Chemical Sensors

Solid-contact potentiometric sensor based on polyaniline-silver composite for the detection of dopamine

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Abstract

A solid-contact potentiometric sensor for the dopamine determination has been developed on the base of glassy carbon electrode covered with polyaniline and silver nanoaggregates. For this purpose, the electropolymerization of the aniline from sulfuric acid followed by the drop casting of a silver suspension obtained by chemical reduction of Ag^+ ions with thiacalix[4]arene bearing catechol fragments in the substituents at the lower rim was employed. The influence of the quantities of the coating materials and experimental conditions of the operational characteristics and sensitivity of the sensor response were investigated. Under optimal conditions, the potentiometric sensor showed Nernstian signal function on the dopamine concentration in the range from 2×10^{-5} to 1×10^{-2} M and the slope of about 30 mV/pC indicating two-electron oxidation of the dopamine in accordance with the Nernst equation. The interfering influence of ascorbic acid was suppressed by additional layer of thiacalixarene and neither uric acid nor albumin affected the dopamine signal of the sensor.

Keywords: Solid-contact potentiometric sensor; Dopamine; Polyaniline; Thiacalixarene; Silver nanoparticles

1. Introduction

Recently, many efforts have been made to develop simple and reliable sensors for dopamine (DA) detection. DA also known as 3,4-dihydroxyphenylethylamine is essential for several physiological functions that play important role in human health. It is vitally related to the diagnosis of various kinds of diseases, e.g., Parkinson's [1], Alzheimer's [2] and Schizophrenia [3]. Low DA levels are also related to HIV infection. For this reason, a number of sensors have been proposed for the DA determination in biological samples [4-6]. In addition to that, many principles of signal transduction have been explored for electrochemical DA detection in model aqueous solution. Most of them utilize voltammetric transducer modified with transient metal complexes [7-9], nanoparticles of noble metals [10-12], carbon nanotubes [13, 14] and polymers applied as supports or discriminators for anionic interferences, e.g. ascorbate [15-18]. Biosensors based on biocatalytic DA oxidation in the presence of laccase [19, 20] and cytochrome *c* [21] were also reported. The voltammetric DA sensors show excellent selectivity and sensitivity of the response providing sub-ppb levels of DA concentrations detected. However, potentiometric devices being much simpler in preparation and operation are quite applicable for the determination of DA levels in some pharmaceuticals and food additives. Open circuit measurement can be utilized with conventional ionometers and does not require solution deaeration and electrode recovery. Thus, the potentiometric electrode with internal filing was described for the DA determination on the base of DA-picrylamine associate, dissolved in a plastic membrane [22]. Recently, solid-contact sensor with molecularly imprinted polymer obtained by co-copolymerization of methacrylic acid and ethyleneglycol dimethacrylate in the DA presence was described [23]. However, the concentrations detected (10^{-4} – 10^{-1} M) were rather high and demonstrated only the applicability of the molecular imprinting for such purposes.

Recently we have described voltammetric sensor for the DA determination based on Ag nanoparticles obtained by chemical reduction of Ag^+ ions with thiacalixarene bearing catechol fragments as the substituents at the lower rim [24]. The modifier exhibited high mediation activity and made it possible to detect down to 0.5 nM of DA. In this work, we have described the solid-contact potentiometric sensor based on the same modifier implemented in polyaniline (PANI) film obtained by electropolymerization.

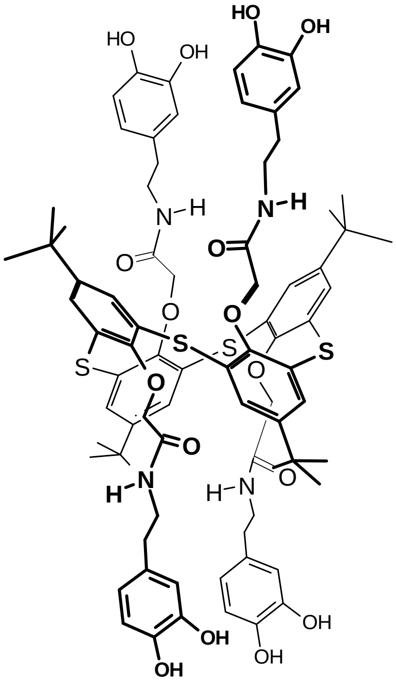
Electropolymerization is a powerful tool for the deposition of thin electroconductive films which can be used as supports for the receptor / mediator immobilization of implementation of auxiliary reagents in the sensor assembly. For DA detection, PANI based composites were described in voltammetric sensors with Au nanoparticles [10, 25] and Ru complexes [26]. The use of PANI in the assembly of solid-contact potentiometric sensors is dictated by its mixed electron-ionic conductivity which makes it possible to exclude internal filling and simplify the design of the potentiometric sensor. Previously, solid-contact PANI based sensors were described for potentiometric determination of ammonia [27], sulfite [28], other redox-active species [23-31], silver cations [32] and pH measurements [33-35]. However, to the best of our knowledge, PANI based composites have not been yet utilized for potentiometric DA determination.

2. Experimental Details

2.1. Reagents and Apparatus

Dopamine and ascorbic acid were purchased from Sigma-Aldrich, Germany. All the reagents were of analytical grade and used as received without additional purification. Millipore® water was used for the solutions preparation.

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrakis-[1-(2’-hydroxyethyl)-N-(3’’, 4’’-dihydroxyphenyl)-amidocarbonyl)-methoxy)-2,8,14,20-tetrathiacalix[4]rene in the *1,3-alternate* conformation (thiacalix[4]arene **1**) was synthesized at the Organic Chemistry Department of Kazan Federal University as described elsewhere [24].



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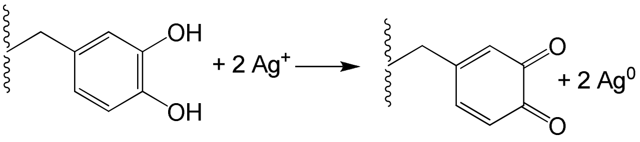
(1)

Briefly, the tetraacid derivative of thiacalix[4]arene was consecutively treated with $SOCl_2$ and dopamine hydrochloride in THF followed by the addition of triethylamine. After 12 h incubation, the reaction mixture was refluxed for 2 h in argon atmosphere. The sediment was neutralized with solid $NaHCO_3$, re-suspended from THF by water and recrystallized from acetone. The structure of the product was confirmed by physical methods and elemental analysis [24]. The purity of the thiacalixarenes used was about 99% in accordance with HPLC data. Silver nanoparticles were synthesized by mixing equal volumes of thiacalix[4]arene **1** solution in acetone and $AgNO_3$ solution in water to final molar ratio of 1:8. The mixture was left to stay for 24 h at 4°C. Then an aliquot of 2 μL was placed onto the surface of glassy carbon electrode (and dried at ambient temperature. The electrode was washed with water and EDTA solution to remove free Ag^+ ions. The reaction of catechol fragments of thiacalixarene with Ag^+ ions is presented in eq. (2).



(2)

The formation of Ag nanoparticles was confirmed by TEM (Figure 1). The average size of the particles was 3-5 nm depending on the incubation period. The nanoparticle size was characterized with Jeol 1200 EX transmission electron microscope (Japan) operating at 80 kV. The samples were mounted on Formvar coated 100-mesh copper grid. The laced structure of the aggregates is supported by thiacalix[4]arene molecules able to self-aggregate in the presence of Ag^+ ions [36].

Electrochemical measurements were performed in non-thermostated 10 ml cell at ambient temperature. The electropolymerization was performed by multiple potential scanning with AUTOLAB PGSTAT 302N (Metrohm Autolab b.v., Netherlands) and BAS CV-51W (BAS Inc.). The potential was measured in open-circuit mode with four-channel computer-aided digital ionometer "Ecotest-001" (Econix-Expert, Moscow). Home-made glassy carbon electrodes were used for sensor preparation. Glassy-carbon rods of 2.7 mm in diameter were pressed into the polytetrafluoroethylene tube and then the end was polished to mirror-like surface. Stainless steel wire was fixed from the opposite side of the electrode by screw joint and used as current collector. Pt auxiliary electrode and double-junction Ag / AgCl /3 M KCl reference electrode (BAS Inc.) were used

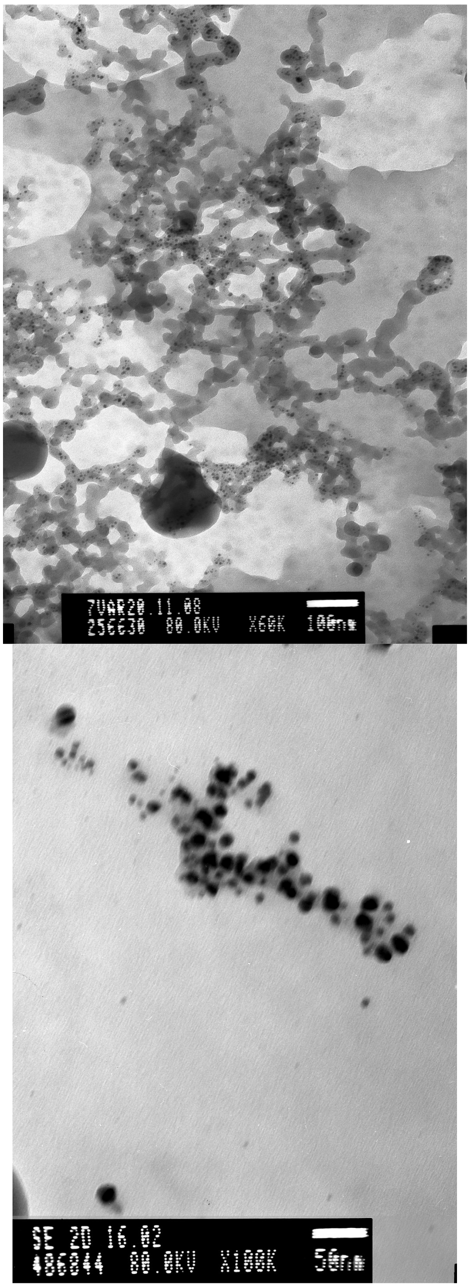
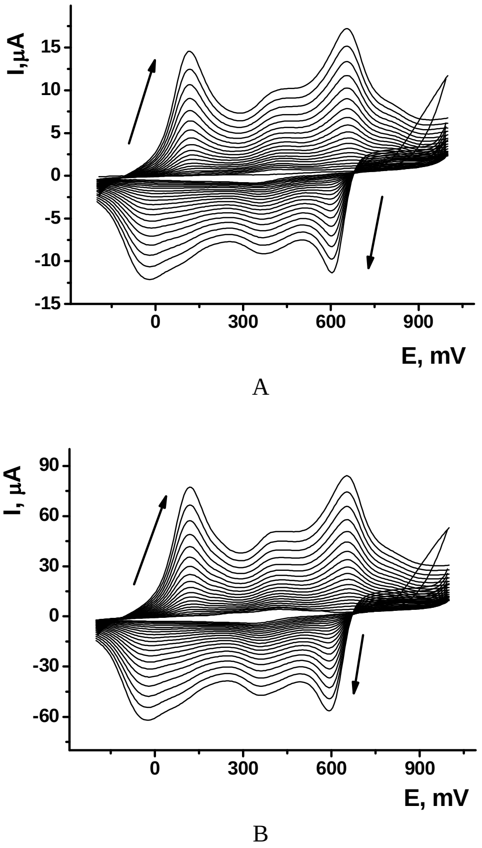


Figure 1. TEM images of silver nanodispersion obtained by mixing of 5×10^{-5} M thiacalix[4]arene **1** and 4×10^{-4} M $AgNO_3$ solutions.



A

B

Figure 2. Multiple voltammograms recorded in 0.2 M sulfuric acid containing 0.07 M aniline at glassy carbon electrode covered with 10 nanomol of thiacalix[4]arene **1** (A) and that with silver nanoparticles obtained at stoichiometric ratio of Ag^+ ions (B) . Scan rate 50 mV/s, the arrows show the direction of the cycle number increase.

in all electrochemical measurements.

2.2. Potentiometric sensor preparation and DA determination

Prior to use, glassy carbon electrode was cleaned with acetone, KOH and H_2SO_4. PANI was electrodeposited by 10 min cycling the potential between -0.2 and +1.2 V at 50 mV s^{-1} in 0.2 M H_2SO_4 containing 0.07 M aniline. The concentration of aniline was determined from previous experiments [32] and provides the formation of a homogeneous strongly acidic solution required for polymerization. After electrolysis, the electrode was rinsed with distilled water and fixed upside down. Then 2-10 μL of 0.1 mM thiacalix[4]arene **1** solution or corresponding amount of the Ag nanoparticles suspension were placed onto the electrode surface and let dry for 10 min. In all the cases, the molar ratio of thiacalix[4]arene and $AgNO_3$ taken for suspension synthesis corresponded to the stoichiometry of reaction (1:8). In some experiments, the modifiers were deposited onto the electrode prior to PANI electropolymerization. The conditions of PANI electrosynthesis as well as optimal surface concentration of thiacalix[4]arene was established previously to reach maximal reproducibility and fast potentiometric response [32].

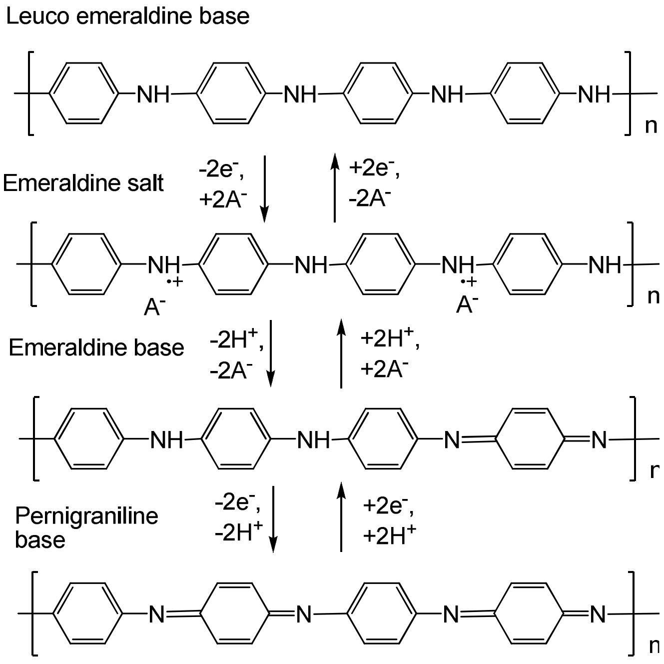
For the DA determination, the potentiometric sensor was placed together with Ag/AgCl reference electrode in the working cell containing 5 ml of 0.05 M phosphate buffer solution, containing 0.1 M $NaNO_3$, pH = 8.0. After the potential equalization, the DA solution was injected and the stationary potential recorded when the drift of the potential reached the value of 0.1 mV/min. For the sensor recovery it was washed with water and twice with working buffer solution.

3. Results and Discussion

3.1. Characterization of the electrode modification

The electron transfer conditions are important for the performance of the solid-contact potentiometric sensors. PANI is redox-active polymer which is able to redox conversion which depends on the pH and standard potential of the solution [35, 37] (3).

The appropriate redox peaks can be observed on voltammograms during the synthesis of PANI at -20 …+110 mV for leuco-emeraldine/emeraldine and +600…+650 mV for emeraldine/pernigraniline pairs (Figure 2). The intermediate peaks are referred to the deamination products of partial oxidation of aniline and its oligomers. Multiple cyclic voltammograms recorded on glassy carbon electrode covered with thiacalixarene 1 (0.2 nanomol per electrode) and silver nanoaggregates obtained with the same amount of thiacalix[4]arene showed better reversibility of main redox reactions and lower contribution of quinoic by-products than those recorded on bare glassy carbon. The improvement of the electropolymerization conditions achieved by thiacalix[4]arene **1** / nanoAg aggregates has been also confirmed by higher symmetry of the peaks and reversible response toward ferricyanides (Table 1) which did not depend on the direction of the concentration shift. The addition of either thiacalix[4]arene **1** or its aggregate with Ag nanoparticles resulted in increase of appropriate slope to its Nernstian value corresponding to one electron transfer in the pair $[Fe(CN)_6]^{3-/4-}$.



(3)

The addition of Ag nanoparticles in the surface layer increased both the currents of aniline polymerization and the reversibility of the electron transfer. The effect is more

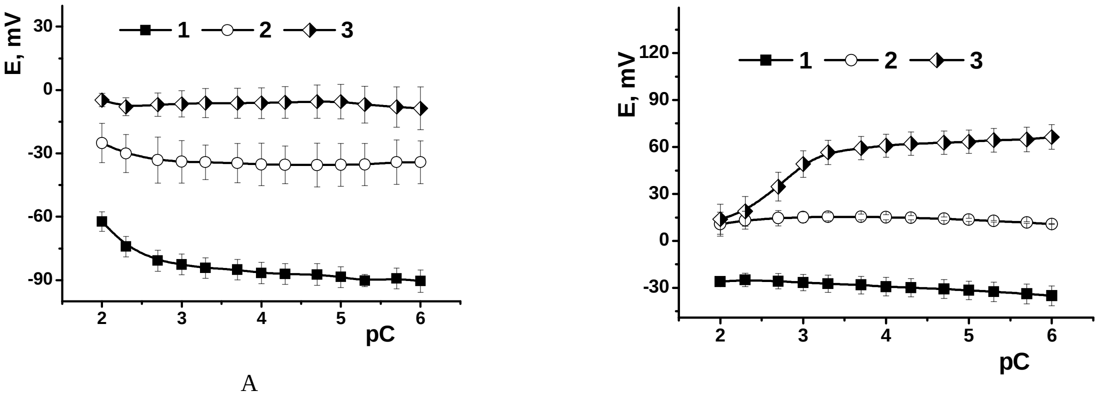
Table 1. The dependence of the stationary potential of the glassy carbon electrode modified with PANI, thiacalx[4]arene **1** and nanoAg aggregates on the ratio of the ferricyanide ions concentrations. $E = a + b \times \log \frac{[Fe(CN)_6^{3-}]}{[Fe(CN)_6^{4-}]}$

Mean±S.D. values are calculated for six replications

Modifier	**a**	**b**	**R^2**
PANI	235.9±0.5	52.4±0.6	0.9995
Thiacalix[4]are **1**/ PANI	233.8±0.7	59.8±0.9	0.9990
Thiacalix[4]arene **1** / Ag / PANI	235.3±2.6	57.2±3.5	0.9834

Table 2. Analytical characteristics of the DA determination with potentiometric sensors based on PANI / nanoAg coating (0.9 nanomol per electrode), E, mV = *a* + *b*×logC. Mean±S.D. are calculated for six replications.

pH	**Concentration range, M**	***a***	***b***	**R^2**
3.0	2×10^{-3} - 1×10^{-2}	153.6±5.4	29.5±2.3	0.9880
4.0	5×10^{-4} - 1×10^{-2}	108.7±11.3	30.5±4.2	0.9285
5.0	5×10^{-4} - 1×10^{-2}	122.3±3.2	17.2±1.2	0.9817
6.0	5×10^{-4} - 1×10^{-2}	107.5±4.2	18.8±1.6	0.9733
6.8	5×10^{-4} - 1×10^{-2}	19.4±5.3	23.6±2.0	0.9727
8.0	2×10^{-4} - 1×10^{-2}	-46.2±9.6	30.0±3.3	0.9495
9.0	1×10^{-4} - 1×10^{-2}	-94.3±5.4	26.7±1.8	0.9747



A

B

Figure 3. Determination of DA on glassy carbon electrode covered with PANI (1), PANI / thiacalix[4]arene **1** (2) and PANI / thiacalix[4]arene **1** / nanoAg aggregates (3). Measurements in phthalate buffer, pH 9.2 (A) and phosphate buffer, pH 8.0. 1.2 nanomol thiacalix[4]arene per electrode.

pronounced if PANI is deposited onto the modifier. The pH dependence of the response is linear in the range pH = 3.0 – 8.0 with the slope of 51 mV/pH for PANI and 56 mV/pH for that deposited onto the thiacalix[4]are **1** / nanoAg aggregate. This confirms high reversibility of the reactions in the layer promoted by implementation of silver nanoparticles.

The amounts of PANI deposited in 15 cycles of polymerization were estimated by integration of cyclic voltammograms assuming two-electron transfer per monomer unit. The average electrode coating was found to be 10±1 nanomol/cm^2 for the electrode covered with thiacalix[4]arene **1** and about 22±4 nanomol/cm^2 for electrode modified with equal amount of Ag nanosuspension. This exceeds the values typical for formation of the monolayer and coincides with previous investigations indicating full coverage of the electrode surface with PANI [32].

3.2. DA determination

The potentiometric sensor with PANI deposited on the thiacalixarene / nanoAg aggregates showed remarkable potentiometric signal toward DA in the pH range from 3.0 to 9.0. Contrary to that, neither PANI nor PANI / thiacalix[4]arene **1** coatings exerted response in the same experimental conditions. The characteristics of the DA determination depended on the buffer system and pH. Figure 3 shows the calibration curves obtained in phthalate and phosphate buffer as example. The characteristics of the DA determination are summarized in Table 2 for the thiacalix[4]arene loading of 1.2 nanomol per electrode. The concentration range is extended with the pH value so that best results were obtained in basic media. Phtalate and TRIS-buffer solutions were found to be inappropriate due to low slope of the dependence.

Increasing amounts of nanoAg suspension resulted in extension of the concentration range determined. The limits of detection (LOD) estimated from S/N=3 ratio decreased in the same direction from 1×10^{-4} to 5×10^{-6} M. The slope of the curve corresponds to the transfer of two electrons in accordance with (2). The optimal amount of silver calculated from thiacalix[4]arene **1** loading and 1:8 molar ratio of the reaction was found to be 9-18 nanomol per electrode (Table 3).

Table 3. The dependence of the analytical characteristics of DA determination on the amount of elemental silver in the surface coating (m(Ag)): E, mV = *a* + *b*×logC. Mean±S.D. are calculated for six replications.

m(Ag), nanomol per electrode	Concentration range, M	*a*	*b*	R^2	LOD, M
3.6	1×10^{-3} - 1×10^{-2}	-33.6±3.6	9.2±1.4	0.9326	1×10^{-4}
5.4	2×10^{-4} - 1×10^{-2}	-49.3±7.4	23.7±2.6	0.9440	1×10^{-4}
7.2	2×10^{-4} - 1×10^{-2}	-52.2±7.2	21.8±2.5	0.9385	5×10^{-5}
9.0	2×10^{-4} - 1×10^{-2}	-46.2±9.6	30.0±3.3	0.9412	2×10^{-5}
18.0	5×10^{-5} - 1×10^{-2}	-67.8±4.9	33.0±1.5	0.9856	1×10^{-5}
36.0	2×10^{-5} - 1×10^{-2}	-17.0±6.0	27.5±1.7	0.9690	5×10^{-6}
54.0	5×10^{-6} - 1×10^{-2}	-119.3±15.9	63.7±4.2	0.9585	1×10^{-6}

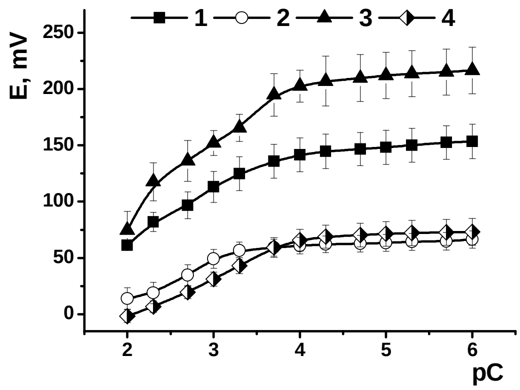


Figure 4. Determination of DA on glassy carbon electrode covered with PANI / thiacalix[4]arene **1** / nanoAg aggregates for different thickness of the surface layer and silver amounts. 5 (1, 3) and 10 (2, 4) cycles of PANI polymerization; 9 (1, 2) and 18 (3, 4) nanomol silver per electrode. Measurements in 0.05 phosphate buffer solution, pH 8.0.

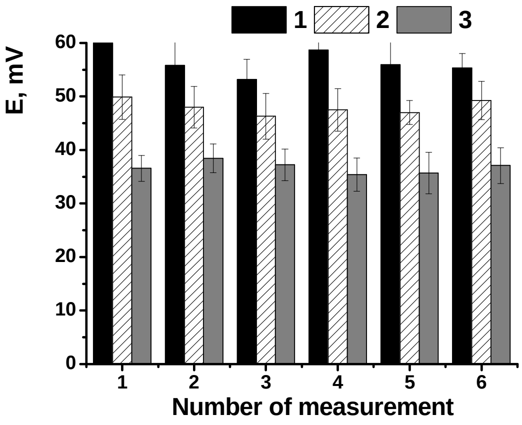


Figure 5. The potential of potentiometric sensor based on glassy carbon electrode modified with PANI / thiacalix[4]arene **1** / nanoAg aggregates prior to (1) and after addition of 10.0 µM (2) and 1.0 mM (3) of DA. 9 nanomol of Ag in the surface coating.

The efficiency of the electron transfer between the redox centers of the surface coating and DA depends on the thickness of PANI. The increase in the number of potential cycling during the electropolymerization from 5 to 10 results in consecutive decrease of the slope of DA calibration curve from 36-43 to 30-33 mV/pC reaching the theoretical value corresponding to two-electron transfer (Figure 4). The excess of the theoretical value observed for thin PANI films and for high amounts of silver in the layer (see Table 3, 54 nanomol of silver per electrode) can be referred to interfering with chloride ions. DA hydrochloride was used for model solution preparation so that the concentration of chloride ions was equal to that of DA in all the experiments. However, we did not find any dependence of the sensor potential on chlorides taken in the concentration range from 10^{-6} to 10^{-1} M, i.e., comparable to those of the DA detected. Shielding the Ag nanoparticles with thicalix[4]arene molecules and PANI layer is one of the reason for such a behavior. Lower quantities of PANI and higher amounts of silver do not protect the silver particles from interactions with chlorides and hence the slope of appropriate calibration curve takes an intermediate value between one-electron (chloride ions) and two-electron (DA) transfer.

The response toward DA was found to be quite reproducible. In the series of alternating concentrations (10^{-5} and 10^{-3} M) the repeatability of the response was found to be 4.5% for a single sensor (six replications) and the reproducibility of six sensors about 7.8% (Figure 5). The potentiometric sensors developed can be used for at least six days for continuous measurements in aqueous solutions at ambient temperature without any losses of sensitivity toward DA.

3.3. Interfering influence

Ascorbic acid exerts an interfering influence of the DA response due to its ability to reduce the PANI layer and hence decrease the stationary potential of the sensor similarly to the DA effect. Indeed we have found that the potential of the PANI covered glassy carbon decreases with the amounts of ascorbic acid in the range from 10^{-6} to 10^{-2} M. The implementation of thicalix[4]arene 1 / nano Ag aggregates in the PANI layer resulted in the shift of the potential so that the S-shaped calibration curve was obtained with a narrow linear range (10^{-3} – 10^{-5} M). The suppression of the interferences related to anionic species, e.g., ascorbic and uric acids, can be achieved by additional deposition of polycationic species which repel the anions from the exchange centers of the coatings. We have deposited a Nafion layer from 2 µl of 0.2% dispersion per electrode. However, this resulted only in a slight decrease in the sensitivity which remained similar to that to DA (Table 4). The additional deposition of thiacalix[4]arene **1** onto the nanoAg particles was found to be more successful (Figure 6). Probably, catechol groups of the substituents present in the thiacalix[4]arene **1** effective eliminate the influence of ascorbate ions due to significant shift of the stationary potential of the sensor (see increment values in Table 4).

Besides ascorbic acid, the influence of uric acid and albumin on the sensor response toward DA was estimated. For

Table 4. The dependence of the analytical characteristics of the sensor potential toward ascorbate ion: E, mV $= a + b\times\log C$. Mean±S.D. are calculated for six replications.

Modifier	**Concentration range, M**	***a***	***b***	**R^2**
Thiacalix[4]arene **1**/ Ag/ PANI	5×10^{-6} - 1×10^{-2}	-115.0±10.4	58.7±2.7	0.9790
Thiacalix[4]arene **1**/ PANI / **1**	5×10^{-4} - 1×10^{-2}	201.8±6.4	19.2±2.4	0.9422
Thiacalix[4]arene **1**/ Ag (1:4) / PANI	1×10^{-5} - 1×10^{-2}	-78.0±19.3	67.6±2.9	0.9876
Thiacalix[4]arene **1**/ Ag / PANI / 2 µl of 0.1% Nafion	1×10^{-5} - 1×10^{-2}	-93.6±5.1	55.7±1.4	0.9944

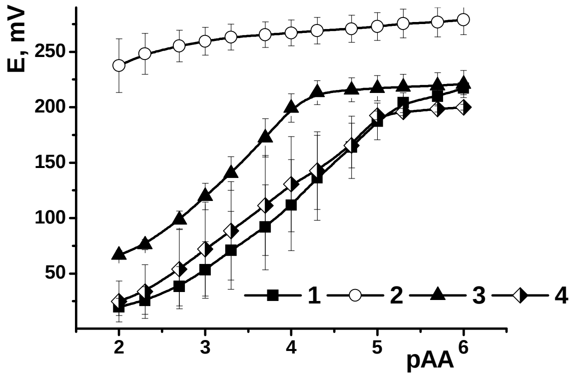


Figure 6. The determination of ascorbic acid with glassy carbon electrode modified with PANI / thiacalix[4]arene **1** /nanoAg (9 nanomol) (1), PANI / thiacalix[4]arene **1** /nanoAg (9 nanomol) / thiacalix[4]arene **1** (2), PANI / thiacalix[4]arene **1** /nanoAg (5 nanomol) (3), PANI / thiacalix[4]arene **1** /nanoAg (9 nanomol) / Nafion (4). Measurements in acetate buffer solution, pH 4.0.

uric acid, no interference with DA measurements was found. In 10^{-5} – 10^{-1} M solutions, uric acid exerted a weak cationic function (slope of about -10 mV per decade) which is fully suppressed in the presence of DA (no significant difference in the slope in the presence of 10^{-3} M uric acid). As regards albumin, its presence in amounts up to 10 mg/l did not change the DA response but significantly decreased the lifetime of the sensor probably due to adsorption and mechanical suppression of the analyte access.

4. Conclusions

The combination of PANI and thiacalixarene bearing catechol fragment in the substituents at the lower rim showed high potential in the development of potentiometric sensors for the DA determination. The implementation of silver nanoparticles obtained by chemical reduction with the thiacalixarene improved the electronic transduction of the layer, the reversibility and the reproducibility of the signal. The response toward DA is due to its redox with participation of silver nanoparticles and probably PANI. However, the latter route is ineffective so that no significant response toward DA was found for the sensors based on PANI without silver in the assembly. The solid-contact sensor developed showed Nernstian response toward DA in the range of concentrations down to 5.0 µM. The LOD values decrease with the increasing amounts of the Ag nanoparticles but at their higher quantities the response is probably related to the counter ion but not DA itself. This can be easily controlled by the slope of calibration curve. The sensitivity of the sensor developed is significantly lower than those reported for a conventional potentiometric sensor based on DA ionic associate [22] and imprinted polymer as recognition element [23]. The sensitive layer of the sensor can be easily prepared by electropolymerization and casting the reagents on its surface. Although the solid-contact potentiometric cannot be recommended for the DA determination in biological fluids where the sensitivities on sup-ppb levels are required, it can be used in drug analysis and the industrial control of the DA synthesis.

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