Science
Tomsk, Russia
Postgraduate Student
selikhova.n@mail.ru

Quinoxalines (benzopyrazines) play essentially important roles in many fields of chemistry, chemical technology and related disciplines.They are represent one of the most significant groups of aza-aromatics forfundamental organic chemistry and its applications to biomedicine and materials science.
5,6,7,8-Tetrafluoroquinoxaline and its previously unknown deriativeswere obtained[1]by reaction between polyfluorinated 1,2-diaminoarenes and glyoxal (Scheme 1).



Scheme 1. Synthesis of quinoxalines

The reactions 5,6,7,8-tetrafluoroquinoxalinewith somenucleophiles, suchas sodium methoxide and dimethylamine, wascarried out to obtain 5,7,8-trifluoro-6-substituted or 5,8-difluoro-6,7-disubstituted quinoxalines depending on the reaction conditions.



$Nu^- = MeO^-, (CH_3)_2N^-$

Scheme 2. Nucleophilic substitutions

References

[1] Makarov A.G. New fluorinated 1,2-diaminoarenes, quinoxalines, 2,1,3-arenothia(selena)diazoles and related compounds/ A.G. Makarov, N.Yu. Selikhova, A.Yu. Makarov et. al.//Journal of Fluorine Chemistry. – 2014. – Vol 165. – p 123-131

OLIGOMERIZATION OF THE RRM2 DOMAIN OF TDP-43 PROTEIN AT REDUCING CONDITIONS STUDIED BY NMR DIFFUSOMETRY

Shaban A.[1],*Rabdano S.O.*[2]

[1]Faculty of Physics, SPbSU, St. Petersburg, Russia
[2]Laboratory of Biomolecular NMR, SPbSU, St. Petersburg, Russia
Student
shaban-a@mail.com

TAR DNA-binding protein 43 (TDP-43) is 414-a.a.protein, which plays an important role in RNA control and transcription [1]. TDP-43 constitutes a major component of the inclusion bodies formed in the brains of the patients with frontotemporal lobar degeneration (FTLD) [2]. Inclusion bodies are largely comprised of the C-terminal fragments (CTF) of TDP-43 with molecular weight 20-25 kDa (so-called "TDP-25") [3,4].

As it turns out, formation of CTF is a consequence of proteolytic cleavage within theRNA-recognition motif (RRM2) domain of TDP-43. RRM2 is a 65-residue globular domain with known structure (PDB ID 1WF0, 3D2W, 4BS2). Proteolytic cleavage within RRM2 leads to the loss of Nuclear Localization Signal located at the N-terminus of TDP-43 and exposure of Nuclear Export Sequence encoded in the RRM2. Consequently, TDP-25 are exported from nucleus into the cytoplasm, where they form the inclusion bodies. We hypothesize that proteolytic cleavage in RRM2 occurs as a result of a transient unfolding caused by oxidative stress.

Our goal is to determine the oligomerization status of the domain RRM2 under reducing conditions. In order to do that we determined the diffusion coefficient for RRM2 using a pulsed-field gradient NMR (pulse sequence – Stimulated Echo) for protein dissolved in buffer, which contained reducing agent — dithiothreitol. The diffusion coefficient was $1.21 \cdot 10^{-8} m^2/s$. Then we determined the molecular mass of the diffusing particle using modified Stocks-Einstein formula. Average molecular mass of diffusing particles is (20 ± 2) kDa.

Obtained average molecular mass of diffusing particles suggests that under reducing conditions some part of RRM2 molecules interacts noncovalently, what causes formation of RRM2 oligomers.

Studies were performed at the Centre for Magnetic Resonance, Center for Thermogravimetric and Calorimetric Research and Center for Molecular and Cell Technologies, St. Petersburg State University, Research Park.

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MOLECULAR RECOGNITION IN EXPLORINGPANCREATIC BETA-CELL FUNCTION AND DIABETES

Sharoyko V.V., *Tennikova T.B.*
Saint Petersburg State University, Institute of Chemistry
Saint Petersburg, Russia
Research fellow
sharoyko@gmail.com,v.sharoyko@spbu.ru

Highly specific molecular recognition represents one of the fundamental principles of the function of living systems and causes all the most important molecular biological processes, such as hormone-receptor interactions, matrix biosynthesizes, enzymatic reactions, transmembrane transport of substances, etc. In a broader sense, molecular recognition is a key concept of supramolecular chemistry, representing a process of targeted binding, where one molecule called as a receptor interacts with high affinity and selectivity with another molecule called as a ligand. As a consequence, a biological response is initiated [1]. Above described complex events occur in pancreatic β-cells, which release hormone insulin. Insulin is a key anabolic hormone controlling carbohydrate metabolism in the body. The deficiency in insulin causes a diabetes mellitus.

Many compounds with imidazoline moiety are effective stimulators of insulin release in pancreatic β-cells. Imidazoline compound BL11282 (5-chloro-3-(4,5-dihydro-1H-imidazol-2-yl)-2-methylindole hydrochloride; **Fig. 1**) is potentially new therapeuticagent to be possibly used for treatment of Type 2 Diabetes (T2D). The molecular recognition is a key event in signal-transduction pathways in the mechanism of BL11282 insulin-releasing effect. In β-cells BL11282 recognizes a number of targets, which are important for insulin release (**Fig. 1**).The cAMP-GEFII•Rim2 (cAMP-regulated protein complex) is involved in BL11282-stimulated insulin release. The insulinotropic effect of BL11282 involves the release of arachidonic acid by Ca^{2+}-independent phospholipase A_2($iPLA_2$) and its metabolism to epoxyeicosatrienoic acids through the cytochrome P450 pathway [2].

If process of molecular recognition is perturbed, a pathological condition in the body, such as diabetes, might be developed. A single mutation (G>Aat chromosome 6) recently identifiedin the human *TFB1M* gene, which was associated withthe risk of T2D [3].TFB1M is the transcription factor B1, mitochondrial,also known as mitochondrial S-adenosylmethionine-6-N′,N′-adenosyl(rRNA)-dimethyltransferase 1,(**Fig. 2**). In mitochondria, TFB1M dimethylates two adjacent adenine residues in the hairpin loop at the 3′ end of 12S rRNA (**Fig. 2**); this covalent modification is a mandatory step in the function of the small subunit of the mitochondrial ribosome.

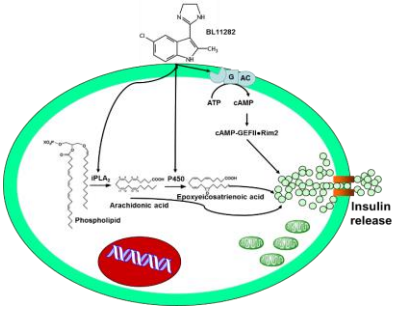

Fig. 1. Molecular recognition is a key event in the mechanism of action of BL11282 in pancreatic beta-cells.

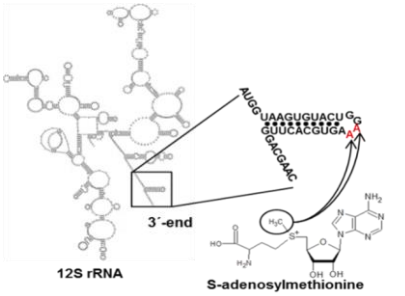

Fig. 2. Molecular recognition in 12S rRNA complexis controlled by TFB1M-dependent dimethylation of adjacent adenine residues.

Deficient 12S rRNA methylation results in perturbation of proper molecular recognition between ribosome subunits, leading to severely impaired synthesis of mitochondrial DNA-encoded proteins and therefore decreased ATP synthesis via oxidative phosphorylation. As a consequence, insulin secretion from pancreatic β-cells is decreased and further T2D is developed [4].

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Acknowledgements

Support was received from Saint Petersburg State University (project numbersare 12.38.220.2015 and 12.50.1193.2014), EFSD, Crafoordska, Knut and Alice Wallenberg, Lars Hiertas Minne, Söderberg, O.E. och Edla Johansson, and Albert Påhlsson foundations, and The Swedish Research Council.

SYNTHESIS OF 1,1-DICYCLOPROPYL- AND TRICYCLOPROPYLHYDRAZINES

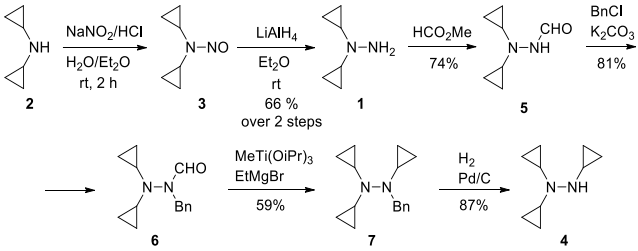
Shestakov A.N.[1], *Kuznetsov M.A*[1].

[1]Saint Petersburg State University,
Saint Petersburg, Russia
Postgraduate Student
shestakov@chemomsu.ru

Hydrazine derivatives display a wealth of biological activities[1] and a combination of hydrazine and cyclopropyl fragments –privileged scaffolds in library design and drug discovery – is very promising towards new pharmaceutically active lead compounds. No wonder there are about 30 patents for pharmaceutical applications of different acyl and alkyl derivatives of mono- and 1,2-dicyclopropylhydrazines[2]. Herein we would like to report synthesis of previously unknown 1,1-dicyclopropyl- and tricyclopropylhydrazines.

At the onset of our work 1,1-dicyclopropylhydrazine **1** was prepared in two synthetic steps from dicyclopropylamine **2** according the "classical way": nitrosation of dicyclopropylamine followed by the reduction of N-nitroso-dicyclopropylamine **3** with $LiAlH_4$. After that, tricyclopropylydrazine **4** was obtained in an overall four-step sequence featuring the de Meijere – Chaplinski modification of the Kulinkovich reaction as a key step – introduction of the additional cyclopropyl ring (Scheme 1).

Scheme 1. Synthesis of 1,1-diyclopropyl- and tricyclopropylhydrazines



Reactions of 1,1-dicyclopropylhydrazine **1** with typical carbonyl compounds were investigated. Our current efforts are focused on the developing synthetic routes to tetracyclopropylhydrazine – the last unknown member of the cyclopropylhydrazine family.

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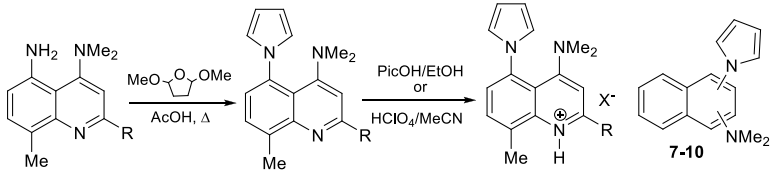
DIMETHYLAMINO NAPHTHALENE AND QUINOLINE DERIVATIVES CONTAINING A PERI-POSITION PYRROLYL MOIETY

Shmoilova E.A., *Pogosova O.G.*
Scientific adviser: *Dyablo O.V., Pozharskii A.F.*

Department of Organic Chemistry, Southern Federal University
Rostov-on-Don, Russia
Postgraduate student
haloinreverse@inbox.ru

First *peri*-dimethylamino(pyrrol-1-yl)quinoline derivatives **3** ,**4** were synthesized by Klausson-Kaas reaction of 5-aminoquinolines **1**, **2** to study a possibility of *NH-π* type intramolecular H-bonding formation. They are pyrrolyl analogs of "quinoline proton sponges"[1,2].



1, 2 **3, 4** **5, 6**

R = Me (**1, 3, 5**), NMe_2 (**2, 4, 6**); X= ClO_4^- (**5**), $PicO^-$ (**6**)

1-pyrrol-1-yl, 8-NMe_2 (**7**); 1-pyrrol-1-yl, 5-NMe_2 (**8**); 1-pyrrol-1-yl, 2-NMe_2 (**9**); 2-pyrrol-1-yl, 1-NMe_2 (**10**)

In ^{1}H NMR spectra of compounds **5**, **6** *NH*-protons resonate as broad singlets at ~ 9.5 and ~10.3 ppm, respectively, rather indicate protonation of *aza*- than *NMe_2*- group. X-ray structural analysis of the quinoline (**4**) showed that in the case of protonation of 4-*NMe_2* group intramolecular H-bonding between the nitrogens is more likely formed rather than *NH-π* type one. Besides, 1-(8-dimethylaminonaphth-1-yl)pyrrole (**7**) and its isomers (**8**-**10**) were obtained. In contrast to the 1,8-isomer **7**, which decomposes under the acid action, compounds **8**-**10** give stable salts with the localization of the proton, as would be expected, on the *NMe_2* group. X-ray analysis of 1-(5-dimethylaminonaphth-1-yl)pyrrole picrate showed that the proton is located on the 5- *NMe_2* group (*N-H* 0.88 Å), and the intermolecular hydrogen bonding is carried out not with the participation of the pyrrole ring, but with one of the oxygen atoms of the counterion (*O...H* 1.88 Å).

References

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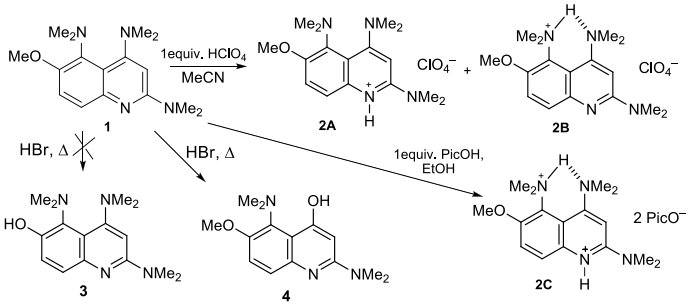
SYNTHESIS AND SOME PROPERTIES OF 6-METHOXY-N^2,N^2,N^4,N^4,N^5,N^5-HEXAMETHYLQUINOLINE-2,4,5-TRIAMINE

Shmoilova E.A., Savchenko A.O.
Scientific adviser: *Dyablo O.V., Pozharskii A.F.*
Department of Organic Chemistry, Southern Federal University
Rostov-on-Don, Russia
Postgraduate student
haloinreverse@inbox.ru

The first representative of methoxy-substituted quinoline proton sponges[1,2] - 2,4,5-tris(dimethylamino)-6-methoxyquinoline (**1**) was synthesized in five steps starting from *p*-anisidine. Measured in CD_3CN by competitive method basicity of key triamine **1** (p*K*a 18.8) is somewhat higher than that for 1,8-bis(dimethylamino)naphthalene (p*K*a, 18.6[3]).



Treatment of slight excess of the base **1** with $HClO_4$ led to monoperhlorat. According to the ^{1}H NMR spectrum (CD_3CN) the salt exists as a pair of cation **2A** and **2B** (ratio 13:87). *Peri*-NMe_2 chelated proton (form **2B**), resonates at 17.98 ppm, while the proton bound to the pyridine nitrogen (form **2A**), gives a signal at 9.49 ppm. Interaction of the base **1** with one equiv. of PicOH in EtOH has unexpectedly led to the formation of dipicrate **2C**. Only one signal of *NH*-proton at 16.96 ppm is visible in the ^{1}H NMR spectrum in CD_3CN, the second *NH*-proton is not seen, perhaps, due to fast exchange between the *aza*-group and picrate anion. Treatment of quinoline **1** with HBr resulted to formation of compound **4** instead of the expected 6-hydroxyquinoline **3**.

References

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[2] Shmoilova, E. A.; Dyablo, O. V.; Pozharskii, A. F. *Chem. Heterocycl. Compd.* **2013**, *49*, 1308.
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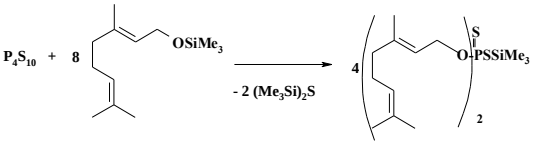
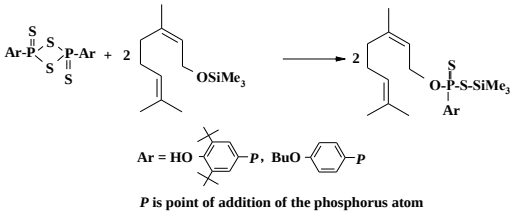
TRIMETHYL SILYL DERIVATIVES OF DIPRENOID ALCOHOLS IN DITHIOPHOSPHORYLATION REACTIONS

Shumatbaev G.G., Terenzhev D.A., Nizamov I.S., Cherkasov R.A.,NizamovI.D.
Kazan (Volga region) Federal University
Student
isnizamov@mail.ru

Isoprenoids and their functionalized derivatives are a prospective class of non-toxic bioregulators for the creation of new drugs. Over the past few years we have been involved in developing new synthetic routes to dithiophosphorylated derivatives of diprenoid alcohols. Compounds prepared in dithiophosphorylation reactions may be used as source for obtaining new fungicidal and bactericidal compounds. To avoid the formation of mixtures of organophosphorus products in the reactions of diprenoid alcohols with phosphorus sulfides, we have applied the silyl protection of the hydrogen atom of hydroxyl group of alcohols. Tetraphosphorus decasulfide has brought about to react with S-trimethylsilyl derivatives of geraniol or nerol in benzene at 55ºC for 1 h with the formation of S-trimethylsilyl esters of O,O'-bis(dienyl)dithiophosphoric acids.



S-Trimethylsilyl derivatives of geraniol or nerol were readily dithiophosphorylated by 2,4-diaryl-1,3,2,4-dithiadiphosphetane-2,4-disulfides in benzene at 40-45ºC for 2-4 h to form S-trimethylsilyl O-dienyl aryldithiophosphonates.



The reaction of racemic linalool with 2,4-diaryl-1,3,2,4-dithiadiphosphetane-2,4-disulfides in benzene at 55ºC for 2 h have been found to bring about the formation of S-trimethylsilyl O-3-(3,7-dimethyl-1,6-octadienyl) aryldithiophosphonates.

Acknowledgements. The study was performed with financial support of the Russian Foundation for Basic Researches (Grant No. 14-03-00897-a).

SYNTHESIS OF INDOLES LINEARLY LINKED TO THE 3-POSITION WITH SELENADIAZOLE AND THIADIAZOLE RINGS

Shustova E.A., Ionova V.A., Velikorodov A.V.

Astrakhan State University
Astrakhan State University, Russia
Student
morfei1990@rambler.ru

Previously, we have demonstrated the possibility of obtaining selenadiazole and thiadiazole with phenylcarbamate fragmen t[1]. In furtherance of thosestudies, we obtained thiosemicarbazone(I) and semicarbazone(II) of methyl 3-acetyl-5-[(methoxycarbonyl)amino]-2-methyl-1*H*-indole-1-carboxylate [2] and explored their heterocyclization into the corresponding1,3,4-oxadiazole and 1,2,3-selenadiazole derivatives. It is found that thiosemicarbazone ofindole(I)by refluxingin acetic anhydridefor 4 hoursis converted intoacorrespondingindole with oxadiazole moietyatC3 atomin 81% yield.

I III

The oxidation ofindolesemicarbazone(II)with selenium dioxidein glacialaceticacidwas obtainedmethyl 5-(methoxycarbonylamino)-2-methyl-3-(1,2,3-selenadiazole-4-yl)-1*H*-indole-1-carboxylate (IV)with 78%yield.

II IV

The structure ofcompounds(III, IV)is provedusing IR,^{1}H-NMR spectroscopy.

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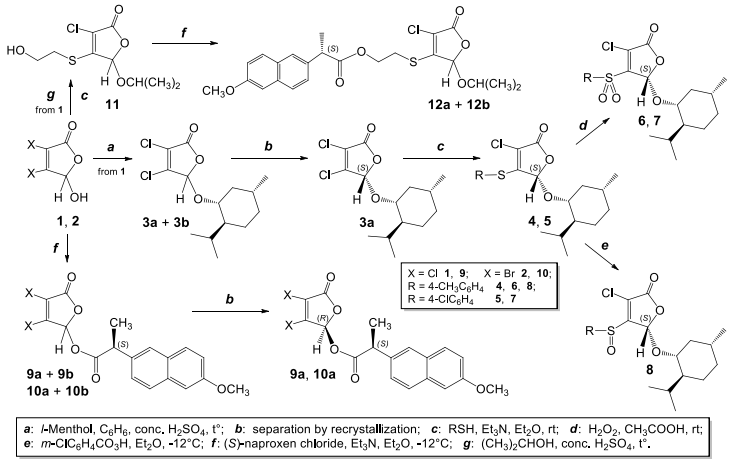
[2] Velikorodov A.V., Mochalin V.B.*Zh. Org. Khim*,**1998**, *34*

NEW CHIRAL 2(5*H*)-FURANONE DERIVATIVES POSSESSING *L*-MENTHOL AND *S*-NAPROXEN MOIETIES

Sibgatullina R.R., Latypova L.Z., Chmutova G.A., Kurbangalieva A.R.

Kazan Federal University
Kazan, Russia
Student
Regina.Sibgatullina@mail.ru

The 2(5*H*)-furanone subunit characterizes many naturally occurring and medicinally important compounds with diverse biological activities such as antifungal, antibacterial and antiinflammatory. Most biological molecules and pharmaceutical targets exist in enantiomerically pure form. In this study, the pharmacophore units of *l*-menthol and *S*-naproxen (a non-steroidal anti-inflammatory drug) as chiral auxiliaries were introduced into the lactone ring in order to obtain the optically pure 2(5*H*)-furanone derivatives. We have allowed mucohalic acids **1** and **2** to react with *l*-menthol and *S*-naproxen and isolated pure diastereomers **3a**, **9a** and **10a** from the obtained diastereomeric mixtures. Thiilation of furanone **3a** and subsequent oxidation reactions of thioethers **4**, **5** result in the formation of enantiomerically pure sulfones **6**, **7** and sulfoxide **8**. We have developed also the three-step synthesis of thioether **12** that combines both 2(5*H*)-furanone and *S*-naproxen moieties. Novel furanone based compounds have been characterized in detail by IR, NMR spectroscopy and single crystal X-ray diffraction.



The work is performed according to the Russian Government Program of Competitive Growth of Kazan Federal University

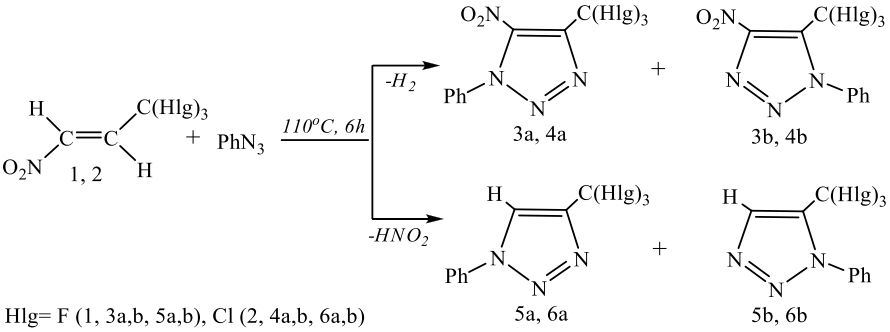
1-NITRO-3,3,3-TRIFLUORO(CHLORO)PROPENES IN THE REACTION WITH PHENYLAZIDE

Slobodchikova E.K.[1], *Egorova A.A., Anisimova N.A., Kuzhaeva A.A.*[2]
[1]Herzen State Pedagogical University of Russia
48 Moika emb., St. Petersburg, 191186, Russia
[2]Saint Petersburg State Technological University of Plant Polymers
4 Ivana Chernih str., St. Petersburg, 198095, Russia

According to the referenced at a nitro alkenes that are functionalized by trihalogenmethyl groups are perspective synthons of the modern organic synthesis and they are interesting for the obtaining of various types of organic compounds including carbo- and heterocyclic systems [1] which are potentially biological active substances [2].

One of the methods of functionalized heterocycles obtaining is the 1,3-dipolar cycloaddition reaction with participation of nitroalkenes as dipolarophiles that consist a trihalogenmethyl group at β-position in their structure. The examples of the interaction of 1-nitro-3,3,3-trifluoro(chloro)propenes with the representatives of nitrones are known in the reference [3,4]. Note that the said dipolarophiles have not been involved in reactions with diazo compounds and azides hitherto.

The interaction between 1-nitro-3,3,3-trifluoro(chloro)propenes (1,2) and phenylazide is investigated in this paper. It have been shown that the reaction proceeds at reflux in toluene (6 h) and thereaction finishes with formation of the isomeric nitrotriazoles (3a,b, 4a,b) which differ among themselves by the reciprocal location of the phenyl substitute regarding the trihalogen group.



Besides these adducts (3a,b, 4a,b), triazoles (5a,b, 6a,b) which do not consist the nitro group have been isolated (by column chromatography) from the reaction mixture. Obtainedtriazoles (3a,b-6a,b) are the result of intramolecular

processes of denitration and dehydration of triazolines which are formed initially.

The structure of obtained compounds (3a,b-6a,b) is proved by modern physical-chemical research methods and the formation of these compounds does not contradict with reference data on such adducts obtaining in reaction of 1,3-dipolar cycloaddition with the same structure type nitroalkenes which contain CO_2R and $P(O)(OR)_2$ groups instead of the $C(Hlg)_3$ substitute in their structure [5,6].

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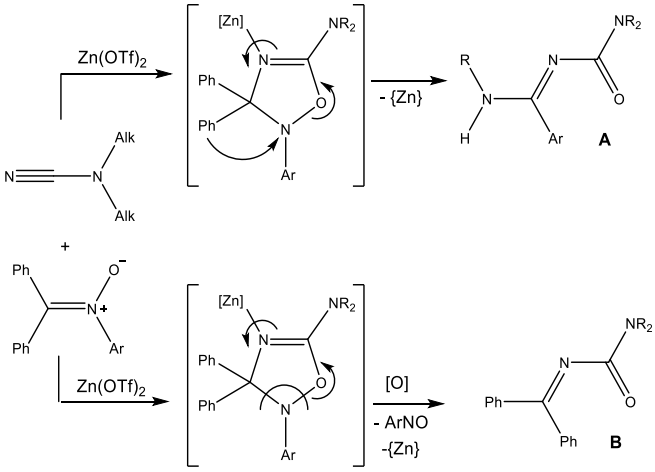
ZINC PROMOTED REACTION OF CYANAMIDES WITH NITRONES: SUBSTITUTED UREAS FORMATION

Smirnov A.S., Butukhanova E.S.
Saint Petersburg State University
Saint Petersburg, Russia
Postdoc
Andrewsmir@yandex.ru

Dipolar cycloaddition (DC) is very useful reaction for construction heterocyclic molecules. Thus, reaction of substituted cyanides and isocyanides with different dipolarophiles leads to broad range of heterocyclic systems [1]. In the framework of our current project «CN triple bond activation to nuclephilic reactions and dipolar cycloaddition by metal salts» we study DC to activated RCN substrates. Recently [2] it was demonstrated that reaction of ketonitrones $Ph_2C=N^{(+)}(Alk)O^{(-)}$ with dialkylcyanamides $NCNR_2$, promoted by zinc(II), resulted in formation of 1,3-dihydrooxadiazoles in mild conditions

with good yields. In the current report we will discuss the dependence of products of the reaction on the structure of starting ketonitrone $Ph_2C=N^{(+)}(R')O^{(-)}$ (R' = Alk, Ar). *N*-Alkyl ketonitrones react with cyanamides $NCNR_2$ with formation cycloadduct otherwise *N*-aryl ketonitrones give linear products – substituted ureas (Scheme).



Scheme. Zn-promoted reaction of *N*-aryl kenonitroes with cyanamides.

Beside major product, viz. urea type **A**, minor product **B** was isolated. Formation of **B** can be explained by oxidation cleavage of hypothetical cycloadduct. Mechanism of the reactions and product structural features will be discussed in the report.

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(2) Abstracts book of conference "Advances and Problems of modern chemistry" Saint Petersburg, Saint Petersburg State university 10-13 Nov 2014

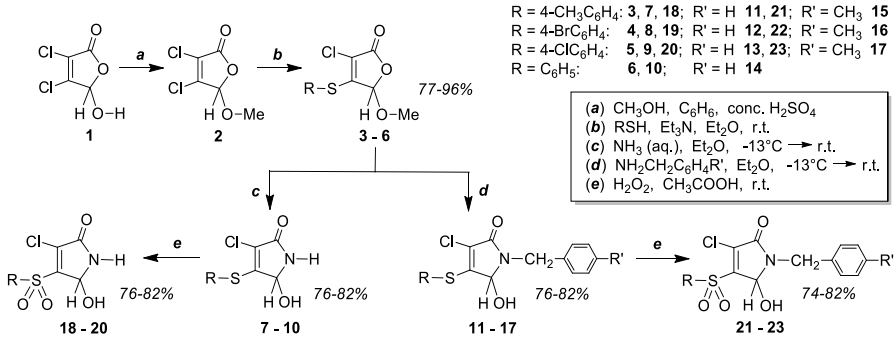
Acknowledgments
The authors express their gratitude to SPBU for postdoc fellowship (grant 12.50.1557.2013). Research work was carried out in collaboration with resource centers of Saint Petersburg University Research Park (Center for Magnetic Resonance, the Center for Chemical Analysis and Materials Research, the Research Center for X-ray Diffraction Studies, and the Center of Thermal Analysis and Calorimetry)

SULFONES OF THE 3-PYRROLIN-2-ONE SERIES: SYNTHESIS AND BIOLOGICAL ACTIVITY

Smirnov I.S., Khabibrakhmanova A.M., Latypova L.Z., Trizna E.Y., Kayumov A.R., Kurbangalieva A.R.

Kazan Federal University
Kazan, Russia
Student
smirnov453@gmail.com

Nitrogen-containing heterocycles attract considerable attention of researchers due to the presence among them of a large number of physiologically active substances and potential drugs. In this study we developed a facile approach to the preparative synthesis of novel sulfonyl derivatives of 5-hydroxy-3-pyrrolin-2-one **18**–**23** from commercially available mucochloric acid **1** based on the following steps: 1) thiilation of 3,4-dichloro-5-methoxy-2(5*H*)-furanone **2** in the presence of triethylamine, 2) ammonolysis and amination reactions of thioethers **3**–**6**, 3) oxidation of 3-pyrrolin-2-one thioderivatives **7**–**17** to sulfones with excess 33% hydrogen peroxide in acetic acid at room temperature.



The ability of the synthesized compounds **1**–**23** to inhibit the growth and the biofilm formation by various bacteria was studied. The minimal concentrations of sulfones **18**–**23** required for the complete inhibition of growth and for the biofilm formation by *Staphylococcus aureus* and *Staphylococcus epidermidis* were determined. It is shown that these furanones do not possess mutagenic and cytotoxic activity at concentrations which inhibit the growth of bacteria and biofilm formation.

This work was performed under the Russian Government Program of Competitive Growth of Kazan Federal University

ENCAPSULATION OF MACROMOLECULAR BIOTECHNOLOGICAL PRODUCTS (PROTEINS AND POLYNUCLEOTIDES) INTO THE BIODEGRADABLE POLYMER PARTICLES

Sobinina I.M., *Korzhikov V.A.*
Saint Petersburg State University
Saint Petersburg, Russia
Student
yulia.sobinina@yandex.ru

The study of macromolecular biotechnological products (proteins and polynucleotides) entrapment into the biodegradable polymer particlesis of significant interest because it allows solving of various biochemical and pharmaceutical problems. One of such issues is the development of systems for targeted delivery of bio macromolecules into diseased tissues and organs. The formation of such polymer systems could be performed via double emulsion method. This method includes the primary emulsification of an aqueous solution of the protein (or other biomolecule) in the oil phase, which represents the solution of biodegradable aliphatic polyester in volatile organic solvent (dichloromethane, ethyl acetate, acetone) and further formation of double "water in oil in water" emulsion with application of the excess of aqueous phase, containing polymer stabilizer. Then the gradual removal of organic solvent occurs by evaporation or diffusion mechanism. This processes result in the formation of a suspension of polymer particles, which contain the encapsulated protein into their internal cavity.

However, due to the fact that the effect of the w/o/w encapsulation procedure on protein stability and structure has only been studied on occasion, many issues are not clear. The main difficulty of this method is to determine the conditions which allow one to keep the structure of the double emulsion, specifically water in oil in water and prevent the association of internal and external aqueous phases. Such a phase merger inevitably leads to a decrease in encapsulation efficiency (EE). Therefore, this research was aimed at optimizingthe conditions for obtaining biodegradable particles by the double emulsionto increase the EE. The protein release kinetics and its dependence on polyester structure were also of particular interest.

In this work we have studied the influence of experimental conditions on encapsulation efficiency of model protein - bovine serum albumin (BSA). For this purpose we have synthesized polylactic acid (PLA, MW = 15 000) copolymerof lactic and glycolic acids (PLGA, MW = 20 000), polypentadecalactone (PPDL, MW = 24 000), and polycaprolactone (PCL, MW = 21 000). The stabilizers choice and organic solvent removal mechanism

were tuned in order to maximize the BSA EE. Also the concentration of stabilizer and pH of second water phase were varied in order to obtain a stable emulsion and microparticles with the smallest size. The obtained particles were separated by centrifugation and the concentration of free BSA in the supernatant was determinedby the Lowry method. Moreover BSA release kinetics from the obtained particles was studied. It was shown that protein release is affected by chemical composition of polyester, which was applied for encapsulation.

This research has also discovered the influence of encapsulation on the activity of enzyme L-chymotrypsin, which was encapsulated in different polymers: PLA, PCL, PPDL with various solvents, stabilizing agents (lecithin+SDC, DMAB+SDS), via the measurement of Michaelis-Menten constant. The encapsulation efficiency of L-chymotrypsin in the microspheres has also been evaluated. Other goal of this work was to test the biological activity of enzyme after in vitro release. The release conditions which minimize the activity loss of L-chymotrypsin were found.

This work was supported by Russian Scientific Foundation (agreement #14-50-00069).

PHOTOCHEMICAL REACTIONS OF KYNURENIC ACID WITH AMINO ACIDS AND EYE LENS PROTEINS

Sormacheva E.D.[1,2], *Zelentsova E.A.*[1,2], *Sherin P.S.*[2], *Duzhak T.G.*[2], *Tsentalovich Yu.P.*[1,2]

[1]Novosibirsk State University,
[2]International Tomography CenterSB RAS, Novosibirsk, Russia
Student
kate.sormacheva@gmail.com

Cataract is the most common form of the blindness in the world. Solar UV radiation is traditionally considered as one of the factors for the cataract initiation and progress. Lens proteins, crystallins, have no turnover during the lifespan of an individual and they constantly accumulate post-translational modifications (PTMs). Some of these PTMs could be induced by the reactions between crystallins and kynurenines (KNs), intrinsic chromophores of the lens. KNs act as UV filters in the eye lens but they form reactive triplets, which could initiate the undesirable reactions. Though the yield of KN triplets is low, such reactions could result in significant protein modification during the individual lifespan. The goals of this work are: (i) to study the quenching reactions of the triplet state of kynurenic acid (KNA) with amino acids and crystallins and(ii) to analyze the modifications of crystallins resulting from photo-induced reactions.

The quenching of KNA triplets by amino acids proceeds via electron transfer mechanism with the formation of corresponding radicals. Tryptophan and tyrosine are the most effective quenchers among the studied amino acids. Reactions of KNA triplets with alpha and beta crystallins results in the formation of both tryptophan and tyrosine radicals. Only the signal from tyrosine radicals was observed in the case of reactions with gamma-crystallin.

The formation of large molecular weight aggregates is the major outcome ofthe photolysis of aqueous solutions of β- and γ-crystallins (in native and denatured states) in the presence of KNA under anaerobic conditions. Another modification observed for all crystallins is the formation of new absorption band with maximum at ca. 325 nm corresponding to products, which fluoresce in the near UV region. Mass spectrometric analysis has showna monotonicdegradation of crystallin monomers and tyrosine residues during the photolysis. The obtained results show that the photo-induced modifications of crystallins result in significant changes of the properties of these proteins that, in turn, couldplay an important role in the cataractogenesis.

Acknowledgements.This work was supported by RSF (14-14-00056) and by RFBR (14-03-31189, 14-03-00027).

MACROPOROUS MOLECULARLY IMPRINTED POLYMER MONOLITHS FOR THE HPLC ANALYSIS OF MACROLIDE ANTIBIOTICS

Stepanova M.A.[1], *Vlakh E.G.*[1,2], *Tennikova T.B.*[1,2]

[1]Saint Petersburg State University, Institute of Chemistry, St. Petersburg, Russia
[2]Institute of Macromolecular Compounds Russian Academy of Sciences
St. Petersburg, Russia
Postdoc
maristepanova@gmail.com

The development of artificial receptors represents one of the actual directions of the modern biomedical chemistry. The simple and effective tool allowing the solvation of this task is the molecular imprinting represents. The approach is based on formation of a molecular fingerprint of the target compound (template) in the polymer matrix [1].

Erythromicin (ERY) is an antibiotic of the macrolide class. Macrolide antibiotics are the safest group of drugs with a broad spectrum of antimicrobial activity. Therefore, ERY is most widely used in human and veterinary medicine. The widespread administration of this drug in veterinary medicine represents a potential risk, because its residues may persist in the animal body and may result in the development of drug-resistant bacterial strains or allergies. The existing analytical techniques to determine the ERY are very laborious and difficult for sample preparation [2].

Molecularly imprinted polymer utilized as artificial receptor for ERY may be used for the highly selective separation and for the analysis of ERY and its analogues directly into biological substrates.

In this work, a series of new macroporous monolithic imprinted HPLC columns with different content of molecular prints of ERY were prepared by *in situ* thermo-initiated polymerization using 2-hydroxyethyl methacrylate as a functional monomer, ethylene glycol dimethacrylate as a cross-linker, 1-decanol–toluene as a porogenic solvent and 2,2'-azobisizobutironitrile as a initiator. The developed stationary phases were characterized by number of parameters such as average pore size, porosity, specific surface area, permeability. The surface morphology of polymers obtained were studied by scanning electron microscopy. The retention of ERY on the developed imprinted columns were compared with the standard non-imprinted sorbent and imprinting factors were calculated.

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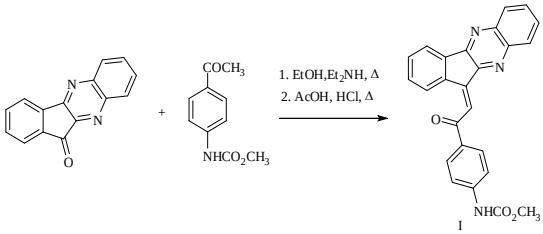
This work was financially supported by grant of Russian Science Foundation (№ 14-13-00940).

SYNTHESIS OF DIHYDROSPIRO[INDENO[2,1-b]QUINOXALIN-11,3′-PYRAZOLE WITH CARBAMATE GROUP

Stepkina N.N., *Velikorodov A.V.*

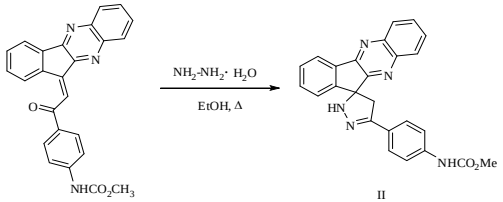
Astrakhan State University
Astrakhan State University, Russia
Student
nadenka_stepkin@mail.ru

By aldol-crotoniccondensation of 11*H*-indeno[1,2-*b*]quinoxalin-2-one with methyl*N*-(4-acetylphenyl)carbamate in absoluteethanol in the presenceof diethylamineandsubsequent heatingin glacialAcOHin the presence ofhydrochloricacidwas prepared (*E*)-methyl4-(2(11-*H*-indeno[2,1-*b*]quinoxalin-11-yliden)acetyl)phenylcarbamate(I)in 90% yield.



I

In order to obtainspiro-fusedindeno[1,2-*b*]quinoxaline withpyrazoleringthe interaction ofthe chalcone(I)withhydrazinehydratewas studied. It is founded, that the reactionaffordsto the formation of methyl4-(2′,4′-dihydrospiro[indeno[2,1-*b*]quinoxalin-11,3′-pyrazol]-5′-yl)phenylcarbamate (II) in97% yield.



II

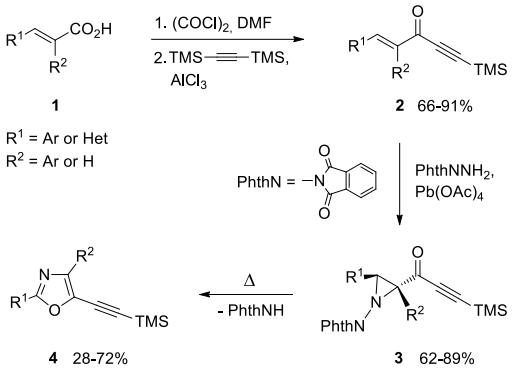
The structure ofnew compoundsis provedusing IR, ^{1}H, ^{13}C NMR spectroscopy.

SYNTHESIS OF 5-(TRIMETHYLSILYLETHYNYL)OXAZOLES FROM DIVERSELY SUBSTITUTED ACRYLIC ACIDS

Stukalov A.Yu., Pankova A.S., Kuznetsov M.A.

Saint Petersburg State University,
Saint Petersburg, Russia
Postgraduate Student
alexstukal@rambler.ru

An oxazole scaffold occurs in a number of synthetic bioactive molecules and natural compounds [1]. The possibility of an easy functionalization of the oxazole ring is important for the construction of complex structures based on it. In this respect, a terminal triple bond offers a wealth of practical synthetic transformations. It is well known, that the Sonogashira reaction is successfully used for introducing the acetylenic moiety into (hetero)aryl rings, but applying this strategy for the synthesis of 5-alkynyloxazoles has been limited so far because of the commercial inaccessibility of the starting halogeno- or triflate heterocyclic electrophiles. This prompted us to develop a novel synthetic route to 5-alkynyloxazoles. Bis(trimethylsilyl)acethylene and diversely substituted acrylic acids **1** are used as the starting materials for the preparation of the enynones **2**. Oxidative addition of N-aminophthalimide to these ketones provides the key 2-acylaziridines **3** that are further utilized in the thermal ring expansion to afford the target oxazoles **4**. The available starting materials and only three simple steps make our method quiteattractive. Last but not the least, the protective TMS group can be easily removed from the ethynyl substituent and it allows to perform further useful transformations.



Picture 1. Synthesis of 5-(trimethylsilylethynyl)oxazoles

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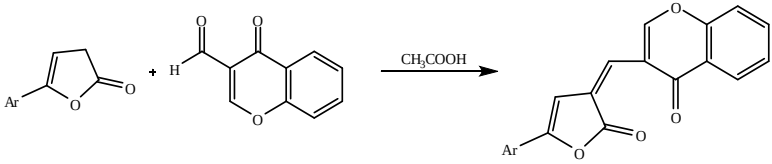
The authors thank theRussian Scientific Fund (research grant 14-13-00126) for thefinancial support.

5R-3*H*-FURAN-2-ONES IN THE SYNTHESIS OF NITROGEN HETEROCYCLES

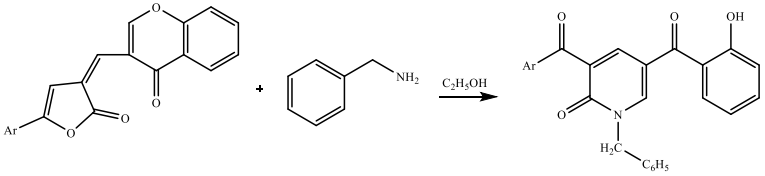
Stulova E.G.[1], *Osipov A.C.*[2], *Yegorova A.Yu.*
Saratov State University of N.G. Chernyshevsky (SSU)
Saratov, Russia
Student
evgenia257@bk.ru

Arylmethylene derivatives of 3*H*-furan-2-one are multifunctional and promising class of heterocyclic compounds. Introduction various aromatic and heterocyclic substituents at the C-3 position of heterocycle significantly expands the range of the synthetic possibilities of these compounds, making them attractive for studying many aspects of theoretical and applied organic chemistry.

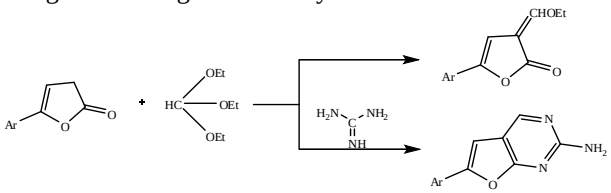
We developed amethod for the synthesis of 3-arylmethylene-3*H*-furan-2-ones, including in their content achromone fragment, giving riseadditional reaction centers and opens new opportunities for thefurther study of obtained compounds,especially the creation of practically important substances, including modern medicine. The interaction of3*H*-furan-2-one with 3-formylchromonewasconducted at an equimolar ratio of the reactants in acetic acid for 20-25 minutes.



The reaction of 3-[(5-aryl-2-oxofuran-3(2*H*)-ylidene)methyl]-4*H*-chromen-4-one with benzylamine leads to individual products, which were characterized by NMR spectroscopydata, including two-dimensional spectroscopy (HSQC, NOESY), as3-(aroyl)-1-benzyl-5-(2-hydroxybenzoyl)pyridin-2(1*H*)-one.This compound is formed due to the high reaction activity of chromone cycle, which easy decyclised under the action of benzylamine.



Three-component condensation offuranone with orthoester and guanidine is apromising synthesis to form polyheterocyclic structures, the reaction proceedsthrough the formation of 3-ethoxymethylene-3*H*-furan-2-oneswhich are intermediates in this reaction.Variation of the nucleophilic components allows obtaining a wide range of heterocyclic structures.



Structure of the obtained reaction products weredemonstrated by NMR spectroscopy, including the two-dimensional spectroscopy (HSQC, NOESY).

This work was financially supported by RFBR (project 13-03-00318).

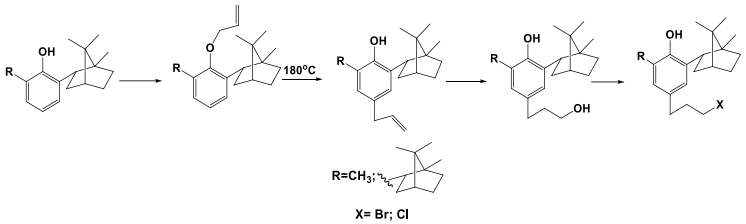
SYNTHESIS OF NEW FUNCTIONAL DERIVATIVES BASED ON TERPENOPHENOLS

Sukrusheva O.V. ,Chukicheva I.Y.

Komi Chemistry Institute of Scientific Centre of Ural branch of Russian Academy of Sciences,
Syktyvkar, Russia
Postgraduate Student
Sukrusheva@mail.ru

At present, sterically hindered phenols are the most representative and popular class amongst synthetic antioxidants. These compounds are biologically active substances, which effectively slows the lipid peroxidation and oxidative stress of organism. One of the most promising methods to improve the efficiency of phenolic antioxidants is to obtain a polyfunctional (hybrid) antioxidants, the molecules of which contain multiple reaction centers capable of inhibiting oxidative processes by means of various mechanisms. [1,2].

It is known that the terpenophenols synthesized at the Institute of Chemistry,the Komi Science Centre exhibit antioxidant activity and are promising compounds for drug development [3], the introduction of additional functional groups into their molecules being the subject of special interest. According to the method developed by A.E. Prosenko halogen atoms (Br, Cl)were introduced in molecule terpenophenols.



Picture 1.Synthesis of new functional derivativesbased on terpenophenols

The resulting compounds are among the intermediates in organic synthesis and have great potential for further synthesis.

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OBTAINING DISPERSIONS OF THE MARINE COLLAGEN FOR THE PRODUCTS OF MEDICAL AND COSMETIC APPOINTMENTS

Tarankova O.A., Geraskina E.V., Kuznetsova Yu.L., Valetova N.B., Semenycheva L.L

Lobachevsky State University of Nizhny Novgorod
Nizhny Novgorod, Russia
Postgraduate student
olyatarankova@mail.ru

The use of collagen as a medical material is presently clamed in various fields of medicine and cosmetology. This is due to its properties such as the stimulation of the regeneration of the human body's own tissues, high mechanical strength, the ability to bind water, and along with it to form complexes with biologically active substances, the absence of toxicity and carcinogenicity. Collagen is used as a substrate, a protective agent and drug transporter. This is collagen film for ophthalmology, sponge coating of wounds and burns, capsules and tablets, gels, tolerance inducers used in the treatment of rheumatoid arthritis. Collagen plays a leading role in tissue engineering as bioconstructional material where it is used for temporary replacement of bone and skin, as a component in artificial blood vessels and valves implant in cosmetic surgery.Important to note, marine collagen has several advantages

compared with collagen of terrestrial animals. It is hypoallergenic, as 96% is identical to the human protein,it has transdermal properties. On the content of chemical elements collagenous materials, derived from hydrobionts, favorably differ from similar materials of terrestrial animals [1, 2]. Thus, it is important to provide a method for the extraction of collagen, which is primarily determine the quality and direction of its further use. The preliminary study of fish skin - a potential raw material for collagen production, estimated the content of the protein component in it. For representatives of salmon there is 15-20% of protein component in feedstock and for the representatives of the cod there is 15-18%. We isolated collagen by the method [3]. We proposed to carry out the extraction by using solutions of various organic acids, because a further field of application of the product is significant limitation in the choice of acid. The extraction efficiency of collagen with various types of extractants is results in Table 1.

Table 1. Comparative table of the extraction efficiency of collagen proteins from salmonids skin

Features of the collagen substance	Extractant				
	Ascorbic acid	Citric acid	Succinic acid	Acetic acid	Salicylic acid
Mass fraction of collagen, %	4.75	4.56	4.96	5.70	1.48
Yield of collagen relatively feedstock, %	23.75	22.80	24.80	28.50	7.40

From this data it is evident that solutions of the commercially available organic acids allow to achieve the complete recovery of collagenous proteins. However, extracts of acetic acid must be further purified (neutralized, dried), due to a strong irritant effect on human's the skin. Many more viable option for creating the soft forms (creams, gels) in this regard are weak organic acids (succinic acid, citric acid, salicylic, ascorbic). Determination of the qualitative and quantitative composition of the obtained solutions of biopolymers produced by the method [4].Thus, the data can be successfully used in the future to obtain a wide range of products for medical and cosmetic purpose.

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Acknowledgements: Work carried out in the LobachevskyState University of Nizhny Novgorod supported by the Ministry of Education and Science of the Russian Federation (task № 2014 / 134, the agreement of 27 August 2013. № 02.V.49.21.0003) using equipment NBI "New materials and energy saving technologies" (project RFMEFI59414X0005).

DYNAMIC SURFACE PROPERTIES OF LYSOZYME/UREA AND LYSOZYME/GUANIDINE HYDROCHLORIDE SOLUTIONS

M.M. Tihonov, O.Yu. Milyaeva, B.A. Noskov [1]

[1]*Institute of Chemistry, Saint-Petersburg State University*
Saint-Petersburg, Russia
herr-morgenstern@yandex.ru

The dynamic surface properties of lysozyme/urea and lysozyme/guanidine hydrochloride (GuHCl) solutions were investigated by the methods of surface dilational rheology and ellipsometry. Measurements of the kinetic dependencies of the dynamic surface elasticity and ellipsometric angles show that these two denaturants have different influence on the adsorption layer structure. The dynamic surface elasticity and surface tension decrease gradually with the increase of urea concentration up to 9 M but the kinetic dependencies of the ellipsometric angle Δ and consequently of the adsorbed amount do not display any significant changes. These results are connected with a gradual transformation of the lysozyme globules in the surface layer into the molten globule state without tightly packed interior of the globule and with a dynamic tertiary structure similar to the corresponding transition in the bulk phase at the increase of urea concentration [1]. Lysozyme preserves its molten globule state in the course of adsorption and the interface has no specific effects unlike the case of bovine serum albumin (BSA) and β-lactoglobulin (BLG) solutions [2]. On the contrary, the increase of GuHCl concentration leads to an abrupt transition from monotonic to non-monotonic kinetic dependencies of the dynamic surface elasticity of lysozyme solutions in a narrow concentration range and to strong changes of the ellipsometric data. These peculiarities indicate the beginning of the globule unfolding in the surface layer but the observed effect is not as strong as in the case of BSA and BLG solutions. The disulfide bonds between remote aminoacid residues of the protein chain restrict the mobility of the partially unfolded lysozyme molecule and do not allow formation of long loops and tails in the surface layer. The obtained results demonstrate the high sensitivity of the surface dilational rheological properties to protein conformations at the liquid – gas interface.

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Acknowledgements:
The work was financially supported by the Russian Foundation of Basic Research (project No. 14-03-00670 _a) and St. Petersburg State University (project No. 12.38.241.2014).

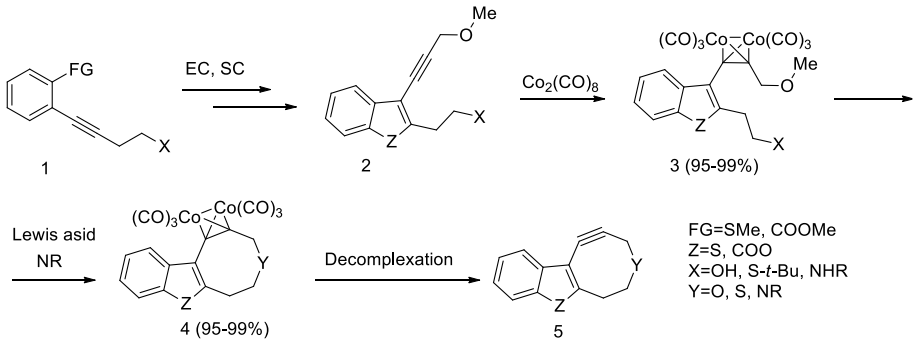
NICHOLAS REACTION AS A USEFUL TOOL FOR THE SYNTHESIS OF HETEROCYCLOOCTYNES

Tikhomirov A.O., Danilkina N.A., Balova I.A.

Saint Petersburg State University
Student
tixmir_spb@mail.ru

Cyclooctynes represent an important class of compounds widely used as special reagents in biological and biochemical studies [1]. This is because of their high reactivity in strain-promoted alkyne-azide cycloaddition (SPAAC) [2], a type of click reaction.

Heterocyclooctynes fused to a heterocyclic core **5**, which are supposed to be highly reactive in SPAAC, were chosen as target synthetic structures. The synthetic approach used is based on the electrophilic cyclization (EC) and the Sonogashira coupling (SC) on initial steps followed by the Nicholas reaction (NR) as a macrocyclization technique. This strategy proved to be very efficient for the synthesis of Co-protected heterocyclooctynes fused to five- and six-membered heterocycles **4**. The final Co-deprotection step is under investigation.



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This study was supported by Saint Petersburg State University (research project 12.38.195.2014) and by the grant of President of the Russian Federation for young scientists (MK-3322.2014.3). The research was carried out using equipment of the resource centres of Saint Petersburg State University: Centre for Magnetic Resonance, Centre for Chemical Analysis and Materials Research.

SYNTHESIS AND INVESTIGATION OF PHOTOCHEMICAL PROPERTIES OF7-HYDROXY-1,1-DIFLUORO-2 (*1H*) - NAPHTHALENONE AND ITS DERIVATIVES

Trofimova D. V.[1,2], *Zaikin P. A.*[2], *Borodkin G. I.*[1,2], *Shubin V.G.*[2]

[1]NovosibirskState University,
[2]N. N. Vorozhtsov NovosibirskInstitute of Organic Chemistry
SiberianBranch of the RussianAcademy ofSciences, Russia
Student
trofimchem@mail.ru

Photocontrolled drug delivery systems in which drug molecule is covalently attached to polymer backbone by a photocleavable coumarin linker are of interest in medical applications for treatment of cancer [1] and secondary cataract [2].

We consider that 7-OR_1-1,1-difluoro-2 (*1H*) -naphthalenones (R_1 = H, Me, Ac) can be used as photoactivelinkers. These compounds were synthesized by the electrophilic fluorination of 2,7-substituted naphthalene derivatives (R_2 = H, Me, Ac) with F-TEDA-BF_4 reagent in acetonitrile, aqueous buffer solution and in solvent-free conditions.The influence of fluorophore structure on the fluorescence spectra was studied (Fig. 1).

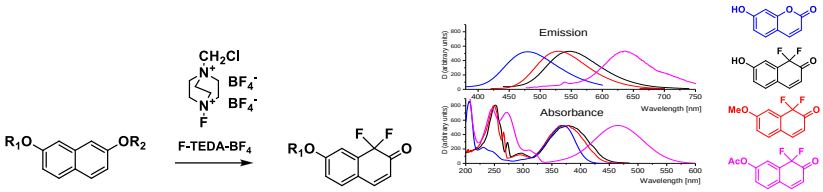
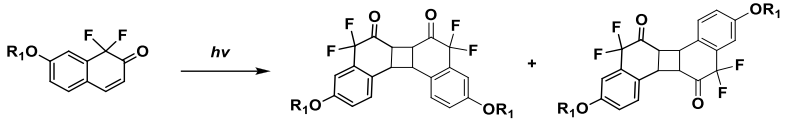


Figure1.Fluorescence spectra of difluoronaphthalenones

The compounds obtained were subjected to photochemical dimerization:



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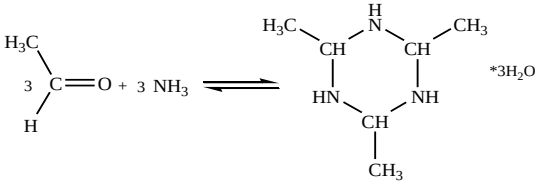
THE STUDY OF ACETALDEHYDE AND AMMONIA INTERACTION KINETICS

Tuguldurova V.P., Malkov V.S., Dahnavi E.M., Fateev A.V., Vodyankina O.V.

National Research Tomsk State University,
Tomsk, Russia
Postgraduate student
tuguldurova91@mail.ru

The reactions between carbonyl compounds and ammonia and its derivatives underlie synthesis ofvaluable heterocyclic compounds. However, these processes usually carried out in water solutionsremain poorly understood in terms of chemical kinetics and reaction mechanisms. In this context, the objective of the present work was to study the kinetics and mechanisms of acetaldehyde and ammonia interaction.The product of this condensation, 2,4,6-trimethyl-1,3,5-hexahydrotriazine trihydrate (acetaldehyde-ammoniatrimer) (Scheme),was isolated from the reaction mixture and analyzed by IR-spectroscopy, and melting point was determined.



Scheme. Reaction between acetaldehyde and ammonia

A series of experiments was carried out using the*in situ* spectrophotometric equipmentto determine acetaldehyde concentration in this reaction. Several mechanisms of acetaldehyde-ammonia trimer formation were proposed based on [1-3].All mechanisms proposed andcorresponding kinetic models were verified using experimental data obtained, and theoretical curves were calculated according to the quasi-steady-state approximation.

In the presentwork quantum-chemical calculations were carried out at B3LYP/6-31+G** to optimize the proposed structures of transition states as well as reveal stationary points on the potential energy surfaces.

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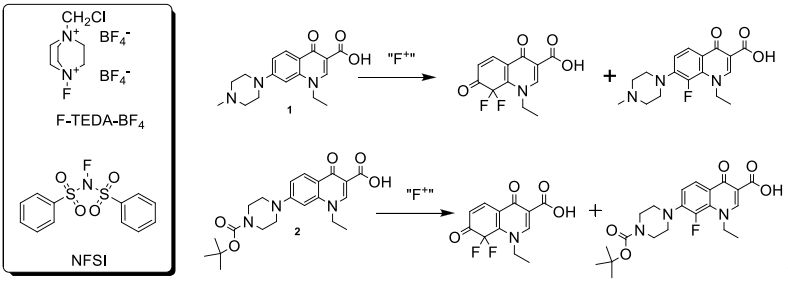
ELECTROPHILIC FLUORINATION OF 1-ETHYL-7-(4-METHYLPIPERAZIN-1-YL) - AND 1-ETHYL-7-(4-*TERT*-BUTOXYCARBONYLPIPERAZIN-1-YL)-4-OXO-1,4-DIHYDROQUINOLINE-3-CARBOXYLIC ACIDS WITH NF-REAGENTS

A. N. Usoltsev[1,2], *P. A. Zaikin*[1], *G. I. Borodkin*[1,2], *V. G. Shubin*[1]

[1] Novosibirsk Institute of Organic Chemistry
[2] Novosibirsk State University
Student
e-mail: usoltcev@nioch.nsc.ru

Nowadays there are a lot of publications devoted to about improvements of synthesis methods of synthesis of bicyclic and tricyclic fluoroquinolones, increase of yield and quality of the products. A number of studies is dedicated to synthesis of new fluoroquinolones to obtain achieve new medicines preparations with a high antibacterial activity [1].

We have shown that fluorination of 1-ethyl-7-(4-methylpiperazin-1-yl)-4-oxo-1,4-dihydroquinoline-3-carboxylic acid (**1**) and 1-ethyl-7-(4-*tert*-butoxycarbonylpiperazin-1-yl)-4-oxo-1,4-dihydroquinoline-3-carboxylic acid (**2**) with NF-reagents NFSI and F-TEDA-BF_4 proceeds predominantly at the 8 position of quinoline fragment in acetonitrile, water and in solvent-free conditions. The main products of the fluorination reaction are presented in the scheme:



This work was gratefully supported by Division of Chemistry and Material Sciences of RAS (project 5.1.4).

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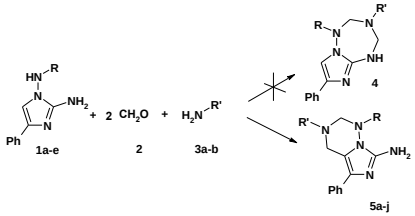
THREE-COMPONENT CONDENSATION OF 1,2-DIAMINOIMIDAZOL WITH A PRIMARY AMINE AND FORMALDEHYDE

D.Yu. Vandyshev, H.S. Shikhaliyev, A.Yu. Potapov.
Voronezh State University, Russian Federation,
394006 Voronezh, University Sq., 1.

The high reactivity of diaminoimidazol allows including them in a variety of reactions as two - and three-component condensation, leading to various azaheterocycles.

We have investigated the three-component condensation reaction **1a-e** with formaldehyde and primary amines **3a-b**. For the process of our study, we found optimum conditions: boiling in isopropyl alcohol the equimolar amount of diaminoimidazol, amine and two moles of formaldehyde (as a 40 % aqueous solution) for 0.5-2 hours.

The formation of triazipin formation cycle was initially assumed **4**. However, when examining the ^{1}H NMR spectra, we found that the cyclization was not two amino groups, and amino hydrazine moiety and the carbon atom of the imidazole ring, leading to new 1,2,3,4-tetrahydro [5, 1-f] [1,2,4] triazin-7-amine **5a-j**.



R = H **(1a, 5a, 5f)**; $CH_2C_6H_5$ **(1b, 5b, 5g)**; $CH_2(4\text{-}CH_3)C_6H_5$ **(1c, 5c, 5h)**; $CH_2(3\text{-}Cl)C_6H_5$ **(1d, 5d, 5i)**; $CH_2(4\text{-}CH_3O)C_6H_5$ **(1e, 5e, 5j)**;
R' = $CH_2C_6H_5$**(3a, 5a-5e)**; $C_2H_5OCH_3$**(3b, 5f-5j)**.

Found that imidazotriazines **5a-j** react by acylating the amino group to form acetyl derivatives **6a-j**.

The structures of all the obtained compounds are also proved by mass spectroscopy and elemental analysis.

POLYMERIC NANOGELS AS SYSTEMS FOR DRUG DELIVERING

Voeykov R.V. [1,2], *Abakumova T.O.* [3], *Chehonin V.P.* [3,4], *Kabanov A.V.* [2,5], *Nukolova N.V.* [2,3]

[1]Lomonosov Moscow State University, Department of Material Scinces
[2]Lomonosov Moscow State University, Faculty of Chemistry
[3]The Serbsky State Scientific Center for Social and Forensic Psychiatry
[4]Russian National Research Medical University
[5] University of North Carolina at Chapel Hill

Selective delivery of drugs in the body is the focus of many research groups in the world. One of the promising nanocontainers is nanogel – soft nanoparticles, consisting of hydrophilic or amphiphilic polymeric chains. Nanogels have beneficial characteristics: high loading capacity, stability and sensitivity to environmental changes (pH, ionic strength and temperature). We can use nanogels with biodegradable cross-links to avoid long-term accumulation of nanocontainers in the body. The aim of this work was to synthesize nanogels and to study loading and release kinetic of anticancer drug Doxorubicin.

Nanogels were synthesized from block-copolymer polyethylene glycol-*b*-polymethacrilic acid (PEG-b-PMAA). Synthesis consists of several steps: 1) formation of polymer polyelectrolyte complexes with oppositely charged ions (e.g. Ca^{2+}); 2) cross-linking of formed nanoparticles by ethylendiamine using carbodiimide; 3) removing Ca^{2+} ions from nanoparticles through chelating with EDTA and dialysis. Cystamine was used instead of ethylendiamine for synthesis of biodegradable nanogels. We used glutathione as reducing agent. Loading of drug into nanogels was processed by their mixing overnight (25ºC, 10 h). Loaded nanogels were purified by multiple centrifugation on Amicon filters (MWCO 30 kDa). Concentration of loaded drug was calculated with help of spectrophotometric analysis. Release of drug was studied at different pH (5.4 and 7.4). DLS method was used for determination size and ζ-potential of nanogel.

Stable negatively charged biodegradable nanoparticles with cross-linked core were synthesized and characterized. Using DLS method we found that size and ζ-potential of nanogel change after loading. It was shown that after adding glutathione release of Doxorubicin is 2 times more effective. Also we studied release of drug from non-biodegradable nanogels at different pH (5.4 and 7.4) and at lower pH it is 2 times more effective too.

Both biodegradable and non-biodegradable nanogels gives an opportunity for selective release of drug in tumor cells.

This work is supported by grants of RSF 14-15-00698, contract №182-MRA between non-profit organization for higher education "Skolkovo Institute of Science and Technology", MSU and MIT (USA).

THERMAL AND SOLUTION-BASED TECHNIQUES OF COCRYSTAL SCREENING: EVALUATING THE EFFECTIVENESS

Voronin A.P., *Manin A.N.*

G.A.Krestov Institute of Solution Chemistry of Russian Academy of Sciences
Ivanovo, Russia
Ph.D. student
flox-av@yandex.ru

In the recent decade, cocrystallization has been admitted as a promising approach [1] increasing the bioavailability of active pharmaceutical ingredients (API) suitable for patenting as novel solid drug form.

The main problem occurring at the early stages of cocrystal search is the choice of an effective screening technique. Among the most popular techniques of obtaining cocrystals are crystallization from solution, crystallization from melt and solvent-drop grinding. The present research represents a comparative analysis of the following screening techniques: DSC cocrystal screening method [1], thermal microscopy [2] and saturation temperature method [3]. The obvious advantage of these techniques over convenient X-Ray-based algorithms is the possibility of performing analysis starting right from physical mixture without preliminary treatment. However, their practical applicability has not been studied yet.

The efficiency of different techniques of cocrystal screening was checked in 18 systems using solvent-drop grinding/powder X-Ray diffraction method combination as benchmark. Benzamide and benzoic acid derivatives were chosen as model systems due to their ability to form a robust acid-amide supramolecular heterosynthon.

The screening has confirmed the formation of 6 new cocrystals. The screening by the saturation temperature method has the highest screen-out rate but the smallest range of application. DSC screening has a satisfactory accuracy and allows screening over a short time. Thermal microscopy is most efficient as an additional technique used to interpret ambiguous DSC screening results. The study also included an analysis of the influence of solvent type and component solubility on cocrystal formation.

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Acknowledgements:

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DEVELOPMENT IN THE INVESTIGATIONS OF EFFICIENCY OF SULFUR CATION-EXCHANGE RESINS USED IN THE P-TERT-BUTYLPHENOL PRODUCTION

I.O. Voronin[1,2], *N.V. Bilenchenko*[1], *T.N. Nesterova*[1]
[1]Department of Chemical Technology, Samara State Technical University
Galactionovskaya st. 141,443100 Samara, Russia
[2]Novokuybyshevsk petrochemical company, Novokuybyshevsk, Samara region, 446214, Russia
E-mail: bilenchenkonv@yandex.ru

p-*Tert*-butylphenol (PTBP) is an important basic organic synthesis product. It is used in the paint and varnish, pharmaceutical industry and, for example, as a component of the motor fuel additives.

In industrial scale its production is organized in 1978 at the Novokuibyshevsk Petrochemical company (NPC), which is currently the only producer of PTBP in Russia.

The requirements for this product is very high, but there are not so many ways to improve quality without reducing of the process efficiency. At the NPC implemented process of the PTBP producing by catalytic alkylation of phenol with isobutylene with the subsequent transalkylation of reaction mass to improve the quality of the product. The approved oneself catalysts for this process are strong-acid sulphur cation-exchange resins (sulphocationites).

We have conducted experiments with the most active and selective catalysts such as Amberlyst 36 Dry, KU-23 and Tulsion T-66 MP. At 353-403K in the range of relations tert-Bu / Ar = 0.1-1.5 (mol / mol) the kinetics of transalkylation in the system «phenol + tert-butylphenol» in the presence of CS-23, Amberlyst 36 Dry and Tulsion T-66 MP are studied. The kinetic characteristics of the studied transformations are defined. It is shown that in passing from Amberlyst 36 Dry to CG-23 10/60 the pre-exponential factor for reaction t-butylphenol + phenol ↔ p-tert-butylphenol + phenol (I) increased by 10 times, and for 2,4-di -t-butylphenol + phenol ↔ 2 × p-tert-butylphenol (II) - 2,000 times. The most high-rate reactions in the overall system of transformations are transalkylation of 2,6-di-TBP and 2,4,6-tri-TBP to phenol and PTBP.

Thermodynamic properties for reaction (I) are calculated in the range of 353-523 K on the basis of experimental and literary data. For the reaction (II) thermodynamic properties are experimentally defined in the range of 353-403 K. It is established that values of enthalpy and entropy effects in both reactions are respectively equal. The difference in values of the equilibrium constants of these reactions is explained.

Also the influence of moisture on the rate of transformations of all types was investigated, and shown that the studied sulphocationites have different sensitivity to the presence of moisture in the system.
On the basis of the executed research recommendations for the terms of conducting process on each of the studied catalysts are made.
Results of research of equilibrium provided a basis during the work with kinetic information which total analysis allowed to establish:
1. The rate of reaching of equilibrium in the "phenol-*tert*-butylphenol" system increases in presence of the considered cationites in the next line: KU 2-8 < KU-23 << Amberlyst 36 Dry < Tulsion T-66 MP.
2. At the increasing of moisture content in reaction mass more than 0.1 % the reaching of an equilibrium state by system is carried out faster in the presence of Amberlyst 36 Dry.
3. The formation of m-*tert*-butylphenol (m-TBP) proceeds with a slower rate compared with main reactions and its concentration in the reaction system is far from the equilibrium value. Nevertheless, even in the small amounts its presence has negative influence to physical and chemical properties of commodity p-TBP. Synthesis conditions (moisture content and temperature in the system) in which the concentrations of meta-isomer in alkylate is minimized at the acceptable rate of target reactions are chosen.
Acknowledgments. This work was financially supported by The Ministry of education and science of Russian Federation within the framework of the basic part of governmental tasks of Samara State Technical University (project code 1708)

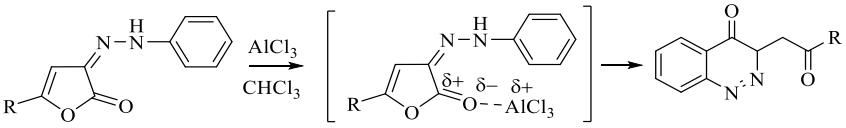
THE USE OF LEWIS ACID IN TRANSFORMATION OF ARYLHYDRAZON-SUSBTITUTED 3*H*-FURAN-2-ONES

Yegorova A.Yu.[1], *Maksimov Ye.A.*[1], *Grinev V.S.*[2], *Mayorova O.A*[1]

[1]Chernyshevsky Saratov State University,
[2]Institute of Biochemistry and Physiology of Plants and Microorganisms,
Russian Academy of Sciences,
PhD student
Beloousova011@yandex.ru

Heterocyclic compounds containing in their structure the hydrazone fragment are of considerable interest due to a variety of chemical reactions,which products exhibit a pronounced biological effect[1].
We found that by using of anhydrous $AlCl_3$, the Lewis acid as a catalyst, the reaction leads to bicyclic product. The reaction was carried out by heating the substituted furanones and $AlCl_3$ at a molar ratio of 1: 2 in chloroform solution. Underthe studied conditions we propose that $AlCl_3$induces the polarization of double bond C=O in furanone fragment. The possible further formation of a

complex with $AlCl_3$ leads to the cleavage of heterocycle ring, and the intermediate undergoes C,C-cyclization at the*ortho*-carbon atom of the aryl substituent of hydrazone function by self-acylation reaction of positive chargedmoiety. It leads to the formation of the corresponding 3-(2-oxo-2-R-ethyl)-3*H*-cinnoline-4-ones.



R = Ph, 4-Me-C_6H_4

^{1}H NMR spectra of resulting compounds recorded in $CDCl_3$ fully confirm the existence of the proposed structure. The spectra contain a triplet of methine groupproton (5.80-5.93 ppm, 1H), a doublet of doublets of methylene units protons (2.65-2.71ppm, 2.85-2.92 ppm), and a multiplet of aromatic protons (7.27-8.13 ppm).

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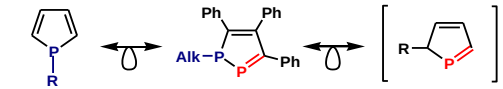
Acknowledgements
This work was financially supported by RFBR (project 13-03-00318).

THE CHEMISTRY OF 1-ALKYL-1,2-DIPHOSPHOLES

ZagidullinA.A.[1], *Oshchepkova E.S.*[1], *Burganov T.I.*[1], *Zvereva E.E.* [1], *Miluykov V.A.*[1], *Katsyuba S.A*[1]., *Sinyashin O.G.* [1], *Hew-Hawkins E.*[2]

[1]*A.E. Arbuzov Institute of Organic and Physical Chemistry,Kazan, Russia*
[2]*Institute of Inorganic Chemistry, Leipzig University, Leipzig, Germany*
Kazan, Russia
Research assistant
zagidullin@iopc.ru

The pioneering work of the synthesis of monophosphole in the 1970s spurred the development in this novel area of chemistry that resulted in novel highly effective catalysts, materials for light-emitting diodes, nonlinear optics, conductive polymers and drugs.[1] Recently, we have found that it is possible to combine the thermal stability of 1*H*-phospholes and the high reactivity of 2*H*-phospholes in one molecule - 1-alkyl-1,2-diphospholes.[2]



Cycloaddition reactions of 1-alkyl-1,2-diphospholes proceed under mild conditions with high regio- and stereoselectivity that open possibilities to construct new chiral polycyclic phosphines with chiral bridgehead phosphorus atoms for asymmetric catalysis.[3] At the same time, the simulations ([TD]-DFT) allowed a detailed interpretation of the experimental UV spectra of these compounds and revealed relationships between the chemical modification of 1,2-diphospholes and their light absorption properties.[4] Moreover, recent experimental work demonstrates the possibility of fine-tuning of the aromaticity as well as reactivity of 1-alkyl-1,2-diphospholes by choosing the appropriate substituents at the phosphorus atom. New 1,2-diphospholes containing electron-withdrawing groups are less stable but more reactive in cycloaddition reactions.[5]For this 'aromaticity' reason, 1,2-diphospholes with electron-donating substituents in the *para*-position of phenyl moieties were investigated as new building blocks for organophosphorus π-conjugated systems.[6]

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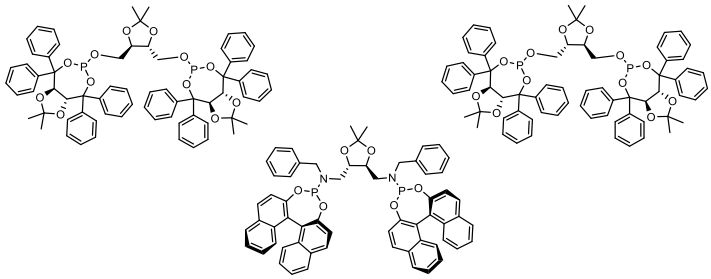
P, P-BIDENTATE PHOSPHITE-TYPE LIGANDS BASED ON TARTARIC ACID DERIVATIVES

Zakharov S.I.[1], *Shiryaev A.A.*[1,2], *Groshkin N.N.*[1], *Zheglov S.V.1* ,*Vaganova U.A.*[1]

[1]S. A. Esenin Ryazan State University, Ryazan, Russia.
[2]Ryazan State Radioengineering University
S. A. Esenin Ryazan State University, Ryazan, Russia
Student
Zakharov177@mail.ru

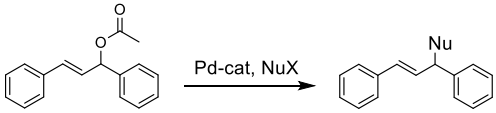
The synthesis of new *P, P*-bidentate phosphites and amidophosphites, formed starting from (*R,R*)-TADDOL ((4*R*,5*R*)-2,2-dimethyl-1,3-dioxolane-4,5-diyl)bis(diphenylmethanol), (S_a)-BINOL ((S_a)-[1,1'-binaphthalene]-2,2'-diol) as well as 4*R*,5*R*-, ((4*S*,5*S*)-2,2-dimethyl-1,3-dioxolane-4,5-diyl)dimethanoland

1,1'-((4S,5S)-2,2-dimethyl-1,3-dioxolane-4,5-diyl)bis(*N*-benzylmethanamine), is described.



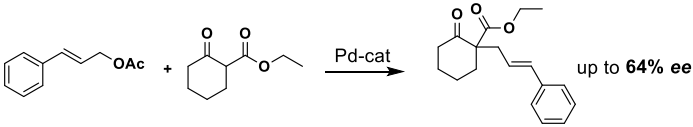
The structure and stereochemical features of intermediates and target compounds are determined based on ^{1}H, ^{13}C, ^{31}P NMR spectroscopy, mass spectrometry, polarimetry and elemental analyses.

Novel ligands were used as asymmetric inductors for Pd-catalyzed allylic sulfonylation and alkylation:



Nu = $CH(CO_2Me)_2$, X = H up to **73% *ee***

Nu = SO_2pTol, X = Na up to **78% *ee***



It should be noted that Pd-catalyzed enantioselective synthesis of a quaternary carbon center is a formidable challenge.

The reported study was partially supported by Ministry of Education and Science of the Russian Federation,research Project No. 2014/378.

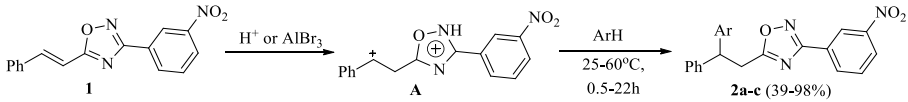
HYDROARYLATION OF(*E*)-3-(3-NITROPHENYL)-5-STYRYL-1,2,4-OXADIAZOLE

Zalivatskaya A.S.[1], *Lisakova A.D.*[2], *Ryabukhin D.S.*[3], *Karunnaya M.V.*[4]

[1]Saint Petersburg State Forest Technical University,
[2]Saint Petersburg State Technological Institute (Technical University),
[3]Saint Petersburg State University,
[4]Yaroslavl State Technical University
Saint Petersburg, Russia
Student
anansaaaw@mail.ru

1,2,4–Oxadiazoles are important subjects in biochemistry and medicine. They have a wide range of application in the pharmacology. 3,5-Substituted-1,2,4-oxadiazoles show various types of biological activities: potent muscarinic agonist, anthelminitics and antitussives, inhibitors of tyrosine kinases. Moreover these heterocycles are used as reactivators of organophosphonate – inhibited human acetylcholinesterase, and may cause coronary vasodilation, local analgesia and used as liquid crystalline mesophaser.

Superelectrophillic activation of (*E*)-3-(3-nitrophynyl)-5-styryl-1,2,4-oxadiazole **1** under the action of Bronsted superacids CF_3SO_3H leads to cationic intermediate **A**only at 60°C, which then reacted with arenes (benzene, o-dichlorobenzene and anisole) to afford oxadiazoles **2a-c** in yields of 39-89%. Hydrophenylation of oxadiazoles **1** with strong Lewis acid $AlBr_3$ or conjugate Bronsted-Lewis acid CF_3SO_3H-SbF_5 takes place even at 20°C, giving compound **2a** in yield of 84 and 98% respectively.The use of $AlCl_3$ at 20°C does not afford compounds **2**, increase the reaction temperature up to 60°C leads to oligomeric compounds.



2, Ar = C_6H_nR [R = H (**a**), 4-OH (**b**), 3,4-Cl_2 (**c**)]

This project was supported by the Russian Foundation for Basic Research (grants no. 15-03-02936-a). A HRMS study was performed at Center for Chemical Analysis and Materials Research of Saint Petersburg State University.

RATIONAL DESIGN OF D-AMINO ACID OXIDASE TO IMPROVEENZYME PROPERTIES

Zarubina S.A.[1,2], *Golubev I.V.*[1,2], *Tishkov V.I.*[1,2,3]

[1]Department of Chemical Enzymology, Chemistry Faculty, M.V. Lomonosov Moscow State University, Moscow, Russia,
[2]Innovations and High Technologies MSU Ltd, Moscow, Russia,
[3]A.N. Bach Institute of Biochemistry, Russian Academy of Sciences, Moscow
Moscow, Russia
Postgraduate student
zarubina.sophia@gmail.com

D-amino acid oxidase (DAAO) is a FAD-containing enzyme whichplays essential physiological functions in living organisms. The enzyme is used in fine organic synthesis, biosensors and medical treatment. Moreover, the most large-scale and perspective field of DAAO application is made use of cephalosporin antibiotics production. There is two-step biocatalytic conversion of Cephalosporin *C* (CephC) into 7-aminocephalosporanic acid.

In our laboratory the rational design is used to obtain mutant forms of DAAO from yeast *Trigonopsis variabilis* (TvDAAO). Positions were determined by simulating mutant structures. Amino acid changes in active site resulted in mutant enzymes with enhanced catalytic efficiency with CephC. Mutations in cofactor-binding domain increased catalytic efficiency with many D-amino acids and thermal stability.

In current work, we combined these amino acid changes into multi-point mutants. The plasmids with mutations in *tvdaao* gene providing triple and quaternary amino acid substitutions were obtained. Mutant enzymes were expressed in *E.coli* cells, purified and characterized. Chromatographic activity determination with CephC was performed. It was found that new multi-point mutants of TvDAAO showed enhanced catalytic activity and thermal stability compared to initial enzymes.

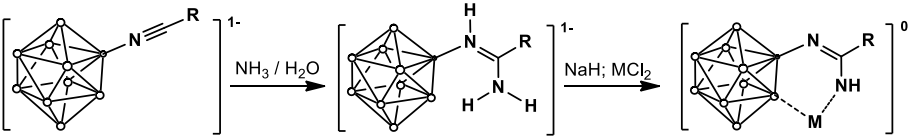
This work was supported by Russian Foundation for Basic Research (grants 14-04-00865-a, 14-04-32064-mol_a and 14-04-31194-mol_a).

SYNTHESIS AND CHEMICAL PROPERTIES OF $[2\text{-}B_{10}H_9NH{=}C(NH_2)R]^-$ (R = Me, Et, ^{t}Bu, Ph) ANIONS

Zhdanov A.P., *Zhihin K.Yu.*

Institute of General and Inorganic Chemistry of N.S. Kurnakov RAS (IGIC RAS)
Moscow, Russia
Ph.D., Research Assistant
zhdanov@igic.ras.ru

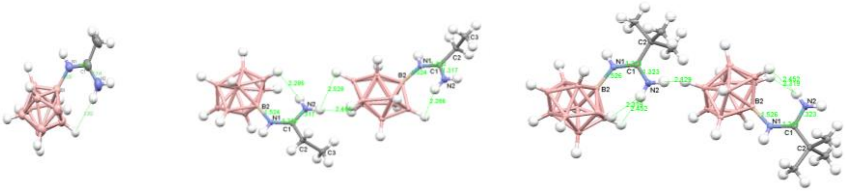
We have found that nucleophilic addition of one molecule of ammonia to nitrilium derivativesof *closo*-decaborate anion lead to the unsubstituted amidines:



R = Me, Et, ^{t}Bu, Ph

M = Zn, Co, Ni

This process is possible to carry out in aqueous solution, which greatly simplifies apparatus of the reaction and the isolation of the desired product. X-ray data and multinuclear NMR spectroscopy of the products indicate that amidine substituent is stabilized by an intramolecular hydrogen bond and a *Z*-configuration (Pic. 1). Also, increasing the steric effect of the R-substituent of nitrilium group promotes the formation of intermolecular hydrogen bonds and coordination substituted *closo*-decaborates in polymer chains (Pic. 1 *b* and *c*).



a *b* *c*

Picture 1. Crystal structure of $[2\text{-}B_{10}H_9\{Z\text{-}NH{=}C(NH_2)CH_3\}]^-$ (*a*), $[2\text{-}B_{10}H_9\{Z\text{-}NH{=}C(NH_2)C_2H_5\}]^-$ (*b*) and $[2\text{-}B_{10}H_9\{Z\text{-}NH{=}C(NH_2)C(CH_3)_3\}]^-$ (*c*) anions

Also we have studied the complexation reaction between the anhydrous metal halides and deprotonated amidine-substituent of closo-decaboratewhich areformed *in situ*. Preliminary data show that neutral complex compound generates in these processes.

Financial support by RFBR, grants 14-03-31789mol_a, 13-03-00525 a.

Section 4.

Quantum chemistry and computer modeling

INTERACTIONS OF DNA WITH BIOMEMBRANES IN THE PRESENCE OF CALCIUM IONS: INSIGHT FROM MOLECULAR DYNAMICS SIMULATIONS

Antipina A.Yu.[1,2], *Gurtovenko A.A.*[2,1]
[1]Saint Petersburg State University
[2]Institute of Macromolecular Compounds RAS
Saint Petersburg, Russia
PhD student
aaju@yandex.ru

Formation of complexes of DNA and biomembranes is important from the point of view of the development of novel efficient and non-toxic vectors for delivering genetic material into the cells. While experimental studies have shown that negatively charged double helixes of DNA can bind to zwitterionic (neutral) phospholipid membranes in the presence of calcium ions, the underlying mechanism of the DNA-membrane complex formation is still unknown. To address this problem, in the present work we employ atomic-scale molecular dynamics simulations to gain a better understanding of the process of formation and the structure of complexes of DNA with phospholipid bilayer membranes. As Ca-DNA-lipid systems can experimentally be prepared in different ways, here we consider two possible scenarios: (1) Ca ions are added to aqueous solution simultaneously with a lipid membrane and DNA placed parallel to the membrane surface; and (2) Ca ions are first allowed to adsorb on a lipid membrane and then DNA is placed in the vicinity of the membrane with pre-adsorbed cations. The atomistic force-fields AMBER parmbsc0 and AMBER Lipid14 were used to describe a double helix of DNA and phospholipid molecules, respectively. With the use of supercomputer facilities microsecond-long molecular dynamics simulations were carried out and a wide range of structural and dynamic characteristics of the Ca-DNA-lipid membrane systems is evaluated. This allowed us for a first time to get an atomistically-resolved insight into Ca-mediated formation of DNA-phospholipid complexes as well as into their structure and stability.

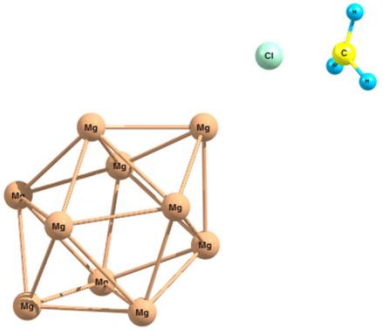
The authors wish to acknowledge the use of the Lomonosov supercomputer at the Moscow State University and the computer cluster of the Institute of Macromolecular Compounds RAS. This work was partly supported by the Presidium of the Russian Academy of Science through the grant program ”Molecular and Cellular Biology” and also by the Russian Foundation of Basic Research through Grant No. 14-03-01073.

QUANTUM CHEMISTRY STUDY OF SINGLET AND TRIPLET SURFACES OF MG_{10} CLUSTER REACTION WITH ORGANOCHLORIDES

Barsukov Y.V.[1], *Porsev V.V.*[2], *Tulub A.V.*[2]

[1]LLC "Geolink Technologies",
[2] Saint Petersburg State University
Saint Petersburg, Russia
Chemist Reseacher
barsukov.yuri@gmail.com

It was found at [1] that magnesium clusters reacts with organofluorides during metal vapor synthesis where cluster Grignard reagent RMg_nF is a product of reaction. We proposed the mechanism of Grignard reagent formation which is based on our quantum chemistry calculations for magnesium [2] and zinc [3] metals.



Picture 1. Transition state CH_3 radical formation in reaction of CH_3Cl with Mg_{10} cluster at D_{4H} symmetry

Nevertheless, intrigue remains about triplet surface effect on the activity of clusters. It was found in calculations the singlet-triplet crossing during isomerization reaction of Mg_{10} cluster. Total energy of triplet state for geometry of Mg_{10} cluster with high D_{4H} symmetry is lower than one for singlet state. It is feature of magnesium cluster, it was not found for Zn_{10} cluster. It is known in literature [4] that magnesium in triplet state is generated during laser ablation and react with methyl halides diluted in argon. Grignard reagent is one of the products of reaction. Thus, in view of the found crossing of singlet and triplet surfaces it is interested to study how Mg_{10} react with organohalides on triplet surface. Quantum chemistry study of CH_3Cl with Mg_{10} clusters with C_{3V} and D_{4H} symmetries are performed. Calculation shows the higher reactivity of cluster at triplet state.

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THE STRUCTURE OF MOH·*n*DMSO (M = Na, K) COMPLEXES: A QUANTUM-CHEMICAL VIEW

Bobkov A.S., *Litvintsev N.N.*, *Orel V.B.*
Irkutsk State University,
Irkutsk, Russia
Student
bas_1995@mail.ru

Activity of the superbasic systems MOH/DMSO is strongly dependent on the nature of the alkali metal cation. The KOH/DMSO system is successfully used in superbasic catalytic reactions, while the NaOH/DMSO system seldom provides significant yields and shows even no activity in some reactions at all.

The step-by-step addition of DMSO ligands to the non-dissociated potassium and sodium hydroxide molecules were considered within the MP2/6-311++G**//B3LYP/6-31+G* approach with non-specific solvation effects included via the polarizable continuum model (PCM).

Quantum-chemical calculations predict the immediate solvation shell of non-dissociated sodium and potassium hydroxides to contain four and five DMSO molecules, respectively.

The first three (or four in case KOH) DMSO molecules are mainly coordinated to the metal cation oxygen atom of DMSO and to the oxygen atom of the hydroxyl group with one proton (type **1**) or two protons (type **2**) of the DMSO methyl groups. The latter is more thermodynamically favorable for MOH·1÷3DMSO complexes found. The last DMSO molecule is located by oxygen atom of the metal cation at the apex of the bipyramid with methyl groups coordinated to the oxygen atom of one of equatorial DMSO ligands.

The enthalpies of formation of the most stable MOH·*n*DMSO complexes are identical for the sodium and potassium hydroxides. The calculated thermodynamic stabilities of the complexes increase monotonically when next DMSO molecules added (see Table 1).

Table 1. The enthalpies of formation of the most stable MOH·*n*DMSO complexes

n	NaOH	KOH
1	-7.6	-6.3
2	-13.7	-12.0
3	-23.7	-20.9
4	-30.9	-28.7
5	–	-34.9

The M–OH bond lengths increase against ones in isolated alkali molecules by 0.305 Å in the NaOH·4DMSO complex and by 0.454 Å in the KOH·5DMSO one. Thus, the solvation shell extension causes loosening of the M–OH bond and increases activity of the base. This effect which is more pronounced for the potassium hydroxide.

Acknowledgements

The financial support from RFBR (Project No. 15-03-03880a) and the Russian Ministry of Education (Project No. 4.1504.2014/K) are gratefully acknowledged.

THE STRUCTURE AND SPECTROSCOPIC PROPERTIES OF 3,4-DIARYLPYRROL-2,5-DIIMINES AND 3,4-DIARYLMALEIMIDES. THEORETICAL AND EXPERIMENTAL STUDIES

Boyarskaya D.V., Afanasenko A.M., Boyarskaya I.A., Panin A.I., Chulkova T.G.
Institute of Chemistry, Saint Petersburg State University,
Saint Petersburg, Russia
Student
dina-bo@mail.ru

Maleimide derivatives such as arcyriarubin and arcyriaflavin, which are isolated from the fruiting bodies of the slime mold (*Arcyria denudata*) [1], correspond to a core structure of selective inhibitors of protein kinase C (PKC) or DNA topoisomerase [2]. The ability of selective inhibition or regulation of the metabolism of cells makes them therapeutically important anticancer agents [3]. On another matter, some of maleimides exhibit luminescence. Films of N-methylated derivatives have been applied for fabrication of red light-emitting diodes (LEDs) [4].

In this study, the structural and spectroscopic properties of maleimide derivatives, 3,4-diarylpyrrol-2,5-diimines and 3,4-diarylmaleimides, were investigated.

The molecular structure of the 3,4-diarylpyrrol-2,5-diimines and 3,4-diarylmaleimides were studied by density functional theory using hybrid potential B3LYP [5-7] and standard basis functions 6-31+G(d,p) and 6-311G(d). The geometries and energies of tautomers were determined. The electronic excited states, UV-Vis and IR spectra of 3,4-diarylpyrrol-2,5-diimines and 3,4-diarylmaleimides were calculated. The band assignment in the experimental spectra was performed using the calculated data. The influence of electronic effects of the aryl substituents in 3,4-diarylpyrrol-2,5-diimines and 3,4-diarylmaleimides on the UV-Vis spectra was studied.

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The authors thank Saint Petersburg State University for a research grant (2013-2015) and Russian Fund for Basic Research (grant 13-03-12411). We also thank the Educational Resource Center of the Institute of Chemistry, the Centre for Optical and Laser Materials Research, and the Research Centre for X-ray Diffraction Studies of Saint Petersburg State University, where the IR, UV-Vis, and XRD studies were performed.

CHARACTERISTICS OF HALOGEN BONDS IN THE CRYSTAL OF IODINE WITH RELATIVISTIC EFFECTS

Bulatova L.M., *Yushina I.D.*, *Bartashevich E.V.*

South Ural State University (NRU)
Chelyabinsk, Russia
Undergraduate student
Luciyabulat@yandex.ru

Molecular crystals with halogen bonds are of fundamental interest for studies of intermolecular interactions and properties of functional materials. The aim is to compare the geometric and electronic characteristics of halogen bonds in the crystal of iodine, obtained under conditions of periodic calculations taking into account relativistic effects at the level of the choice of basis sets and pseudopotentials core [2-5] with those obtained from High-precision X-ray diffraction data [1]. The challenge also lies in choosing the optimal basis set for subsequent quantum topological analysis (QTAIM) electron density (ED). The calculations are performed by B3LYP in the program CRYSTAL14. Tested basis sets: 1) Stuttgart many-electron full-relativistic pseudopotentials of 28 and 46 core electrons, valence is often described bases VTZ type; 2) basis set DZVP and its truncated analogue of 11 shells; 3) DZP adjusted Douglas-Kroll-Hess (DKH).

It was found that most accurately reproduces the length of covalent $\Delta R_{I\text{-}I}$ = 0.004 Å and halogen bonds $\Delta R_{I\cdots I}$ = –0.001 Å using DZVP. The core pseudopotentials lead to an overestimation of the length of a covalent bond I–I and severely underestimating the halogen bond I…I. As reference values chosen ED at the critical points I–I/I…I, obtained in the experiment with the subsequent multipole refinement ED [1]. It turns out that the basis sets spanning pseudopotentials underestimate the ED for covalent bond. DZP-DKH underestimates the length of halogen bond and thus overestimates the ED at the critical point of the halogen bond for about 0.007 a.u.

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Acknowledgements
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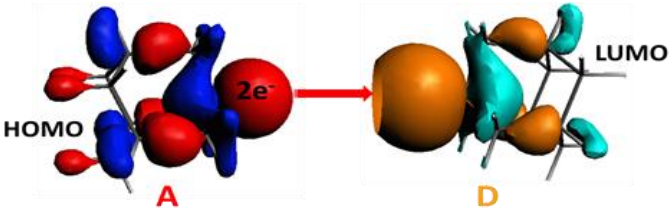
CHEMICAL BONDING ANALYSIS IN COMPLEXES OF E-X (E = B, AL; X=N, P) CONTAINING LEWIS SUPERACIDS BY EDA

Majid El-Hamdi and Alexey Y. Timoshkin

Inorganic Chemistry Group, Institute of Chemistry, St. Petersburg State University, University Pr. 26, Peterhoff, 198504 St. Petersburg, Russian Federation
majidelhamdi6@gmail.com; timoshkn@gmail.com

Density functional theory calculations of donor-acceptor complexes between group 13 element adamantane and fluorinated adamantane derivatives $E(C_9H_{15})$ and $E(C_9F_{15})$ (E = B, Al) and different Lewis bases (XH_3, $X(CH_3)_3$, $X(C_9H_{15})$; X=N, P) have been performed at the BP86/TZ2P level of theory. The electronic structure and chemical bonding have been investigated with energy decomposition analyses (EDA) of the interaction energy. A combination of better electrostatic (ΔE_{elstat}) and orbital interactions (ΔE_{oi}) is mainly responsible for the larger stability of complexes with fluorinated adamantine derivatives, while deformation energies of the fragments and Pauli repulsion (ΔE_{Pauli}) are of less importance. The analysis of molecular orbitals expectedly reveals that the HOMO of donor molecules interact with LUMO of group 13 element acceptors evolving bonding and antibonding σ orbitals.



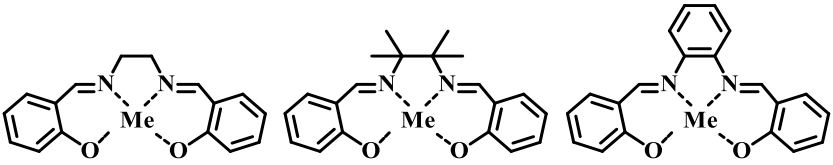
FROM SOLUTION TO POLYMER FILM: SELF-ORGANIZATION OF METAL-SALEN COMPLEXES NEAR SOLID SURFACES.

Hrom S.I., *Sizov V.V.*, *Vanin A.A*
Saint Petersburg State University
grom_sergei_90@mail.ru

Coordination polymers based on transition metal (Me) complexes with SalEn-type Schiff-base ligands possess a number of unique properties, such as high redox conductivity, rich electrochemical behavior and selective catalytic activity in heterogeneous reactions. These features suggest potential use of such compounds in various important applications (sensors, catalysts, supercapacitors).

The properties of poly-[MeSalEn] polymer films formed from monomeric [MeSalEn] units via electropolymerization are largely determined by the packing of monomers at the surface of the electrode. In the present work the self-organization of [MeSalEn] molecules in solution at a graphitic surface is studied by computer simulations.

Molecular dynamics and simulated annealing studies were performed for solutions of [MeSalEn] complexes in acetonitrile. Six SalEn-type Schiff-base ligands were considered: SalEn, SaltmEn, SalPhen, and their methoxylated derivatives (see Figure).



SalEn *SaltmEn* *SalPhen*

In all simulated systems [MeSalEn] complexes were observed to form dense films at the solid surface. These films displayed distinct layered structure, with the majority of [MeSalEn] molecules being aligned parallel to the surface. However, orthogonal and diagonal orientations could also be observed. The packing density and inter-layer distance in the films were significantly influenced both by the structure of the imine bridging fragment and the presence of substituents in aromatic rings. Typical stacking motifs were identified using a variety of structure analysis tools.

STRUCTURE-CONDUCTIVITY DEPENDENCE IN YTTRIA-STABILIZED ZIRCONIA: A MOLECULAR DYNAMICS STUDY

Ivanov M.A., Snegurov P.A., Sizov V.V.
Saint Petersburg State University
Saint-Petersburg, Russia
Student
mikhail.ivanov.1995@gmail.com

Yttria-stabilized zirconia, $[ZrO_2]_{1-x}[Y_2O_3]_x$, is a well-known material, which is widely used as electrolyte in solid oxide fuel cells because of its good ionic conductivity. The ability of this material to conduct oxygen ions results from the doping of ZrO_2 by another oxide, such as Y_2O_3. As the Zr^{4+} ions are replaced in the cationic sub-lattice by Y^{3+} ions, vacancies emerge in the anionic sub-lattice due to the electroneutrality condition. Along with the content of dopant cations in the system, their distribution is another important factor influencing the conductivity of the doped oxide. For example, clustering of dopant cations may lead to formation of local bottlenecks, hindering the overall conductivity of the solid oxide.

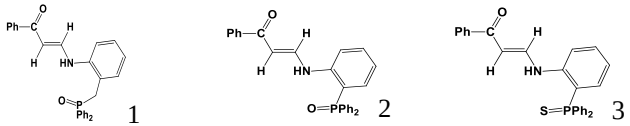
In this work we present the results of a systematic simulation study of the dependence of oxygen diffusion on the structural parameters of YSZ samples. Molecular dynamics simulations were carried out at several temperatures for YSZ samples containing up to 14 mol. % of yttria. The most prominent feature of this study is the use of multiple random distributions of Y^{3+} ions over the cation sub-lattice for every YSZ composition. Oxygen diffusion coefficients obtained for each of these random configurations are subsequently averaged to give the final oxygen diffusivity for a given YSZ composition. Extensive ensemble averaging can significantly improve the accuracy and reliability of simulations because the averaged diffusion coefficients are likely to be free from structural bias. Furthermore, the abundance of computational data for each YSZ composition provides the basis for efficient search of structure-diffusivity correlations, which may suggest possible routes to improving the performance of solid electrolytes by fine-tuning their structure.

We report the overall magnitude of diffusivity fluctuations and the observed correlations between the calculated oxygen diffusion coefficient and the distribution of cations in the simulated sample. Finally, we provide practical recommendations on the use of ensemble averaging for evaluating the conductivity of YSZ and similar solid oxides by molecular dynamics simulations.

POLARITY OF (THIO)PHOSPHORYLATED ENAMINOKETONES IN SOLUTION

Khanafieva R.R.[1], *Alimova A.Z.*[1], *Chachkov D.V.*[2], *Ishmaeva E.A.*[1], *Aleksanyan D.V.*[3], *Kozlov V.A.*[3], *Vereshchagina Ya.A*[1]
[1]Kazan Federal University,
[2] Joint Supercomputer Center of the Russian Academy of Sciences (Kazan Branch),
[3] A.N. Nesmeyanov Institute of Organoelement Compounds,
Kazan, Russia
Student
khanafieva.rezeda@mail.ru

Functionalized enaminoketones 1-3 capable of forming unsymmetrical metal complexes owing to the presence of different donor centers are of interest in coordination and organometallic chemistry as convenient models for investigation of metal binding modes, high-performance catalysts and so on [1]. We have determined previously unknown polarities of compounds 1-3 according to the second Debye method based on the measurement of the dielectric constant of the dilute solutions of the polar substance in a nonpolar solvent at 25°C. The dielectric permittivities of solutions of 1-3 were determined on a BI-870 instrument. The refractive indices of solutions were determined on a RA-500 refractometer. The values of dipole moments are sufficiently high (scheme 1).



1 μ_{exp} = 6.07 D 2 μ_{exp} = 6.82 D 3 μ_{exp} = 6.08 D

Scheme 1. Experimental dipole moments of 1-3 in benzene

Also we performed quantum chemical calculations of the dipole moments and the relative energies of all possible conformations of 1-3 by the DFT B3PW91/6-31G(df,p) method and calculated their polarities according to the vector-additive scheme. The obtained results will be discussed. Compounds 1-3 were synthesized according to procedure [1].

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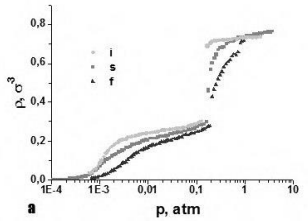
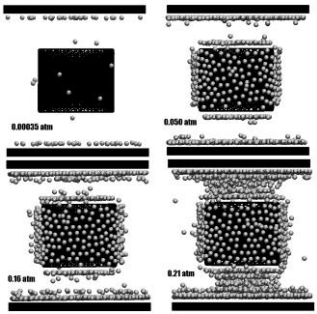
THE SIGNIFICANCE OF EDGE EFFECTS FOR ADSORPTION IN PORES

Kopanichuk I. V.
Saint Petersburg State University
Petrodvorets, Saint Petersburg, Russia
Student
kopan239@gmail.com

The goal of this work is to find differences in adsorption behavior between finite and infinite pores named “edge effects”. They have maximum in the area at the edge of the adsorbing surface, where the values of the adsorption field of finite and infinite slits reaches the greatest difference. The significance of edge effects increases for narrow pores: the presence of the edge at the adsorbing surface changes the adsorption isotherm and the mechanism of filling. In wide pores edge effects lead only to a slight decrease in the density of the adsorbate at low pressures, leaving the general form of the adsorption isotherm and the mechanism of filling unchanged. This is confirmed by the adsorption isotherm and instant snapshots of system configurations.



Picture 1. Adsorption isotherms of narrow pores. (i) – infinite, (s) – asymmetric, (f) - finite.



Picture 2. Main stages of the adsorption mechanism in the asymmetric pore.

This work is financially supported by the Russian Foundation for Basic Research under Grant No. 13-03-01081-A.

CORRELATION AND MODELING OF THERMOCHEMICAL PROPERTIES OF THE SYSTEM WITH ESTER SYNTHESIS REACTION ON THE BASE OF UNIFAC AND NRTL MODELS

Letyanina I.A., Tsvetov N.S.,Toikka A.M.
Saint Petersburg State University,
Saint Petersburg, Russia
PostDoc
irina-letyanina@mail.ru

Esterification reaction is one of the most convenient methods to obtain esters which have important scientific and practical importance. For the synthesis and separation processes optimization various thermodynamic data and computation methods are needed. The multicomponent system with *n*-propyl acetate synthesis reaction (*n*-propanol + acetic acid + *n*-propyl acetate + water) is considered in this work. The purpose of our study was to determine experimentally the excess enthalpy of the mixing for binary sub-systems of the mentioned quaternary system at T = 313.15 K with following correlation and modeling by various approaches. In spite the applications of different models for the analysis of H^E data are discussed in literature the case of reacting systems needs additional consideration.

The measurements of the H^E values were carried out with the C80 calorimeter with membrane mixing cells manufactured by Setaram Instrumentation (France). The C80 calorimeter works on the Tian-Calvet heat flow principle. Principally, esterification reaction can occur in the mixtures during the calorimetric measurements and influence on results. But the approbated by us experimental technique allow to claim the negligible influence of the reaction.

For the preliminary correlation of experimental H^E data we used the traditional methods such as Redlich-Kister equation and its modified version. Then UNIFAC and NRTL models have been used to predict and to correlate the excess enthalpy data. The application of UNIFAC model for the prediction of H^E values leads to significant differences between experimental and calculated data (in the case of considered systems). Accordingly this approach needs improvement for thermochemical data consideration. Relatively good agreement has been archived between experimental and calculated H^E data by means of the NRTL model. The discussion of other opportunities for the modeling of H^E data will be also presented.

Acknowledgements

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SPONTANEOUS FORMATION OF ALUMINUM-NITROGEN RINGS IN THE GAS PHASE: QUANTUM-CHEMICAL AND MASS SPECTROMETRIC STUDY

Lisovenko A.S.[1], *Timoshkin A.Y.*[1], *Binnewies M.*[2], *Milke E.*[2]
[1]Saint Petersburg State University, St. Petersburg, Russia
[2]University of Hannover, Hannover, Germany
lisovenkoanna@gmail.com

The chemical vapor deposition (CVD) method is one of the leading ways for production of 13-15 binary materials, such as aluminum and gallium nitrides. In the condensed phase reaction between $AlMe_3$ and NH_3 proceeds as follows:

Gas phase chemistry is not yet fully understood. Although it is known that laser irradiation of $AlMe_3$ and NH_3 mixtures at low temperatures results in formation of cluster compounds [1], thermal activation for the cluster formation has not been documented. In the present work gas phase reactions between trimethylaluminum and ammonia (deutero-ammonia) were examined by mass spectrometry. It is found that spontaneous reaction in vapors at 388 K results in formation of oligomeric products (including $[Me_2AlNH_2]_{2,3}$ rings). In order to understand the gas phase chemistry, initial reactivity between $AlMe_3$ and NH_3 has been studied computationally [2]. It was shown that the first methane elimination from the $AlMe_3NH_3$ complex is a rate-limiting step of the reaction and formation of the dimeric ring $[Me_2AlNH_2]_2$ is very favorable thermodynamically. In the present work we extend our computational studies to explore reaction $3[Me_2AlNH_2]_2 = 2[Me_2AlNH_2]_3$. Structures of all compounds and transition states were optimized at B3LYP/def2-TZVPP level of theory, thermodynamic characteristics and activation barriers were obtained. Reactions of dimeric and trimeric amidoalanes $[Me_2AlNH_2]_{2,3}$ with $AlMe_3$ and NH_3 were also considered.

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GRAPHENE-INDUCED CHANGES IN MECHANICAL PROPERTIES OF A CRYSTALLIZABLE POLYIMIDE R-BAPB

Mikhailov E.A.[1], *Nazarychev V.M.*[2], *Falkovich S.G.*[2], *Larin S.V.*[2], *Lyulin S.V.*[2,3]
[1]Saint-Petersburg State Polytechnic University, Saint-Petersburg, Russia
[2]The Institute of Macromolecular Compounds of RAS, Saint-Petersburg, Russia
[3]Saint-Petersburg State University, Saint-Petersburg, Russia
Saint-Petersburg, Russia
Student
mihalko2008@gmail.com

Thermoplastic polyimides (PI) are widely used as thermostable polymer matrices in modern nanocomposites. Having good thermal and electric properties they still exhibit worse mechanical properties than metals. Different reinforcing nanofillers are usually embedded to the polymer matrix to improve mechanical properties. Recently, influence of carbon nanofillers (carbon nanotube and graphene sheet) on structural properties of crystallizable thermostable PI R-BAPB synthesized in the Institute of Macromolecular Compounds RAS based on 1,3-bis-(3′,4-dicarboxyphenoxy)-benzene (dianhydride R) and 4,4′-bis-(4′′-aminophenoxy)-diphenyl (diamine BAPB), has been investigated using molecular dynamics (MD) computer simulation. It was shown that graphene induces structural ordering near the surface of nanofiller more strongly than carbon nanotubes. These changes could significantly affect mechanical properties of the nanocomposites.
In the present simulation the study of influence of a graphene-induced ordering of polyimide matrix on its mechanical properties was carried out. Simulations were performed with GROMACS MD package using GROMOS 53a5 force field. Graphene sheet was removed from the sample and the system was additionally equilibrated during 20 ns. The developed technique allowed us to investigate properties of the pure polymer oriented by graphene. Young's and shear moduli of the R-BAPB samples were estimated at the room temperature. The sample oriented by graphene manifests spatial anisotropy of mechanical properties. Furthermore, average value of Young's modulus of oriented sample is higher as compared to non-oriented one.

Acknowledgements
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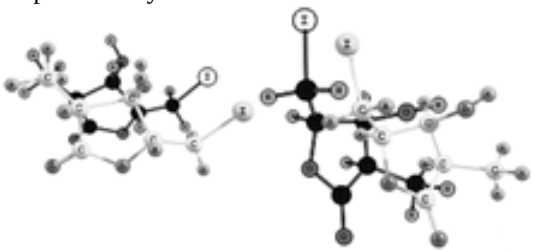
ANALYSIS OF HALOGEN BONDS OF IODINE IN ORGANIC CRYSTALS FROM DIMERIC APPROACH

Nasibullina S.E., *Bartashevich E.V.*
South Ural State University (NRU)
Chelyabinsk, Russia
Undergraduate student
svetlaya.n.e@yandex.ru

Noncovalent halogen-halogen interactions are the subject of much interest in crystal engineering. They define the structural, thermodynamic, thermal and other properties of materials. A halogen bond [1, 2] R–Hal…D is the non-covalent interaction, where R–Hal is the halogen bond donor, D is the halogen bond acceptor, R is a group covalently bound to Hal.

The aim of theoretical research consists of the analysis of iodine halogen bonds in organic crystals from the position of the dimeric approach. To investigate iodinated of molecular compounds the Kohn-Sham methods（B3LYP/6-311G (d, p), B3LYP/6-311+G (d, p) и B3LYP/DZP-DKH) have been used. The theoretical study revealed that after localization of the equilibrium geometry of the dimers, halogen bond (type II interactions) is stored in the isolated dimers. It was found that the smallest changes in the interatomic distances between atoms involved in halogen bond C–I…I–C formation occurred in the dimers, which has been optimized by B3LYP/DZP-DKH.



Picture 1. Example of geometry changing in the dimer structure: lighter shade marked structure observed in the crystal, dark - the result of the optimization

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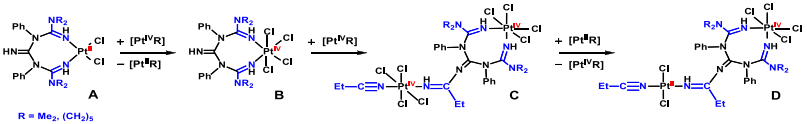
Acknowledgements
The work was supported by the Russian Ministry for Education and Science GZ729, and was carried out on a supercomputer "TORNADO" SUSU.

GENERATION OF MIXED-VALENCE DIPLATINUM SPECIES VIA COUPLING OF PLATINATED TRIGUANIDES WITH PLATINUM-ACTIVATED NITRILES: A THEORETICAL STUDY

Novikov A.S.
Institute of Chemistry, Saint-Petersburg State University
Stary Petergof, Russian Federation
Postdoctoral Fellow
ja2-88@mail.ru

Di-nuclear platinum species are compounds of paramount importance broadly used in catalysis, organic synthesis, material science, photophysical chemistry, and chemotherapy [1]. The majority of studied dinuclear platinum complexes are symmetrical systems, whereas asymmetric, particularly mixed-valence, species are rather rare. Our group developed a novel strategy for facile generation of asymmetric dinuclear platinum systems, including mixed-valence Pt^{II}/Pt^{IV} species, exploiting synthetic potential of the platinum-mediated nitrile–imine reaction, viz. coupling of platinated triguanides with Pt-activated nitriles (Scheme 1) [2]. This communication deals with the quantum-chemical (DFT) study of the possible mechanism of this coupling. Based upon our theoretical calculations, the following reaction path was postulated, viz. the platinated triguanides **A** acts as a reducing agent, and redox reaction between the Pt^{IV}-complexes *trans*-$[PtCl_4(EtCN)_2]$ [$\mathbf{Pt^{IV}R}$] and **A** furnishes oxidized form of platinated triguanides **B** and the Pt^{II}-complexes *trans*-$[PtCl_2(EtCN)_2]$ [$\mathbf{Pt^{II}R}$] followed by the nucleophilic addition **B** + [$\mathbf{Pt^{IV}R}$] resulting in generation of Pt^{IV}/Pt^{IV} species **C**. Afterwards, **C** reacts with [$\mathbf{Pt^{II}R}$] accomplishing mixed-valence Pt^{II}/Pt^{IV} species **D** and [$\mathbf{Pt^{IV}R}$]. Furthermore, we analyzed from thermodynamic viewpoint reasons and driving forces for redox instability of species **D** leads to formation of the Pt^{II}/Pt^{II} compounds as well as some by-products.



Scheme 1. Generation of asymmetric dinuclear platinum systems including mixed-valence Pt^{II}/Pt^{IV} species.

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Acknowledgements

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QUANTUM-CHEMICAL STUDY ON THE STRUCTURE OF KOH·5DMSO·H_2O COMPLEXES

Orel V.B., Bobkov A.S., Vitkovskaya N.M.
Irkutsk State University,
Irkutsk, Russia
Research Fellow
bobinbaba@gmail.com

The widely used KOH/DMSO superbasic catalytic media usually contains some amount of water coming either from the base and DMSO or forming as a by-product of the reaction. Moreover, in some cases, water is added to the reaction system on purpose.

Coordination of water molecule towards the KOH·5DMSO complex (Fig. 1, [1]) through both faces (F) and edges (E) of the potassium cation octahedral surrounding were considered within the MP2/6-311++G**//B3LYP/6-31+G* approach with non-specific solvation effects included via the polarizable continuum model (PCM).

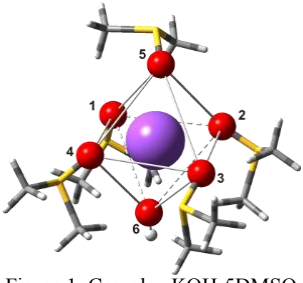

Figure 1. Complex KOH·5DMSO

Five stable complexes found differ in enthalpy by less than 3.1 kcal/mol. The most thermodynamically stable complex corresponds to coordination of water molecule to the **F_{146}** face with the enthalpy decrease by ΔH = –12.5 kcal/mol (see Table 1). Water coordination gives rise to separation of K^+OH^- ion pair: the K–O interatomic distance under **F_{126}** coordination increases by 1.157 Å with respect to KOH·5DMSO itself. Water molecule is not prone to substitute a DMSO ligand in the nearest solvation shell of the potassium cation.

Table 1. Enthalpy of KOH·5DMSO·H_2O formation from KOH·5DMSO and H_2O

Coordination type	**F_{146}**	**E_{36}**	**F_{126}**	**E_{35}**	**E_{34}**
ΔH kcal/mol	-12.5	-11.5	-10.4	-10.4	-9.3

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Acknowledgements

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INCREASING THE RESOURCE EFFICIENCY OF GASOLINE BLENDING USING A COMPUTER MODELING SYSTEM

Sakhnevich B.V., *Kirgina M.V.*
[1]National Research Tomsk Polytechnic University,
Tomsk, Russia
Student
sugar92_bv@mail.ru

Gasoline is one of the most desired products of oil refinery all over the world. According to expectations, in 2020 its production in Russia will be increased up to 46.7 MT/Y. Due to this fact, gasoline production companies set as the main goal to increase the volumes of production as well as to upgrade the key quality characteristics of gasoline.

The process of gasoline blending is one of the most difficult multistage technologies for optimization. This is primarily due to the large number of involved components, the composition of which varies considerably during rerefinery processes. Moreover, chemical and physical properties such as octane numbers do not follow the law of additivity.

Thus, optimization of gasoline blending is only possible on the basis of complex system with models of the main rerefinery processes - catalytic reforming and isomerization. This system is developed on the Chemical Engineering of Fuels and Chemical Cybernetics Department of Tomsk Polytechnic University. The system calculates gasoline blending recipes taking into the account the non-additive nature of octane numbers and changes in feedstock. It provides precise counting of hydrocarbon composition and detonation characteristics of gasoline which satisfies all the quality criteria.

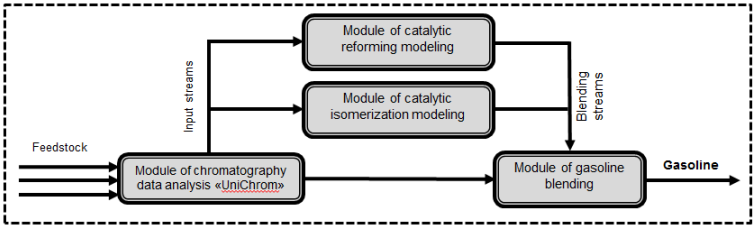


Figure 1. The structure of complex modeling system

Applying such an approach allows avoiding unnecessary overruns of expensive and difficult-to-obtain blend components as well as providing essential economic benefit for a refinery in general. In this work, it was shown that increasing the concentration of key components in isomerization unit feedstock (n-pentane and n-hexane) to 2-3 wt. % leads to the increase of product octane number up to 2-3 points. As a result, it determines the blending components ratio. In practice it is possible to save 2 wt. % of MTBE and 1 wt. % of alkylate when producing the Premium-95 gasoline.

ALKYLATION OF BENZENE WITH PROPYLENE OPTIMIZATION AT THE OJSC OMSKY KAUCHUK USING A MATHEMATICAL MODEL

Salischeva A.A.[1], *Chudinova A.A.*[1,2], *Gavrikov A.A.*[1], *Nurmakanova A.E.*[1], *Ivashkina E.N.*[1],
[1]National Research Tomsk Polytechnic University,
[2]OJSC Omsky Kauchuk
Tomsk, Russia
graduate student
SalischevaAA@yandex.ru

Synthetic α-methylstyrene rubbers are the products obtained at Omsky Kauchuk refinery alongside with other petrochemical products, such as octane additives, phenol and acetone.

At the beginning of the 2000th years, an undesirable component was found in the trade α-methylsterene (α-MS) which is used for rubber production in a process of emulsive polymerization with butadiene. Later, it was named as X-component, because until now it is impossible to determine its exact formula. The X-component cannot be separated in a rectification stage due to relatively equal boiling temperatures of the mixture. For this reason, it was hypothesized that the X-component is a product of n-propylbenzene (NPB) conversion that comes with raw materials of dehydrogenation process, isopropylbenzene (IPB), for production of the α-MC. NPB content varies from 0.1 to 0.2 % wt. while the maximum accepted values do not exceed 0.05 % wt.

The only way to achieve the reduction of NPB content is to vary technological conditions of the reactor block in a process of alkylation of benzene with propylene.

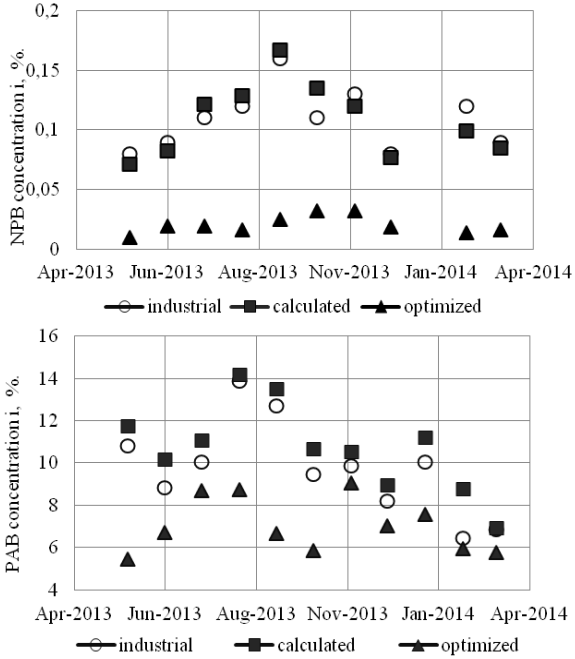
The performed monitoring of alkylation production unit allowed receiving the data about those operational parameters which influence the NPB output. As an experimental data analysis shown, it is possible to achieve the NPB content reduction by changing a reactor temperature, a molar ratio of raw flows and volumetric a feedstock flow rate.

To avoid significant span time and materials cost when searching for an optimal parameters values, we developed a mathematical model of the process [1]. It was implemented in Borland «Delphi 7» workspace and supplemented with the mathematical optimization function. Its working principle is to find parameters values for defined boundary conditions, or maximum conditions of the objective function.

The developed mathematical model was verified by comparing an industrial and calculated data for different alkylation production regimes (Figures 1-2). By using of the developed optimization module, such values of raw flowrates and catalyst temperatures in the reactor were identified, which provide high

outputs of isopropylbenzene (with n-propylbenzene content no more than 0.5 % wt).

Mathematical model approbation was performed with an industrial data. We achieved reducing of PAB (polyalkylbenzene) concentration down to 35% wt. that is the cause of the selectivity decline in a isopropylbenzene production process. The results of optimization calculations are presented in Figures 1-2 in a form of average values for period of 2013-2014 years.



Figures 1-2. Results of comparing of the industrial, calculated and optimized values of concentration of NPB and PAB in the product mixture.

The executed numerical dependencies allowed developing the technological solutions for optimal production regimes in a alkylation process at the OJSC Omsky Kauchuk .

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STRUCTURE OF METAL COMPLEXES WITH XENON AND KRYPTON: QUANTUM CHEMICAL STUDY

Shakhova V.M.[1], *Semenov S.G.*[2], *Makarova M.V.*[1]

[1]Saint Petersburg State University,
[2]Saint Petersburg Nuclear Physics Institute,
Saint Petersburg, Russia
Student
verahcnkrf@gmail.com

Inclusion of noble gas atoms (Ng) into the first coordination sphere of the metal complexes gained the increasing interest soon after the first successful synthesis and X-ray analysis of $AuXe_4^{2+}(Sb_2F_{11}^-)_2$ salt, the product of gold(III) fluoride, xenon and antimony pentafluoride reaction in hydrofluoric acid solution [1]. In this compound, which is stable at temperatures below -40 °C, gold is in the rare Au(II) valence state and forms coplanar chemical bonds with four Xe atoms located at the corners of the square [1]. Quantum chemical calculations of the free $AuXe_4^{2+}$ cation performed using HF, B3LYP and MP2 methods also verified the unusual structure of the gold and Xe containing compound, which was characterized by D_{4h} point group [1].

In this work the symmetry, equilibrium structural parameters and stability of gold, silver, copper, mercury, cadmium, zinc and barium with xenon and krypton complexes ($MtNg_4^{2+}$, $MtNg_3^{2+}$, $MtNg_4^{+}$, $MtNg_2^{2+}$ and $MtNg_2^{+}$) were studied using quantum chemical (U)PBE0/SDD and (U)MP2/SDD methods and Gaussian09 computer program [2]. The instability of $MtNg_4^{2+}$ complexes for Au (II), Ag(II), Cu(II), Hg(II), Cd(II) and Zn(II) with Xe or Kr was explained by the calculated free energies of $MtNg_2^{+}$ and Ng_2^{+} decay reactions. The symmetry of $AuNg_4^{2+}$, $AgNg_4^{2+}$ (D_{4h}); $CuNg_4^{2+}$ (**D_{2d}**, a flattened tetrahedron); $HgNg_4^{2+}$, $CdNg_4^{2+}$, $ZnNg_4^{2+}$ and $BaNg_4^{2+}$ (T_d), their internuclear distances and charge distribution between the Mt and Ng atoms indicate a significant covalent bonding.

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AN EQULIBRIA STUDY AND MODELLING FOR ACETIC ACID + 1-PROPANOL + 1-PROPYL ACETATE + WATER SYSTEM

Sjukkalova E.A.[1], *Toikka M.A.*[1], *Naumkin P.V.*[1]

[1]Saint Petersburg State University,
Saint Petersburg, Russia
Postgraduate Student
Ifgenika@gmail.com

Esters as individual products or intermediates are widely used as flavor additives, adhesives, pharmaceuticals, emulsifiers, solvents, plasticizers and monomers. The traditional way for esters manufacture is the esterification reaction between carboxylic acid and alcohol over acidic catalyst. Product yield of the esterification is commonly correlated with chemical equilibrium of the reaction and equilibrium between liquid phases.

Therefore experimental data on phase and chemical equilibrium are used to develop separation and purification methods. So the combination of these data is the fundamental principle for the development of reactive mass transfer processes which accordingly able to increase the product yield and simplify a process flow design.

In order to create the estimation scheme that allows obtaining equilibrium data without experiment, we suggest following steps:

● Chemical equilibrium at 353 K, vapor-liquid equilibrium (VLE) and liquid-liquid equilibrium (LLE) study for acetic acid + 1-propanol + 1-propyl acetate + water system. Quantitate information from obtained results and lower temperature data [1] for the system, which also were investigated by our work group, are used for VLE calculation; ● UNIFAC model prediction of activity coefficients for the suggested system and a results comparison with VLE and LLE experimental data; ● Calculation and analysis of thermodynamic properties for the system; ● Geometry optimizations and vibrational frequencies evaluation from quantum chemistry calculation at the HF/6-311G (++, 2d, 2p) level. The analysis of above mentioned steps helps us to create a simulation for the esterification processes which include chemical reaction and separation stage.Investigated experimental data, a contribution and a connection of the steps of calculation, will be discussed on the conference.

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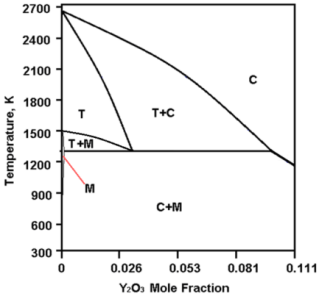
Acknowledgments: This research was supported by Russian Foundation for Basic Research (grant 13-03-00985A). Pavel Naumkin is also grateful to SPbSU for financial support in the frame of the grant (12.50.1195.2014).

MOLECULAR DYNAMICS SIMULATION OF IONIC CONDUCTIVITY IN YTTRIA-STABILIZED ZIRCONIA: THE ROLE OF PHASE COMPOSITION

Snegurov P.A., Ivanov M.A., Sizov V.V.

Saint Petersburg State University
Saint-Petersburg, Russia
Master student
alandeilokart@gmail.com

Molecular dynamics (MD) simulations were carried out to study ionic transport in cubic and tetragonal $[ZrO_2]_{1-x}[Y_2O_3]_x$ solid oxide (yttria-stabilized zirconia, YSZ) at 1373 K, 1673 K, and 1973 K for samples containing up to 12 mol.% of Y_2O_3. Calculated oxygen diffusion coefficients were averaged over twenty random cation distributions for each YSZ composition to ensure correct evaluation of the dependence of diffusivity on yttria content. The data obtained from MD simulations were used in conjunction with experimental phase diagram (Picture 1) to estimate the oxygen transport performance of YSZ samples, including those containing more than one phase. For heterogeneous samples (T+C and T+M) the quantities of coexisting phases were obtained from the phase diagram using the lever rule.



Picture 1. Phase diagram of yttria-stabilized zirconia.
C – cubic phase, T – tetragonal phase, M – monoclinic phase.

The dependencies of oxygen diffusion coefficients on yttria content for cubic and tetragonal YSZ were essentially similar. The phase diagram-based approach used in the present work for evaluating the conductivity of heterogeneous YSZ samples demonstrated a significant improvement over single-phase predictions. As a result, we were able to reproduce the available experimental data and to provide a molecular-level insight into the phenomena observed in experimental studies.

VALENCE ELECTRONIC STRUCTURE OF BROMOBENZENE: GREEN'S FUNCTION THEORETICAL STUDY

Soshnikov D.Yu.[1,2], *Trofimov A.B.*[2,1]

[1] Favorsky's Institute of Chemistry, SB RAS, 664033 Irkutsk, Russia
[2] Irkutsk State University, 664003 Irkutsk, Russia
Ph.D. student
lebron23cavaliers@rambler.ru

Halogenobenzenes are important models for systematic studies of substitution effects in benzene aromatic ring. The valence-shell electronic structure of these molecules can be probed by synchrotron radiation photoelectron spectroscopy yielding a wealth of experimental data that can further be interpreted using Green's function (electron propagator) methods of quantum chemistry [1].

In the present work we study the valence electronic structure of bromobenzene using the third-order algebraic diagrammatic construction (ADC(3)) scheme for the one-particle Green's function [2], the non-Dyson (nD) ADC(3) approach [3], and the outer-valence Green's function (OVGF) method [2]. The cc-pVDZ and cc-pVTZ basis sets were used in the ADC(3) calculations, whereas the OVGF results were obtained for the cc-pVXZ (X=D,T,Q,5) and aug-cc-pVYZ (X=D,T,Q) basis sets. The calculated vertical ionization energies and photoelectron intensities were used to interpret the recent experimental data obtained by D.M.P. Holland and co-workers [4].

The calculated and experimental spectral profiles are in good quantitative agreement with each other, allowing most of the features observed up to 19.5 eV to be unambiguously assigned. The inner valence region of the spectra is dominated by various shake-up transitions reflecting the breakdown of the one-electron ionization picture at higher binding energies. The low-lying shake-down satellite of $^2B_2$ symmetry was predicted near 12.6 eV. The vibrational structure seen in X^2B_1, A^2A_2, B^2B_2, and C^2B_1 photoelectron bands was investigated using Franck-Condon approximation.

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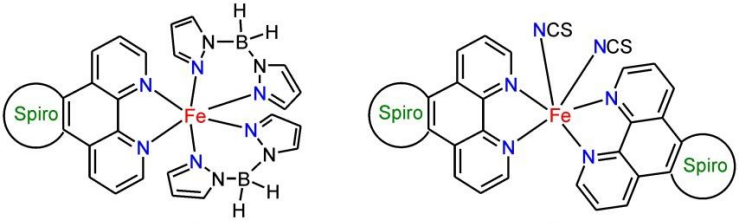
Acknowledgements.
This work was supported by grant from the Ministry of education and science of the Russian Federation.

SPIN CROSSOVER IN IRON COMPLEXES WITH PHENANTHROLINE LIGANDS MODIFIED BY PHOTOCHROMIC SPIROCYCLIC FRAGMENTS: COMPUTATIONAL MODELING

Starikova A.A., *Minkin V.I.*

Institute of Physical and Organic Chemistry at Southern Federal University
Rostov-on-Don, Russia
Junior researcher
alstar@ipoc.sfedu.ru

Switching of magnetic properties of coordination compounds through irradiation is a practically feasible way to control magnetic characteristics. The most well-known photomagnetic effects are light-induced excited spin-state trapping (LIESST) and ligand-driven light-induced spin change (LD LISC) [1]. The significant progress in the using of mechanism for the controlled change of the magnetic properties under the irradiation has been recently achieved by two independent research groups, studying phenanthroline iron complexes with annelated photochromic dithienylethene fragment [2, 3]. In order to find the compounds possessing photoinduced spin crossover we suggest using phenanthroline containing photochromic spirocyclic fragments (spiropyran, spirooxazine, chromene) as a ligand. On the basis of density functional theory quantum-chemical calculations with the use of various functionals (B3LYP*, TPSSh and OLYP), the possibility of reversible photoswitching of spin states of Fe(II) complexes **1** and **2** have been examined [4].



1 **2**

Spiro = spiropyran, spirooxazine, chromene

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MATHEMATICAL MODELLING OF THE CATALYTIC CRACKING PROCESS OF VACUUM DISTILLATE

Stebeneva V.I.,[1] Kiseleva S.V.[1], Nazarova G.Y.[1]

[1] National Research Tomsk Polytechnic University,
Tomsk, Russia
Student
stebeneva_valeriya@mail.ru

Catalytic cracking has crucial significance for advanced petroleum refining. The problem of technological mode optimization of catalytic cracking industrial unit can be solved by the development of adequate mathematical model of the process based on physical and chemical regularities of catalytic cracking reactions.

The calculation of thermodynamic parameters of vacuum distillate catalytic cracking reactions were carried out in this work.

Using theoretical data about chemism of catalytic cracking process, and experimental data from industrial plant, the list of passing reactions was composed.

The thermodynamic probability of each reaction was estimated by value of the Gibbs energy change ΔG during the reaction at the process conditions (temperature 504 °C, pressure 0.108 MPa). The ab initio (non-empirical) method DFT – Density Functional Theory, implemented in Gaussian software, was used for the evaluation of each individual hydrocarbon formation thermodynamic properties. Theoretical approximation was model B3LYP (Becke's density functional theory (B3) with theoretical approach using Li Yang and Para electron correlation (LYP), basis 3-21G.

It was found that the endothermic cracking reaction of high molecular weight linear paraffins (ΔH = 81,30 kJ/mol, ΔG = -62,52 kJ/mol) and isoparaffins (ΔH = 81,36 kJ/mol, ΔG = -62,011kDzh / mol) and hydrogen transfer (ΔG = -115,54 kJ/mol) with a positive heat effect ΔH = -133,48 kJ / mol are thermodynamically probable reactions of the process.

The formalized scheme of hydrocarbons conversions of the catalytic cracking process with taking into account thermodynamic and kinetic regularities and aggregation of hydrocarbons in groups by chemical features, was developed. The scheme also contains the reactions of cyclization and isomerization of n-paraffins, dealkylation of aromatics, condensation and coke formation reaction.

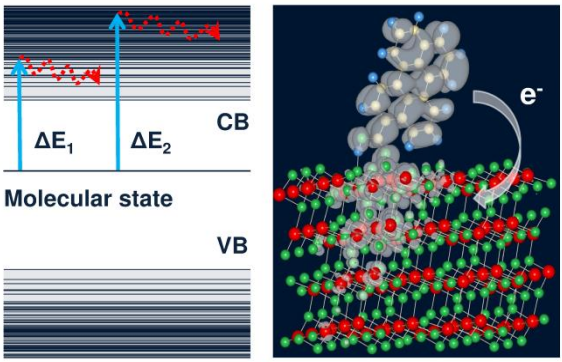
According to the created formalized scheme of hydrocarbons conversions, the kinetic model of catalytic cracking process was developed. It is a differential equation system of reactant concentrations changing by contact time with initial conditions: τ=0, Ci=Ci0.

PHYSICAL FACTORS INFLUENCING EXCITED STATE CHARGE TRANSFER AT THE PERYLENE – TITANIUM OXIDE INTERFACE

Syzgantseva O.A.[1,2], *Laasonen K.*[1], *Puska M.*[2]

[1]Aalto University, Department of Chemistry
[2] Aalto University, Department of Applied Physics
Espoo, Finland
Postdoctoral researcher
olga.syzgantseva@aalto.fi

Physical factors, affecting the amount and the rate of dynamical excited state charge transfer (CT) at the anchored perylene molecule (PeCOOH) – titanium oxide (TiO_2) interface, are considered within Real-Time propagation Time-Dependent Density-Functional Theory (RT-TDDFT) and Ehrenfest Dynamics (ED) formalisms [1], implemented in the GPAW program [2]. The influence of ionic dynamics on the rate and amount of interfacial CT is analysed. The impact of the anchor group and the energy of the initial excitation on the process dynamics is assessed. The dependence of CT characteristics on the surface coverage by the dye molecule is demonstrated. By the increase of the size of the TiO_2 system the transferred charge saturates toward one electron, and electron injection rates become coherent with available experimental and theoretical literature data [3].



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Acknowledgements
We acknowledge PRACE for awarding us access to resource Curie based in France at CEA. We thank CSC – IT Center for Science Ltd. and Aalto Science-IT project for providing computational resources.

FULLERENE DIFFUSION IN POLYIMIDE BASED NANOCOMPOSITES: MOLECULAR DYNAMICS SIMULATION

Volgin I.V.[1], *Larin S.V.*[2], *Falkovich S.G.*[2], *Nazarychev V.M.*[2], *Lyulin S.V.*[1,2]
[1]Faculty of physics, Saint-Petersburg State University, 198504, Saint-Petersburg, Ulyanovskaya str. 1
[2]Institute of Macromolecular Compounds of Russian Academy of Sciences, 199004, Saint-Petersburg, Bolshoj pr. V.O., 31
i.v.volgin@gmail.com

Atomistic molecular dynamics simulation of polyimide-based nanocomposites filled with two types of fullerenes (fullerene C_{60} and its derivative PCBM) has been carried out on a microsecond time scale. Composite microstructure and dynamical properties of the filler in polymer matrix have been studied for three polyimides with small differences in their chemical structure. Influence of the polyimides chemical structure and nanofiller type on the polymer matrix ordering has been examined. A dynamical behavior of the fillers has been investigated by evaluating mean-squared displacement, van Hove correlation functions, and intermediate scattering functions. A fullerene diffusion in PI matrices reveals a non-classical behavior that can be described by jump diffusion.

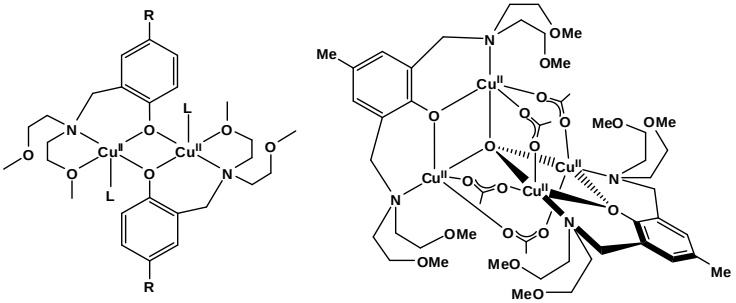
Acknowledgements
This study has been supported by Russian Foundation for Basic Research (grant No. 15-03-07614). The simulations have been carried out using the computational facilities of the Institute of Macromolecular Compounds of Russian Academy of Sciences, and the Chebyshev and Lomonosov supercomputers at Moscow State University.

DFT MODELING OF THE CATECHOLASE ACTIVITY OF NEW MULTICOPPER(II) COMPLEXES WITH MANNICH-BASE LIGANDS

Zhigulin G.Y., *Rychagova E.A.*, *Ketkov S.Y.*

G.A. Razuvaev Institute of Organometallic Chemistry RAS
Nizhny Novgorod, Russia
Postgraduate Student
gzhigulin@gmail.com

Synthetic analogues of catechol oxidase have been studied extensively in recent years [1] in order to understand the structure-function relationships and to find out various external factors affecting the activity of these systems. The reactions of new multicopper(II) complexes **1**-**5** bearing Mannich-base ligands (Figure 1) with 3,5-di-*tert*-butylcatechol have been investigated in this work by DFT calculations at the PBE/TZ2P and B3LYP/DGDZVP levels. The B3LYP/DGDZVP approach has been used mainly to analyze electronic structures of the complexes and their intermediates. The faster PBE/TZ2P computations have been employed to estimate energy changes corresponding to the catalytic steps. Experiments reveal complex **5** to decrease catecholase activity as H_2O content in MeCN changes from 0 to 25% while complexes **3**-**4** demonstrate an opposite trend. The calculations predict a possibility of complex **5** decomposition on reaction with H_2O which can explain its anomalous behavior. Complexes **1** and **2** show different catalytic activities and the solvent effects. These differences were interpreted in this work on the basis of analysis of energetic changes accompanying the reactions with 3,5-di-*tert*-butylcatechol. Possible catalytic cycles involving multicopper complexes have been proposed as a result of the DFT calculations.



1 R = Cl, L = NO_3 **3** R = Me, L = OAc
2 R = Cl, L = OAc **4** R = Me, L = Cl

Figure 1. Multicopper(II) complexes with Mannich-base ligands

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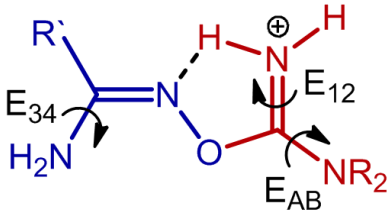
Developing the molecular structure of *O*-carbamidine amidoximes: molecular dynamics and *H*-bondings

Zimin D.P.[1], *Kulish K.I.*[1], *Novikov A.S.*[1], *Bokach N.A.*[1]

[1]Saint Petersburg State University,
Saint Petersburg, Russia
Student
dimzzz_oz@mail.ru

Nucleophilic addition to nitriles, RCN, represents an attractive route to new organic and coordination compounds with a variety of laboratory and industrial applications.[1] Metal *mediated* nitrile–nucleophile coupling was found to be a key step in some routes to important classes of nitrile-derived organic compounds such as amidines, acylamides, 1,3,5-triazapentadienes, carboxamides (and related species), phthalocyanines and 1,2,4-oxadiazoles.

Yields of 1,2,4-oxadiazoles depends on internal parameters of *O*-carbamidine amidoxime[2] which include a number of features of the molecule such as hydrogen bond, hindered rotation and etc. We compared known literature data about similar compounds like amides and guanidinium salts for a better understanding of the obtained data. Therefore, the aim was to study structure of previously unknown *O*-carbamidine amidoximes: intramolecular *H*-bond, barrier activation energy of rotation in amide group and X-ray parameters (Picture 1).



Picture 1. Barrier activation energy of rotation in amide group.

Studies of molecular structure were prepared by temperature depending 1H NMR spectroscopy and quantum calculations, thus, we compare experimental and theoretical data.

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Acknowledgements

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Section 5.

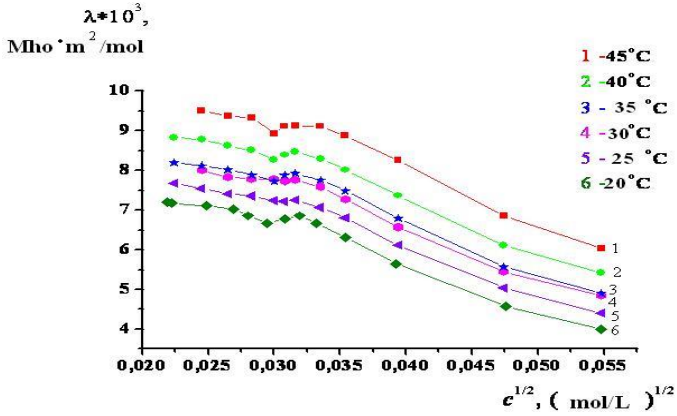
Modern techniques in analytical chemistry

INVESTIGATION OF HYDRATION OF ANIONIC SURFACTANT

Andranovich O.S[1],*Kopnina R.A.*[2], *Demyantseva E.Yu.*[3],*Korotkikh O.P.*[4], *Kochurova N.N.*[5]

[1,2,3]Saint Petersburg State Technological University of Plant Polymers,
[4,5]Saint Petersburg State University,
Saint Petersburg, Russia
Student
ilonichka3377@mail.ru

Investigation of electroconductivity of aqueous solution of sodium nonyl sulphate was carried out at concentrations before and after CMC and temperatures 20÷45°C. For these temperatures the limit equivalent electroconductivity of anion NS^-, molecular and ions coefficients of diffusion have been calculated. In particular our experimental data testify that mobility of NS^- ions decreases when temperature increases. It's seemed too that temperature influences on type of hydration of ion NS^-. Determined CMCs in these temperatures are correlated with [1]



Picture 1. Plots of $\lambda*10^3$ versus $c^{1/2}$ from electroconductivity data before and after CMC and temperatures 20÷45°C.

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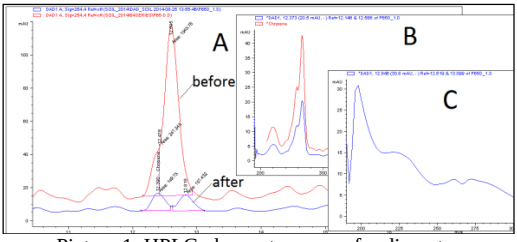
Acknowledgements. This work was supported by the Council on Grants of the President of the Russian Federation (Programme for Support of Leading Scientific Shcools, project no NSh – 2744.2014.3 and project SpbU no 0.37.179.2014)

USE OF SOLVENT EXTRACTION FOR ADDITIONAL CONFIRMATION OF THE RESULTS OF CHROMATOGRAPHIC ANALYSIS OF SEDIMENTS

Antonchyk V.V.[1], *Leschev S.M.*[2]

[1] Republic centre of analytical control in the field of environmental protection,
[2] Belorussian State University
Minsk, Belarus
Main specialist
vicky_chemist@tut.by

The comparative study of extraction properties of some polar organic solvents and ionic liquids has been made for polycyclic aromatic hydrocarbons (PAH) [1]. It was established that the least distribution constants and the maximal effectiveness of extraction of PAH is typical for systems with low or moderate value of solvophobic effect of the polar phase, characterized by the value of the increment of the methylene group, for instance, hexane – acetonitrile. As a result, some new, simple and effective methods of preconcentration, separation and determination of PAH, as well as of additional confirmation of the results of chromatographic determination of PAH in different objects, have been developed. In particular, after HPLC determination of PAH in a sample of sediments (Fig.1 (A) before) the extraction of hexane extract of PAH by an equal volume of acetonitrile was carried out (Fig.1 (A) after). Basing on the obtained distribution constants and spectra of chrysene (Fig.1 (B)) and unknown substance (Fig.1 (C))), it is easy to see that chrysene is identified correctly and it is presented in the sample. The interference of unidentified substance is reduced on 90%. So, the distribution constants of substances, together with retention times of peaks, may be used for the additional confirmation of the results of chromatographic analysis.



Picture 1. HPLC-chromatograms of sediments.

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FABRICATION AND PROPERTIES OF REACTION-BONDED SILICON AND BORON CARBIDE COMPOSITES

Antonova E.S.

State research center of Russian Federation OJSC «ORPE «Technologiya»
Obninsk Institute of Nuclear Energy (branch) of the National Research Nuclear University «Moscow Engineering Physics Institute»
Obninsk, Russia
Student
antonovadugina@mail.ru

The reaction-bonded silicon (RBSC) and boron (RBBC) carbides are actively used abroad in multi-layer impact-resistant barriers. In the present study the new lightweight high impact RBSC and RBBC were developed from powders of Russian production – JSC «UNIHIM s OZ», Yekaterinburg. The compositions of SiC and B_4C powders mixtures were chosen by varying the ratio of the volume parts of the grain fraction and particle size fractions to obtain maximum packing density in the compacts. According to XRD analysis RBSC mainly consist of plate-like morphology β-SiC, small amount of α-SiC and residual Si. RBBC mainly fabricated β-SiC around B_4C, $B_{13}C$, $B_{10}C$ phases, the ternary $B_{12}(C,Si,B)_3$ phase and residual Si. Silicon carbide and ternary phase were attributed to the dissolution-precipitation process. RBSC and RBBC are the product of the reactive infiltration process of a green silicon and boron carbides compacts with molten silicon according to reactions

$$B_4C_s + Si_{liq} \rightarrow SiC_s + B_{12}(B, C, Si)_3,$$

$$Si_{liq} + C_s = SiC''_s.$$

The formation of secondary SiC, $B_{12}(C,Si,B)_3$ allows to obtain the structure of continuous carbide framework to provide improved mechanical properties to the composites. In this work established the physical and mechanical properties of the composites depend on phase, fractional composition and dispersion of the powders mixtures and conditions of the reactive infiltration. RBSC was obtained with density values about 3,11 g/cm^3, flexural strength 380 MPa, fracture toughness about 4,9 MPa·m$^{1/2}$, hardness 26 GPA by the ratio of the volume parts of fractions V_2/V_1 as 0,6 and grain size fractions powders d_1/d_2 over 9. Containing 70 % fraction of F 240 and 20-30 % fraction 6U-13 RBBC show density values about 2,55 g/cm^3, flexural strength 340 MPa, fracture toughness about 4,1 MPa·m$^{1/2}$, hardness 28 GPA.

STEPWISE INJECTION DETERMINATION OF ANTIPYRINE IN SALIVA SAMPLES COUPLED WITH EFFERVESCENCE ASSISTED DISPERSIVE LIQUID-LIQUID MICROEXTRACTION

Aseeva[1] D., Medinskaia[1] K., Andruch[2] V., Bulatov[1] A., Vakh[1] K.

[1]Saint Petersburg State University
[2]University of P.J. Šafárik
Saint Petersburg, Russia
Postgraduate student
ksmed90@gmail.com

Sample preparation plays an important role in chemical analysis. As usual it includes the separation and/or preconcentration of the analytes from the sample matrix with the improvements of selectivity and sensitivity. One of the common sample preparation methods in the flow analysis is liquid-liquid extraction (LLE). To improve the analytical performance of LLE and satisfy the requirements of Green chemistry several microextraction techniques such as single drop, dispersive and hollow-fiber liquid-phase microextraction have been developed. Implementation of these microextraction techniques in flow analysis improves the reduction of organic solvents consumption and, as the results, the reduction in the amount of waste generated, thus leading to the lower cost and the environmentally-safety of analysis. Nevertheless, all these microextraction techniques have both advantages and disadvantages, which lead to the further development of new sample pretreatment methods.

New automated effervescence assisted dispersive liquid-liquid microextraction (EADLLME) based on a flow system have been proposed. The EADLLME assumes the dispersion of an extraction solvent by CO2 bubbles into a mixing chamber of flow system. In this case a sample and all required aqueous reagents are aspirated and mixed into the mixing chamber and then extraction solvent, carbonate-ions and acids solution are simultaneously injected at high flow rate into the water phase. The main EADLLME advantages are environmental friendliness and rapidity. Unlike conventional DLLME, in the case of EA-DLLME the organic disperser solvent as well as centrifugation procedure for disruption of the cloudy state are not used. The extraction procedure has been optimized and used for the determination of antipyrine as model analyte in saliva samples.

This work was supported by the Russian Foundation for Basic Research (project No. 13-03-00031-a and 14-03-31092 mol_a). Scientific researches were performed at the Center for chemical analysis and materials research of St. Petersburg State University.

STUDY AND MINIMIZATION OF MATRIX EFFECT DURING DETERMINATION OF 1-METHYL-*1H*-1,2,4-TRIAZOLE BY HEADSPACE SOLID-PHASE MICROEXTRACTION AND GC-MS IN SOILS CONTAMINATED BY UNSYMMETRICAL DIMETHYLHYDRAZINE ROCKET FUEL RESIDUALS

Bakaikina N.V., Yegemova S.S., Kenessov B.N.

al-Farabi Kazakh National University
Almaty, Kazakhstan
Student
bakaikina@cfhma.kz

Determination 1-methyl-*1H*-1,2,4-triazole (MTA), the main and the final transformation product of the hydrazine-based rocket fuel is very important for environmental risk assessment of heavy rocket launches from Baikonur cosmodrome [1]. Analytical methods used for determination of MTA and other transformation products of UDMH in soil samples require time and labor intensive sample preparation. A screening method based on solid-phase microextraction (SPME) in combination with gas chromatography – mass spectrometry (GC-MS) was proposed for quick and inexpensive detection of MTA and other UDMH metabolites [1]. However, matrix effect does not allow their accurate quantitative determination [1-2].

This work was focused on study and minimization of the effect of soil type, moisture and organic carbon content during determination of MTA by SPME-GC-MS. Results of experiments showed that MTA extraction efficiency from soil of different origin vary by the factor of 10. Highest response was observed for sandy soils, the lowest - for heavy loam. Increase of moisture content from 5 to 25% led to the decrease of MTA extraction efficiency for all studied soils except heavy loam.

To minimize matrix effect, isotopically labeled standard (MTA-d3) dissolved in excess water (5 mL) was added to 1 g of soil prior to analysis followed by intensive agitation during 15 min. This approach allowed considerable increase of method accuracy and determine concentrations being very close to spiked values (recoveries 50-120%). Method detection limit was 1 mg kg^{-1}. Compared to other available methods, the developed one is very simple, fast and fully automated using any SPME-capable autosampler.

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Acknowledgements

This work was conducted under the project “Development and implementation of “green” methods for determination of organic pollutants in soils” funded by the Ministry of Education and Science of the Republic of Kazakhstan.

VOLATILE ORGANIC COMPOUNDS MONITORING IN AIR OF ALMATY CITY BY USING GAS CHROMATOGRAPHY MASS SPECTROMETRY AND SOLID-PHASE MICROEXTRACTION

Bektasov M.A.[1], *Zagainova M.*[1], *Baimatova N.KH.* [1], *Kenesov B.N.* [1]

[1]Al-Farabi Kazakh National University
Almaty, Kazakhstan
Student
bektasovmarat@gmail.com

The major pollutants of the Almaty city are particulate matter, nitrogen oxides, aromatic and polycyclic aromatic hydrocarbons, concentrations of them are much higher than in developed countries.

One of main stages to reduce air pollution is its monitoring. The most difficult and time-consuming task in air monitoring is determination the concentrations of volatile organic compounds (VOCs). This makes significantly complicate the organization of monitoring this group of compounds in the cities of Kazakhstan.

The aim of work was to study the possibility of using solid-phase microextraction (SPME) coupled with gas chromatography-mass spectrometry (GC-MS) for monitoring of time weighted average concentrations (TWA) of benzene and its methyl derivatives (BTEX) in atmospheric air of Almaty.

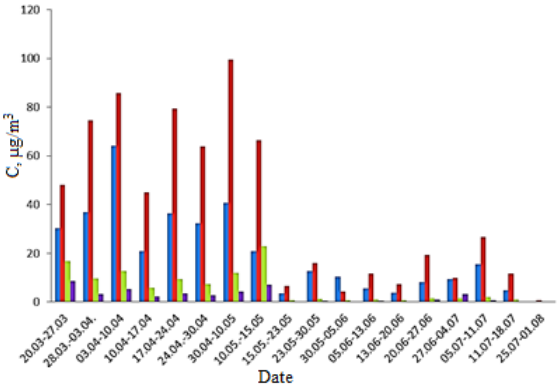


Figure 1. Screening of benzene, toluene, ethylbenzene and o-xylene in air of Almaty city by CAR/PDMS fiber

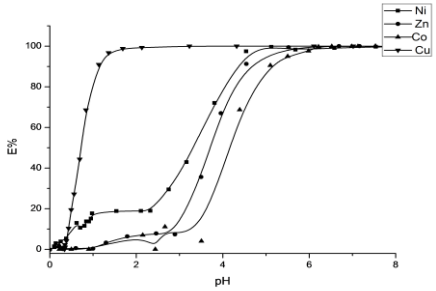
In May, benzene concentration in air decreased by 3-5 times. In March and April toluene concentration reached 100 µg/m^3. The maximum concentration of ethylbenzene was 29 µg/m^3. The average concentration of ethylbenzene was 7.6 µg/m^3. The maximum concentration of o-xylene during monitoring was 8.0 µg/m^3.

THE EXTRACTION OF TRANSITION METALS WITH N-(O,O'-DI-2-ETHYLHEXYL)PHOSPHORYLMETHYLSARCOSINE

Chibirev E.O., Garifzyanov A.R., Cherckasof R.A.

Kazan Federal University
Kazan, Russia
Postgraduate Student
chibirevegor@mail.ru

Brand new extraction systems that involve the usage of functionalized phosphorylated substances as extraction agents can serve as the basement for the creation of innovative extraction, concentration, separation techniques and for the rare elements analysis. An application of aminophosphoryl compounds into an extraction processes is poorly described in science literature. These compounds represent the group of species that combine the structure attributes of two extraction reagents types: phosphorus organic compounds and amines.
The goal of presented exploration is the study of N-(O,O'-di-2-ethylhexyl)phosphorylmethylsarcosine extraction properties relative to zinc, nickel, cobalt and copper ions. The relation between extraction degree and the pH of aqueous phase for the some ions is represented at the picture below. The concentration of extraction agent in chloroform was always 0.1M.



Picture 1. Extraction degree dependence on the pH of aqueous phase for the some ions.

According to the graph, extraction agent mentioned above shows great selectivity relative to the copper ions in acid medium.

This work was funded by the subsidy allocated to Kazan Federal University for the project part of the state assignment in the sphere of scientific activities(№ 4.413.2014/к).

Cu(II), Co(II), Cd(II) and Ni(II) SORPTION CHARACTERISTICS ON SILICA GEL FUNCTIONALIZED FORMAZAN GROUPS

Danilova A. B., Konshina D. N., Konshin B. B.

Kuban State University
Krasnodar, Russian Federation
Postgraduate Student
Anny.Furina@yandex.ru

Monitoring of heavy metals in natural and waste waters at their maximum permissible concentrations is an important analytical task. To solve it important to use methods of preconcentration, allowing separate defined elements of a large volume of salt solution of complex composition, lower detection limits, eliminate or significantly reduce the influence of the matrix effect. Thus considerable interest in acquiring expansion of the sorption materials.

We have previously was found that Cu (II), Co (II), Cd (II) and Ni (II) to exhibit the highest affinity towards extraction by silica gel covalent grafting formazans group (Table 1). The mutual influence of heavy metals in their simultaneously extraction, without various anion and in the presence of macro-components in amounts typical of river and sea water, carried out in a static mode were study. The residual concentration of analytes in solution determinations were performed by ICP-AES. The findings suggest that the high affinity of the surface to the copper ions in the competitive sorption. However, when implementation dynamic mode sorption, varying the velocity passing the solution from 3.8 to 1.1 ml / min was achieved quantitative sorption of Cu (II), Co (II), Cd (II) and Ni(II), which allows the simultaneously preconcentration of heavy metals.

Table 1: The coefficients of distribution and rate constants, activation energies, and the maximum capacity of the sorbent for Cu, Co, Ni, Cd

Me	Kd	A max, mmol/g	K of rate, g/mmol*s	Ea, кJ/mol
Cu	0,7± 0,1	0,03± 0,01	2,0 ± 0,2	31,8± 0,2
Co	0,5± 0,1	0,4± 0,1	5,7 ± 0,2	36,2± 0,2
Ni	2,2± 0,1	1,0± 0,1	7,7 ± 0,2	21,4± 0,2
Cd	1,7± 0,1	0,8 ± 0,1	9,2 ± 0,2	43,6± 0,2

The study was performed using the equipment of the Center for Joint Use "Ecological and Analytical Center". This work was also supported by Grants of the President of the Russian Federation (MK-4160.2014.3) and State Support (Pr. no. 14/55t (359)).

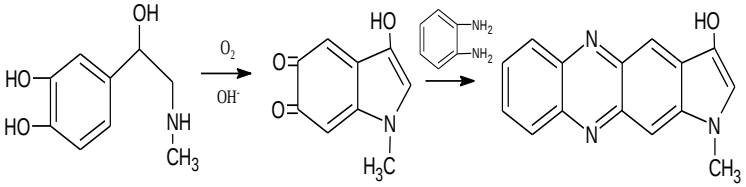
FLUORIMETRIC DETERMINATION OF EPINEPHRINE IN HUMAN URINE

Davletbaeva P.N., Falkova M.T.,Michaylov.E.V. Bulatov A.V.

Saint Petersburg State University
Saint Petersburg, Russia
Student
poli1993@yandex.ru

In our time the main goal of analytical chemistry is development of sensitive and rapid analysis of biological samples to obtain accurate and reproducible results. Catecholamines are the physiologically active substances responsible for biochemical reactions of the adaptation to acute stress. At various diseases they are secreted in the increased or reduced amounts. Accordingly, the determination of the exact value of the concentration of catecholamines allows us to use it for diagnostic purposes.

A sensitive fluorimetric method for the quantative determination of epinephrine was developed. It was based on the reaction of epinephrine with o-phenylenediamine with addition of acetone for increasing fluorescence intensity and further micellar concentration of the reaction product:



The micellar concentration of the reaction product in nonionic surfactant Triton-X114 with followed centrifugation and separation of organic phase allows to increase the sensitivity of the fluorimetric determination of epinephrine by 10 times compared with previously developed methods. The limit of detection (LOD) was assessed as $1{,}4 \cdot 10^{-12}$ mol/l. The developed method has been verified on the real biological samples (human urine). The accuracy of the results was confirmed by the added-found method and HPLC.

Part of the research was done using the equipment of Educational Resource Center of Chemistry of Research Park St. Petersburg State University.

BATCH-INJECTION DETERMINATION OF CEFOTAXIME AT THE ELECTRODE MODIFIED BY MIXED-VALENCE RUTHENIUM OXIDES

Degteva M.A., Leksina Y.A., Chelnokova I.A., Shaidarova L.G.

Kazan Federal University,
Kazan, Russia
Postgraduate
Degteva_marina@rambler.ru

Cefotaxime (CEF) belongs to semisynthetic cephalosporin antibiotics and is widely used to treat bacterial infections, mostly respiratory and urinary infections, because it is active against many bacteria. It is also illegally used in food preservation and processing, etc. Therefore, it is necessary to develop sensitive and selective methods for the determination of this compound in biological fluids and food industry.

From now on, different analytical methods have been reported for the determination of CEF, including high-performance liquid chromatography, spectroscopic methods and electrochemical methods. At the same time, electrochemical methods become popular because of their higher sensitivity, lower cost and faster operation than other methods.

Catalytic activity of mixed-valence ruthenium oxides electrodeposited on the glassy carbon electrode toward the oxidation of CEF was studied.

The oxidation of CEF at bare glass carbon electrode occurs at a very high positive potential. Mixed-valence ruthenium oxides electrodeposited onto the glassy carbon electrode, show catalytic activity in the electrooxidation of CEF. It is exhibited in decreasing of overvoltage of substrate oxidation and in increasing of oxidation current of modifier. This sensor shows sensitive and selective response at the oxidation of CEF.

The method of amperometric detection of CEF at this modified electrode in conditions of batch-injection analysis (BIA) is suggested. The dependence of the analytical signal from the electrochemical and hydrodynamic parameters of the system was determined. Working conditions for analytical signal registration were obtained. Under BIA conditions, the sensitivity, rapidity and productivity of the analysis increase compared to the stationary conditions. The dependence of the analytical signal from CEF concentration is linear in the range from 5×10^{-7} to 5×10^{-3} mol/l.

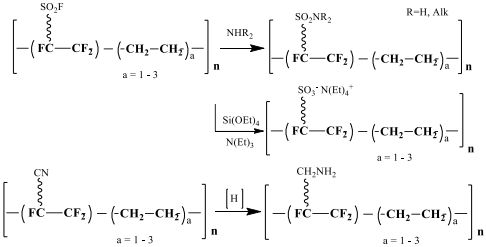
SYNTHESIS AND APPLICATION OF NEW POLYFLUORINATED POLYMERS IN CHROMATOGRAPHY AND CAPILLARY ELECTROPHORESIS

Dzema D.V.[1], Kartsova L.A.[1], Emelianov G.A.[2], Nayden S.V.[2]

[1]Saint Petersburg State University,
[2] Institute of synthetic rubber,
Saint Petersburg, Russia
Student
dasha.dzema@gmail.com

Topicality of fluorinated polymers in chromatography caused not only by high inertness and thermal stability but also by unique affinity to fluorine-containing compounds, hydro- and oleophobicity.

In this study copolymers of ethylene and perfluoro(3,6-dioxa-4-methyl-8-nonene) sulfonylfluoride with a different molecular weight and blockiness were synthesized and described. They were subjected to polymer-analogous transformations of sulfonylfluoride therminal groups to the sulfonate and sulfamide groups in order to control the solubility in water-organic solvent and complexion properties of these polymers. Also the polymers with amino therminal groups were prepared by copolymerization of ethylene and perfluoro (2,6-dioxa-2-methyl-7-octene)cyanide followed by reduction of therminal cyano group with $BF_3/NaBH_4$ system (pic. 1).



Picture 1. Polymer-analogous transformations

Columns for gas-liquid chromatography with synthesized copolymers as a stationary phase were prepared and tested. It was shown that application of both polymers as a buffer solution modifier in capillary electrophoresis stimulates increase of efficiency and selectivity for the separation of endogenic steroid hormones that are one analyte eluted in the absence of polymers additives. Also by HPTLC determination of water-soluble vitamins and amino acids, the addition of copolymers with sulfonate and sulfamide groups into eluent results in high separation efficiency because of covering the surface of silica gel and blocking of silanol groups. Prepared polymers with an amino-terminal groups are promising candidates for dynamic coating the walls of the quartz capillary in capillary electrophoresis and also are high thermo- and alkalistability materials.

DISPERSIVE LIQUID–LIQUID MICROEXTRACTION FOLLOWED BY MICROVOLUME UV-VIS SPECTROPHOTOMETRIC DETERMINATION OF SURFACTANTS IN WATER

Evdokimova E.S., Vakh Ch.S., Bulatov A.V.

Saint Petersburg State University
Saint Petersburg, Russia
Student
kotieva93@mail.ru

Sample preparation plays an important role in chemical analysis. As usual it includes the separation and/or preconcentration of the analytes from the sample matrix with the improvements of selectivity and sensitivity. However, conventional pretreatment methods such as liquid-liquid extraction (LLE) and solid-phase extraction are time consuming, labor intensive and require large amounts of organic solvents. Currently, the efficiency of preconcentration, miniaturization and significant reduction of toxic solvents volume are the main demands, which correspond to the concept of Green analytical chemistry.

Nowadays, despite the environmental toxicity, surfactants are widely used in both domestic and industrial areas. For the determination of surfactant spectrophotometry is commonly used. This procedure is based on the ion-pair extraction of surfactant with organic dye into a suitable organic solvent. Unfortunately, the volumes of the solvent requiring for the extraction are very large which is contrary to the concept of Green chemistry. To solve this problem is possible by the using of dispersive microextraction.

The novel and simple methods for the sensitive determination of surfactants in water are developed by combination of effervescence assisted dispersive liquid-liquid microextraction (EADLLME) and microvolume UV-vis spectrophotometry. The methods are based on the ion-pair extraction of cationic and anionic surfactants with organic dyes – methyl orange and azure A, respectively, into CHCl3 using EADLLME technique. The EADLLME assumes the dispersion of CHCl3 by CO2 bubbles, which are formed by the injection of carbonate-ions and CHCl3 mixture into acidic sample solution. The analytical performances of proposed EADLLME procedures were compared with the convectional dispersive liquid-liquid microextraction (DLLME). The appropriate experimental conditions for EADLLME and conventional DLLME were investigated.

ELECTROPHORETIC ON-LINE CONCENTRATION OF STEROIDS AND BIOGENIC AMINES USING IONIC LIQUIDS BASED ON IMIDAZOLIUM

Gallyamova V.F. , Bessonova E.A. , Kartsova A.A.

Saint Petersburg State University
Saint Petersburg, Russia
Student
valeria.gallyamova@mail.ru

Ionic liquids (ILs) - organic salts, melt at or below 100 ◦C and are characterized by high conductivity, ability to dissolve polar and non-polar analytes. The important thing about ILs is that varying the cation or anion may significantly affect physical and chemical properties: hydrophobicity, hydrophilicity, polarity, solubility etc. This makes them promising materials for using as components of chromatographic and electrophoretic phases. The method of capillary electrophoresis (CE) is an alternative and complementary to HPLC, with some advantages: high separation efficiency, small volume of samples, but the sensitivity to UV detection at 2-3 orders of magnitude lower than for HPLC. In our laboratory we found out that the introduction of ILs based on imidazole with a hydrophobic alkyl radical (C12, C16) in background solution (BGS) leads to the dynamic modification of the capillary wall of silica, and at concentrations above the critical micelle concentration, may form IL micellar phase, thereby increasing selectivity. It is hoped that using them in on-line sample preconcentration techniques (stacking, sweeping, dynamic pH junction) will lead to lower detection limits of biologically active analytes, which is important for solving medical and biological problems and find out additional characteristics of the ILs.

Underway we establish the possibility of ILs when introduced into the BGS to reduce the detection limits of diagnostically important biologically active analytes - hydrophobic (steroid hormones) and hydrophilic (catecholamines, catechins) analytes - in a capillary zone electrophoresis and micellar electrokinetic chromatography. The basic factors which allow increasing the efficiency and selectivity of separation: the influence of the concentration of ILs, the pH of the BGS, the input method of the sample. We obtained quantitative estimates of the effectiveness of on-line concentration. According to the obtained results scheme of electrophoresis analysis of biological objects were suggested.

The research was supported by Chemistry Educational Centre of St. Petersburg State University.

DISPERSIVE LIQUID–LIQUID MICROEXTRACTION PROCEDURE FOR SPECTROPHOTOMETRIC DETERMINATION OF FERROCENE IN GASOLINE

Gorbunov I.S., *Shishov A.Y.*, *Bulatov A.V.*

Saint Petersburg State University
Saint Petersburg, Russia
Student
i.gorbunov_chem@mail.ru

The present-day gasoline is produced by blending of components from different petroleum refining processes and different octane booster additives. Ferrocene was widely used as octane booster additive, but now its application is forbidden. From this point of view it is necessary to determine the ferrocene in gasoline to establish its falsification.

The first spectrophotometric method based on dispersive liquid-liquid microextraction of ferrocene into the aqueous phase and its oxidation with subsequent UV-VIS spectrophotometric detection is represented in this work. Under optimal experimental conditions the absorbance of the colored extract at the 620 nm obeys Beer's law in the range of 25-250 μM of ferrocene in gasoline. The proposed method was successfully applied to the determination of ferrocene in gasoline and the analytical results agreed fairly well with the results obtained by reference AAS method.

This work was supported by the Russian Foundation for Basic Research (project No.13-03-00031-a and 14-03-31092_mol-a). Scientific researches were performed at the Center for chemical analysis and materials research of St. Petersburg State University.

BIOLABELS BASED ON LUMINESCENT QUANTUM DOTS: ANALYTICAL APPLICATION

Goryacheva I.Yu.

Saratov State University, Professor

goryachevaiy@mail.ru

Presentation will cover state of the art of the luminescent quantum dots development and application as biolabels in analytical chemistry. Luminescent quantum dots are semiconductor light-emitting particles of nanometer scale that have emerged as a new class of luminescent labels for chemical analysis (first of all bio- and immunoassay), molecular imaging and biomedical diagnostics. Small size, bright luminescence, photostability and turnable spectral characteristics are well suited for s detection of multiple analytes with ultrahigh sensitivity. For successful development of new immunoassay methods two basic aspects for obtaining satisfactory sensitivity and reproducibility exist. The first key point is to exploit highly efficient signal-transduction labels (tags). Another important issue is to adapt a simple and sensitive signal-transduction method.

Properties of quantum dots, their synthesis and modification, variants of quantum dots' based labels, conditions of signal generation together with advantages and disadvantages will be discussed. Firstly used for bioimaging, they later became useful tools for immunoassay in the traditional microtiter plate format (fluorescent-linked immunoassay, FLISA) and after in sensors and rapid tests. The interest to this kind of labels for analytical applications could be even wider because the related toxicity (the main restriction of QDs application for in vivo imaging) is not so critical for in vitro goals.

Examples of luminescent quantum dots applications in analysis will be presented, perspectives for rapid tests, sensors as well as for modification of classical methods

The work was supported by Russian Scientific Foundation (project 14-13-00229).

VOLTAMETRIC DETERMINATION OF THE ACYCLOVIR AND GANCYCLOVIR IN DRUGS USING ELECTROCATALYTIC RESPONSE OF GLASSY CARBON ELECTRODE MODIFIED BY THE FILM OF RUTHENIUM HEXACHLORORUTHENATE

Ishnazarova L.R., Zhaldak E.R., Gedmina A.V., Shaidarova L.G.

Kazan Federal University,
A.M. Butlerov Chemical Institute
Kazan, Russia
Student
ishnazarova-88@mail.ru

Acyclovir (Acv) and gancyclovir (GAcv) are a basis of many drugs which are widespread as antiviral preparations. For control of Acv and GAcv content are employed various methods. The use of voltametry at the chemically modified electrodes (CME) with electrocatalytic properties allows increasing considerably sensitivity and selectivity of organic compounds determination.

Possibility of voltametric determination of ATsV and GTsV in model solution and drugs using glassy carbon electrode (GCE) modified by inorganic film of ruthenium hexachlotoruthenate (RuRuCl6) is studied.

Oxidation of Acv and GAcv in acid solutions on the bare GCE proceeds irreversibly and with overpotential. It is established that film immobilized by RuRuCl6 shows catalytic activity towards to Acv and GAcv oxidation. The catalytic effect is employed in decreasing of the potential and multiple increasing of the oxidation current of these compounds on this film electrode. Optimum conditions of receiving greatest catalytic effect at the film of RuRuCl6 are revealed. Kinetic parameters of electrooxidation of ACv and GACv at the CME with RuRuCl6 film were calculated.

Modes of voltametric determination of Acv and GAcv on CME with RuRuCl6 film are developed. The linear dependence of the catalytic current from analytes concentration is observed in range from 0.5 M to 5.0 M. CME with RuRuCl6 film was used in the analysis of drugs.

NON-ELECTROCHEMICAL SENSING OF INDIVIDUAL ION ACTIVITY: A NOVEL CONCEPT AND ITS VERIFICATION

Kalinichev A.V., *Peshkova M.A.*

Saint Petersburg State University
Saint Petersburg, Russia
Student
andre.kalinichev@gmail.com

Chemical sensors is an area of interest throughout many decades. Recently, a number of articles tagged "optical sensor" has drastically increased. Optical sensor (optode) is a device which translates activity of the analyte in the sample into optical signal. Optodes do not require electrical connection with neither power source nor detector, they can be miniaturized down to nano-size devices, are insensitive to the electric interferences, can provide minimally invasive and remote measurements which is attractive for *in vivo* applications. The response mechanism of bulk optodes is determined by ion-exchange (for cation-selective optodes) or co-extraction (for anion-selective optodes) [1].

Optode response depends on the ratio or product of the two ion activities: of the analyte ion and of the reference ion. This means independent data on the reference ion activity is required to unequivocally measure the analyte. Solution to this problem increasingly attracts attention of the researchers but no general concept of single-ion optical sensing was introduced so far [2].

Here we propose an approach for developing single-ion optode with the pH-sensitive colorimetric optode as an example. The ionic strength interference typical for this type of optodes will be overcome. In [3] it was shown that the single-ion optical sensor is eventually an analog of the galvanic cell with a liquid junction. This analogy can be achieved by adding to the membrane phase moderately lipophilic electrolyte, e. g. tetrabutylammonium tetrabutylborate (TBATBB), which distributes between the phases and stabilizes the interfacial Galvani-potential. In this contribution we describe the verification of the proposed approach with optical as well as electrochemical measurements. Composition of the optode membrane capable of individual sensing of pH is optimized for the respective physiological levels of ions. Ultimately, a theoretical model linking composition of the developed optode membrane with its response will be proposed.

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Acknowledgements

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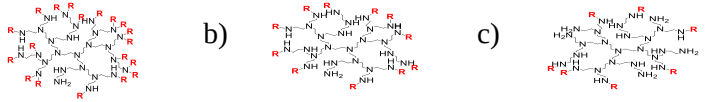
APPLICATION OF OLYGOSACCHARITED HYPERBRANCHED POLY(ETHYLENE IMINE)S AS NEW CHIRAL SELECTORS FOR DRUGS ENANTIOMERS SEPARATION IN HIGH PERFORMANCE THIN LAYER CHROMATOGRAPHY

Kapizova D.A., Dzema D.V., Kartsova L.A.
Saint Petersburg State University,
Saint Petersburg, Russia
Student
kapidiana@yandex.ru

The importance of the monitoring of drugs enantiomeric purity is explained by various actions of the enantiomers on the human organism (it can be also the toxic and mutagenic action). The aim of this investigation was to identify the possibility of hyperbranched polymers as chiral selectors in high performance thin layer chromatography (HPTLC) for the separation of enantiomers of nonsteroidal anti-inflammatory drugs (ibuprofen, ketoprofen and ketorolac) and β-blockers (propranolol, carvedilol and sotalol) in it pharmaceuticals. Hyperbranched polymers under consideration consist of functionalized dendritic core (poly(ethyleneimine) – PEI (5 and 25 kDa) with different degree of substitution of amino groups by oligosaccharide (maltose, lactose and maltotriose) and were used as the components of stationary phase (Picture 1).

a) b) c)



Picture 1. PEI-OS: a) structure A (77% modified terminal amino groups), b) the structure B (32%), c) the structure C (16%).

During the searching of optimal chiral separation conditions several factors were varied: the composition of eluting systems, structure of polymer selectors (core weight (5 and 25 kDa), the chemical nature (maltose, lactose, maltotriose) and density (structure A, B and C) of OS shell), concentration of polymer in the modified solutions, one-dimensional (1D) and two-dimensional (2D) eluting way. In case of β-blockers the best chiral separation were achieved by using hb PEI polymers with the maltose and lactose shells. Optimized chiral separation conditions were realized by the analysis of drugs "Anaprilin", "Akridilol", "Ibuprofen" and "Sotageksal", that were as racemate. It is of interest, that the separation of carvedilol enantiomers was achieved only by simultaneous using of two chiral selectors: *L*-prolin in the mobile phase and PEI-OS modified stationary phase. The maximal values of enantioselectivity factors (α = 6,4) were observed only with a PEI-Lac-A 5 kDa (2 mg/ml) stationary phase and *L*-proline modified mobile phase(3,4%). Thus, hb poly(ethylenimine) polymers surrounded by olygosaccharided shell should be recommended as a chiral selectors for TLC effective separation of β-blockers.

ELECTRONIC TONGUE IN ARTIFICIAL SALIVA – ONE MORE STEP TOWARDS THE ARTIFICIAL MOUTH

Khaydukova M.M.[1], *Immohr L.I.* [2], *Pein M.*[2], *Kirsanov D.O.* [1]

[1]Saint Petersburg State University,
[2] Heinrich-Heine University Duesseldorf,
Saint Petersburg, Russia
PhD student
khaydukova.m@gmail.com

Oral administration is a convenient way for drug delivery, but active pharmaceutical ingredients (APIs) often possess an unpleasant taste. One common way to taste-mask solid oral dosage forms is delaying the API release. This technique allows for minimizing the contact time between taste buds and the API, thus avoiding taste identification by the patient. According to the Pharmacopoeias the drug release rate for solid dosage form has with regard to quality assurance to be estimated with defined dissolution tests. As a result, a dissolution profile is obtained, reflecting the functional connection between residence time in the medium and amount of released APIs.

For taste-masking studies, usually water or artificial saliva (AS) are applied as dissolution media. However, no specification of the AS composition is provided by the Pharmacopoeias and due to that the compositions of AS vary widely [1]. In our study, AS contained inorganic salts, mucin and α-amylase to simulate ionic, protein and enzyme composition of human's saliva. This composition allows for approaching to *in vivo* conditions vs. commonly applied *in vitro*. Usually, the API concentration can be detected by UV spectroscopy. In case of the used complex AS, spectrophotometric method was not applicable due to intense absorption of the AS itself. Thus, applicability of potentiometric multisensor system ("electronic tongue") for dissolution profiling was investigated. The tests were performed in water and protein based AS for two types of tablets.

The obtained results suggest that multisensor systems can be successfully applied for dissolution profiling in complex media which are not compatible with optical spectroscopy methods. Nonetheless, current multisensensor system requires several improvements, such as reducing sensors size to address hydrodynamic issues in standard dissolution test vessel.

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NEW AERO-HYDRAULIC SCHEMES IN STEPWISE INJECTION ANALYSIS

Khydiakov U.S.[1], *Mozzhyhin A.V.*[1], *Moskvin A.L.*[2]
[1] ZAO NPO Granit-NEMP.
[2] Saint Petersburg State University. Department of Analytical Chemistry.
Saint Petersburg, Russian Federation
Research Assistance
uhs83@mail.ru

A new method of flow analysis - proposed in 2007 [1] stepwise injection analysis (SWIA) has a several of important advantages regarding the method flow-injection analysis (FIA). However, a disadvantage of SWIA relatively FIA is a long time of analysis. The study of SWIA allowed to change the initial hydraulic circuit and twice reduce the time of determination. The time of analysis became same time of the analogue techniques in FIA. In figures 1, 2, 3 aero-hydraulic circuits SWIA are presented.

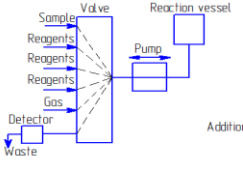

Figure 1. The original scheme SWIA [1]

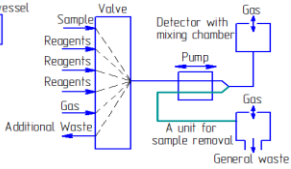

Figure 2 A new scheme SWIA with the introduction of solutions into the cell through the bottom

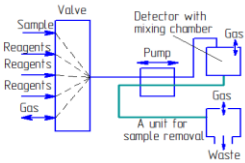

Figure 3 A new scheme SWIA with the introduction of solutions into the cell through the top

The techniques of determination of Mn (II) and nitrite were made using the presented schemes. Times of measurements according to the presented diagrams in figures 1, 2, 3 ions Mn(II) were 7.5, 4.5 and 3.8 min, nitrite ions 8, 5, and 4.5 min, respectively. Reducing the time of analysis were 38-40 % according to the scheme in Fig. 2 and 45-50 % according to the scheme in Fig. 3.

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HAIR SURFACE ANALYSIS USING GAS CHROMATOGRAPHY − MASS-SPECTROMETRY

Kislyakova Y.Y., Sheshko T.F., Serov Y.M.

Russian People's Friendship University
Moscow, Russia
Postgraduate student
rupf@mail.ru

Hair surface analysis for different organic exogenous compounds is one of the main parts of toxicological hair analysis. Gas chromatography – mass-spectrometry is one of the most popular and effective method for hair surface analysis but it is also useful for hair decontamination procedure effect estimation for further internal area analysis of this biological object.

According to literature analysis four main schemes of sample preparation and hair surface decontamination procedures for the further hair analysis using chromate-mass-spectrometry were selected. Experimental estimation of the selected schemes was done and the universal methodology for hair surface analysis and decontamination was proposed.

Schemes estimation was done using model hair samples prepared with special technic with exactly known amount of external pollutant which was imitated phenylalkylamines. Instrumental analysis was provided using gas chromatography method with mass-selective detection (GC-MS) on equipment by Agilent Technologies (USA), consisted of gas chromatograph 5890 and one quadrupole mass-detector 5975C. Chromatograph was equipped with capillary column DB-5MS length 30 m, thickness 0,25 mm and internal diameter of sorbent − 0,25 microns.

According to obtained experimental data comparison new universal method of hair surface analysis and hair decontamination procedure during toxicological internal hair area study were suggested.

THE ROLE OF IONIC LIQUIDS IN SELECTIVE ELECTROPHORETIC DETERMINATION OF HYDROPHOBIC AND HYDROPHILIC ANALYTES IN NATURAL OBJECTS

Kolobova E.A., Kartsova L.A., Bessonova E.A.

Saint Petersburg State University
Saint Petersburg, Russia
Postgraduate students
ekatderyabina@mail.ru

Ionic liquids (ILs) are salts with melting points below 100 ^{0}C. As a rule they consist of large a organic cation and a organic or inorganic anion. Despite the fact that ILs have been known long, their potential in separation methods has been demonstrated only recently.

The influence of ILs based on imidazolium (C_{12}MImCl, C_{16}MImCl) on electrophoretic migration parameters of hydrophilic (amino acids and catecholamines) and hydrophobic (steroids) solutes was investigated in the work.

It was shown that introduction of ILs into the running buffer resulted in the dynamic modification of the quartz capillary wall at pH=2,0. This fact was confirmed by the existence of the reverse electroosmotic flow (EOF). When the IL concentration in the buffer electrolyte was less than the critical micelleformation concentration (CMC) – the condition of capillary zone electrophoresis (CZE) – the efficiency growth for amino acids and catecholamines enlarged 2-3 times. The separation selectivity increased in the micellar electrokinetic chromatography when the IL served as a pseudo-stationary phase.

It was found that the incorporation of the ionic liquid in the electrophoretic C_{12}MImCl system allowed to determine amino acid glycine which was not absorbed in UV-area of spectrum under the indirect detection at 220 nm.

Amino acid ionic liquids (AAILs) C_4MIm^+L-Pro^- и C_6MIm^+L-Pro^- were synthesized. The obtained compounds were characterized by NMR-spectra. AAILs were used as chiral selectors in ligand separation of racemic mixtures of amino acids.

IONIC LIQUIDS ARE EXTRACTANTS OF STEROID HORMONES AND AMINO ACIDS

Kolobova E.A., Kartsova L.A., Bessonova E.A.
Saint Petersburg State University
Saint Petersburg, Russia
Postgraduate Student

ekatderyabina@mail.ru

The use of ionic liquids (ILs) in separation methods has been the object of intense interest for about a decade. ILs are quaternary salts of organic bases with the melting point below the room temperature or close to it. They are called *«room temperature - ionic liquids»* (RTILs). Those substances are good solvents for a wide range of organic compounds due to their low volatility and negligible vapor pressure, good thermal stabilities, and electrolytic conductivity. They are also applied in solid-phase and liquid-liquid extractions at the sample preparation.

Extraction processes of amino acids and steroid hormones into hydrophobic ILs ($C_6MImNTf_2$, C_6MImBF_4, C_8MImBF_4) were investigated in research.

It was established that the highest extraction degrees of amino acids from aqueous solutions (pH = 2.0) were achieved by using the ionic liquid $C_6MImNTf_2$. The formation of the inclusion complex between the protonated amino group of amino acids and macrocycle 18-crown-6 favored the amino acid transition from the aqueous phase into the ionic liquid. The back extraction was carried out with 0.3 M borate solution (pH = 9.3) .

In the case of steroid hormones other patterns were found: the extraction degrees increased with the increase of the length of the alkyl radical of the IL, and when under using an anion in IL such as tetrafluoroborate BF_4^-.

The scheme of urine sample preparation was proposed for the electrophoretic analysis of amino acids with the extractions degrees 92-100 %.

ANALYSIS OF THE REACTION MASSES OF XYLENE'S ALKYLATION BY PROPYLENE

Kondratev O.I., Vostrikov S.V., Nesterova T.N.

Samara State Technical University,
Student
olkondor95@gmail.ru

Isopropylxylene (*iso*-PX) are raw materials for xylenols production - starting materials for the preparation of highly effective antioxidants and polymers with valuable properties.

As a result of alkylation of any of the xylenes, a complex mixture is formed and it contains compounds such as polymethylbenzenes, isopropyltoluenes (*iso*-PT) and *iso*-PX. Thus, development of quantitative analysis with the utmost separation of the components of the reaction mixture was made.

Component identification was carried out the following way:

- Structure of substances identified by chromato-mass-spectrometric analysis
- Benzene, toluene, polymethylbenzenes and all xylenes identified by addition of individual substances
- Components in the group mono-*iso*-PT identified by a special experiments: in the alkylation, 4- *iso*-PT и 2- *iso*-PT dominated in the kinetic mode, 3- iso-PT и 4- iso-PT dominated in the thermodynamic mode with the substantial absence of 2- *iso*-PT
- *iso*-PX identified similar to *iso*-PT:

Isopropyl-p-xylene (*iso*-P-*para*-X): in the group mono-*iso*-P-*para*-X we have one component – 2-*iso*-P-*para*-X.

In the group di-*iso*-P-*para*-X – 2,5-di-*iso*-P-*para*-X > 2,6-di-*iso*-P-*para*-X with increasing predominance of 2,5- di-*iso*-P-*para*-X in the transition from kinetic mode to thermodynamic mode of alkylation.

Isopropyl-m-xylene (*iso*-P-*meta*-X): in the group mono-*iso*-P-*meta*-X in the kinetic mode of alkylation –

4-*iso*-P-*meta*-X > 5- *iso*-P-*meta*-X >> 2- *iso*-P-*meta*-X.

In the thermodynamic mode of alkylation we can observe significant predominance 5-*iso*-P-*meta*-X concentration in the reaction mass over 4-*iso*-P-*meta*-X and 2-*iso*-P-*meta*-X. In the group di-*iso*-P-*meta*-X – 4,6-di-*iso*-P-*meta*-X > 2,5 di-*iso*-P-*meta*-X >> 2,4-di-*iso*-P-*meta*-X, with a decrease in predominance of 4,6-di-*iso*-P-*meta*-X over 2,5-di- *iso*-P-*meta*-X and 2,4-di-*iso*-P-*meta*-X in the reaction mass in the transition from kinetic mode to thermodynamic mode of alkylation.

Isopropyl-o-xylene (*iso*-P-*ortho*-X): in the group mono-*iso*-P-*ortho*-X – 4-*iso*-P-*ortho*-X > 3-*iso*-P-*ortho*-X with increasing predominance of 4-*iso*-P-*ortho*-X concentration in the transition from the kinetic to the thermodynamic alkylation's mode. In the group di-*iso*-P-*ortho*-X in both modes of alkylation we can observe ratio of components - 3,5-di-*iso*-P-*ortho*-X > 3,6-di-*iso*-P-*ortho*-X >> 4,5-di-*iso*-P-*ortho*-X

As a result of work done we developed a quantitative analysis of the reaction mixture of alkylation xylenes with propylene with limit separation of the components of the reaction mixture.

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DEVELOPMENT OF THE TECHNIQUE OF ARC EMISSION SPECTRAL ANALYSIS OF TOBACCO WITH PRE-MINERALIZATION

Kononov A.S., *Savinov S.S.*, *Drobyshev A.I.*
Saint Petersburg State University,
Saint Petersburg, Russia
Student
kononov-sashulya@mail.ru

It is difficult to imagine our world without tobacco products: according to the World Health Organization today 1.3 billion of the world population are addicted to the tobacco. Most of the people know what damage to health nicotine and tar (basis of tobacco) cause. But besides them tobacco contains heavy metals, which could provoke irreparable harm. As far as tobacco smoke is directly contacts with the lungs, these elements easily penetrate into the human organism.

Many heavy metals, such as Fe, Cu, Zn, Mo involve in biological processes and in certain amounts are necessary for the normal functioning of plants, animals and humans. On the other hand, some heavy metals and their compounds are carcinogenic and can accumulate in tissues and organs, causing some diseases and disastrous impact on the human organism. For example, an excessive content of Pb (the presence of which has been proved in tobacco) in the body leads to the affection of the hematopoietic and nervous systems, kidneys. High content found in tobacco Cd results in increasing of the risk of "earn" lung cancer, a renal dysfunction, an increase blood pressure, and then a stroke. Therefore the determination of heavy metals in tobacco is important problem of modern toxicology.

Such highly sensitive and most commonly used methods as ET-AAS and ICP-AES require complex sample preparation, including mineralization of samples. In the literature there is a large number of substantially different (in duration, equipment and reactants used) performances of this step. The purposes of this study are the experimental comparison of different ways of sample mineralization and its optimization for subsequent determination of heavy metals and other elements. Identification of the tobacco elemental composition and assessment of the content of detected elements are also presented. Thereto we use an alternative to ICP-AES and ET-AAS – a.c. arc AES analysis of liquid samples, previously developed in our laboratory and successfully showed itself to advantage in the analysis of biological fluids.

Part of the research was done using the equipment of Educational Resource Center of Chemistry of Research Park St. Petersburg State University.

USAGE OF THE HIGH-PERFORMANCE LIQUID CHROMATIGRAPHY ASSESSMENT METHOD BY BENZO(A)PYRENE URBAN POLLUTION

Konysbayeva A.B.[1], *Bakhov Zh.K.*[2]
[1]M.Auezov South Kazakhstan State University Shymkent city, Kazakhstan
[2]M.Auezov South Kazakhstan State University, Shymkent city, Kazakhstan
Postgraduate
a.konysbayeva@gmail.com

In recent years, Kazakhstan has been an intense increase in the number of vehicles. This paper presents the results of experimental studies of environmental pollution (snow and soil) Shymkent benzo(a)pyrene under the influence of vehicles. Atmospheric pollution of Shymkent recording by the system of state control. Evaluation of air pollution on the highways and in the surround in residential area is based on the definition in the air content of the main components of exhaust gases (carbon monoxide, nitrogen oxides, sulfur dioxide, and formaldehyde).

In the course of research on the individual components of pollutants established qualitative and quantitative laws between the content of benzo(a)pyrene. In determining benzo(a)pyrene in the environment used method of high performance liquid chromatography (HPLC) [1], which was implemented on the device "Varian Pro Star 500" in the test laboratory of engineering profile SKSU named after M. Auezov.

Snow cover is an inartificial natural tablet drives of aerosol. The study of the spatial dynamics of the distribution of contaminants in the snow reveals the sources of aerosol emissions, to differentiate footprint and propagation distance, perform an assessment of the total output and the characteristics of the particulate composition [2]. Analysis of the average annual concentrations (mg/m^3) of pollutants in the atmosphere of Shymkent for 2008-2014 year shows that the CO concentration is in the range between 1250-2100 mg/m^3, NO_2 - 40-55, SO_2 - 3-5 mg/m^3 Formaldehyde - 12.9 mg/m^3.In general, these figures though are the maximum permissible limits, in some periods, especially during adverse weather conditions, in the busiest transport stations in the city there is an excess of nitrogen dioxide and formaldehyde. For these areas of the city of Shymkent characterized by an increased content in the soil and snow cover benzo(a)pyrene. The research results can be used to monitor mutual observations of the snow and the surface air of the city, to make decisions to improve the environmental situation in the city.

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PHOSPHOLIPID DETERMINATION IN BIOSAMPLES BY MALDI MASS SPECTROMETRY

Kotryakhov I.A.[1,2], *Milman B.L.*[2]

[1]Saint Petersburg State University,
[2] FSBSI "Institute of Experimental Medicine"
Saint Petersburg, Russia
Student
ivankotof@gmail.com

Metabolomics is a relatively new and rapidly expanding field of research. An integral part of it is lipidomcs, which specifically studies lipidom – full complex of lipids, participating in intracellular metabolism reactions. The rapid development of techniques for analysis of biosamples in a past decades, mainly mass spectrometry, made possible a more deep understanding of a intracellar metabolism. In this report, we use MALDI-TOF (matrix-assisted laser desorption/ionization time-of-flight mass spectrometry) technique to determine the qualitative composition of the lipid mixtures, and to explore possibilities of using this technique as a quantitative analytical tool. To achieve this goal we choose to study composition of phosphocholines (PC) and lysophosphocholines (LPC), the most abundant parts of lipidom and the main components of cell membranes.

All measurements were made on a Bruker ultrafleXtreme mass spectrometer. The biological samples were human blood plasma and mouse lung lavage. Two common MALDI matrices, 2, 5-dihydroxybenzoic acid (DHB) and α-cyano-4-hydroxycinnamic acid (HCCA), were used. Lipid compounds were identified by nominal and exact ion masses including product ions generated by the technique of tandem mass spectrometry (LIFT technique). Quantitative data were obtained by spiking biosamples or their extracts with the pertinent standard.

Analytical procedures under consideration led to reliable identification of several tens of LPCs and PCs, including such abundant bioanalytes as LPC(16:0), LPC(18:2), PC(34:2), PC(36:2) etc. Also, the similarity in precursor ion fragmentation pathways were observed between MALDI-LIFT and the well-known combination of electrospray and ion collision activation. In quantitative analysis, several mass peak intensity ratios, e.g LPCs/PCs were measured. The repeatability and reproducibility of the ratios were found out to be not high. That restricts the use of MALDI in very accurate analytical measurements and make it possible to discriminate between significantly different samples, e.g. some lavage ones from healthy and infected mice.

We want to thank our colleagues Natalya Lugovkina for her help with the sample treatment and Yana Zabrodskaya, who kindly provide lavage samples.

DETERMINATION OF CARBON IN REACTOR-GRADE METALLIC SODIUM

Kozhukhova A.E.[1], *Nizovtsev A.A.*[2], *Krasikova E.A.*[2], *Ilicheva N.S.*[2]

[1]IATE MEPHI
[2]SSC RF-IPPE
Obninsk, Russia
Student
alina_18031994@mail.ru

Input control of the carbon concentration and regular control during operation of the cooling circuit are necessary to ensure the normal exploitation of sodium cooled fast reactors. Sodium coolant must comply with the technical requirements on the carbon concentration [1].

Currently, distillation-potentiometric method is accepted for the determination of carbon concentration in metallic sodium [1]. This method combines, except distillation, simultaneous processes of distillation residue combustion and potentiometric titration. Run time of the unit analysis with prepared work solutions and tuned equipment is three hours. This technique is labor consuming and is characterized by essential ratio error (± 75%).

The aim of this work was to determine the carbon in metallic sodium using express analyzer.

Following equipment was used for determination of carbon in sodium samples: sampler-distillator, radiation-protective glove-box 7BP1-OS Plexiglas, carbon analyzer «METAVAK-CS30». Sodium samples were distillated in vacuum at 350 °C in precalcined quartz crucibles than were made up in an argon gas atmosphere in glove-box and were combusted in an oxygen flow at 1300 °C using the carbon analyzer. The generated carbon dioxide was transported on the IR-detector, and the carbon concentration in the sample was calculated. The average content of the carbon in the analyzed samples of metallic sodium was attained at 28 ± 5 ppm. The values obtained are precision and are characterized by ratio error of 18%. Thus, the determination of carbon concentration in metallic sodium using express analyzer reduced the labor consume and lowered the time of analysis.

References

[1] Industry Standard 95 10582-2003

THE INFLUENCE OF THE REDOX POTENTIAL OF THE MEDIUM ON THE PROPERTIES OF POLYANILINE ACTUATOR

Krylov A.A.

Tver State University,
Tver, Russia
Student
tolya21@yandex.ru

Changing the geometric dimension of polyaniline's (PANI) layers under the current flow is described in several publications. At the same time, it is known, that changing of the redox potential of the medium can also effect on the degree of oxidation of the PANI (redox actuator), and consequence, on the actuator's properties. For research we used a thin platinum foil coated on its surface with one hand PANI's layer by electrochemical oxidation by the classic method. Such design makes it easy to evaluate the change in geometric dimensions of PANI's layer on the degree of curvature platinum foil or substrate. To create the necessary redox potential of the system we used redox buffer solution based on Fe^{2+}/Fe^{3+}. All experiments were performed in an acid medium. Experiments have revealed that the degree of curvature of the actuator depends on the redox potential and the deviations has linear relation in the range from 200 mV to 600 mV. It was found, that the pH has a significant impact on the magnitude of the response of the actuator. With increasing pH from 0 to 3,5 response, naturally, decreases, and at higher values actually disappears completely. This can probably be explained by the fact that at a pH of greater than 4 electrical conductivity of PANI is absent. Changing of the redox potential from the least value to greatest promotes rapid changes in position of the actuator. However, changing the potential from high to low occurs deceleration of response. That is, observe a kind of hysteresis. The magnitude of the hysteresis is dependent on the acidity of the medium. In a highly acidic medium hysteresis is minimal and at pH of 3, 5 has a maximum value. The response of the actuator is saved when you repeatedly change the redox potential of the medium, resistant to small mechanical stress, and doesn't lose its properties by drying. Based on the obtained regularities developed redox indicator with direct readout. This detector represents as a long coiled platinum foil, one surface of which is covered with a layer of PANI. The inner end of the spiral are fixed and on the outside has a pointer as an arrow, with which you can take readings by the scale. In order to eliminate the influence of hysteresis before the measurements the device must be placed for a short time in a medium with a redox potential of 300 mV. This sensor was used to determine the redox potential of model mixtures and showed good results. When placed in an environment with the selected redox potential the stable readings are formed for a few seconds.

STEPWISE INJECTION DETERMINATION OF NITRITE AND NITRATE IN NATURAL WATER

Kudriashova V.A. [1],*Khudiakov U.S.*[1], *Zakharenko V.M.*[1], *Mozzhykhin A.V.*[1], *Moskvin A.L.*[2]

[1] ZAO NPO Granit-NEMP.

[2] Saint Petersburg State University. Department of Analytical Chemistry.

Saint Petersburg, Russian Federation

Research Assistance

varvarakudryashova@mail.ru

The photometric technique was developed for the determination of nitrite and nitrate ions in natural fresh and salt waters by stepwise injection analysis (SWIA). The technique is based on the catalyzed by nitrite ions oxidation of Mn (II) by H_2O_2. The determination of nitrate ions is produced after their recovery with copper-plated Cd-reducer. The ranges of determined concentrations for nitrite ions is $5 \cdot 10^{-3}$ – 0.4 mg/dm^3 and for nitrate ions is 0.1 - 10 mg/dm^3. The limits of detection are $5 \cdot 10^{-4}$ mg/dm^3 and $2 \cdot 10^{-2}$ mg/dm^3 respectively. The time of one measurement is not more than 7 minutes. The error of measurement is not more than 15%. The technique was tested by additive and dilution method for different types of waters and by reference method and also the effect of salinity was studied. Main advantages of the technique are removing of toxic Griess-Ilosvaya reagent, saving reagents and reducing the amount of drain, high sensitivity and selectivity. The technique is used for automatic determination of nitrite and nitrate ions in the continuous mode with speed 9 analysis / h, or in the mode with delay between tests. Aero-hydraulic circuit for the operations of sample preparation and measurements is presented in figure. Values of absorbance of the background solution and solution with catalytic reaction are transmitted to the PC. The PC calculate concentrations of nitrite and nitrate ions by calibration graph.

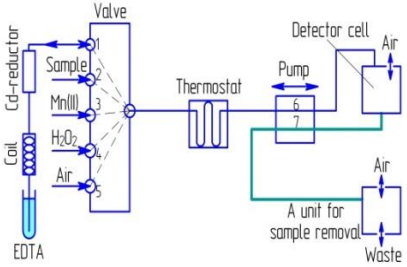

Figure. Aero-hydraulic circuit for the nitrite and nitrate determination.

COMPOSITION OF SHALE OIL SUPERADIABATIC PYROLYSIS PRODUCTS

Kudryavtseva E.V.[1], *Davydova G.I.*[2], *Dorofeeva T.V.*[2], *Kolesnikova Yu.Yu.*[2], *Shunina I.G.*[2]

[1]Lomonosov Moscow State University,
[2]Institute of Problems of Chemical Physics (Russian Academy of Sciences)
Moscow, Russia
Student
elenakudryavts@yandex.ru

Shale oil is valuable for industrial production. Oil is obtained by thermal decomposition of kerogen - solid organic material located in the shale deposits. During the processing of shale oil a number of useful chemicals are produced, but it`s main part is used as a synthetic alternative fuel source, which is important due to the exhaustion of the world's oil resources [1]. Due to the necessity to improve the technology of processing of oil and gas shale the investigations are carried out in this area. One of the most important stages of the process is the determination of chemical composition of shale oil by different analytical methods.

Shale oil samples were obtained by filtration combustion of shale at the superadiabatic mode [2]. Initially, vacuum distillation of original shale oil was carried out in the temperature range 100 – 250 °C. The first fraction was about 10% by volume of the initial resin and contained a large amount of water, which was separated by separatory funnel.

The initial oil and the distillation residue obtained after distilling off the low-boiling fraction were investigated by infrared (IR) spectroscopy. The spectra obtained were virtually identical, because the volume of the distillation residue was about 90% of the original resin. The spectrum revealed bands, which were characteristic for the following classes of compounds: saturated and unsaturated hydrocarbons, benzene homologues, aromatic aldehydes [3]. By elemental analysis the initial oil composition corresponded to the following: C (~80%), H (~10%), O (~10%), S (~0%).

A detailed qualitative and quantitative composition of the first low-boiling fraction was analyzed. Putative organic substances which are presented in the mixture were identified by gas chromatography - mass spectrometry (GC-MS) method using a spectra library. When analyzing data were obtained, we revealed that the sample contained representatives of the following classes of organic substances with the number of carbon atoms from 5 to 12: alkanes, alkenes, dienes hydrocarbons, cyclic hydrocarbons, aromatic compounds, polycyclic aromatic compounds, aromatic aldehydes, saturated and unsaturated ketones. Certain functional groups of atoms were identified by the method of infrared spectroscopy. The data of IR spectroscopy confirmed the results

obtained during the analysis by GC-MS. Also, elemental analysis of the first fraction was carried out. The structure included the following elements: C (~78%), H (~10%), O (~12%), S (~0%).
Thus, compounds that may inhibit hydrotreating processes (unsaturated and aromatic compounds, oxygen-containing compounds) were detected in the composition of resin. Therefore, investigated mixtures are difficult to refine, and this process requires highly efficient hydrotreating catalysts. The data obtained could be useful to improve the methods of processing of oil shale by selection of a suitable catalyst of hydrotreating, as well as for the following investigations in the area of the production of alternative fuels.

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VOLTAMMETRIC DETERMINATION OF HYDROGEN PEROXIDE H_2O_2 ON ELECTRODES MODIFIED BY MESOPOROUS STRUCTURES BASED ON IRON OXIDE (III) NANOPARTICLES.

Golubeva A.A.

Saint Petersburg State University,
Saint Petersburg, Russia
Student
golubeva__nastya@mail.ru

1. The electrochemical behavior of iron oxide (III) nanoparticles is studied in nafion films planted on the gold electrodes and the ITO surfaces.
2. By the cyclic voltammetry it is found that the peaks on the voltammograms correspond cathode reduction and anode oxidation of iron oxide nanoparticles.
3. Injection of hydrogen peroxide additions into solution leads to the disappearance of the electrolytic reduction peaks of iron (III) nanoparticles and the appearance of catalytic oxidation / reduction peaks of hydrogen peroxide H_2O_2.
4. Current of the peaks of catalytic reduction of hydrogen peroxide linearly depends on its concentration in the range of 4 * 10-7 ÷ 10-7 M.

MODERN METHODS IN THE ANALYSIS OF RECENT SEDIMENTS FROM THE DELTA OF LENA RIVER

Kurtukov V.V.[1], *Chekantsev N.V.*[1], *Goncharov I.V.*[2]

[1]Tomsk Polytechnic University,
[2]Joint Stock Company "Tomsk Oil and Gas Design and Research Institute"
Tomsk, Russia
Student
artisticpossum@gmail.com

The study is dedicated to modern methods of soil sample analysis. For better clarity, a set of soil samples from the delta of Lena river was taken as an object of research. The first stage of the analysis is sample preparation. Soil particles were ground and then passed on to the stage of 'Rock-Eval' pyrolytic analysis where thermal modelling of the source bed evolution is carried out. During gradual heating, amount of evaporated free hydrocarbons and bound hydrocarbons is evaluated. Judging by these two values and the Total Organic Carbon (TOC), one can assess oil potential of a sample.

After deciding which samples are to be further analyzed, the chosen batches are undergoing cold extraction in Soxhlet extraction apparati in order to get materials appropriate for chromatomass-spectrometry. Chromatomass-spectrometry is then performed in the linear temperature programming mode. Resulting mass-fragmentograms are processed and analyzed.

The full cycle of research was carried out for 17 samples from delta of Lena river and the results were acquired and interpreted.

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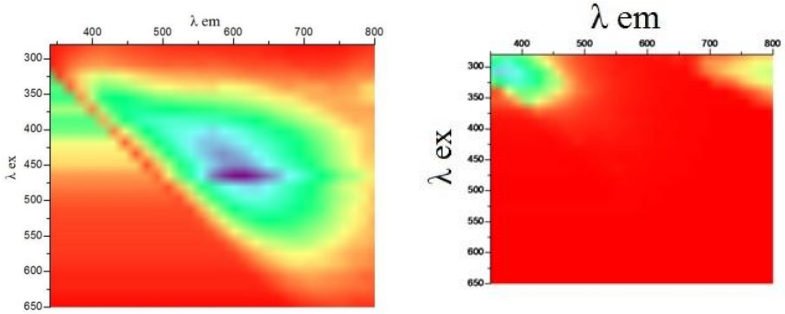
FLUORESCENCE OF LIGNINS

Kuznetsova M.V., Kosyakov D.S., Ladesov A.V., Bogolitsyn K.G.

Northern (Arctic) Federal University named after M.V. Lomonosov,
Arkhangelsk, Russia
PhD student
Marie.89@mail.ru

2D excitation-emission fluorescence spectra of lignin preparations in solid state and in solution were recorded using the Horiba Fluorolog-3 double monochromator luminescent spectrometer. The presence of long wavelength emission bands in visible region of spectrum is shown for solid lignin samples, which is not usual for polymer solutions (Picture 1). Spectra show the quenching of fluorescence due to solvation effects.



Picture 1. 2D excitation-emission spectra of lignin samples recorded in front face mode: dioxane lignin in solid state (left) solution of dioxane lignin (right). Color changes from red to violet are showed an increase in fluorescence intensity.

The obvious dissimilarity in excitation-emission spectra and fluorescence intensities for lignins of different origin is demonstrated. These facts are of great significance for the rapid identification of lignins and their determination in lignocellulosic materials. Effect of lignin functional composition on its fluorescent properties and the role of carbonyl groups in fluorescence quenching are studied. The excitation energy transfer in lignin macromolecules is discussed.

Acknowledgements

The authors are grateful to Russian Foundation for Basic Research (project No. 14-03-31593) and Ministry of Science and Education for financial support. Research was done using equipment of Core Facility Center “Arktika” Northern (Arctic) Federal University named after M.V. Lomonosov

FRACTIONATION OF WOOD USING BINARY MIXTURE ACETATE 1-BUTYL-3-METHYLIMIDAZOLIUM-DIMETHYLSULFOXIDE

Ladesov A.V., Kosyakov D.S., Bogolitsyn K.G., Falev D.I., Pokryshkin S.A.
Northern (Arctic) Federal University named after M.V.Lomonosov
Arkhangelsk, Russia
Engineer
lokoal13@gmail.com

The imidazolium based room temperature ionic liquids are known as promising green solvents for wood dissolution and fractionation leading to obtaining of lignin and polysaccharide parts.

Earlier we proposed 1-butyl-3-methylimidazolium acetate as the media with extremely high dissolution power towards lignin and perspective cooking agents for plant biomass chemical treatment.

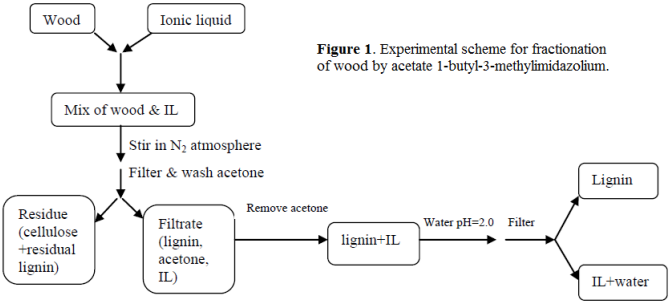


Figure 1. Experimental scheme for fractionation of wood by acetate 1-butyl-3-methylimidazolium.

In present work the treatments of softwood with ionic liquid acetate 1-butyl-3-methylimidazolium their binary mixtures with DMSO at different temperatures were done. It was found that wood is completely dissolved in ionic liquid and IL-DMSO system at 150°C. The method of sequential sedimentation of lignin and polysaccharide fractions from solution was proposed. The obtained products were characterized using the IR and NMR spectrometry as well as the pyrolytic gas chromatography mass spectrometry methods. The molecular weight distributions of lignins were determined by size exclusion chromatography. Gaseous products evolved during the treatments were identified by gas chromatography-mass spectrometry technique.

Acknowledgements. We thank Joint use center of scientific equipment “Arctica” of Northern (Arctic) Federal University named after M.V.Lomonosov, where all experiments were conducted.

VOLTAMMETRIC DETERMINATION OF HISTAMINE AT THE ELECTRODE MODIFIED BY GOLD NANOPARTICLES

Leksina Y.A., Degteva M.A., Chelnokova I.A., Shaidarova L.G.

Kazan Federal University,
Kazan, Russia
Student
Degteva_marina@rambler.ru

Histamine is an paracrine hormone of the body with a heterocyclic diamine structure. It is involved in numerous physiological processes like the regulation of sleep-wake cycles, control of cardiovascular functions and gastric juice secretion. Beside this histamine also acts as neurotransmitter in the central nervous system and is an important mediator of inflammation.

Conventional procedures such as spectrophotometry and chromatography are used to estimate the histamine concentration. But these methods have certain disadvantages such as lack of selectivity and need for expensive instrumentation. In contrast, electrochemical method has attracted significant attention as an alternative method because of its inherent advantages of simplicity, high sensitivity and relatively low cost.

Chemically modified electrodes (CME) with electrocatalytical properties are widely used in electroanalytical chemistry. Noble metals are universal catalysts for many electrochemical reactions. The catalytic activity of noble metals depends on the size of particles deposited on the electrode surface.

In the present work, the influence of the surface morphology and particle size of gold particles electrodeposited on the surface of glassy carbon electrode (GCE) on the catalytic properties of metal toward the oxidation of histamine was studied.

Gold nanoparticles electrodeposited onto CGE show catalytic activity in the electrooxidation of histamine. It is exhibited in decreasing of overvoltage of substrate oxidation and in increasing of oxidation current of modifier. The image of the electrode surface topography was obtained; the sizes of gold particles were estimated by the atomic force microscopy. These data were correlated with the voltammetric parameters of the histamine electrooxidation. As the dispersity of gold nanoparticles electrodeposited on the GCE surface increased and their size diminished, the catalytic activity of the metal increased. CGE modified by gold nanoparticles shows sensitive and selective response at the oxidation of histamine.

A voltammetric method for histamine determination using the electrocatalytic response of the electrode modified by gold nanoparticles was developed. The catalytic current was a linear function of analyte concentration in the range from 5×10^{-6} to 5×10^{-3} mol/l. The proposed method was used to determine histamine in drugs.

NOVEL WATER HARDNESS SENSORS

Levin M.B., *Mikhelson K.N.*

Saint Petersburg State University
Saint Petersburg, Russia
Ph.D. Student
doom666er@gmail.com

Magnesium cation, like many other analytes is accessible by ion-selective electrodes (ISEs). Control of Mg^{2+} is of interest for clinical analysis [1] due to its importance for human physiology. Unfortunately, despite a strong demand for Mg^{2+} monitoring in body liquids, no sensor with adequate selectivity has been developed. All known Mg^{2+}-ISEs suffer strong interference from Ca^{2+}, and therefore are hardly suitable for real applications [2].

Mg^{2+} sensing is also relevant in view of the water hardness control in industry, to prevent limescale formation in various facilities. Known water hardness ISEs are based either on decanol-1 (liquid membrane), or on 4-(decyloxy)butane-1-ol (DOB) (PVC membrane) [3]. Both suffer strong interference from alkali cations.

In this work we describe novel Mg^{2+} and water hardness sensors based on newly invented ionophores (Fig. 1). The sensors combining neutral ionophore 6-C16 with charged ionophore hemi-Calcium bis[4-(1,1,3,3-tetramethylbutyl)phenyl]phosphate ($CaDOPP_2$) allows obtaining ISEs with remarkable selectivity to Mg^{2+} and Ca^{2+} over alkali metal ions.

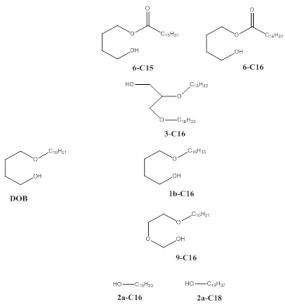


Fig 1. Structures of the ionophores

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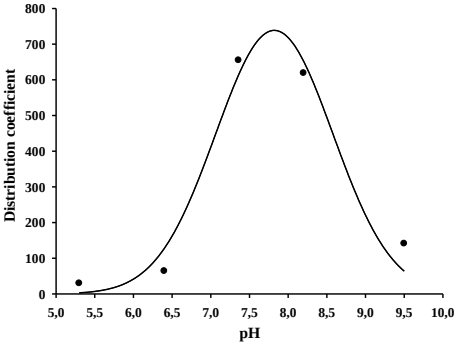
SOLVENT SUBLATION OF Ho (III) FROM DILUTE AQUEOUS SOLUTIONS

Louconin R.E., Horoshih T.A., Berlinskiy I.V., Lobacheva O.L.

National Mineral Resources University (Mining University)
Saint Petersburg, Russia
Student
LouconinR@yandex.ru

This process can be considered as a solvent extraction with the additional removal mechanism (air or purge gas stripping). The technique has advantage over ion flotation or solvent extraction. Although the adsorptive bubble separation techniques have been studied extensively, the literature on the subarea of solvent sublation (SS) is rather sparse. The determination of trace elements in water requires highly sensitive as well as accurate analytical methods. If a water sample is complicated like sea or wastewater, it becomes very difficult to analyze the sample due to very low concentration of impurities. With the use of SS technique the preliminary concentration of impurities (e.g. trace elements) for further analytical determination can be realized. Separation in SS is due to the ability of some species to orient themselves in the air-water interface, and the adsorption on the bubble surface is due to the presence of certain functional groups. In SS equilibrium state cannot be established in the bulk of the system but only at the aqueous-organic interface. In a particular experiment in SS process, surface-active material will be present in a bulk aqueous phase, on top of which is placed an immiscible liquid. Gas bubbles are generated in the aqueous media and are buoyed upward into the organic phase. The bubbles selectively adsorb surface active material while in the water (as in any adsorptive bubble process) and transport this material to the nonaqueous phase. The material is either deposited in the top phase after the bubbles burst at the air-liquid interface or dissolved during the passage of the bubble through the immiscible phase. In fact, the name – "Solvent Sublation" arises from that an ionic species, called the *colligend*, is removed by addition of a surface-active collector of opposite charge to that on the colligend. The complex formed by coulombic attraction is called the "Sublate", and the process of lifting the sublate by gas bubbles – "Sublation". According to F. Sebba, it is not necessary that the sublate dissolve fully in the organic layer, only that the salt be wetted by the solvent. Thus, both the formation of true solutions and suspensions of the sublate in the organic phase should be possible. In this paper we present our results on separation and pre-concentration of a trace of Ho (III) by the perspective separation method – SS. Water example solution was placed to the flotation cell 2.5 cm in diameter and 50.0 cm in height. According to the SS technique the surfactant (sodium

dodecylsulfate - NaDS) was added to the bulk aqueous phase containing trace amounts of Ho(III). The initial concentration of Ho^{+3} is equal 10^{-3} mol/l. Picture 1 present experimental data on distribution coefficient of Ho^{+3} between organic (2-octanol) and water phases accordingly.



Picture 1. Distribution coefficient of Ho (III) in nitrate solutions at different pH with NaDS.

The advantage of S.S. over foam separation or air stripping is that higher removal efficiencies are possible (98% of Ho^{+3} can be removing from nitrate solutions).

Acknowledgements

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STEPWISE INJECTION DETERMINATION OF CAFFEINE IN HUMAN URINE AND SALIVA SAMPLES COUPLED WITH SOLID PHASE EXTRACTION

Medinskaia K., Nikolaeva L., Kirsanov D., Vakh K., Bulatov A.

Saint Petersburg State University
Saint Petersburg, Russia
Postgraduate student
ksmed90@gmail.com

CYP_1A_2 contributes to the metabolism of a number of therapeutic drugs including a number of long-term pharmacotherapies used in the treatment of psychosis and depression. Due to difference in a drug metabolizing efficiency between patients it can lead to failure to achieve therapeutic efficacy or conversely an adverse effect. Caffeine, due to its ease of administration and safety, is the most widely used probe to measure CYP_1A_2 activity.

This study has investigated the use of caffeine as a probe to measure CYP_1A_2activity in saliva and urine samples.

The aim of this study was to develop a simple, fast, sensitive and automative method for determination of caffeine in saliva and urine samples. Therefore, the solid phase extraction coupled with caffeine selective electrode under stepwise injection system was applied for extraction and preconcentration of caffeine in saliva and urine samples.

The extraction under static and dynamic conditions was studied using different membranes. Their sorption kinetic, sorption isotherms, influence of pH and surfactants were investigated.

This work was supported by the Russian Foundation for Basic Research (project No. 13-03-00031-a and 14-03-31092 mol_a). Scientific researches were performed at the Center for chemical analysis and materials research of St. Petersburg State University.

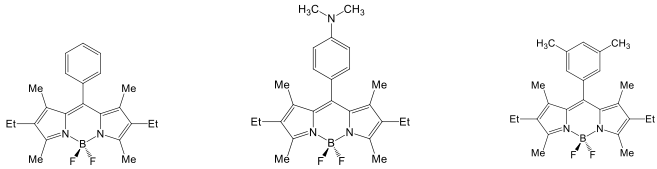
SYNTHESIS AND SPECTRAL PROPERTIES OF POTENTIAL MOLECULAR ROTORS BASED ON 8-SUBSTITUTED BODIPY

Merkushev D.A., *Marfin Yu.S.*, *Rumyantsev E.V.*

Ivanovo State University of Chemistry and Technology,
Ivanovo, Russia
Student
ununnamed911@gmail.com

Boron-dipyrromethene complexes (abbreviation: BODIPY) may be used as sensors for selective spotting cations, anions, pH measurements. The BODIPY molecules could be attached to different biomolecules for biochemical needs. But the newest way of BODIPY studies – is using them as molecular rotors.

Molecular rotors are a class of compounds, which molecules consist of at least 2 parts and can form a twisted state. This mechanism opens the way to the measurement of local dynamical viscosity through molecular rotors. This method of viscosimetry is going to replace traditional techniques for viscosity measurements. Molecular rotors makes possible the viscosity measurements of microsystems in real-time, what can be useful in the analytical control of polymerization processes (e.g. Sol-gel synthesis) and conformational transitions. In this work, three BODIPY complexes with different substituents in 8- position were synthesized and investigated.



Picture 1. Structures of investigated compounds

The photophysical properties of complexes were measured in several polar and nonpolar solvents and their mixtures with different viscosities in condition of varying the temperature. The results show that all the presented compounds obtain molecular rotor properties and show themselves as intensive ones.

It was shown that the nature of the solvent and the substituent plays a great role in rotary properties. It was found that every rotor has its own optimal viscosity range where it shows the best rotary properties.

The work was supported by the grant of the President of the Russian Federation for young scientists and graduate students engaged in advanced research and development in priority directions of modernization of the Russian economy (2013 – 2015) (Grant No. SP-1742.2013.1) and the Russian Foundation for Basic Research (No 14-03-31888).

DEVELOPMENT OF PROCEDURES FOR THE FULLERENES C_{60} AND C_{70} DETERMINATION IN THEIR AQUEOUS DISPERSIONS

Mikheev I.V.[a,b], *Volkov D.S.*[a,b], *Korobov M.V.*[a], *Proskurnin M.A.*[a,b]
[a] Chemistry Department, Lomonosov Moscow State University
[b] Analytical Centre of Lomonosov Moscow State University / Agilent Technologies Authorized Partner Laboratory
Moscow, Russia
Postgraduate Student
mikheev.ivan@gmail.com

Unique properties of carbon nanomaterials, especially fullerenes and their solutions find increasingly wide acceptance in basic science and applied technologies. During the last decade, they are in demand in up-to-date energy systems and fine-chemical and drug synthesis. Recently, much attention has been paid to their use in medicine e.g. for drug delivery into cells or for attaching various substances to cell membrane surface. Here, one of the difficulties is the synthesis of non-toxic water-soluble fullerene compounds that can be introduced into human body. In this regard, of importance are aqueous dispersions of unmodified fullerenes (AFD). Nonetheless, AFDs show certain difficulties and often call for a chemical modification or the use of the toxic organic solvents. In addition, the aggregation properties of AFDs have not been studied in full. Thus, this hinders their use in medicine. The aim of this study is to develop approaches to the analysis of the fullerene aqueous dispersions and related materials.

AFDs of C_{60} and C_{70}, and a technical mixture of C_{60} and C_{70} were prepared according to the procedure of solvent-exchange protocol. Total organic carbon analyzer was used for developing the procedure for carbon total concentrations in AFDs. In addition, the content of fullerenes in their aqueous dispersions at a very low level (ppm) makes the use of classical methods of chemical analysis almost impossible. Thus, to solve this problem, low concentrations of fullerenes were determined using thermal-lens spectrometry. To prove the state of the unmodified fullerene in AFDs, their UV-visible absorption spectra as well as spectra of the toluene extracts were recorded; the data show that the majority of fullerene in AFDs is not chemically modified. In addition, MALDI confirmed the unmodified state of fullerenes in their AFD. An important parameter (because the cell membrane is able to pass a very limited size of the molecule clusters or aggregates into the cell) is the distribution of fullerene clusters size, which was implemented by DLS and PEM. As well, for the first time ultrasonic-assisted extraction of fullerenes from AFDs is reported, and the physicochemical parameters of this process are estimated.

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TECHNIQUE TO EXTEND THE RANGE OF MEASURED CONCENTRATIONS IN STEPWISE INJECTION ANALYSIS WITH PHOTOMETRIC DETECTION

Mozzhykhin A.V.[1], *Khydiakov U.S.*[1], *Moskvin A.L.*[2]
[1] ZAO NPO Granit-NEMP.
[2] Saint Petersburg State University. Department of Analytical Chemistry.
Saint Petersburg, Russian Federation
Research Assistance
uhs83@mail.ru

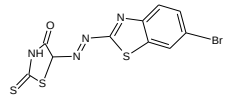
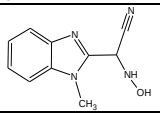
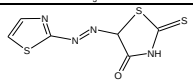
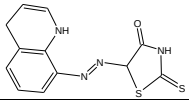
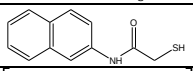
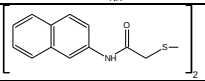
One of the most common methods of detection in flow-injection analysis (FIA) is photometric. The disadvantage of this method is the relatively narrow range of measured concentrations, due to the limit of the optimal range of absorbance with boundaries of 0.1 - 1.2 units of absorbance. During environmental monitoring of nature water equipped FI analyzers ecological boat passes tens of kilometers. On a large territory the composition of the water may change. Thus, the concentrations of monitored component go out of the measuring range of techniques. It requires changes in the hydraulic circuit, the configuration analyzer, preparation new solutions and new calibration curve. These operations take a few hours and lead to the disruption of continuous monitoring. The method of stepwise injection analysis (SWIA) solves this problem. The use of a single hydraulic line and separate execution of each operation allow change the volume of reagents or samples automatically and thereby to change the measurement range. Introduction of criteria of the changing the range allows the program of SWI analyzer change the volume of solutions automatically and use calibration curve another measurement range. The proposed method was successfully verified during the development of techniques for measuring ions Mn (II) and nitrite ions. The measurement range of the ions Mn(II) 1 - 300 μg/dm3 includes two subranges 1 - 30 and 20 – 300 μg/dm3. The transition between the subranges is performed automatically from smaller to larger and back. The range of measurements of nitrite ions 5 – 1000 μg/l includes two subranges 5 - 200 and 150 - 1000 μg/dm3. The proposed method allows to increase the range of measured concentrations 5-10 times or more with the introduction of the third subrange.

NEUTRAL AND CHARGED CARRIERS OF CADMIUM (II) IONS

Nuralieva U.G., Tataeva S.D., Magomedov K.E., Ramazanov A.Sh
Dagestan State University,
Student
uma.honey@mail.ru

Cadmium - metal, the application of which is continuously expanding. The range of its content in natural and industrial objects of analysis is very high and ranges from ppm to tens of percent. Cadmium metal has not toxic properties. Cadmium compounds, regardless of their state of aggregation (dust, smoke, cadmium oxide, vapors, mist) are poisonous. Cadmium poisoning can occur when heated metal or alloy smelting of ores and in the production and application of paints and alloys to which it is included. According to its toxicity of mercury or cadmium is similar to arsenic. A lot of pollution on the environment cadmium has a chemical current sources (one small battery will pollute the soil a few square meters). Values were calculated lipophilicity alleged ionophores on cadmium ions (II) with the help of a software package ACD / ChemSketch (Vers. 6.0), the values of which are presented in Table

Table. Lipophility values of different ionophores.

№	Carriers	Lipophility Value
1		4.09±0.95
2		1,94±0,72
3		1,66±0,9
4		1.08±1.14
5		2,79 ± 0,32
6		5,56±0,46

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[1] Magomedov K.E., Tataeva S.D., Goryachaya V.S. Potentiometric sensor cadmium ions (II). Bulletin of the Dagestan State University. 2013. Vol. 6.
[2] Magomedov K.E., Tataeva S.D. Potentiometric sensor for cadmium ions (II) «Mendeleev 2014» VIII All-Russian Conference with international participation of young scientists in chemistry. Abstracts. Section 3. New analytical methods in chemistry. St. Petersburg. 2014. pp 302-303.

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SINGLET OXYGEN DETERMINATION IN THE GAS STREAMS BY THE METHOD OF "CHEMICAL TRAPS"

Ovechkin A.S.[1,2], *Reingeverts M.D.*[2], *Kartsova L.A.*[1]

[1]Saint Petersburg State University,
[2]*FSUE "RSC" Applied Chemistry"*
Saint Petersburg, Russia
Postgraduate student
Lacksser@gmail.com

Singlet oxygen is a pollutant of the atmosphere, a component of the photochemical smog. Its quantification is complicated by the lack of standard samples. The generator capable of producing gas streams with a given concentration of singlet oxygen is developed in CJSC “OPTEC”. For its standardization, it is necessary to develop a technique of the determination of singlet oxygen in the gas streams.

To solve the problem method of “chemical traps” with GC analysis was chosen. It includes passing of sampled gas through the sorption tubes, filled with polystyrene sorbent XAD-2, coated with α-terpinene, and subsequent GC analysis of ascaridole – the product of [4+2]-cycloaddition of singlet oxygen to α-terpinene. The proposed method takes into account the thermal instability of ascaridole and the influence of the amount of α-terpinene on the singlet oxygen capture efficiency. It was established that the generator produces approximately 1.06 μg/m^3 of singlet oxygen. The possibility of using PTFE as a carrier of α-terpinene was also investigated.

For comparison, analysis with the 9,10-diphenylanthracene as a "chemical trap" was performed. The amount of 9,10-diphenylanthracene endoperoxide, which is formed by capturing singlet oxygen, was determined by HPLC with DAD. 9,10-Diphenylanthracene endoperoxide was photochemically synthesized for quantitative analysis of singlet oxygen. PTFE or XAD-2 were used as a sorbent. In the first case, the amount of fixed singlet oxygen was 0.033 μg/m^3, in the second case, 0.144 μg/m^3.

ANOMALOUS TEMPERATURE DEPENDENCE OF GAS CHROMATOGRAPHIC RETENTION INDICES OF POLAR COMPOUNDS ON NON-POLAR PHASES

Pavlovskii A.A , Zenkevich I.G.

St. Petersburg State University
St. Petersburg, Russia
Postgraduate Student
alex.pavlovsky@mail.ru

Retention indices (RI) are the most reproducible retention invariants in gas chromatography. However, there are several factors that reduce their reproducibility. The main source of interlaboratory variation of RI is their monotonous temperature dependence RI(T) which is often approximated with linear regression: RI(T) = RI(T_0) + β(T – T_0).

For most of organic compounds the temperature coefficients are β = dRI/dT > 0. At the beginning of the 2000s, the examples of anomalous temperature dependence RI(T) were first revealed for some polar organic compounds (alkanones, nitroalkanes, etc.) on non-polar phases. The essence of this anomaly is an impermanent sign of temperature coefficients dRI/dT, which leads to the appearance of RI minima.

Verification of the anomalous dependence RI(T) of different polar analyte classes (dimethyl formamide, dimethyl sulfoxide, alcohols, and others) was carried out using a WCOT column with an apolar stationary phase (BPX-1). It has been established that such anomalies are not associated with overloading of the chromatographic column. The form of this dependence is not fixed; it depends on the amount of analytes injected. For example, three types of RI(T) dependencies were found by varying the amount of dimethyl formamide in a chromatographic zone of 0.6 μg (I), 4.3 μg (II) and 16.9 μg (III) according to: increasing (I), with a minimum (II) and monotonously decreasing (III) (Figure).

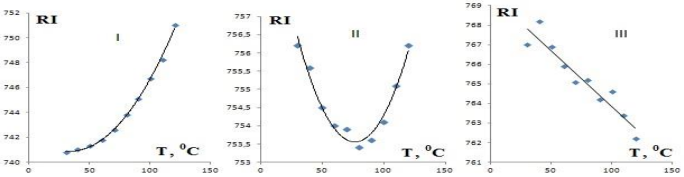


Figure. RI(T) dependencies for different amounts of $(CH_3)_2NCHO$.

Hence, previous recommendations on the interpretation of temperature coefficients dRI/dT should be reconsidered.

CRITERIA FOR OVERLOADING OF GAS CHROMATOGRAPHIC SYSTEMS

Pavlovskii A.A , Zenkevich I.G.

St. Petersburg State University
St. Petersburg, Russia
Postgraduate Student
alex.pavlovsky@mail.ru

Retention indices (RI) are widely accepted in gas chromatography (GC) as a means of identification. Since these indices are low-sensitive to GC conditions, they obey interlaboratory reproducibility. However, some factors influence RIs values. One of these factors is mass overloading of GC systems. The term "overloading" does not have an unambiguous definition and it is often perceived intuitively.

Our work is devoted to re-examination and comparing of criteria for mass overloading, namely:

I. The variations of RIs *vs.* masses of analytes injected into a column, i.e., RI = *f(m)*. These dependencies possess no anomalies in the expected region of overloading of the column.

II. The dependence $H/\omega_{0.5} = f(m)$, i.e., variations of the ratios of heights of chromatographic peaks (H) to their widths (e.g., $\omega_{0.5}$) *vs.* masses of analytes injected. Fig. 1 illustrates the typical dependence of $H/\omega_{0.5}$ *vs.* mass of the dimethyl formamide at 100 °C.

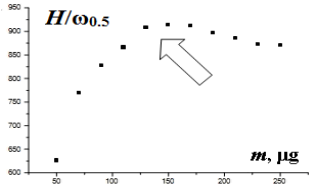


Figure 1. Graphical illustration of overloading criterion II. The arrow indicates the beginning of the overloading.

III. The dependence $A = f(m)$, i.e., variations of the chromatographic peaks asymmetry factors (A*) *vs.* masses of analytes injected. The character of dependencies $A = f(m)$ varies greatly depending on the polarity of the analytes. Fig. 2 shows the dependence of A *vs.* mass of the dimethyl formamide at 100 °C.

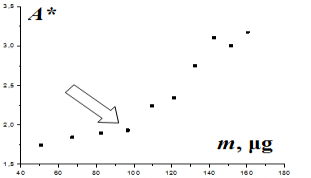


Figure 2. Graphical illustration of overloading criterion III. The arrow indicates the beginning of the overloading.

Both criteria **II** and **III** easily indicate the beginning of the mass overloading of GC columns and these dependencies are concordant with the limiting overloading values.

DETERMINATION OF FLUOROQUINOLONES IN URINE

Pochivalov A.S., Vakh Ch.S.
Saint Petersburg State University
Undergraduate student
alexpochival@bk.ru

Antibiotics found widespread application in medical practice as pharmaceuticals. Relatively new group of synthetic antibiotics is a fluoroquinolones. Despite their pronounced antimicrobial activity, these drugs cause a great toxic effect to human body. Because of this point of view, the determination of fluoroquinolones in different biological fluids is the highly important task.

Taking into account the low levels of fluoroquinolones effective preconcentration of the target analytes from the sample matrix is a necessary step of sample preparation. In analytical practice liquid-liquid extraction as a pretreatment method is widely used. However, it requires large amounts of toxic organic solvents that is contrary to the concept of Green analytical chemistry. Microextraction is much more preferable procedure for sample preparation. In the field of its so-called switchable hydrophilicity solvents has been proposed as an alternative to toxic organic extractants. The SHS effectively become miscible with the addition of carbon dioxide and form two phases when it removed from the solution. In this work possibility of application of SHS for microextraction of fluoroquinolones from urine with following HPLC determination with fluorescence detection is considered.

DETERMINATION OF HYDROQUINONE IN AQUEOUS SOLUTIONS BY INTERRUPTED VOLTAMMETRY

Semenova E.A., Ermakov S.S.
Saint-Petersburg State University
Saint-Petersburg, Russia
Postgraduate student
semenova.e.a.0506@gmail.com

Analytical capabilities of the direct interrupted voltammetric method were investigated using determination of hydroquinone as an example.

The study of the background curves obtained on the gold, the platinum, the glassy carbon and the composite electrodes was performed in order to choose the optimal material of a working electrode. It was found that the composite electrode is characterized by the lowest values of the background current.

The limiting background current dependence on the hydroquinone concentration and voltage scan rate were registered on the composite and glassy carbon electrodes. It was found that the analytical signal is linear in the range from $1*10^{-7}$ to $5*10^{-6}$ M for the composite electrode, and is linear over the entire range of concentration from $1*10^{-5}$ to $1*10^{-3}$ M for the glass carbon electrode.

THE DEPENDENCE OF THE BACKGROUND CURRENT FROM THE COMPOSITE ELECTRODE POTENTIAL AND THE GAIN IN THE CIRCUIT VOLTAMMETRY

Poduretc A.A.

Saint Petersburg State University,
Saint Petersburg, Russia
Student
bonparishk@mail.ru

1. Principle of a method.

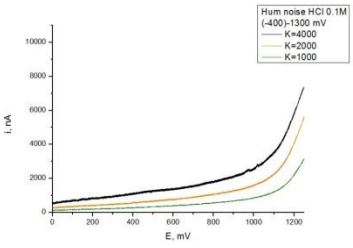
A theoretical analysis of the method can be carried out using Randles equivalent circuit, which simulates the electrochemical processes in a cell. It contains a kommutator for interruption effect. In a result of periodic interrupt of current circuit of the electrochemical cell, the interference in the form of the charging current is not formed, and a current mainly contains informative capacitive component proportional to concentration of the ion, and a small of Faraday's part.

2. Vindication of report.

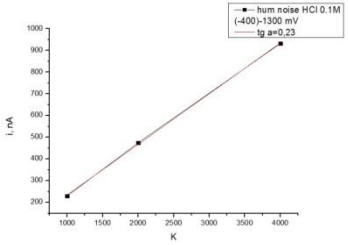
The current I_n deal with non-ideal polarizability of electrode, appears due to the processes, which does not depend on the charging of DES. Therefore, as the current associated with the electrochemical reaction, it will depend on the gain K. Previously, it was shown that the composite electrode is the optimum for the method of interrupted amperometry, so it was chosen for voltammetry mode.

Objective:

Measurements were made according to the background current I_n and three gain K of composite electrode in switching voltammetry mode.



Picture 1. The dependence E-I



Picture 2. The dependence K-i

Conclusions: The achieved dependence is close to the theoretical: the measured current is directly proportional to the gain. The data indicates that there I_n occur through the processes that are related to the charging of DESand quasi-faradaic processes.

LATERAL FLOW ENZYME IMMUNOASSAY - NEW RAPID METHOD FOR PROGESTERONE DETERMINATION

Safronova V.A.[1], *Samsonova J.V.*[1, 2], *Osipov A.P.*[2]

[1]Department of Chemistry, M.V.Lomonosov Moscow State University
[2]National University of Science and Technology "MISIS"
Moscow, Russia
Postgraduate student
Safronova.Valentina88@gmail.com

Actual problem of modern medical and veterinary diagnostics is the creating of simple biosensor devices that enable the rapid analysis of various biologically active substances. These methods should have high sensitivity, reproducibility, the possibility to be applied in field conditions, as well as low cost. Among rapid methods having above advantages one of the current approaches is a lateral flow immunoassay (immunochromatographic assay), wherein colloidal gold nanoparticles is often used as a label for visualization of the final product. This biosensor device is based on a test strip consisting of several adjoining porous membranes, through which analysed sample is moved from sample application point towards the end of a strip. The analysis resulted in the appearance of colored line in the test region, the intensity of which depends on target analyte concentration. These portable systems have the following advantages. Since the device contains all necessary specific components (to perform analysis it is enough to add a few sample drops) it is easy to use. The analysis is rapid (colored lines usually develop in 5-10 minutes after sample application). The results can be quantified visually or by means of special portable detecting device.

In order to increase the sensitivity of the competitive immunoassay a new method of lateral flow enzyme immunoassay (LFEIA) for the determination of progesterone was developed. To visualize the final product of immunoassay reaction horse radish peroxidase was used as a label. The principle of the method was based on the competitive interaction of free progesterone in a sample and enzyme-labeled progesterone for binding sites of specific antibodies immobilized on analytical membrane of a strip. Specific immunoreagents were obtained and characterized, membrane components were selected, the kinetics of formation of immunochemical complexes in lateral flow mode was explored, conditions of analytical signal registration were optimized. It has been shown that the use of enzyme label allows to increase sensitivity of LFEIA in an order compared to the use of colloidal gold as a label. Detection limit of progesterone was 1 ng/ml, and the analysis time was 15 minutes. The applicability of the developed system for the quantitative determination of progesterone in whole cows' milk for the purposes of early pregnancy detection was confirmed.

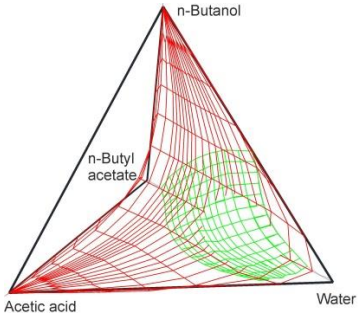
THE EXPERIMENTAL STUDY OF PHASE EQUILIBRIUM FOR THE SYSTEM ACETIC ACID + N-BUTANOL + N-BUTYL ACETATE + WATER

Samarov A.A.[1], *Toikka A.M.*[1], *Toikka M.A.*[1]

[1]Saint Petersburg State University,
Saint Petersburg, Russia
Postdoc
samarov@yandex.ru

Actual direction of energy saving resources is the use of biofuels. As biofuel is a long-chain saturated and unsaturated methyl esters, to evaluate the kinetic and thermodynamic parameters are often used model compounds. Using small-chain methyl esters such as alkyl formates, acetates and propanoates was proposed in [1].

The experimental study of CE and LLE was carried out at 293.15 – 313.15 K by gas chromatographic (GC) analysis (Cristal 5000, Chromatec, Russia) with the internal calibration standard detection method. New experimental data on CE were obtained for homogeneous and heterogeneous regions. We also used the data that had been obtained in our recent work [2]. On the base of experimental data the surfaces of phase and chemical equilibrium were constructed in the concentration tetrahedron (Picture 1). The crossing CE and LLE surfaces (i.e. the establish heterogeneous CE) is discussed.



Picture 1. Quality appearance of the surface of phase (green) and chemical (red) equilibrium.

Various models such as UNIFAC, NRTL and UNIQUAC were used to calculate CE and to estimate the equilibrium constant. The calculated data were compared with available information in the references. On the base of our results the complete topological structure of the liquid phase diagram of acetic acid – n-butanol – n-butyl acetate – water system had been obtained.

References:

[1] O. Herbinet, W. Pitz, C. Westbrook, Combust. Flame 154 (2008) 507–528.

[2] Samarov A.; Toikka M.; Toikka A. Fluid Phase Equilib., 2015, 385, 129-133.

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A NEW APPROACH OF BOVINE LEUKEMIA VIRUS DETECTION BY ELISA AND PCR IN DRIED BLOOD SPOTS

Saushkin N.U.[1], *Samsonova J.V.*[1], *Osipov A.P.*[2], *Kondakov S.E.*[2], *Zhigaleva O.N.*[3], *Komarov A.B.*[3]

[1]Lomonosov Moscow State University,
[2]National University of Science and Technology "MISiS",
[3]Biokom
Moscow, Russia
Postgraduate Student
sushk_90@mail.ru

Bovine leukemia virus (BLV) is an exogenous retrovirus of cattle, which causes enzootic bovine leucosis (EBL). Indirect serological methods such as ELISA and AGID are routinely applied for EBL diagnostics by detecting specific antibodies against virus proteins. Latent progress of disease is a matter of serological tests being ineffective for 2-8 weeks after infection as antibodies are not produced in blood. That doesn't allow to detect and isolate the infected animals in time. To enhance the effectivity of BLV diagnostics PCR is also used, which is able to detect the proviral DNA in blood samples directly.

Dried blood spots (DBS) technology includes the application of blood drops onto the special membrane with further drying. DBS has a lot of advantages in comparison to routine blood collection and has found a wide application in medical diagnostics. DBS can be used as a sample collection technique in field conditions, the dried samples can be delivered to a laboratory without cooling. These advantages make DBS technology attractive for application in veterinary. A new format of sample collection, transportation, storage and analysis of DBS was proposed. Special narrow marked stripes of membranes were used as a carrier. A piece of the membrane with sample was cut with scissors and analyzed.

The original approach for PCR and ELISA detection of BLV using DBS was proposed. The samples of blood (n=287) were measured by conventional way and using DBS technique. Several commercial ELISA test systems were adapted for analyzing dried spots of cattle blood and serum. A new real-time PCR technique was developed for detecting BLV. Different methods of proviral DNA extraction from dried blood spots were applied. PCR and ELISA showed identical results both in liquid and DBS format. Correlation between the results of PCR and ELISA was 92.7%. PCR detected 4 positive results among seronegative samples. The proviral DNA wasn't recovered in 12 seropositive sample. Such result can depend on special aspects of EBL progress and/or poor PCR sensitivity.

QUINAZOLINE DERIVATIVES – POTENTIAL IONOPHORES FOR POTENTIOMETRIC SENSING OF HYDROPHILIC ANIONS

Semenov V.V., *Kirsanov D.O.*

Saint Petersburg State University
Saint Petersburg, Russia
Student
vksemenov@gmail.com

In this study allosteric modulators of the metabotropic glutamate receptors were investigated as potential membrane active components for potentiometric chemical sensors. Metabotropic receptors are molecular membrane receptors of eukaryotic cells which upon binding to their bioligands (modulators) transmit an external chemical control signal into cells, starting a cascade of biochemical reactions and influencing cell metabolism.

We studied electrochemical properties of ten different polymeric membranes based on two different quinazoline derivatives. Polymer membranes were prepared from poly(vinyl chloride) plasticized with 2-nitrophenyl octyl ether (NPOE). Two different ion-exchangers: tridodecylmethylammonium bromide (TDMA) and potassium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (KTFPB) were also employed to modify sensor properties. The active components in polymer membranes were the following quinazoline derivatives: 7-acetyl-6-(4-methoxyphenyl)-3-(methylsulfanyl)-1-oxo-6,7-dihydro-1 H-[1,2,4]triazino[1,6-c]quinazolin-5-ium-2-ide and 7-acetyl-6-ethyl-3-(methylsulfanyl)-1-oxo-6,7-dihydro-1 H-[1,2,4]triazino[1,6-c]quinazolin-5-ium-2-ide.

The sensitivity of the sensors was studied in series of individual compounds solutions in the concentration range from 10^{-7} to 10^{-2} M. The sensors under study showed Nernstian electrode response to sulfate, carbonate, nitrate, bromide and iodide while for acetate, chloride and thiocyanate it was sub-Nernstian. Typical detection limits were around 10^{-6} M of anion. It is noteworthy that selectivity of the sensors studied with fixed interference method was decreasing in the following way: chloride>thyocyanate>iodide>bromide≈sulfate>nitrate>carbonate>acetate. A significant deviation from Hofmeister selectivity can be observed and this gives a good promise for development of a novel class of ligands for hydrophilic anions both for selective and cross-sensitive potentiometric sensors.

ANALYTICAL CAPABILITIES OF DIRECT INTERRUPTED AMPEROMETRY FOR DETERMINATION OF PHENOLIC COMPOUNDS IN AQUEOUS SOLUTIONS

Semenova E.A., *Ermakov S.S.*

Saint-Petersburg State University
Saint-Petersburg, Russia
Postgraduate student
kassumy@mail.ru

Interrupted amperometry is a new highly sensitive electrochemical method in which the capacitive current is an analytical signal. It is provided with the periodical current interrupt of an electrochemical cell. The occurring current consists of an informative capacitive component which is dependent on the concentration of analyte.

The registered current is defined as an unlocking time/ locking time ratio which serves as a gain:

$$i_{av} = \frac{T_{int}}{t_l} i_{elch} = \frac{t_{unl}+t_l}{t_l} i_{elch},$$

where i_{av} is the average current; $\frac{T_{int}}{t_l}$ is the period of interruption (the gain); t_l is the locking time, μs; t_{unl} is the unlocking time, ms; i_{elch} is the current of the electrochemical reaction. This allows us to analyze quite low values of concentration.

The analytical capabilities of direct interrupted amperometry have been investigated using phenolic compounds in aqueous solutions as an example. It is found that the limit of detection is $8{,}8*10^{-9}$ M for phenol and $3{,}1*10^{-8}$ M for hydroquinone.

LATERAL FLOW IMMUNOASSAY AS EXPRESS-METHOD OF PROCALCITONIN DETECTION

Serebrennikova K.V.[1,2], *Samsonova J.V.*[1,2], *Osipov A.P.*[2]

[1]Lomonosov Moscow State University,
[2]National University of Science and Technology "MISiS",
Moscow, Russia
Postgraduate Student
ksenijasereb@mail.ru

During the last decade express-methods of analysis of different compounds with visual detection of results were developed. These methods found wide application in different fields, such as medical diagnostics, pharmaceutical and food industries, ecology, veterinary medicine, etc. These express-methods are based on the principle of lateral flow immunoassay. This type of analysis is performed on special test strips and provides quick results. The reaction proceeds in one step, as this test system already contains all necessary components. No additivities except analyzed sample are required. The result of analysis is observed as colored bands in the test and control zones of analytical membrane. The widespread use of this method is provided by short period of testing (10-15 min), easy detection, which doesn't require any additional devices. Gold nanoparticles are usually used as a label for visual detection of test results. The advantages of such type of labels are simple synthesis, opportunity to obtain particles with different diameter and also unique optical properties, such as phenomenon of surface plasmon resonance.

The express-method of procalcitonin detection in serum using principle of lateral flow immunoassay and colloidal gold as a label was developed. Procalcitonin is a diagnostical marker of severe infections and sepsis. Normal concentration of procalcitonin doesn't exceed 0.1 ng/ml, but during chronical inflammation, caused by bacteria, the level of procalcitonin in blood arises in range from 1 ng/ml to more than 1000 ng/ml. The samples of gold nanoparticles of different sizes were obtained and characterized during this study. The conjugates with specific monoclonal antibodies against procalcitonin were obtained. The efficiency of developed lateral flow immunoassay was confirmed by ELISA test-system for the procalcitonin detection.

A NEW METHOD FOR THE ISOLATION AND CONCENTRATION OF THE PESTICIDES

Shreyner E.V.[1], *Shustov V.E.*[2], *Podolskya E.P.*[1,2], *Alexandrova M.L.*[1]

[1]FSIS Institute of Toxicology FMBA Russia,
[2]Institute for Analytical Instrumentation RAS
Saint Petersburg, Russia
Junior researcher
shreyner.ekaterina@gmail.com

Because of the intensive use of pesticides in modern agricultural industry in the last decades of their content in the objects of environmental increased significantly. In this regard, the development of new highly specific and selective analytical methods for the monitoring and measuring the level of pesticides in the environment is a promising task.

The glyphosate and its metabolite aminomethylphosphonic acid (AMPA) are widespread herbicide as well as in connection with the specific physical and chemical properties (low volatility, lack of chromophore groups, low solubility in organic solvents) determination of these compounds in samples of different nature is a laborious, complicated and expensive process.

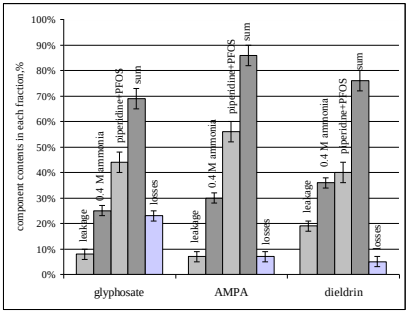


Fig. 1. Results of metal-affinity chromatography LBF Ni (II) stearate for glyphosate, AMPA and dieldrin

We have proposed an entirely new method of extraction and concentration these pesticides from an aqueous solution without a pretreatment of the sample without using any derivatizing agent. This method includes conducting metal-affinity chromatography using a newly developed sorbent based on Langmuir Blodgett film (LBF) in stearate nickel (II) followed by eluting components using different solvents (ammonia, piperidine). LBF are molecular monolayers collapsed for surface water subphase containing metal ions, i.e. the surface of these films mainly composed of the solid is securely associated to metal ions. Quantitative analysis was performed by AES with ICP. The results are shown in Fig. 1. Also, the proposed method was applied to isolate other highly toxic insecticide - dieldrin from mouse blood plasma (Fig. 1). Quantitative analysis was performed by GC/EC.

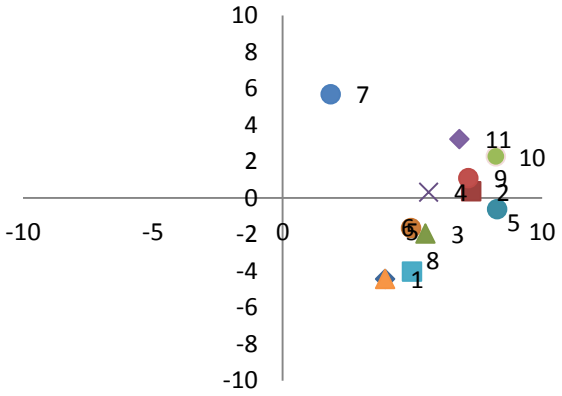
Based on these data, we conclude that isolation of glyphosate, AMPA from aqueous solutions and dieldrin from plasma using LBF-based nickel (II) stearate followed by elution of the compounds is possible.

APPLICATION CHEMOMETRICS IN THE SPECTROLUMINESCENCE ANALYSIS OF ETHANOL

Sidorenko M.Y.

Siberian Federal University
Krasnoyarsk, Russia
Student
sidorenko_93@mail.ru

Identification of authenticity of ethanol and way of its production is a complex analytical problem. In order to solve use such methods as liquid scintillation spectroscopy and gas liquid chromatography/mass spectrometry. The micro-impurities in ethanol possess ability to absorb and luminescence optical radiation, therefore for identification of ethanol it is suggested to use full spectra of luminescence [2] taken on a spectrofluorimeter "Flyuorat Panorama 02". In this paper 10 samples of ethanol of various origin were studied. The received full spectra of luminescence were processed by methods principal component analysis (picture 1).



Picture 1. PCA scores plot of ten samples of ethanol

The sample 7 differs from the others, as confirmed by results GLC/MS.

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[2]. GOST R 52945-2008 Ethanol rectified. Identification of spectraluminecsence method.-M.: Standards Publishing, 2008-14p.

CARBON NANOMATERIALS (REDUCED GRAPHEME OXIDE, CARBON NANOTUBES) AND METAL NANOPARTICLES AS MODIFIERS OF THE ELECTRODE SURFACE IN DESIGNING OF MONOAMINE OXIDASE AMPEROMETRIC BIOSENSORS

Sitdikova R.R., Medyantseva E. P., Brusnitcyn D.V., Varlamova R.M.

Kazan Federal University
Butlerov Institute of Chemistry
Kazan, Russia
Student
sitdikovarr@mail.ru

Promising area of biosensors for the determination of drugs preparations is modification of electrode surfaces with nanostructured materials: carbon materials (carbon nanotubes, reduced graphene oxide) and metal nanoparticles (gold, silver, nickel and copper). Carbon nanomaterials have been dispersed in chitosan solutions with different concentrations. Wherein we varied not only the concentration of modifiers but a component of bioactive part too. During the research we identified the best nano-structured surface modifiers among the proposed nanomaterials.

An amperometric biosensors have been developed for the determination of antidepressants (e.g., the definition of imipramine, tianeptine and moclobemide) based on screen-printed graphite electrodes (3×1), modified by functionalized reduced graphene oxide (RGO-COOH) with different concentrations (CRGO – COOH = 1 and 2 mg/ml), nickel nanoparticles (NiNPs), copper (CuNPs) and immobilized enzyme monoamine oxidase (MAO). Functioning of biosensors is based on the combination of the biochemical reaction and electrochemical oxidation of hydrogen peroxide in the presence of adrenaline substrate. Linear relationship between current magnitude and concentration of antidepressant for MAO biosensors based on nanostructured material RGO-COOH/NiNPs is observed in range of concentration from 1×10^{-4} to 4×10^{-8} mol/l, and from 1×10^{-4} to 1×10^{-8} mol/l for RGO-COOH/CuNPs. The application of nanostructured materials allowed to broaden the range of detectable concentrations, to reduce the lower limit of detectable concentrations, to improve coefficient of correlation compared with biosensors based on unmodified counterparts.

We offered the method of determination of the drug substance in drug preparations : "Melipraminum", "Coaxil", "Auroriks" with a Sr value no more than 0.065 .

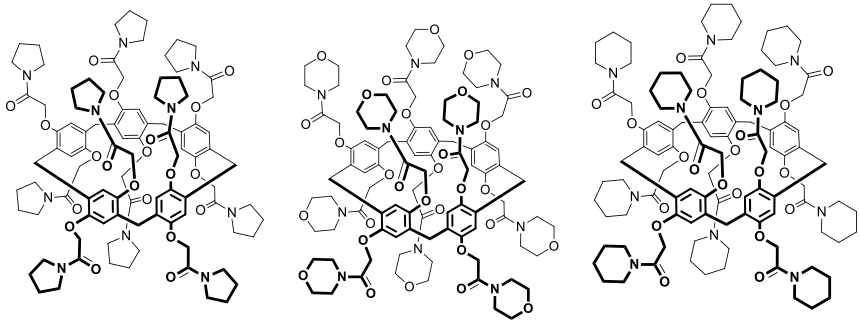
This work was supported by the Russian Foundation for Basic Research (grant № 13-03-01101-a).

SOLID-CONTACT POTENTIOMETRIC SENSOR BASED ON SCREEN-PRINTED ELECTRODE AND SUBSTITUTED PILLAR[5]ARENE FOR COPPER(II) IONS

Sorvin M.I., Gabidullina I.I.

Kazan (Volga region) Federal University
Kazan, Russia
Postgraduate Student
smi9999@mail.ru

New solid-contact potentiometric sensor based on screen-printed electrode has been developed for determination of Cu(II) ions. Three pillar[5]arene derivatives with different substituents as ionophores were implemented in the surface layer. For this purpose, pillar[5]arene derivatives were first dissolved in DMF dispersed on the working surface of carbon screen-printed electrode together with 2 μL of the carbon paste. Then surface layer was dried until a dense film was formed.



1 **2** **3**

Picture 1. Structure of pillar[5]arene derivates.

Optimization of ionophore content and surface layer formation was performed to reach best selectivity and sensitivity of response toward Cu(II) ions. The selectivity of the solid-contact sensors obtained was tested against other metal cations in different pH regions. Best results have been achieved with amidopiperidyl substituents of pillar[5]arene. The concentrations range of potentiometric response to Cu(II) ion was from $1.0*10^{-6}$ to $1.0*10^{-1}$ M with the slope of about 50 mV/pC indicating redox mechanism of signal generation. The results coincide well with previously established characteristics of similar sensor based on polyaniline film and unsubstituted pillar[5]arene.

Financial support of Russian Science Foundation (grant 14-13-00058) is gratefully acknowledged.

EVALUATION OF THE ANALYTICAL CAPABILITIES OF FRUORINE-CONTAINING POLYMERS AS MOBILE PHASE MODIFICATORS FOR THE DETERMINATION OF BIOLOGICAL ACTIVE COMPOUNDS BY HIGH PERFORMANCE THIN LAYER CHROMATOGRAPHY

Sukhomlinova A.E., Dzema D.V., Kartsova A.A.

Saint Petersburg State University,
Saint Petersburg, Russia
Student
SPbAGanchous@yandex.ru

Method of high-performance thin-layer chromatography (HPTLC) with densitometric detection has been actively demanded during rapid determination of biologically active substances due to the simplicity of the modification of the chromatographic phases. This contributes to the efficiency and selectivity of separation of the components of complex mixtures.

Use of fluorine-organic compounds as stationary phases and as additives to the eluent or the working electrolyte in chromatography and electrophoresis is interesting due to their unique properties: thermostability over a wide range of temperature, chemical inertness, unique hydro- and oleophobicity of perflourinated fragments. This paper is devoted to the research on the effect of new ethylene and perflourine(3,6-dioxa-4-methyl-8-nonen)sulfonylflouride copolymers with (Figure 1) different terminal groups (sulfonylflouride, sulfonate and sulfonamide) as additives to the mobile phase (HPTLC) in the determination of amino acids and vitamins.

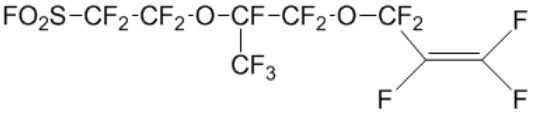


Figure 1. Perflourine(3,6-dioxa-4-methyl-8-nonen)sulfonylflouride monomer structural formula.

It was found that the presence of fluorine polymers with different ionogenic terminal groups in the composition of the eluent provides a significant increase in the efficiency (4-5 times) for the amino acids (lysine, glutamic acid, tryptophan) and vitamins B1 and B12.

It was suggested that these polymers prevents the interaction of the amino groups of the analytes with the silanol groups of the silica gel. In was found that the addition of fluorine copolymer with terminal sulfonate groups leads to the complete separation of catechines mixture with high efficiency, which cannot be done by using other modifier due to their high affinity to the stationary phase (silica gel).

METALL ION-MEDIATED COMPLEX IMPRINTED MEMBRANE FOR DETERMINATION OF OFLOXACIN

Timofeev S.S., Falkova M.T. , Bulatov A.V.

Saint Petersburg State Univercity
Saint Petersburg, Russia
student
wall91@mail.ru

The aim of modern analytical chemistry is reagent usage minimization, ecological safety and decrease of analysis cost. This is particularly important for medicine, because determination of medicinal substances and markers in biological materials is an integral part of diagnosis and treatment of diseases. Presence or absence of the various substances allows to choose the correct individual dose of pharmaceuticals and to determine the functional state of an organism.

Ofloxacin is a second generation antibiotic of the fluoroquinolone class which exhibits high activity against a broad spectrum of gram-negative and gram-positive bacteria. Low cost in comparison with third and fourth generation antibiotics is the reason of widespread use of this pharmaceutical.

In this work a solid phase fluorescence method for the determination of ofloxacin by using of metal ion-mediated complex imprinted polymer membrane was proposed.

The polymer membrane was prepared through in situ polymerization method. It was performed by surface modification of tetrafluoroethylene membrane soaked in polymerization solution containing ofloxacin as a template. Synthesized membrane demonstrates a good selectivity and high affinity to the molecules of ofloxacin. Quantitative determination of ofloxacin adsorbed on the membrane surface was performed by solid phase fluorescence method. Linear response was up to $4 \cdot 10^{-5}$ M. The developed method has been verified on the model solutions. The accuracy of the results was confirmed by the HPLC method.

EMISSION SPECTRAL ANALYSIS OF LIPSTICK USING A. C. ARC

Timofeeva A.D., Savinov S.S., Drobyshev A.I.

Saint Petersburg State University,
Saint Petersburg
timofeeva_aleksa@bk.ru

One of the most popular cosmetic products is lipstick. It is known that during the day about 24 mg of a lipstick from lips are "eaten up", and also some of its components can penetrate into the human body through the skin. In a number of publications the presence of low contents of metals such as Pb, Cd, Cr, Mn, Ti, Al, Co and Zn was demonstrated in lipstick. Considering that heavy metals have a tendency to accumulate in the body, so the question of the control of their content, especially xenobiotics, arises, as they have a detrimental effect on the health. For example, high content of Pb in the body is associated with hypertension, premature labor, anemia and infertility. Skin contact with Cr-contained compounds can cause ulcers. Excessive accumulation of Cd leads to pathological changes of cardiovascular and skeletal systems. So lipstick is a potential source of accumulation in the human body of elements that have a negative impact on the health. Therefore, determination of its microelement composition content is in the area of interest not only of product quality control, but also medicine.

Such highly sensitive techniques like AAS-ETA or ICP-AES require a complex sample preparation, including mineralization of samples. AES with spectrum excitation of dried residue of the liquid sample from the end of carbon electrode in an a. c. arc could be an alternative technique. The aim of this work was: the selection and development of a simplified method of lipsticks sample preparation for subsequent excitation of its emission spectra and determination of the presence of elements (including metals-xenobiotics) using the calibration samples, prepared on the basis of a multi-element water standard solution CertiPUR IV with a concentration of elements 1 mg / ml.

Part of the research was done using the equipment of Educational Resource Center of Chemistry of Research Park St. Petersburg State University.

SPECTRAL DETERMINATION OF MICROELEMENTS IN WINES USING A.C. ARC

Titova A.D., *Savinov S.S.*, *Drobyshev A.I.*
Saint Petersburg State University,
Saint Petersburg
s.sergei.s@mail.ru

In recent years the variety and size of wine sales in Russia are being steadily increased. At the same time poor quality and / or counterfeit goods are appeared more and more on the market, leading to poisoning and increasing of mortality of people. Therefore, the control of the authenticity and quality of wine production is an urgent problem.

The problem of identification of wines on a regional basis is added up to the establishing of connection between component composition of wines and soils, which relevant to geographical area of growing grapes. Those components whose content in wine is not changed during the production of the beverage can be markers of regional identity.

Methods of determining of organic compounds as well as trace elements included in wine composition are required to solve these problems. It's well known, that the content of trace elements depends on the grape variety, ripeness, its place of growth, agricultural techniques and processing technology. For example, concentrations of Pb, Cd, Zn, Cr, Ni are indicators of environmental safety; the content of B, Mn, Ba, Co, Ti, V characterizes regional belonging of wines; the content of Na, K, Mg, Ca reflects the technological processes of production. Since some of the elements are contained in wine at concentrations of less than 0.1 mg/l, highly sensitive atomic emission technique of element determination with the spectrum excitation of the dried liquid sample residue from the end of the carbon electrode in an a.c. arc was used for the analysis.

The aims of the work included the study of trace-element composition and the possibility of its changes during storage of wine samples, the optimization of technique of sampling, the identification of elements-markers to determine the authenticity and recognize the regional origin of wines.

Part of the research was done using the equipment of Educational Resource Center of Chemistry of Research Park St. Petersburg State University.

NEW DUAL SURFACTANT ELECTROOSMOTIC FLOW MODIFICATION SYSTEM FOR ELECTROPHORETIC ISOTOPIC SEPARATION OF CATIONIC SPECIES

Tkach K., Kamentsev M.Y.

Saint Petersburg State University,
Saint Petersburg,
Student
kir14-94@mail.ru

To determine the content of isotopes in various samples, the methods based on mass spectrometry are usually used. However, due to the high cost, the development of lower-cost alternative for these purposes is very relevant. In particular capillary electrophoresis (CE).

The most commonly used method of isotope separation in CE is based on a modification of the electroosmotic flow (EOF), oppositely directed movement of the isotopes in the capillary during the analysis under the influence of an electric field. By modifying the electroosmotic flow, which serves as a factor retarding the movement, one can achieve the optimal speed for the separation of isotopes. The main drawback of the method is low reproducibility of the migration time.

The goal of this work is to optimize conditions of previously described method of Li isotope separation to achieve maximum reproducibility of the migration times of Li isotopes. The influence of migration times, concentration of surfactants, and capillary conditioning on migration time repeatability have been studied.

Cationic surfactants CTAOH and TTAB in combination with non-ionic Tween 20 were proposed as EOF modifiers, allowing to achieve a high reproducibility of the migration times (RSD <2.1%) in a wide range of EOF velocities.

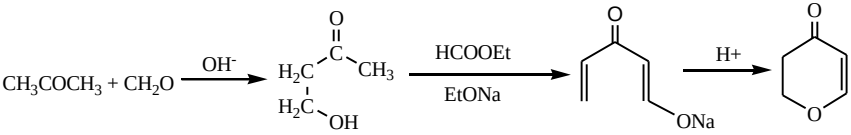
Optimal composition of the background electrolyte giving the most reproducible migration times has been found experimentally.

DERIVATIVES OF A DIHYDROPYRANE - 4 - ON, AS EXTRAGENTS OF METALS AND INHIBITORS OF CORROSION OF METALS

Umbetaliyeva A. S., Kalugin S. N., Burkitbayeva S. D.,Bektasov M. A., Yelibayeva N. S.
Kazakh National University named after Al-Farabi
Almaty, Kazakhstan
Undergraduate
arailym.uas@gmail.com

Derivatives of dihydropyrane - 4 - on as β-dicarbonyl compounds, represent practical interest as perspective extragents of metals and inhibitors of corrosion of metals in the different ranges of pH.

Dihydropyrane-4-on is received by ester condensation of β-oxyethylmethylketone with ethylformiate in the presence of an ethylate of sodium. While acidization the created enolate form is transferred to enol form and further into a cyclic form.



The structure of a product is proved by spectral methods and chemical transformations. Thus, while interaction with ammoniac solution of oxide of silver, colloidal silver is emitted, and while interaction with solutions of chloric iron and chloride of copper the painted complex connections are formed.

The received results prove a possibility of use of derivatives of a dihydropyrane as extragent of metals and also as inhibitors of corrosion of metals.

Inhibition of the zinc in the alkaline environment has been proved by electrochemical and gravimetric methods. The inhibitive effect is 99%. The inhibition of steel is performed with less effect which is caused by insolubility of dihydropropyrane - 4 - on in acid environments.

For the purpose of increase of solubility emulsifier (OP-10) has been used. The received steady emulsion inhibits a steel with high effect in sulfuric, hydrochlorid-acid and hydrosulphuric environments.

Now the researches of synthesis of other derivatives of dihydropyrane - 4 - on, containing substitutes in a cycle, as well as the researches of studying of their complexable and inhibiting capability are being conducted.

This Work has been performed within the framework of scholar financing by MES of RK of the projects 1266/GF4 and 2290/GF4.

BAKER'S YEAST ASSISTED SIMPLE POTENTIOMETRIC METHOD FOR SUGAR DETERMINATION

Voitechovic E.

[1]Saint Petersburg State University,
Saint Petersburg, Russia
Postdoc
voitechovic.edita@gmail.com

The sugar content provides information about food and beverages, which is necessary for various fields: dietary, medicine, gastronomy, food quality. There are a lot of methods, which are usually employed for sugar content determination, e.g. titrimetry, chromatography, spectrophotometry. Numerous biosensors and chemical sensors were developed for quantitative and qualitative analysis of different sugars. The biggest drawback of the suggested methods is the need in special reagents and high-cost equipment. Enzyme based sensor systems are promising, but because of the complicated enzyme purification procedure and low enzyme stability these systems are quite expensive and have short life time. The cost-effective and sensitive methods for sugar determination are highly demanded.

Here we introduce baker's yeast assisted simple potentiometric method for sugar determination in beverages. The ability of commercially available baker's yeast to ferment sugars and proportionally increase environment acidity was tested using plain glass pH electrode. The conditions for analysis and yeast fermentation were optimized. The developed method was tested during the determination of sugar amount in different apple juices. It was shown, that proposed method can be applied to determine total sugar amount in the fruit juices.

Acknowledgements. E. Voitechovic would like to acknowledge the financial support from St. Peterburg State University Postdoc Grant #12.50.1191.2014

EXPRESS METHOD FOR DETERMINING THE TOTAL CARBON IN BORON CARBIDE BY USING A VARIO EL CUBE ELEMENTAL ANALYZER

Vorozhtsov D.L., Sokolova O.V.

Lobachevsky State University of Nizhni Novgorod
Nizhni Novgorod, Russia
research fellow
dmvorozh@gmail.com

Boron carbide finds wide use in various industries. It is used to fabricate abrasive and grinding materials and chemical glassware and as a semiconductor material in electronics. B_4C ceramic plates serve to create high-strength light-weight body armor. In nuclear power engineering, boron carbide is used as a material for rods controlling the course of nuclear reactions. This compound has the characteristic feature of its composition depends on the conditions of a synthesis. This leads to significant variations in the physicochemical properties of the resulting material. Thus, control of the carbon content in the final product becomes critically important. Elemental analyzer Vario El cube (Elementar Analysensysteme, Germany) designed for elemental analysis of organic and inorganic samples. The duration of a single CN analysis is 5-6 minutes. Thus, it is possible to develop a rapid procedure of analyzing samples of boron carbide.

The goal of our study was to develop a rapid method for determining the total carbon in boron carbide samples by using a Vario El cube elemental analyzer. Metrological characteristics of the proposed method were measured. The modification of the fluxing agent composition enabled a 1.5 times decrease in the time of oxygen dosing in oxidation of a sample, which substantially prolonged the service life of the reducing tube of the device. The key advantages of the suggested analytical procedure are the high rate of analysis and simplicity [1].

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Acknowledgements

The study was carried out with support from the Ministry of Education and Science of the Russian Federation on the equipment of the Collective Usage Center “New Materials and Resource-saving Technologies” (Lobachevsky State University of Nizhni Novgorod, project RFMEFI59414X0005).

SIMULTANEOUS STEPWISE INJECTION DETERMINATION OF METHANOL AND ETHANOL IN BIODIESEL USING PERVAPORATION

Zabrodin A.V., Shishov A.Y., Penkova A.V., Ermakov S.S., Bulatov A.V.

Saint Petersburg State University
Saint Petersburg, Russia
Student
artemikon@gmail.com

Biodiesel is a relatively new source of renewable energy which is composed of the mixture of mono-alkyl esters of long chain fatty acids, obtained through a transesterification reaction of vegetable oils or animal fats with methyl or ethyl alcohol in the presence of alkali or acid catalysts. An excess amount of alcohols in biofuel affects the efficiency of its combustion in the engine and accelerates its deterioration. In this regard it is essential to determine the content of methanol and ethanol in order to control biofuel quality.

The aim of this work was to develop fully automated procedure for determination of methanol and ethanol in biodiesel in conditions of stepwise injection analysis (SWIA). The method involves the injection of biodiesel sample into donor chamber of a pervaporation module. The methanol and ethanol evaporate into the headspace and then diffuse across an aromatic polyamide membrane into a mixing chamber of SWIA equipped with screen printed electrodes for voltammetric detection. Optimal experimental conditions for an on-line determination of methanol or ethanol were investigated. The detection limits were for found to be 0.5 mg g^{-1} with a sampling frequency of 10 h^{-1}. The method was successfully applied to the analysis of biodiesel samples. The SWIA data was validated versus GC-MS.

Acknowledgements:
This work was supported by the Russian Foundation for Basic Research (project No. 13-03-00031-a 14-03-31092 mol_a). Scientific research was performed at the Center for Chemical Analysis and Materials Research, at the Center of Thermal Analysis and Calorimetry, and at the Interdisciplinary Resource center for Nanotechnology of the St. Petersburg State University and Resource center for Chemical Education.

FULLY AUTOMATED SPECTROPHOTOMETRIC DETERMINATION OF GLYCEROL IN BIODIESEL

Zabrodin A.V., Shishov A.Y., Bulatov A.V.

Saint Petersburg State University,
Saint Petersburg, Russia
Student
artemikon@gmail.com

Biodiesel is an important alternative fuel, produced from animal fats or natural vegetable oils. Biodiesel is generally produced by catalytic transesterification reaction of oils in presence of alcohol during which the glycerol is obtained as a byproduct. The presence of glycerol causes the formation of soap and deteriorates combustion of fuel. At present several methods for glycerol determination in biodiesel with the usage of liquid and gas chromatography, mass spectrometry, capillary electrophoresis are developed. However, most of them require high-cost instrumentation, skilled analysts and complex and time-consuming sample pretreatments. Also, these methods are not efficient enough and generate large amount of wastes.

Flow analysis provides higher efficiency, allows decreasing of reagents amount and wastes. Flow injection methods for glycerol determination in biodiesel with spectrophotometric, spectrofluorometric and amperometric detection were reported. But common disadvantage of these methods is the requirement of manually operated extraction of glycerol into aqueous phase and centrifugation of the extract. These procedures are long-time (15-30 min) and don't allow to carry out fully automated procedure.

To solve the problems mentioned above, the new method for flow determination of glycerol in biodiesel was developed using the automated extraction of analyte from the organic phase to aqueous phase by means of membrane separation. Further determination of the analyte is carried out with spectrophotometric detection. The method's linearity range is 20-200 ppm, LOD is 10 ppm.

This work was supported by the Russian Foundation for Basic Research (project No. 13-03-00031-a and 14-03-31092_mol-a). Scientific researches were performed at the Center for chemical analysis and materials research of St. Petersburg State University.

ASSESSMENT OF THE TOXICITY OF WATER BEFORE AND AFTER THE ULTRASONIC TREATMENT IN TERMS OF BIOASSAY USING A MULTISENSOR SYSTEM

Zadorozhnaya O.A.

Saint Petersburg State University,
Saint Petersburg, Russia
Graduate student
Olesya.zadorazhnaya.91@mail.ru

Water quality assessment, as well as its purification and disinfection are important problems. One of the widely used methods for water purification is ultrasonic cleaning; such purification is based on an ultrasonic cavitation – appearance of the collapsing bubbles filled with vapor or gas in the sonicated liquid. Collapsing cavitation bubbles generate the powerful pressure pulses and shock waves in the test liquid. The cavitation may be accompanied by breaking of the chemical bonds of macromolecules and the initiation of chemical reactions. These processes can reduce the toxicity of water in some cases.

To assess the water toxicity a variety of bioassay methods are developed, these methods are based on the study of the reactions of living organisms on potentially contaminated environment.

In this study the bioassay, based on the reaction of *Daphnia magna*, was used as a reference method for the potentiometric multisensor system. This method is using *Daphnia magna* - small crustaceans, their death rate in a sample is express indicator of acute toxicity of water. This technique has a number of drawbacks, such as the need to maintain the special living conditions for daphnia, and the presence of limitations of working with crustaceans, for example, this method can not be used to assess the toxicity of chlorinated water, as *Daphnia magna* is extremely sensitive to chlorine.

In this work, we applied the potentiometric multisensor system, previously calibrated against the samples with known toxicity, as an alternative to biotesting method. We employed an array of cross-sensitive potentiometric sensors, which by means of chemometric methods (PLS regression) was calibrated relative to the response of *Daphnia magna* in four groups of natural water samples both before and after sonication. The relative error of toxicity prediction of using the sensors array was in the range 10-25%. These results give a good promise for multisensor systems to become an alternative method for water toxicity analysis.

STUDYING OF THE SOLID-PHASE EXTRACTION FOR DETERMINATION OF ACROLEIN IN THE AIR

Zavernenkova E.O.

Federal budget scientific institution "Federal scientific centre for medical and preventive health risk management technologies", Russia
zavernenkova@yandex.ru

At present the problem of environmental pollution by harmful organic compounds is extremely urgent. At this case acrolein is of great interest. The referent concentration of acrolein is very low, 0.00002 mg/m^3. The complexity of determining acrolein microconcentration is associated with taking air samples, their storage and the limit of detection of the laboratory equipment. We have studied the possibility of applying the solid-phase extraction to achieve the desired level of method sensitivity we suggest to determine the acrolein content in the air. The detection and the quantification of the acrolein were accomplished by the method of high-perfomance liquid chromatography using a Eclipse XDB-C_{18} column (2.1x150 mm) and fluorescent detection. The method suggested is based on determining acrolein content, acrolein being used in the form of its 7-xydroxyquinoline derivate that is formed as a result of the chemical reaction (Figure 1).

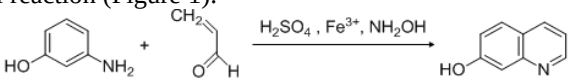

Fig 1. Reaction of derivatization

Sample taking consists of air bubbling through the two Richter devices.

We have studied two type of solid-phase extraction cartridge. They are Oasis HLB 3cc and Oasis Max 3cc. It was found that due to the high acidity of absorbing solution (pH = 1) analyte is not retained on the cartridge.

Alkalization of the reaction mixture led to instability analysis. It makes impossible to use solid-phase extraction for the for the derivate concentrating.

The results of our research will be applied to the development of the method used to determine acrolein content in the atmosphere at the reference concentration level.

FEATURES OF GAS CHROMATOGRAPHIC ANALYSIS OF LOW VOLATILE DICARBOXYLIC ACIDS

Igor G. Zenkevich, *Liliya N. Fakhretdinova*
Saint Petersburg State University,
Saint Petersburg, Russia
Student
l.fakhretdinova2015@yandex.ru

Di- and polycarboxylic acids is the important group of natural biogenic compounds. In this regard, the possibilities of their direct gas chromatographic analysis without derivatization were the subject of interest for us.

Analytical Conditions: GC-MS Instrument: Shimadzu QP 2010 Plus,,
Column: RTX-5 MS, length 30 m, i.d. 0.25mm, film thickness 0.25μm,
Column temperature: 70 – 200 °C, ramp 10 °C/min,
Injector temperature: 220 °C.

Some compounds of this series [e.g., glutaric, retention index (RI) 1286] can be analysed directly without decomposition, for some others the formation of the products of their interaction with solvent are typical (oxalic acid), while in some cases the products of their thermal decomposition are the single compounds registered on the chromatograms.

Oxalic acid is registered as dissolved peak with irreproducible position of its front edge. In addition to that, two products of its interaction with 2-propanol are observed (Fig. 1). First of them is rarely reported monoisopropyl ester of oxalic acid:

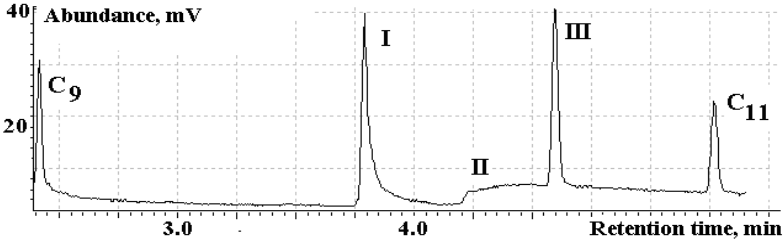

Fig. 1. Chromatogram of oxalic acid solution in 2-propanol; C_9 and C_{11} – reference *n*-alkanes, **I** – monoisopropyl oxalate, **III** – diisopropyl oxalate, **II** – broad peak of oxalic acid.

The behavior of thermally unstable citric acid, which consists of three carboxyl groups, was considered for comparison. In the result of successive dehydration and decarboxylation this compound forms anhydrides of citraconic (RI 948 ± 3) and itaconic (RI 1038 ± 3) acids; both were identified using their mass spectra.

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