ISAC-2017

1st International Seminar on Advanced Calorimetry

ABSTRACTS

KAZAN
19-20 October
2017

19-20 October 2017
Kazan, Russia

ISAC-2017

1ˢᵗ International Seminar on Advanced Calorimetry

ABSTRACTS

**19-20 October 2017
Kazan, Russia**

THE CONFERENCE ORGANIZERS

Ministry of Education and Science of the Russian Federation

Kazan (Volga region) Federal University

Laboratory of fast scanning calorimetry (KFU)

INTERNATIONAL ADVISORY BOARD

Cristoph Schick (Germany)

BorisSolomonov (Russia)

Sergey Verevkin (Germany)

LOCAL ORGANIZING COMMITTEE

Cristoph Schick – Chairman

Boris Solomonov – Co-chairman

Alexander Gerasimov – Secretary

Valery Gorbatchuk

Marat Ziganshin

Timur Mukhametzyanov

Ruslan Nagrimanov

Artur Boldyrev

Liana Usmanova

Askar Gatiatulin

Igor Sedov

PLENARY LECTURES

DETECTION OF SMART PROPERTIES OF CALIXARENES USING SIMULTANEOUS THERMAL ANALYSIS AND FLASH DSC

Gorbatchuk V.V., Ziganshin M.A., Gataullina K.V., Gatiatulin A.K., Gabdulkhaev M.N.

Institute of Chemistry, Kazan Federal University, Kremlevskaya st. 18, Kazan, 420008, Russia
e-mail: Valery.Gorbatchuk@kpfu.ru

Smart properties of solid calixarenes and other hosts were observed boosting their selectivity and clathrate stability. Absolute selectivity of host response to guest inclusion and release was found, which goes far beyond the capability of ordinary key-to-lock mechanism. While current concept of molecular recognition is based on the preferential binding of complementary species, the present work uses specific cooperative properties of host crystals such as their memory of previously bound guest[1-3] and effect of clathrate preparation history on guest inclusion capacity and clathrate stability.[4,5] Thus, small guest molecules having no more than one functional group capable of H-bonding or donor-acceptor interactions can be discriminated even from their close homologues.

An observed ability of several calixarenes to remember previously included and evolved guests does not have any precedents by selectivity. This memory can be read in simultaneous TG/DSC experiment, by DSC or by flash DSC as an exothermic effect of host collapse from loose to dense phase without mass change. The memory parameters (enthalpy and temperature of polymorphic transition) strongly depend on the guest structure. This smart property persists also for guest mixtures.[3] In some cases, such memory effect can be found only after a solid-phase guest exchange in calixarene clathrates.[6] When combined, these effects give a controlled polymorphism of calixarenes with long-chain substituents with H-bonding capability.[2]

References

1. Gataullina K.V., Ziganshin M.A., Stoikov I.I., Gubaidullin A.T., Gorbatchuk V.V. *Phys. Chem. Chem. Phys.* 2015, **17**, 15887.
2. Gataullina K.V., Ziganshin M.A., Stoikov I.I., Klimovitskii A.E., Gubaidullin A.T., Suwińska K., Gorbatchuk V.V. *Cryst. Growth & Design* 2017, **17**, 3512.
3. Safina G.D., Ziganshin M.A Gubaidullin A.T., Gorbatchuk V.V. *Org. Biomol. Chem.* 2013, **11**, 1318.
4. Gorbatchuk V.V., Gatiatulin A.K., Ziganshin M.A., Gubaidullin A.T., Yakimova L.S. *J. Phys. Chem. B* 2013, **117**, 14544.
5. Galyaltdinov S.F., Ziganshin M.A., Gubaidullin A.T., Vyshnevsky S.G., Kalchenko O.I., Gorbatchuk V.V. *CrystEngComm* 2014, 3781.
6. Galyaltdinov S.F., Ziganshin M.A., Drapailo A.B., Gorbatchuk V.V. *J. Phys. Chem. B* 2012, **116**, 11379.

NON-EQUILIBRIUM FAST THERMAL RESPONSE OF POLYMERS

Minakov A.A.

A.M. Prokhorov General Physics Institute, RAS, Vavilov str. 38, Moscow,119991, Russia
e-mail: minakov.alexander@rambler.ru

Non-equilibrium thermal response of polymers in nanosecond and longer time scales is described by the linear differential equation with dynamic heat capacity in the framework of the linear response theory.[1] The equation can be utilized on the length scale of more than 10 nm for semi-crystalline polymers and down to the nanometer scale for amorphous system. The equation can be solved, if the dynamic heat capacity is specified. In general, the dynamic heat capacity is a multi-scale decaying function, which can be presented as a continuous sum of exponential decays with appropriatedistribution of the relaxation-time parameter τ_0. Then, the thermal response of polymers $T(t,\mathbf{r})$ can be represented as a linear combination of solutions with different τ_0, since the equation is linear with respect to $T(t,\mathbf{r})$. Self-consistent analytical solution for non-equilibrium thermal response of polymers in planar and spherical geometries is obtained.
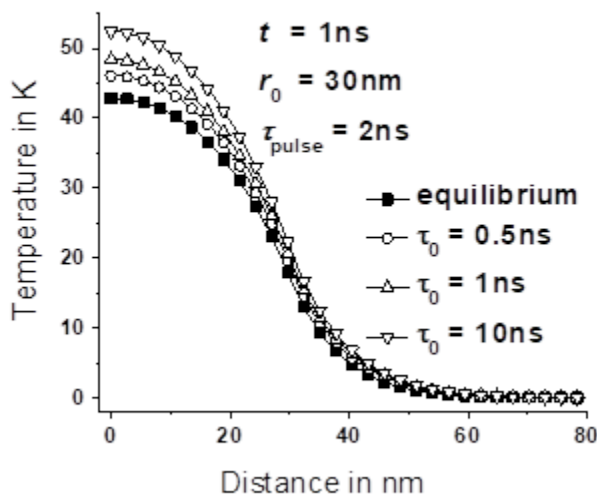
Non-equilibrium thermal response of polymers under pulse heating differs significantly from the thermal response of the material in equilibrium. It is noteworthy that even very fast components of the dynamic heat capacity (with τ_0 in the order of 1 ns) significantly affect the thermal response to the local thermal perturbations (in nanometer scale). The effect is more pronounced in the initial stage of the heating process at t in the nanosecond scale. This can be significant for the heat transfer process at fast formation of crystallites in nanometer scale.

References
1. Landau L.D., Lifshitz E.M., Statistical physics, Part 1, Pergamon press, 1980.

ACHIEVEMENTS AND CHALLENGES IN EXPERIMENTAL AND STATISTICAL THERMODYNAMICS OF ORGANIC COMPOUNDS

Pimerzin A.A.

Samara State Technical University, Samara, 443100, Russia
e-mail: pimerzin.aa@samgtu.ru

Experimental results are extremely important for thermodynamics and thermochemistry, due to the fact that experiment is the only reference point for verifying calculations and the consistency of information obtained from various sources. Traditional thermochemical and thermodynamic methods of research operate with high purity individual compounds. Moreover, the accuracy of the result is directly arise from the purity level of chemicals. Obviously, the requirement for high-purity substances imposes meaningful constraints on authenticity of the obtaining data.

The combination of traditional methods and techniques without mentioned limitations (for example, the method of studying chemical equilibrium) makes it possible to broaden the set of studied compounds, especially for chemicals, which are difficult to obtain in high-purity samples. The suggested simultaneous approach proved effective for various classes of organic compounds. Several examples are given in the report.

The development of molecular modeling and quantum-chemical calculations opens the door to multiple opportunities for prediction the thermodynamic properties of polyatomic organic compounds. However, today these opportunities are not always fully used. The accuracy of the result of calculation depends on several factors that must be performed if we are looking forward to a positive outcome. First and foremost, it is the observance of the assumptions underlying the statistical calculations of thermodynamic properties of compounds. Among them

- The principle of independence of the different types of motion and the additivity of their contributions to thermodynamic functions;

- Approximation of "rigid rotator - harmonic oscillator".

However, the complex structure of polyatomic molecules, the conformational heterogeneity of the compounds, the appearance of intramolecular degrees of freedom with high-amplitude movement, unharmonic character of the vibrational frequencies are very often do not fit into the framework of the established assumptions.

This research analyzes the reasons for the differences between the forecast of the thermodynamic properties (entropy, enthalpy, heat capacity) and experiment. The analysis was performed on the example of the thermodynamic properties of aliphatic, alicyclic, aromatic hydrocarbons, alkylphenols, alkylhalogenbenzenes and its reactions.

Some of the raised issues have been decided. For other ones the methods, which allow detecting their emergence and making estimation, have been proposed. For some problems have yet to find a solution.

# THERMOPHYSICAL PROPERTIES OF THERMALLY LABILE COMPOUNDS

Abdelaziz A.,[a] Zaitsau D.H.,[b] Mukhametzyanov T.,[c] Solomonov B.,[c] Verevkin S.P.,[b] <u>Schick C.</u>[a,b]

[a] *University of Rostock, Institute of Physics & Competence Centre CALOR, Albert-Einstein-Str. 23-24, 18051 Rostock, Germany,*
[b] *University of Rostock, Institute of Chemistry, Dr-Lorenz-Weg 2, 18051 Rostock, Germany,*
[c] *Kazan Federal University, Kremlyovskaya Street 18, Kazan 420008, Russian Federation*
e-mail: christoph.schick@uni-rostock.de

How to obtain reliable thermophysical properties from thermally labile compounds, e.g. biomolecules or ionic liquids? In general, one has to stay at temperatures where decomposition is negligible during the time of the measurement. If possible, one can stay at sufficiently low temperatures avoiding decomposition. However, often this strategy is not applicable because the effect of interest does not occur at such low temperatures or the rate is so low that it is very hard to get any signal from the process under investigation. Typical examples for such situation are the melting of biomolecules, e.g. dry proteins, or vaporization of ionic liquids or sublimation of biomolecules. Then, the only way to obtain reliable data is by speeding up the process under investigation in order to avoid the decomposition, which is usually slower. For example, only if the complete heating-cooling cycle to observe the melting of dry proteins is so fast that decomposition at the highest temperatures is negligible, there is a chance to get melting temperature and heat of fusion of the high temperature transition. Fast scanning calorimetry (FSC) offers a possibility to realize experiments on millisecond time scales and with that to overturn chemical decomposition in many materials.[1,2] The general principle of FSC with heating and cooling rates up to 10^6 K/s will be introduced and applications to the melting of proteins and other biomolecules will be discussed.[3-5] The vaporization of ionic liquids and the sublimation of biomolecules will be discussed too.[6,7]
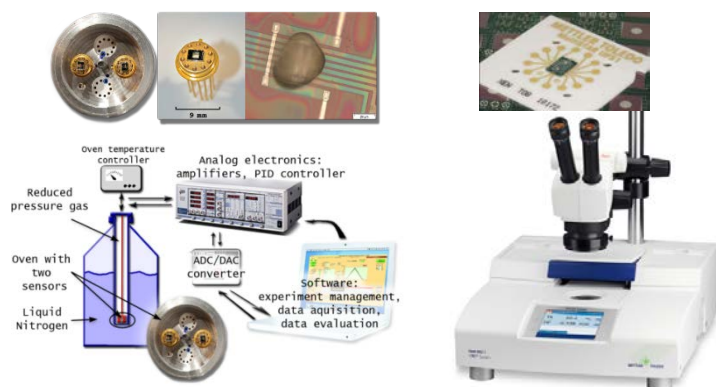
Photographs of available fast scanning calorimeters

Funktional Materials Rostock e.V.   Mettler Toledo

References:
1. Schick C.,Mathot V. Fast Scanning Calorimetry. Springer, 2016.
2. Zhuravlev E. Schick C. *Thermochim. Acta* 2010, **505(1-2)**, 1.
3. Cebe P., Hu X., Kaplan D.L., Zhuravlev E., Wurm A., Arbeiter D.,Schick C. *Scientific Reports* 2013, **3(1130)**,1.
4. Cebe P., Partlow B.P., Kaplan D.L., Wurm A., Zhuravlev E.,Schick C. *Thermochim. Acta* 2015, **615**, 8.
5. Cebe P., Thomas D., Merfeld J., Partlow B.P., Kaplan D.L., Alamo R.G., Wurm A., Zhuravlev E.,Schick C. *Polymer* 2017, **126**, 240.
6. Ahrenberg M., Brinckmann M., Schmelzer J.W.P., Beck M., Schmidt C., Keßler O.H., Kragl U., Verevkin S.P.,Schick C. *Physical Chemistry Chemical Physics* 2014, **16 (7)**, 2971.
7. Ahrenberg M., Beck M., Neise C., Kragl U., Verevkin S.P.,Schick C. *Physical Chemistry Chemical Physics* 2016, **18 (31)**, 21381.

NEW ASPECTS IN THERMOCHEMISTRY OF SOLID-LIQUID PHASE TRANSITIONS OF ORGANIC NON-ELECTROLYTES

<u>Solomonov B.N.</u>

Kazan Federal University, Kremlevskaya st. 18, Kazan, 420008, Russia
e-mail: Boris.Solomonov@kpfu.ru

Solid-liquid phase transitions thermochemistry plays important role in solidification studies of polymers, metals, inorganic salts and low-molecular organic compounds. Enthalpy of fusion is a source of information about intermolecular interactions in materials, crystallinity, mixtures phase diagrams shape, heat transfer in the solidification interval.

In the present chapter we analyze relationship between the fusion enthalpies of aromatic compounds at the melting temperature and the solution enthalpies in benzene at 298.15 K. Sublimation and vaporization thermochemistry are used as an additional source of information about the latter relationship. The equality between the fusion enthalpies at the melting temperature and the solution enthalpies in benzene at 298.15 K is established for a large number of compounds. The influences of solution enthalpy of liquid in benzene and fusion enthalpy temperature dependence on this equality are discussed.

FROM SURFACE TO BULK DEHYDRATION OF MATERIALS.
A KINETIC PERSPECTIVE

Vecchio Ciprioti S.

*Department of Basic and Applied Science for Engineering, Sapienza University of Rome,
Via del Castro Laurenziano 7, 00161 Rome, Italy
e-mail: stefano.vecchio@uniroma1.it*

Hydration is an important process occurring in several classes of materials (i.e., foods, pharmaceuticals, clay minerals, etc.) that may affect their stabilities. For this reason, it is important to determine the temperature ranges (at ambient pressure) where they released water physically or chemically bound to the surface or to the bulk of their structures. Furthermore, the knowledge of the rate at which dehydration takes place at a given temperature is also important.

At a higher temperature several materials may undergo dehydroxylation by removing water molecules through the condensation of hydroxyl groups from their surfaces, and in some cases from the bulk (i.e., OH groups pending inside the layer of hydrogenphosphates of tetravalent metals like Zr(IV) and Ti(IV)).[1] The amount and the temperature ranges at which this process occurs is of paramount relevance to establish some physico-chemical properties of these materials. For instance, when a suitable amount of water is removed via dehydroxylation of kaolin (KAO) in the range 450-600 °C a lattice vacancy is formed and if many vacancies are obtained the structure is deformed into metakaolin.[2]

In particular, for a full comprehension of the properties of gel- and ceramic-glasses with the perspective of their use as bioactive materials a deeper insight into their thermal behavior is provided in this study by means of thermal analysis aiming at investigating the processes occurring during heating from a kinetic point of view, with particular reference to dehydration. A similar approach is proposed to investigate dehydration and dehydroxylation of nanosize tube of halloysite (HNT), whose interest increased significantly during the recent years due to their remarkable properties, like that to entrap negatively charged molecules within the positively charged inner lumen (i.e., drugs, NAD, marine biocides).[3]

Non-isothermal kinetics of this process, which occurs at temperature quite higher than dehydration due to the presence of stronger hydrogen bonds between the OH groups, was extensively studied for different types of KAOs,[4,5] but little is known about the same process occurring in HNTs where early papers used questionable kinetic methods under isothermal conditions. These two case studies will be presented and critically discussed using reliable kinetic methods that are among those recommended by the Kinetic Committee of the International Confederation for Thermal Analysis and Calorimetry (ICTAC).

References
1. Vecchio Ciprioti S., Catauro M., *J. Therm. Anal.Calorim.*2016, **123**, 2091; Vecchio Ciprioti S., accepted for publication, *J. Therm. Anal.Calorim.* 2017.
2. Yeskis D., van Groos A.F.K., Guggenheim S., *Am. Mineral*. 1985, **70**, 159.
3. Duce C., Vecchio Ciprioti S., Ghezzi L., Ierardi V., Tinè M.R.*J. Therm. Anal.Calorim*. 2015, **121**, 1011.
4. Gasparini E., Tarantino S.C., Ghigna P., Riccardi M.P., Cedillo-Gonzalez E.I., Siligardi C., Zema M., *Appl Clay Sci.*2013, **80-81**, 417.
5. Ptacek P., Kubatova D., Havlica J., Brandstetr J., Soukal F. *Thermochim. Acta,*2010, **501**, 24.

SOLUBILITY OF MOLECULAR AND IONIC PRECURSORS IN IONIC LIQUIDS

Verevkin S.P.,[a] Zaitsau D.H.,[a] Held C.[b]

[a] *Institute of Chemistry, Dept. Physical Chemistry, University of Rostock, Dr-Lorenz-Weg-2, 18059 Rostock, Germany,*
[b] *Laboratory of Thermodynamics, Dept. Biochemical and Chemical Engineering, Technical University of Dortmund, Emil-Figge-Strasse 66, 44227 Dortmund, Germany*
e-mail: sergey.verevkin@uni-rostock.de

The success of ionothermal synthesis is crucially dependent on the creative choice of suitable precursors. The main goal of this project is the development of general thermodynamic procedure based on the ePC-SAFT model enabling effective prediction of solubility of liquid or solid precursors in ionic liquids used as suitable solvents for the ionothermal synthesis. As the solid precursors we consider salts close related to the synthesis of metal nanoparticles in ILs. As the liquid precursors the homologous series of organic compounds (alkanes, alkenes, aromatics, alcohols, ethers, esters) will be studied. Development and parametrization of the ePC-SAFT model will be performed by using reliable experimental data. In this context, the subsidiary goal of this project will be the extended experimental study of thermodynamic properties of pure ILs and precursors, as well as properties of their binary mixtures in order to provide reliable input data sets required for the model development and validation. In order to propagate application of thermodynamic parameters obtained from binary mixtures precursor-IL to multi-component systems, an additional validation of the model will be performed by the experimental and theoretical study of two equilibrium systems, where three of four reaction participants as well as the solvent are included. An accumulation of thermodynamic results will allow developing of a general scale of solubility parameters, with the purpose of predicting the performance and aiding the selection of ILs for ionothermal synthesis. This scale has a potential to be extended and improved for application to a broad scope of molecular and ionic precursors.

STRUCTURE-PROPERTY RELATIONS IN VAPORIZATION THERMODYNAMICS: MOLECULAR LIQUIDS vs IONIC LIQUIDS

Zaitsau D.

Institut für Chemie und Kompetenzzentrum CALOR, Universität Rostock, Albert-Einstein Str 25, 18059, Rostock, Germany
e-mail: ZaitsauDz@gmail.com, Dzmitry.zaitsau@uni-rostock.de

Molecular solvents have been used for a long time as main reaction media for synthesis: from cooking food to many stage industrial syntheses of biomolecules. The purification of the target product is the main energy consumption of the industrial synthesis. Ionic liquids (ILs) were recently proposed to be a perspective media for synthesis decreasing the purification costs. These compounds consist of the bulky organic cation and organic or inorganic counter ion. The ion interaction in ILs is suppressed by the steric repulsion of the bulky cations and leads to low melting temperature. The low melting temperature clears the ways for ILs as a synthesis media.

The liquid state of ILs is not the only their positive feature, they also possess extremely low vapor pressure, the wide electrochemical window, and the high conductivity. The great advantage of ILs is numerical degrees of structural freedom which can be applied to design the structure of IL and altering the physical properties (viscosity, density, solubility) together with polarity and aromatic and so on according to needs.

The enthalpy of vaporization is the key value for understanding the inter- and intra-molecular interaction in materials, for example through molecular simulation computation techniques. Experimental determination of the vaporization enthalpies for systems with such extremely low vapor pressure and thermal lability is a challenging task. But during the last ten years, we have come a long way *per aspera* to develop and improve the set of experimental techniques allowing determination of the vaporization enthalpy and in many cases absolute vapor pressures even for systems with low thermal stability. From the other side, plenty degrees of structural freedom in ILs spoils the approach of measuring the enthalpy of vaporization for all ILs as the number of possible ILs is too high ($\sim 10^{18}$).

The only way to solve such problem is creating the simple but reliable correlation between the ILs structure and its enthalpy of vaporization. Application of the additive approaches has shown the similarities as well as significant differences in vaporization enthalpy for molecular and ionic liquids.

Thus, for molecular systems, the additivity of the vaporization enthalpy is an ordinary case and the most observed deviations correspond to strong interactions in molecules like H-bands. But in the case of ILs strong coulomb interaction is an ordinary case and therefore deviations from the additivity are often observed.

The difference in thermodynamic properties of molecular and ionic solvents raise the requirements of the experimental techniques in order to determine the vaporization properties for extremely high volatile compounds without their thermal decomposition. The improvement of the existing techniques and non-conventional application of the calorimetric methods allows the reliable study of the vaporization thermodynamics for ILs.

As a results of the long term study of the enthalpies of vaporization for series of ILs with different cations (imidazolium, pyridinium, and ammonium) and anions (halides, BF_4, PF_6, NTf_2, and so on) the final analysis of the vaporization enthalpy and the CH_2 increment $\Delta_l^g H^o_m(CH_2)$ was carried out. From the first sight, the observed dependences for vaporization enthalpies in ILs are absolutely different to the molecular compounds. The more detailed analysis provides some similarities in vaporization enthalpy but significantly amplified in the case of ILs.

SCIENTIFIC SESSION

THERMODYNAMIC ASPECTS OF THE FORMATION OF SOLID DISPERSIONSBASED ON PROTEINS WITH THE POSSIBILITY TO INHALATION ADMINISTRATION

Boldyrev A.E., Gerasimov A.V., Usmanova L.S.

Kazan Federal University, Kremlevskaya st. 18, Kazan, 420008, Russia
e-mail: ArEBoldyrev@kpfu.ru

Inhalation therapy is one of the methods of express administration of drugs into the human body. Inhaled substances with this method of administration do not undergo changes similar to those observed when administered via the gastrointestinal tract. The substances introduced into the lungs by inhalation have a 10-200 fold greater bioavailability than nasal and gastrointestinal administration because of extremely abundant capillary network and huge surface of lung alveoli. Furthermore, inhalation administration in aerosol form of the drug with controlled parameters can serve as a non-invasive alternative to injecting drugs. Therapeutically useful particulate limited range in diameter from 1 to 5 microns. In this paper, the complex of physical and chemical methods have been optimized composition of the sodium caseinate with a well-established as a model hydrophobic drug compound - phenacetin. The optimum concentrations of the components in solution to produce spherical microparticles with an average diameter of 1.3 microns, which can be used for inhalation delivery of drugs and have increased solubility, are determined. The thermodynamic parameters of the dissolution for produced microspheres were obtained. Preliminary minimum set of methods needed for protein:drug composits by spray dried are: differential scanning calorimetry, X-ray powder diffraction, determination of kinetics of the dissolution process.

DETERMINATION OF SUBLIMATION ENTHALPIES OF SUBSTITUTED BENZIPHENONES, FLUORENES AND DIPHENYL ETHERS BY SOLUTION CALORIMETRY APPROACH

Buzyorov A.V., Samatov, A.A., Nagrimanov R.N., Solomonov B.N.

Kazan Federal University, Department of Physical Chemistry,
Kremlevskaya Str. 18, Kazan, 420008, Russia
e-mail: abuzurov95@gmail.com

Substituted benzophenones, fluorenes and diphenyl ethers are widely used in the pharmaceutical industry and perfumery. Consequently thermochemical properties of these compounds are required for determination the solubility. For examplethe solubility of fluorenes and benzophenones is an important property because many of its derivatives are pollutants.

However, only the sublimation enthalpy of unsubstituted fluorenes and benzophenons were studied well.

As a well-known most popular and accuracy methods for determination ofsublimation enthalpies based on the investigation vapour pressure at wide temperature range. However organic compounds such as benzophenone and fluorene derivatives can decompose at elevated temperature.

For this reason we used method which has been developed in our previous work.[1] This approach based on the difference between solution and solvation enthalpy. Thermochemical data of solution enthalpies of benzophenones, fluorenes and diphenyl ether derivatives were measured by a precision solution calorimeter at 298 K. For the estimation solvation enthalpy of these compounds we used additive approach. The content of this approach is as follows: solvation enthalpy of unsubstituted compounds was defined as a difference between experimental solution enthalpy and well established literature sublimation enthalpy. The contribution due to the substituent group is added to solvation enthalpy of parent aromatic compound. Solvation enthalpies of sixteen substituted benzophenones, fluorenes and diphenyl ethers were calculated by this approach.

We have also found that in a number of cases instead of the solution enthalpy in benzene at 298 K the fusion enthalpy at the melting temperature can be used. A comparison between literature data and the calculated sublimation enthalpies demonstrates a satisfactory performance.

References
1. Solomonov B.,Varfolomeev M.,Nagrimanov R.,Novikov V., Buzyurov A., Fedorova Yu., Mukhametzyanov T. *Thermochim. Acta*2015, **622**, 88.

EFFECT OF MINERAL MATTER AND METAL OXIDE ADDITIVES ON THE THERMAL DECOMPOSITION OF KEROGEN STUDIED BY TG/FTIR TECHNIQUE

Emelianov D., Varfolomeev M.

Kazan Federal University, Kremlevskaya st. 18, Kazan, 420008, Russia
e-mail: dima_emelyan@mail.ru

The tremendous increase in global energy demand and rapid depletion of conventional oil resources has necessitated the use of alternative energy sources. Oil shale is an organic-rich, petroleum-generating source rock that accounts for approximately 35% of the world's reserves, with a large commercial viability.[1,2] Generally, oil shale can be converted into useful forms of energy mainly via pyrolysis or combustion. Investigation of the oil shale combustion is mainly useful for the optimization of the direct energy extraction processes. At the same time the results obtained from the oil shale pyrolysis are necessary for understanding the processes accompanying the in-situ artificial oil shale aging. Recently, thermal analysis techniques have been widely used for investigation of the oil shale oxidative and inert degradation. Their simplicity and an additional opportunity to carry out simultaneous spectral analysis allow one to get more details on the combustion and pyrolysis mechanism.

In the present study we use thermogravimetry equipped by FTIR spectrometer for analyzing the emitted product gases to investigate the pyrolysis of Bazhenov formation kerogen. The studied samples were preliminarily purified from bitumen fraction and demineralized from calcite and silicate matrices. The measurements were performed in the temperature range 25-800 °C in inert (nitrogen) atmosphere. To estimate the pyrolysis process kinetic characteristics the measurements were performed at 5, 10, 15, and 20 K min^{-1} heating rates. It was shown that the TG curve includes two mass loss stages, Δm_n, with the $\Delta m_1 \approx 28\%$ and $\Delta m_2 \approx 9\%$. As a consequence, two clear peaks assigned to the kerogen and pyrite decomposition are observed in the corresponding DTG curves. This assignment was confirmed by the results of IR measurements. The DTG temperature maximum, $T_{max} = 434$ °C (at 10 K min^{-1}), corresponding to the first process coincides with the maximum on the IR-signal in CH stretching region (2800-3100 cm^{-1}) observed during the course of the experiment. In contrast, the second process observed at $T_{max} = 527$ °C is not accompanied by the organic content release as well as no peaks corresponding to organic matter are observed in the gas phase IR spectra at higher temperatures. This fact points out that the fuel generation does not take place at $T>550$ °C. Using the data at different heating rates the kinetic characteristics of the kerogen thermal decomposition were estimated. Comparison of the results obtained from model-free (Friedman and Ozawa-Flynn-Wall) and model kinetic approaches show good agreement indicating the reliability of the found data.

In order to study the rock influence on the kerogen pyrolysis the 15 / 85 (w/w) kerogen / calcite mixtures were also investigated. In agreement with the earlier work by Pan *et al.*[3] it was shown that calcite has no significant influence on the kerogen pyrolysis. For example, the position of the principal peaks on the DTG curves (decomposition of kerogen and pyrite) do not shift in the presence of calcite. The activation energy, however, shows some decrease compared to the value found for the kerogen pyrolysis in the kerogen-pyrite mixture. The effect of MnO_2 additives (1% wt.) – promising nanocatalyst – on the thermal behavior and kinetic parameters of kerogen was also thoroughly studied.

References
1. Taciuk W. *Oil Shale* 2013, **30**, 1.
2. Wang S., Jiang X.M., Han X.X., Tong J.H. *Energy* 2012, **42**, 224.
3. Pan L., Dai F., Huang J., Liu S., Li G. *Thermochim. Acta* 2016, **627-629**, 31.

CONTROLLED SELECTIVITY OF GUEST INCLUSION BY FLEXIBLE CALIXARENES

Gabdulkhaev M.N., Gorbatchuk V.V., Ziganshin M.A., Gatiatulin A.K.

A.M. Butlerov Institute of Chemistry, Kazan Federal University, Kremlevskaya st. 18, Kazan, 420008, Russia
e-mail: muhammet.gabdulhayev@mail.ru

Selective memory for volatile organic compounds and controlled selectivity of clathrate formation and are smart properties of calixarenes, especially those having flexible molecules. In the present work, the mutual influence of two guests benzene and tetrachloromethane in their binary mixture on the memory effect for tert-butylcalix[6]arene (**1**) was studied. The first example was found for an ability of these two guests to erase the host memory for each of them when included simultaneously with formation of a ternary clathrate. This clathrate has a much higher thermal stability than corresponding binary clathrates according to the data of simultaneous TG/DSC method combined with mass-spectrometric analysis of the evolved guest vapors. Besides, to characterize ternary clathrate $1 \cdot 0.3C_6H_6 \cdot 0.9CCl_4$ as a new crystalline phase and not a mechanical mixture of binary clathrates formed separately with each guest, these clathrates and four other ternary products with higher and lower benzene contents were studied using XRPD[1].

(**1**)　　　　　(**2**)

Prepared mixed inclusion compounds perform a unique ability for fractional guest release on the separate steps of clathrate decomposition, which may be used for separation of pure volatile compounds from their mixtures.[1]

For calixarene **2**, the possibility to control the direction of solid-phase guest exchange in its clathrate and the inclusion selectivity for the guest mixture components were studied. The effect of a small additive of the non-included fourth component on the calixarene sorption capacity, the selectivity and direction of the guest exchange process in clathrate has been found. Depending on the content of the fourth component, it is possible to obtain ternary and quaternary clathrates of different composition, or transfer the "host" to a state without guest.

References
1. Gabdulkhaev M., Gatiatulin A., Ziganshin M., Gorbatchuk V. *J Therm Anal Calorim* 2016, **126**, 627.

CYCLOTRIMERIZATION OF ALKALI METALS DICYANAMIDES IN A MACROPOROUS MEDIUM

Galukhin A.V., Bolmatenkov D.N.

Kazan Federal University, Kremlevskaya str. 18, Kazan, 420008, Russia
e-mail: and_galuhin@mail.ru

Thermally induced cyclotrimerization of alkali metals dicyanamides is a convenient model reaction for studying confinement effects of different porous media. The reaction results in formation of substituted 1,3,5-triazine cycle and proceeds unambiguously without formation of any by-products. Its exothermicity makes possible to control reaction progress by DSC. Furthermore, the differences in physical properties of alkali metals dicyanamides allow to study the reaction both in solid state (Na) and liquid state (K, Rb).
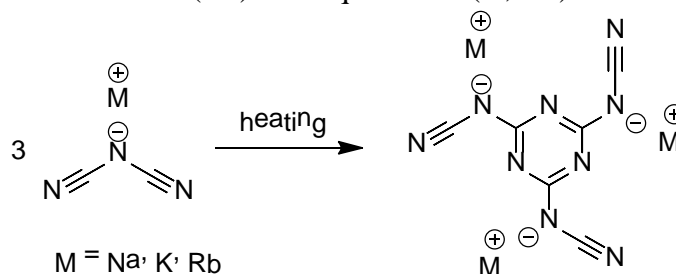
For the first time the highly ordered synthetic opal films will be used as a model porous medium. Synthetic opal films possess such advantages as: the possibility of variation of the pore size, the independence of porosity on the pore size, chemical, thermal and mechanical stability. Kinetics of chemical reactions will be studied by non-isothermal kinetic analysis methods in a broad range of temperatures and heating rates, in particular for the first time the ultra-fast differential scanning calorimetry (heating rates are up to 40 000 K/s) will be applied.

The results obtained in a frame of the project on the dependence of the reactivity of substrates and their state on the parameters of the porous medium will allow to develope fundamentally new approaches for controlling the reactivity of compounds by nanoconfinemet effect.

POLYMORPHISM OF BETA-CYCLODEXTRIN SILYL DERIVATIVE

Gatiatulin A.K., Ziganshin M.A., Gorbatchuk V.V.

A.M. Butlerov Chemical Institute, Kazan Federal University,
Kremlyovskaya str. 18, Kazan, 420008, Russia
e-mail: askar.gatiatulin@gmail.com

Per-6-O-(tert-butyl)(diphenyl)silyl-β-cyclodextrin (**1**) can form a number of crystalline, liquid and glassy polymorphs. This compound is a mono-derivative of β-cyclodextrin modified by primary face. Partially derivatized cyclodextrins with free hydroxyl groups are amphiphilic and have nanocapsule forming properties for drug delivery.[1]

R = SiPh₂t-Bu
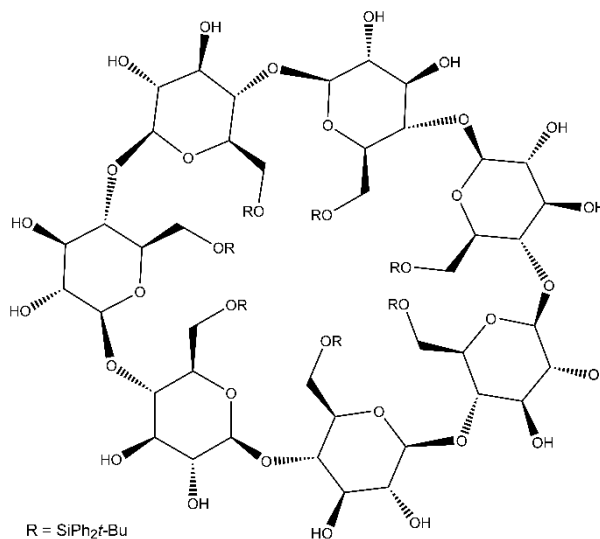
*Figure 1. Per-6-O-(tert-butyl)(diphenyl)silyl-β-cyclodextrin (**1**).*

The studied monosubstituted per-6-O-(tert-butyl)(diphenyl)silyl-β-cyclodextrin was found to exist as a stable liquid in a wide range of temperatures and in two polymorphic forms. Fusion enthalpy of the initial crystalline form prepared from solution in pyridine and heat capacity change at glass transition of the overcooled melt were determined. Conditions of existence for the crystalline, glassy and liquid forms were found. The studied compound can be mixed in any proportion with a number of hydrophilic and lipophilic solvents and has moderate solubility in water.

References
1. Gatiatulin A.K., Ziganshin M.A., Kurochkina G.I., Popkov A.V., Grachev M.K., Gorbatchuk V.V. *Macroheterocycles* 2017, **10(2)**, 233.

PREPARATION, CHARACTERIZATION, AND OPTIMIZATION OF SPHERICAL MICROPARTICLES OF SOLID DISPERSION OF A HYDROPHOBIC DRUG PHENACETIN

<u>Gerasimov A.V.</u>,[a] Ziganshin M.A.,[a] Rakipov I.T.,[a] Klimovitskii A.E.,[a] Usmanova L.S.,[a] Lyadov N.M.[b]

[a] Kazan Federal University, Kremlevskaya 18, Kazan, 420008, Russia,
[b] Kazan Physical-Technical Institute of RAS, Sibirsky Trakt 10/7, Kazan, 420029, Russia
e-mail: Alexander.Gerasimov@kpfu.ru

Inhalation administration is a promising alternative to the invasive drug delivery methods. The particle size required for ideal drug aerosol preparation is between 1 to 3 µm. The application of microspherical particles of solid dispersions enhances bioavailability of poorly soluble drugs due to the solubilization. In the present work, the spray drying process of the production of microspherical particles of solid dispersions of polyvinylpyrrolidone K29-32 with model hydrophobic drug – phenacetin was optimized using the results of DSC, PXRD and viscometry. The Gibbs energy of dissolution in water was shown to be negative for the mixture with polymer:phenacetin mass ratio 5:1. We demonstrate that the optimal size distribution for the inhalation administration is obtained for microspherical particles produced using spray caps with 7.0 µm hole size. The dissolution time of phenacetine from the produced microspherical particles is significantly lower than that of drug tablets. Based on powder X-ray diffraction data phenacetin was shown to stay in amorphous state for 4 months in microspherical particles of solid dispersions. According to the obtained results, strategic application of the spray drying process could be beneficial for the improvement of the pharmaceutical properties of phenacetin and other poorly soluble drugs.

INFLUENCE OF POLYMORPHISM ON RECEPTOR PROPERTIES OF TETRABENZOYLMETHOXY DERIVATIVE OF THIACALIX[4]ARENE

Ionova S.L., Gorbatchuk V.V., Ziganshin M.A., Gabdulkhaev M.N., Gatiatulin A.K.

A.M. Butlerov Institute of Chemistry, Kazan Federal University, Kremlevskaya st. 18, Kazan, 420008, Russia
e-mail: sionovawork@gmail.com

Calixarenes are good model organic compounds for the study of polymorphism. This feature can be important for pharmaceuticals, where it is necessary to detect all possible polymorphs and to develop efficient and reproducible ways of their preparation. Suitable polymorphs of calixarenes may be used in sensors[1] and in separation of gases. In this work, the ability of metastable calixarene **1** polymorphs with a memory of their preparation history to have a controlled inclusion capacity was studied as well as the dependence of calixarene receptor properties on its polymorphic modification. Besides, the possibility of changing the direction of polymorphic transitions was investigated using guest exchange in calixarene **1** clathrates.

1
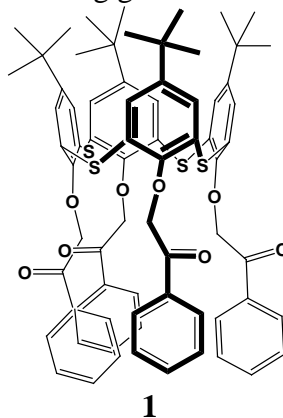
In this work, two polymorphic modifications of calixarene **1** were characterized by simultaneous TG/DSC method and by X-ray powder diffractometry.A method for preparation of polymorphs was developed using solid-phase guest exchange. The vapor sorption capacity and the selectivity of calixarene **1** depends on its polymorphic modification, which may be used for molecular recognition in sensors.

References
1.Safina G.D., Validova L.R., Ziganshin M.A., Stoikov I.I., Antipin I.S., Gorbatchuk V.V. *Sens. and Actuators B: Chemical* 2010, **148**, 264.

NEW ASPECTS OF INTERMOLECULAR INTERACTIONS OF ORGANIC COMPOUNDS IN IONIC LIQUIDS

Khachatrian A.A., **Shamshutdinova Z.I., Varfolomeev M.A., Solomonov B.N.**

Department of Physical Chemistry, Kazan Federal University,
Kremlevskaya 18, Kazan 420008, Russia
e-mail: art220692@yandex.ru

Nowadays rapidly increase interest of new class of molten salts – ionic liquids (ILs). ILs is comprised of a bulky organic cation and coordinating organic or inorganic anion. Much of the interest ILs based on their unique properties such as chemical stability, thermal stability, nonflammability, low vapor pressure, high solvency ability. Also, ILs proved as alternative "green solvents", reaction media for synthesis, different processes catalyst. Still rapidly grow number of new synthesized ILs. Thus knowledge of thermochemical properties of ionic liquids will make their industrial application more available. One of the important aspects is interrelation of the structure of ionic liquids and thermochemical properties. Furthermore, necessary approaches and method of estimation and predictions intermolecular interactions ILs.

In this paper we have studied thermochemistry of solution of substituted aromatic compounds in ILs using direct solution calorimetry technique and to get new values. 1-alkyl-3-methylimidazolium based ionic liquids with tetrafluoroborate ($[BF_4]$), trifluoromethanesulfonate ($[TfO]$) and bis(trifluoromethylsulfonyl)imide ($[NTf_2]$) anion were taken as solvents of this work. As the substituted aromatic compounds o-, m-, p-dichlorobenzenes, o-, m-, p-dinitrobenzenes, o-, m-, p-chloronitrobenzenes were used. There are solutes has a different values of dipole moment.

In this work we studied one of aspects of intermolecular interaction of solutes in ionic liquids. The enthalpies of solvation organic compounds in ionic liquids were analyzed. The absence of influence of dipole moment of organic compound in ionic liquids, do possible to use additivity of group contribution. The enthalpies of solvation NO_2, Cl, OCH_3, NH_2, CH_3, I, Br, $COOCH_3$, tert-Bu groups were derived. These results are very important for estimating intermolecular interaction organic compounds in ionic liquids. Group contribution approach using might be prediction not only enthalpies of solvation and some types of intermolecular interaction also solubilizing ability of organic compounds through to prediction of enthalpy of solution

ENTHALPIES OF THE DIELS-ALDER REACTIONS OF A SERIES OF DIENES WITH TETRACYANOETHYLENE AND 4-PHENYL-1,2,4-TRIAZOLINE-3,5-DIONE

Kornilov D.A., Kiselev V.D.

A.M. Butlerov Institute of Chemistry, Kazan Federal University,
Kremlevskaya 18, Kazan, 420008, Russia
e-mail: Dima_himik2@mail.ru

Considering two pairs of reactions of dienophiles (A_1, A_2) with dienes (D_1) and (D_2), we assumed that the difference in enthalpies of reactions of two dienophiles with a common diene is mainly determined by the difference in energies of the reacting bonds of the dienophiles.

$$\Delta H_{r-n}(D_1+A_1) - \Delta H_{r-n}(D_1+A_2) = K_1[\Delta H_{r-n}(D_2+A_1) - \Delta H_{r-n}(D_2+A_2)] \qquad (1)$$

Correspondingly, for the pairs of reactions of two dienes with a common dienophile, it should be expected that the difference in enthalpies of these reactions would mainly be determined by the difference in energies of the reacting bonds of the dienes.

$$\Delta H_{r-n}(D_1+A_1) - \Delta H_{r-n}(D_2+A_1) = K_2[\Delta H_{r-n}(D_1+A_2) - \Delta H_{r-n}(D_2+A_2)] \qquad (2)$$

It can be expected that the proportionality coefficients K_1 and K_2 would be close to unity. This makes it possible to calculate the enthalpy of a reaction difficult for measuring, for example, $\Delta H_{r-n}(D_1+A_1)$, from the data obtained for three reactions convenient for measurements.

We considered the relationship between the enthalpies of the Diels-Alder reactions in solutions of twenty dienes with two active dienophiles, tetracyanoethylene **1** and 4-phenyl-1,2,4-triazoline-3,5-dione **2**. The comparison of the experimental values of enthalpies of the diels-Alder reactions of dienes with dienophiles **1** and **2** confirms that equations 1 and 2 are fulfilled.

$$\Delta H^1_{r-n} = (20\pm4) + 0.887\Delta H^2_{r-n} \qquad (3)$$

For equation 3 r=0.9896, SD=6.9, and n=16.

The obtained equation 3 allowed us to calculate the enthalpies of reactions **1** with hexachlorocyclopentadiene (**3**), hexabromocyclopentadiene (**4**), 9,10-diphenylanthracene (**5**) and norbornadiene (**6**) equal to -47, -35, -23, and -174 kJ·mol^{-1}, respectively. It is difficult to measure the enthalpy of reaction **1**+**6** because of its very low rate.[1] If the entropy of Diels-Alder reaction is accepted to be -140 J·mol^{-1}·K^{-1},[2-3] the calculated equilibrium constant for reactions **1**+**3**, **1**+**4**, and **1**+**5** at 25 ^{0}C are 8.5, 7·10^{-2}, and 5·10^{-4} L·mol^{-1}, respectively. These data clearly show that attempts to carry out slow and equilibrium processes **1**+**3**, **1**+**4**, and **1**+**5** at elevated temperatures will be unsuccessful. They can be carried out only under conditions of high hydrostatic pressure when the rate and equilibrium constant increase significantly.[4] For reaction **1**+**6**,the high value of the equilibrium constant (higher than 1·10^{23} L·mol^{-1}) allows it to occur at elevated temperatures.

Thus, the high reactivity of 4-phenyl-1,2,4-triazoline-3,5-dione and the enhanced exothermicity of its Diels-Alder reactions with dienes make it possible to calculate the enthalpies of slow and/or equilibrium reactions with tetracyanoethylene and to choose optimum conditions for them.

References
1. Kiselev V.D., Shakirova I.I., Kornilov D.A., Kashaeva H.A., Potapova L.N., Konovalov A.I. *J. Phys. Org. Chem.* 2013, **26**, 47.
2. Kiselev V.D., Konovalov A.I. *J. Phys. Org. Chem.* 2009, **22**, 466.
3. Mielert A., Braig C., Sauer J., Martelli J., Sustmann R. *Liebigs Ann. Chem.* 1980, **1980**, 954.
4. Wurche F., Klarner F.-G. in High Pressure Chemistry, Wiley-VCH, Weinheim, 2002.

LYSOZYME DENATURATION IN GLYCEROL INVESTIGATED BY FAST SCANNING CALORIMETRY

## Mukhametzyanov T.A.,[a] Sedov I.A.,[a] Schick C.[a,b]

[a] Kazan Federal University, Kremlevskaya 18, Kazan, 420008, Russia,
[b] University of Rostock, Institute of Physics, Albert-Einstein-str. 23-24, Rostock,18051, Germany
email: Timur.Mukhametzynaov@kpfu.ru

Fast scanning chip calorimetry is a novel experimental approach allowing investigation of thermal effects upon heating or cooling at rates up to 10^6 K/s.[1]

We have used fast scanning chip calorimetry to study the denaturation of hen egg-white lysozyme at heating rates from 3 to 8000K/s. Because of the small sample size solvent evaporation is a significantconcern. Thus glycerol was used for the preparation of the solution. It was demonstrated that lysozyme forms a native structure and an endothermic peak is observed upon heating of the solution.[2] The lowest protein concentration producing good signal-to-noise ratio was found to be 50 mg/ml, no buffer salts were added to avoid possible precipitation and additional baseline distortion.

The typical endothermal peaks (area normalized) observed during the experiments are presentedin the picture below:
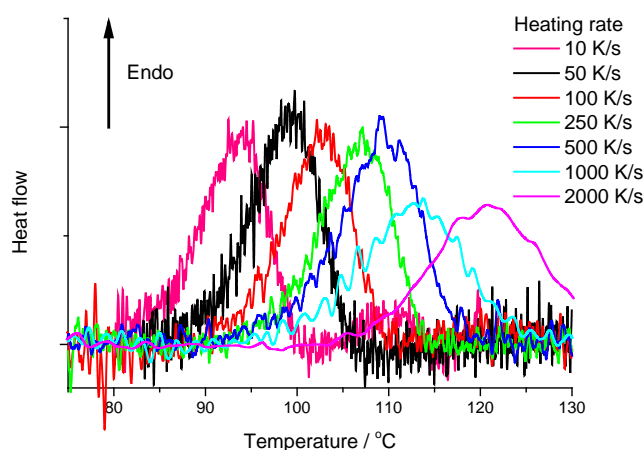
With the heating rate increase, the peak position changes to higher temperatures. No evident peak smearing is observed until the heating rate of about 1000 K/s. The apparent activation energy of the denaturation process as determined from the Kissinger plot is 261±13 kJ/mol. The observed behavior appears to follow a two-state irreversible denaturation mechanism as described by Lepock *et al*.[3]

References
1. Schick C., Mathod V. (Editors) Fast Scanning Calorimetry, Springer, 2016.
2. Burova T.V., Grinberg N.V., Grinberg V.Ya., Rarir R.V., Klibanov A.M. *Biochem. et Biophys. Acta* 2000, **1478**, 309.
3. Lepock J.R., Ritchie K.P., Kolios M.C., Rodahl A.M., Heiz K.A., Kruuv J. *Biochemistry* 1992, **31**, 12706.

NON-ADDITIVITY IN THE SOLVATION ENTHALPIES OF SUBSTITUTED PYRAZOLES AND IMIDAZOLES AT 298 K

Nagrimanov R.N.,[a] Samatov A.A.,[a] Solomonov B.N.,[a] Verevkin S.P.[b]

[a] A.M. Butlerov Institute of Chemistry, Kazan Federal University, Kremlevskaya 18, Kazan, 420111, Russia,
[b] Department of Physical Chemistry, Rostock University, Rostock,18051, Germany
e-mail: rnagrimanov@gmail.com

Thermochemical properties of phase transitions are an important parameter of a pure substance. Conventional methods for determination of these properties are based on the investigation of the process of transition from the condensed phase to gas state at 298.15 K. This procedure is not universal and has some well-known problems, which were discussed in detail.[1]

In this work, we propose a solution calorimetry approach to the determination of the enthalpies of phase transitions directly at 298 K. This approach is based on the well-known relationship between the phase transition enthalpy of compound Ai at 298 K and the enthalpy of solution ($\Delta_{soln}H^{A_i/S}$) and solvation ($\Delta_{solv}H^{A_i/S}$) of compound Ai in solvent S at 298 K:

$$\Delta_{cr(l)}^{g}H^{A_i/S}\ (298\ K) = \Delta_{soln}H^{A_i/S}\ (298\ K) - \Delta_{solv}H^{A_i/S}\ (298\ K) \qquad (1)$$

Solution enthalpy can be measured experimentally. The solvation enthalpy can be calculated using the additive scheme as well as the vaporization enthalpy. However it was shown that the solvation enthalpies as well as vaporization enthalpies at 298 K of pyrazole and imidazole have different values despite the same molecular formula. This difference was analyzed based on substituted pyrazoles and imidazoles with the same molecular formula. And it turned out that this difference is a constant and can be taken into account for calculation the solvation enthalpies of substituted imidazoles.

Also in the present work we have developed an additivity scheme for the calculation of solvation enthalpy of systems with hydrogen bond interactions.[2] A simple additivity scheme was modified taking into account the contribution of hydrogen bonding on the solvation enthalpy values.[2] This contribution was calculated using equations that connected the enthalpy of hydrogen bonds with frequency shifts of N-H stretching vibrations. The efficiency of the scheme for calculating the enthalpies of solvation was tested on the substituted NH containing compounds. We have determined vaporization/sublimation enthalpies of substituted NH containing compounds at 298.15 K using experimentally measured solution enthalpies and estimated values of solvation enthalpies. The values of vaporization/sublimation enthalpies obtained using the solution calorimetry approach are in good agreement with data from transpiration method and data from the literature.

References
1. Verevkin S.P. Elsevier, Amsterdam, 2005.
2. Solomonov B.N., Varfolomeev M.A., Nagrimanov R.N., Novikov V.B., Buzyurov A.V., Fedorova Yu.V., Mukhametzyanov T.A. *Thermochim. Acta* 2015, **622**, 88.

INTERMOLECULAR INTERACTIONS OF AMIDES WITH ORGANIC MOLECULES:COOPERATIVITY EFFECTS

Rakipov I.I., Petrov A.A.

*A.M. Butlerov Institute of Chemistry,, Kazan (Volga region) Federal University,
Kremlevskaya 29/1, Kazan, 420008, Russia
e-mail: ilnaz0805@gmail.com*

Intermolecular interactions has significantly influence on properties of many supramolecular and biological systems. Especially they are important in conformational stability of proteins and nucleic acids. Quantification and analysis of hydrogen bonds in complex biological molecules is a very complicated task, so for their research simple model compounds are used. Peptides and amides of carboxylic acid are the most appropriate facilities for these purposes.

In present work a thermochemistry of hydrogen bond formation of proton acceptors (B) in the medium of linear (N-methylformamide (NMF)) and cyclic amides (2-pyrrolidone (Py)) was studied. These compounds simulate structural fragments of different biological molecules. The infinite dilution solution enthalpies of nitriles, ketones, esters, ethers and amines in amides were measured at 298.15 K. The hydrogen bonding enthalpies of studied solutes with proton acceptor solvents were determined on the basis of experimental data. The hydrogen bond enthalpies of proton acceptors (B) in N-methylformamide and 2-pyrrolidone are significantly lower than the hydrogen bonding enthalpies of systems of amide-base in the complexes 1:1 due to reorganization effects of amides as solvent. The cooperative effects in multi-particle complexes of amides with bases change inversely from proton acceptors abilities of base

THE THERMAL STABILITY OF CLATHRATES OF THE LEU–LEU DIPEPTIDE

Safiullina A.S.,[a] **Ziganshin M.A.,**[a] **Ziganshina S.A.,**[b] **Gerasimov A.V.,**[a] **Gorbatchuk V.V.**[a]

[a] Alexander Butlerov Institute of Chemistry, Kazan Federal University, Lobachevskogo str. 1/29, Kazan, 420008, Russia,
[b] Zavoisky Physical-Technical Institute, Kazan Scientific Center, RAS, Sibirsky tract, 10/7, Kazan, 420029, Russia
e-mail: englishfile94@gmail.com

In the present work, the thermal stability of clathrates of the Leu–Leu dipeptide and thermal properties of the initial Leu–Leu powder was studied by simultaneous thermogravimetry (TG) and differential scanning calorimetry (DSC) analysis with mass spectrometric (MS) evolved gas analysis.

It was found that Leu–Leu saturated with alcohols, pyridine and chloroform vapors forms stable clathrates at room temperature. Dipeptide does not form stable clathrates with acetonitrile, benzene, tetrachloromethane and dichloromethane.

The possibility of using the selectivity of the Leu-Leu dipeptide toward alcohols over nitriles and the low thermal stabilities of clathrates containing large guests for separation of mixtures of organic compoundswas demonstrated. For this, two samples were prepared by saturating the Leu-Leu powders in methanol / acetonitrile and methanol / n-butanol vapor mixtures with a volume ratio of 1: 1. The thermal analysis of the dipeptide saturation products with vapors of organic mixtures, shown in Figure 1.
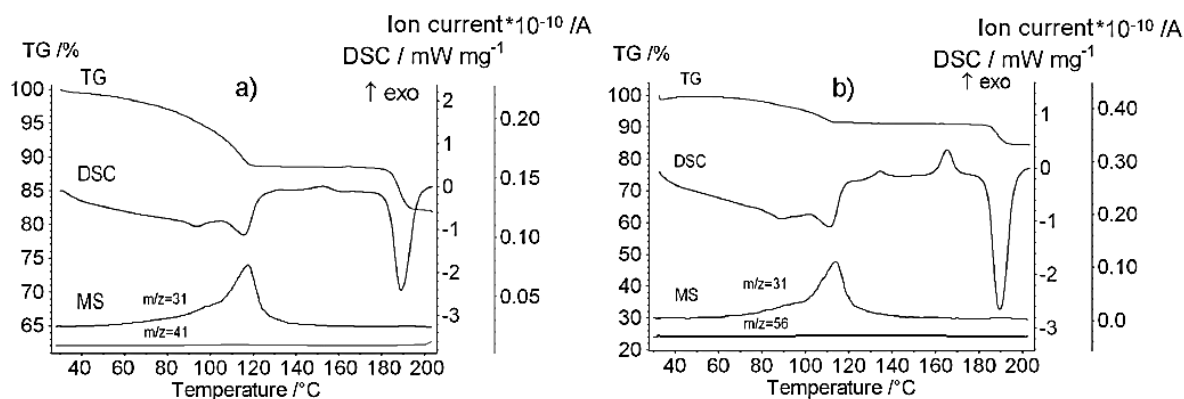

Figure 1. The data from TG/DSC/MS analysis of the product of Leu–Leu powder saturation with vapors of 1 : 1 v/v% (a) MeOH/MeCN and (b) MeOH/n-BuOH mixtures for 3 days. Ion thermograms of methanol (m/z= 31), acetonitrile (m/z=41) and n-butanol (m/z=56). The heating rate is 10 K min⁻¹.

It was found that the evolved gases contain only methanol vapors (mass spectrometric signal m/z = 31).

The obtained results may be useful for the practical application of dipeptides as new sorption materials.

NON-ADDITIVITY IN THE SOLVATION ENTHALPIES OF SUBSTITUTED PHENOLS AND NH-CONTAINING COMPOUNDS. ESTIMATION OF THEIR ENTHALPIES OF VAPORIZATION/SUBLIMATION AT 298,15 K

<u>Samatov A.A.</u>, Nagrimanov R.N., Solomonov B.N.

Department of Physical Chemistry, Kazan Federal University,
Kremlevskaya st. 18, Kazan, 420008, Russia
e-mail: samatov.aizat@gmail.com

Substituted phenols and NH-containing compounds are widely used in various industries. Most drugs, perfume, fungicides contain OH and NH-groups. Most of heterocyclic amines are used for the synthesis of alkaloids and pharmacophores.[1]

Enthalpy of sublimation/vaporization is an important thermodynamic function of pure compound and it can be used to determine intermolecular interactions.

In the present study, we develop the approach for determination of solvation enthalpies of NH-containing heterocyclic compounds and substituted phenols. Different methods[2,3] of calculation of the contributions to the solvation enthalpies related to hydrogen bonds formation are tested and discussed.

According to the approach proposed in this work, the enthalpy of solvation of compound A_i containing n-substituents X can be represented as a sum:

$$\Delta_{solv} H^{A_i/S} = \Delta_{solv} H^{ArH/S} + \sum \Delta_{solv} H^{X_i \to CH/S} + \Delta\Delta H$$

where $\Delta_{solv} H^{ArH/S}$ is the solvation enthalpy of aromatic compound; $\Delta_{solv} H^{X \to H/S}$ is the solvation enthalpy related to the substitution of hydrogen from aromatic compound with substituent X, $\Delta\Delta H$ is the non-additivity contribution related to the hydrogen bond formation.

We have applied the method of calculating sublimation enthalpy, at 298.15 K, using solution calorimetry method for compounds capable of solute-solvent hydrogen bonds. According to this method the sublimation enthalpies of NH-containing compounds and substituted phenols were calculated from experimental solution enthalpies and calculated solvation enthalpies. The latter of mentioned is calculated using an additive scheme for calculation of non-specific part of solvation enthalpy and IR spectroscopic measurement of the H-bonds part. It was shown that the contribution to the solvation enthalpy related to H-bonds enthalpy can be estimated using several different approaches. In general these contributions for studied NH-containing compounds are in the range from (−3) to (+7) kJ·mol−1. The sublimation enthalpies calculated in the present work are in good agreement with the available literature data.

References
1. Luzzio F.A., Zacherl D.P., Figg W.D. *Tetrahedron Lett*. 1999, **40 (11)**, 2087.
2. Marks A.P., Drago R. S. *J. Am. Chem. Soc*. 1975, **97 (12)**, 3324.
3. Spencer J.N., Gleim J.E., Blevins C.H., Garret R.C., Mayer F.J., Merkle J.H., Smith S.L., Hackman M.L. *J. Phys. Chem*. 1979, **83 (20)**, 2615.

SOLVENT EFFECT ON THE ACTIVATION ENERGY OF PROTEIN DENATURATION

<u>Sedov I.A.</u>

A.M. Butlerov Institute of Chemistry, Kazan (Volga region) Federal University,
Kremlevskaya 18, Kazan, 420008, Russia
e-mail: igor_sedov@inbox.ru

It is well known that the majority of water-miscible organic solvents destabilize the native structure of proteins and lower the temperature of denaturation when they are added to the aqueous protein solutions. While the influence of organic denaturants on the temperature, enthalpy and entropy of unfolding has been repeatedly studied in various systems, their effect on the mechanism of unfolding remains virtually unexplored.

The values of the activation energy of unfolding and their dependence on the concentration of denaturants are of a great interest for mechanistic studies, in particular, to establish the presence or absence of intermediates. Spectroscopic methods such as fluorescent and circular dichroism spectroscopy can be used to determine the rate constant of unfolding by monitoring the change of the signal intensity in time. One can determine the activation energy from the temperature dependence of the rate constants. Differential scanning calorimetry technique makes it possible to find the activation energy of unfolding using the dependence of the temperature corresponding to the maximum of denaturation peak from the scanning rate.

We study the influence of various organic denaturants on the process of denaturation of hen-egg white lysozyme. We determined the activation energies of unfolding of lysozyme in mixtures of water with dimethyl sulfoxide, 1,4-dioxane, acetonitrile, and isopropanol at various compositions using differential scanning calorimetry. In all the cases, addition of organic cosolvent leads to a decrease in the activation energy. At the same time, the process of unfolding of lysozyme was studied using full-atom molecular dynamics simulations in the mixture of water with dimethyl sulfoxide. It is shown that the mechanism of disruption of the protein native structure significantly changes even when only 5 mole % of dimethyl sulfoxide is added to water. Simulations reproduce a pronounced acceleration of denaturation in the presence of dimethyl sulfoxide and show the enrichment of the lysozyme solvation shell with the organic component during the course of unfolding.

SOLID DISPERSIONS AS A METHOD OF INCREASING THE BIOAVAILABILITY OF DRUGS

Usmanova L.S., Gerasimov A.V., Boldyrev A.E.

Kazan Federal University, Kremlevskaya st. 18, Kazan, 420008, Russia
e-mail: lian-usman@mail.ru

The formation of solid dispersions is one of the methods of hydrophilization of drugs. The possibility of obtaining solid dispersions of model hydrophobic drugs – phenacetine, sulfanilamide and dipyridamole with biocompatible polymers – polyethyleneglycoles with different molecular masses (PEG-1000 and PEG-1400) and Pluronic F127 was shown by low temperature differential scanning calorimetry method.

The influence of the polymer matrix on the limiting solubility of drugs was investigated by UV-spectrophotometric method. It was shown that the presence of a polymer in the aqueous solution leads to an increase in the solubility of the studied drugs.

Dissolution calorimetry method was used to determine enthalpies of dissolution of polyethyleneglycoles with average molecular weight 1000 and 1400, Pluronic F127, phenacetine in water, and also composites obtained on their basis. Based on the additive scheme, the energies of the intermolecular interactions of polymer-phenacetin were calculated.

The decrease in self-associated phenacetin molecules was observed with increasing polymer content in composites by IR spectroscopy method.

The obtained solid dispersions have a melting point of the polymeric component close to physiological, which makes it possible to use the studied composite materials, both in capsular drugs of internal application, and in ointments of external use and suppositories.

NEW ASPECTS IN THERMOCHEMISTRY OF FUSION AND SOLUTION OF ORGANIC NON-ELECTROLYTES

<u>Yagofarov M.I.</u>, Nagrimanov R.N., Solomonov B.N.

Alexander Butlerov Institute of Chemistry, Kazan Federal University, Kremlevskaya, 18, Kazan, 420008, Russia
e-mail: michaelyago@mail.ru

Thermal effects of fusion and solution are a source of information about intermolecular interactions in materials, crystallinity, mixtures phase diagrams shape, heat transfer during crystallization. In the present work we study the relationship between the fusion enthalpies of aromatic compounds at the melting temperature and the solution enthalpies in benzene at 298.15 K according to Eq. (1):

$$\Delta_{soln}H^{A_i/C_6H_6}(cr,\ 298.15\ K) - \Delta_{soln}H^{A_i/C_6H_6}(l,\ 298.15\ K) =$$

$$= \Delta_{cr}^l H^{A_i}(T_m) + \sum \Delta_{trns}H^{A_i}(T_{trns}) + \int_{T_m}^{298.15} [C_p^{A_i}(l,\ T) - C_p^{A_i}(cr,\ T)]dT \tag{1}$$

Where $\Delta_{soln}H^{A_i/C_6H_6}$ is the enthalpy of solution of compound A_i in benzene, $\Delta_{cr}^l H^{A_i}(T_m)$ is the enthalpy of fusion at the melting temperature, $\sum \Delta_{trns}H^{A_i}(T_{trns})$ is a sum of the enthalpies of solid-solid phase transitions occurring between 298.15 K and the melting temperature and $\int_{T_m}^{298.15} [C_p^{A_i}(l,\ T) - C_p^{A_i}(cr,\ T)]dT$ is a thermal adjustment of the fusion enthalpy to 298.15 K calculated according to Kirchhoff's law.

For the most of non-self-associated aromatic compounds the $\Delta_{soln}H^{A_i/C_6H_6}(cr,\ 298.15\ K)$ values are close to $\Delta_{cr}^l H^{A_i}(T_m)$, indicating weak temperature dependence of the fusion enthalpy.

On the other hand, hydrogen-bonded aromatic compounds (e.g. phenols) have the solution enthalpies exceeding the fusion enthalpies by a constant value $\Delta_{soln}H^{A_i/C_6H_6}(l,\ 298.15\ K)$, which vary insignificantly in the compounds with the same hydrogen-bonding group and different substituents not causing self-association.

Finally, the analysis of Eq. (1) for the non-self-associated compounds having notable distinctions between $\Delta_{soln}H^{A_i/C_6H_6}(cr,\ 298.15\ K)$ and $\Delta_{cr}^l H^{A_i}(T_m)$ leads to conclusion that the heat capacities of aromatic compounds in hypothetical liquid state between 298.15 K and T_m appear to be linear extensions of the heat capacities of the melt.

References

1. Yagofarov M.I., Nagrimanov R.N., Solomonov B.N. *J. Chem. Thermodyn.* 2017, **105**, 50.
2. Yagofarov M.I., Nagrimanov R.N., Ziganshin M.A., Solomonov B.N. *J. Chem. Thermodyn.* 2018, **116**, 52.

THERMALLY INDUCED SELF-ASSEMBLY AND CYCLIZATION OF DIPEPTIDES IN SOLID STATE

Ziganshin M.A.,[a] Safiullina A.S.,[a] Gerasimov A.V.,[a] Ziganshina S.A.,[b] Gorbatchuk V.V.[a]

[a]Kazan Federal University, Kremlevskaya st. 18, Kazan, 420008, Russia,
[b] Zavoisky Physical-Technical Institute, Kazan Scientific Center, RAS, Sibirsky Trakt 10/7, Kazan, 420029, Russia
e-mail: Marat.Ziganshin@kpfu.ru

Short-chain oligopeptides are popular objects for study at the present time, because of their potential advantages for various technologies and their ability to self-assembly with the formation of various nanostructures depending on the conditions. Being biocompatible and environment-friendly oligopeptide-based materials are often considered as good alternatives to inorganic nanomaterials.

The thermal treatment of oligopeptides is one of the methods for synthesis of organic nanostructures. However, heating may lead not only to self-assembly of the initial molecules, but also to chemical reactions resulting in the formation of new unexpected nanostructures or changing in the properties of the existing ones. In the present work, the reaction of cyclization of dipeptides in solid state under heating was studied. The example of dipeptide cyclization is shown in Figure 1.
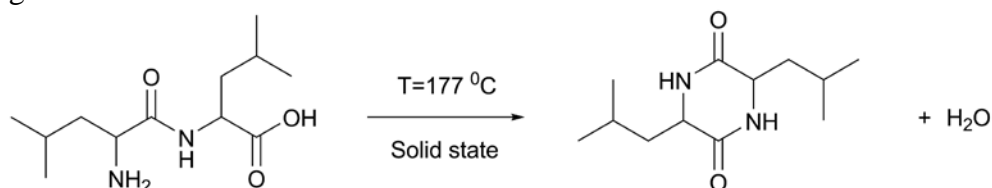

Figure 1. Scheme of the reaction of cyclization of leucyl-leucine in the solid state.

The change in morphology of dipeptide thin film and formation of nanostructures after heating was visualized using atomic force microscopy. This method also was used for demonstration of differences in self-assembly of linear and cyclic dipeptides. Kinetic parameters of cyclization were estimated within the approaches of the non-isothermal kinetics ("model-free" kinetics and linear regression methods for detection of topochemical equation). The results of present work are useful for explanation the changes in the properties of nanostructures based on short-chain oligopeptides after thermal treatment, as well as for the synthesis of cyclic oligopeptides.