SYNTHESIS OF NANODIMENSIONAL FILMS BASED ON HYBRID MATERIALS AND THEIR APPLICATION IN THE ION-SELECTIVE ELECTRODES

N.S. Ivanov, V.D. Khripun, M.A. Trofimov, N.G. Sukhodolov and A.A. Pendin

St. Petersburg State University, Chemistry department, Universitetskii pr., 26, Petrodvorets, St. Petersburg, 198504, Russia

Abstract. Properties of the monomolecular films containing hybrid materials as derivatives of porphyrine, ferrocene and hexacyanoferrates are considered. Surface properties of alkylferrocene monolayers are studied, their transferring conditions on a firm substrate are chosen. The film electrodes are created using obtained structures. The film electrodes usage as reference electrodes and electrodes of the II kind reversible to anion surface-active substances is shown. Standard electrode potential for the system $R_{III}Fc$ - $R_{III}FcF_9Val$ is determined which is equal (0.360 ± 5) V.

1. INTRODUCTION

Hybrid materials containing combined properties of organic and inorganic substances attract increasing interest. Such materials can be obtained by direct synthesis, crystallization, self-organization or Langmuir-Blodgett (LB) method. The LB method allows to change properties of films simply, varying polar part of an amphiphyl molecule structure, monolayer structure, solution (subphase) composition and a transfer condition on a firm substrate. It allows to synthesize organic film coverings with properties characteristic to inorganic substances.

The Langmuir-Blodgett film (LBF) are the regular multimolecular structures (MMS) created by consecutive transfer on a firm substrate monolayers (ML) of insoluble SAS from a water subphase surface [1]. MMS are an example of the nanostructured systems because a thickness of one monolayer is the length of one organic SAS molecule. MMS broad application both in fundamental researches, and in various areas of practical application is caused by the possibility to change their structure and properties from a layer to a layer, relative simplicity of their obtaining [1,2]. For example, LBF built in such way are used as elements in micro- and optoelectronics, in chemical sensors, photo and electron resists of high resolution, etc. LBF application in thin dielectric layers in "metal – dielectric – the semiconductor" systems as the semiconductor of some modern materials (A_3B_5 type) which aren't undergo high-temperature processing [3] is very perspective. Unlike some other formation methods of a dielectric layer, LBF transfer on a material studied doesn't change substrate properties. Moreover, built nanodimensional structures find their application in development of various chemical sensors [2,3].

Electroactive LBF are used for development of ultrathin film electrodes in photochemical devices and information storage devices [2]. There are solid-state sensors using for the analysis of a gas phase on the basis of PLB with copper phthalocyanine on the silicon substrate, reacting to NO_2, NH_3, and SO_2 concentration [2]. LBF formation from proteinaceous

and biologically active agents monolayers on a precious metals substrate allows to obtain biosensors, for example glucose biosensor, in which the arachidonic acid with immobilized glucose oxidase film is put a gold electrode on. Immunosensors on the basis of PLB with immunoglobulin were also developed is caused by the [2,3]. Porphyrine derivatives, [4,5], hexacyanoferrates and ferrocene derivatives are usually introduced into film as active components.

Porphyrine diphyl derivatives. Porphyrine derivatives in mixture with fatty acids are used to build monolayer in this case, but thus units with uneven distribution of porphyrine are formed. It occurs because fatty acids tend to force porphyrine derivatives out from the structure. For example polymeric diphyl materials received by self-assembly allow to get rid of this shortcoming [6-10].

Not only metal ions, but also complex ions can react with a monolayer. Besides electrostatic interaction this one can form coordination bonds with monolayer molecules.

The analogues of the Berlin Azure (ABA) attract a great interest because of a broad range of properties received by magnetic field, light, temperature or pressure influence on them. One of the main reasons of the coordinated nanoparticles building is studying of size influence on collective magnetic properties on the one hand and nanodimensional particles building which magnetic properties set by external influences on the other hand. Such particles can be used for production of information storage devices. In literature several methods of creation of ABA are described [11-32].

Copper hexacyanoferrate nanoparticles are synthesized by Langmuir-Blodgett method by adsorption of negatively loaded nanoparticles dissolved in water on positively loaded monolayer, such as dioctadecyldimethylammonia bromide or octadecylamine. It was found, that two systems can be received in dependence of precursor nanoparticles concentration in a subphase. At high concentration ($>10^{-5}$ M) colloidal ABA are adsorbed on a surface due to electrostatic interaction causing monolayer loosening. Well organized LBF with partial dissociation of colloidal ABA are formed in diluted solutions [33]. Bagkar with coll. reports about LBF containing nickel hexacyanoferrate particles with 100 nm size on DODA monolayer usage as the sensor on potassium ions [34]. Recently, LBF of ABA nanoparticles with 20 nm size with octadecytimetylammonia were obtained by Ohnuki with coll.[35]. These LBF were used as amperometric biosensors on glucose.
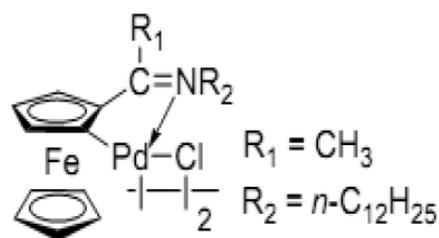

Fig. 1. Ferrocenylammonia cyclopalladate structure, adapted from [37]

The ferrocene derivatives complexes are used not only in electrochemical systems, but also in catalysis.

Cyclometallization in particular cyclopalldization of ferocenium-ligands is studied roughly during last decades. Ferrocenylammonia cyclopalladates are applied as catalysts in conjugated reactions [36]. Synthesis of diphyl ferrocenylammonia cyclopalladate (Fig. 1) and its catalytic application in homogeneous Heck-Suzuki cross-conjugation reactions at ambient and high temperatures are described in the work [37].

Analysis of compression isotherms show that cyclopentadienyl rings are parallel each other and inclined rather quartz substrate due to dense packing of molecules [38]. Successful transfer of a monolayer on a substrate is confirmed by linear dependence of absorption intensity on number of the transferred layers.

Films containing ferrocene derivatives are of great interest due to unique electrochemical properties of the ferrocene.

Physicochemical properties of ferrocene compounds and their oxidized RFc-RFc$^+$ forms (where Fc is the ferrocene core) allows to distinguish a alkyl or aryl-substituted ferrocene as electrode-active substances for various electrode systems . Such properties are the high speed of an one-electron exchange between RFc-and RFc$^+$-forms (RFc $\leftrightarrow$ RFc$^+$ + e) both in homogeneous, and in heterogeneous redox reactions , large ionic radius, small charge and spherical structure of a ferrocene core, practical insolubility of RFc in water and aqueous electrolytes solutions (less the 10^{-6} Mol/l), small solubility of ferrocene salts, in particular alkyl forms, with anions of large size which changes quickly with increase in carbon atoms number in the alkyl substitute . The adsorptive (emulsion) electrodes of the first kind, reversible to corresponding cation Fc$^+$ and RFc$^+$ were obtained. They were used as reference electrodes for practically insoluble RFcA salts (where A = ClO$_4^-$, BF$_4^-$, etc). Electrodes of the sec-

ond kind, reversible to the anions mentioned above were received. Moreover, they stabilize ferrocene salts destruction. Inserting alkyl substituents in a ferrocene ring (RFc) also increases stability of RFc^+- forms to destruction processes and allows to receive monolayers on their basis.

It should be noted that the electrode potential when RFc-RFc^+ system is used as an electrode material will not be affected on pH because neither alkyl-ferrocene, nor alkyl-ferricene compounds demonstrate the acid-base properties in aqueous electrolytes solutions.

The purpose of this work was to research LBF with series of ferrocene compounds synthesis and to apply them in electrode systems.

2. MATERIALS

1. Ferrocene derivatives (ferrum dicyclopentadienyl)
a) octodeconoylforrocene $COC_{18}H_{37}Fc$ [R_1Fc]
b) hexadeconoylforrocene $COC_{16}H_{33}Fc$ [$R_{II}Fc$]
c) octadecylferrocene $C_{18}H_{37}Fc$ [$R_{III}Fc$]
were synthesized as described earlier [8], chromatographic analysis showed more than 95% of the main substance.
2. Stearin acid $C_{17}H_{35}COOH$ [HSt] acid was recrystallized six times from absolute ethanol to 99.8% purity, Mp 69,50C.
3. Potassium salt $(CF_3)_2CFCF_2COOK$ nanofluorovaleric acid [KF_9Val] war synthesized at the State Institute of Applied Chemistry and was used without additional purification.
4. The distilled water with specific conductivity $\kappa = 2 \cdot 10^{-6}$ $S \cdot cm^{-1}$ and surface tension $\sigma = 72.7 mN/m$ was used.
5. The universal buffer mixes were prepared from acetic, phosphoric and boric acids and sodium hydroxide [9].
6. Hexane, Buffer Concentrates and other commercial-grade reagents were used without additional purification.

3. EXPERIMENTAL

Studying of ML surface pressure-area isotherms was carried out by continuous compression on the automatic installation consisting of a dural waxed bathtub in which studied solution was placed. Langmuir's torsion scales with the sensitive sensor and a mobile barrier with the automatic mechanism of movement with a speed of 5 cm/min was connected to the system at $T = 20\pm2$ °C.

The portion of ferrocene derivative was dissolved in n-hexane (concentration C=6÷9·10^{-5} mol/l). 1 ml of this solution was placed on the surface of water solution "substrate" with a 5 ml calibrated pipette between a mobile barrier and a barrier of Langmuir scales. The mobile barrier movement value was transformed to the electric signal by means of the sensor (rheochord). During mobile barrier movement ML contracted and transferred pressure upon Langmuir scales barrier. The sensor produced the electric signal proportional to the force size, operating on a scales barrier.

MMS were formed on a glass plate surface with a conducting layer of SnO_2 on one of the sides on which electrochemical researches were carried out. The plate signal was detected with silver conductor soldered to the conducting side of a plate; Ga was used as a solder, because $Tp(Ga) =28\pm2$ °C, thereby we could be sure that no thermal changes appeared in the received structure at the soldering.

Plates were carefully washed out in hexane before ML forming. Their conducting surface had resistance 0.4-0.6 MOhm.

MMS were received by consecutive transfer of a ferrocene derivative monolayer on a firm basis by Langmuir-Blodgett's method. 10-12 ml ferrocene solution in n-hexane (C=6÷9·10^{-5} of Mol/l) was dropped on the surface of a water phase and after evaporation of solvent gave an insoluble monolayer on a surface. ML received between a mobile barrier and a barrier of Langmuir scales, was squeezed up to the necessary size of superficial pressure by a mobile barrier (V=5 cm/min.), equal to the ML condensed condition of $\pi \approx 20$ mN/m. Then the solid surface was fixed in the immersing device, and back and forth motion of this plate was carried out. The transfer of ML on a surface occurred in both phases of movement (immersion and a raising) that corresponded to U-type of resultant MML structure on a solid substrate.
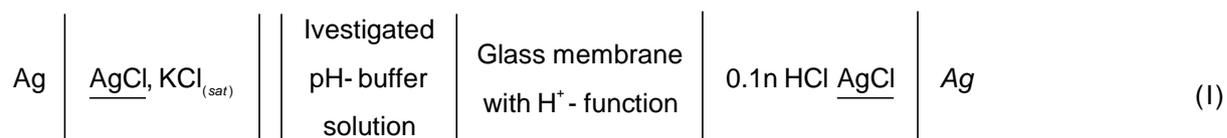
After placing ferrocene on a plate it was necessary to create red-ox system, i.e. to receive the oxidized RF^+ forms and to stabilize them by nonafluorovaleric anion [F_9Val^-]. The direct current power supply (B5-49 type) and platinum electrode were used. The electrode was plunged in the KF_9Val aqueous solution (C=10^{-3}mol/l) with the prepared ferrocene electrode and the 1.5 V voltage was applied for 3 minutes.

The formation technique was changed when ferrocenium cation was stabilized by the stearin acid anion. After ML formation on a water subphase, the solid substrate was fixed on the immersing device. Then ML formation of ferrocene in immersion phase was made, i.e. the device was stopped when the plate was immersed in water. Ferrocene was removed from a water and the stearin acid monolayer
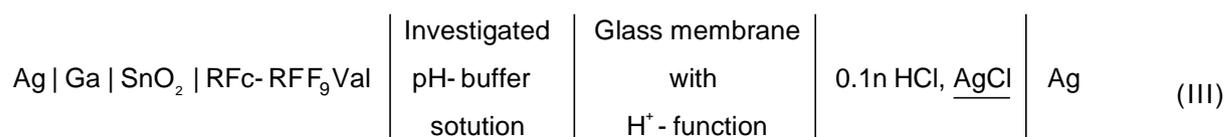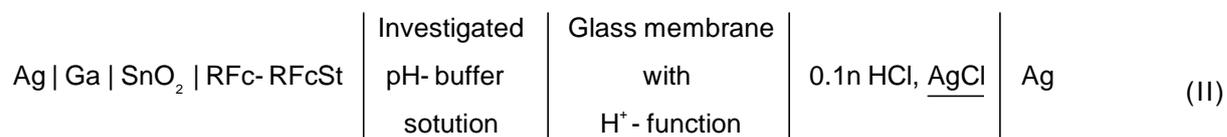
in n-hexane (5-7 ml, $C=10^{-4}$ mol/l) was dropped on the water surface. Further the stearin acid ML was contracted by the mobile barrier to the condensed condition ($\pi \approx 20$ mN/m), then the plate was extracted from water, transferring stearin acid on a solid substrate with ferrocene ML on it. Y-type of the received MMS structure on a solid substrate allows to arrange cations of RFc^+ and anions- stabilizers St^- most closely. Then edges and a place of adhesion were isolated by paraffin.

It was done to avoid potential instability because of the current expiration from SnO_2 solid phase edges with LBF and from gallium solder.
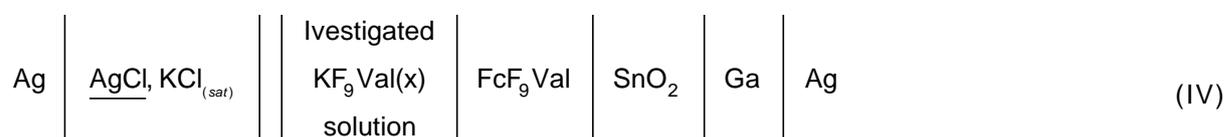
Electrometric measurements were carried out with potentiometer I-130 at (20±2) °C. Glass pH electrode ESL-515 was used for pH measurements. It was previously calibrated in standard pH-buffer solutions. Silver chloride electrode was used as the reference electrode. Galvanic electrode I scheme is following:

$$Ag \left| \underline{AgCl}, KCl_{(sat)} \right| \left| \begin{array}{c} \text{Ivestigated} \\ \text{pH- buffer} \\ \text{solution} \end{array} \right| \begin{array}{c} \text{Glass membrane} \\ \text{with } H^+\text{- function} \end{array} \left| 0.1n\ HCl\ \underline{AgCl} \right| Ag \qquad (I)$$

Galvanic cells II and III were used to study the properties of MML electrodes (RFc-RFcA where A = St^-, F_9Val^-) on SnO_2:

$$Ag \mid Ga \mid SnO_2 \mid RFc\text{- } RFcSt \left| \begin{array}{c} \text{Investigated} \\ \text{pH- buffer} \\ \text{sotution} \end{array} \right| \begin{array}{c} \text{Glass membrane} \\ \text{with} \\ H^+\text{- function} \end{array} \left| 0.1n\ HCl,\ \underline{AgCl} \right| Ag \qquad (II)$$

$$Ag \mid Ga \mid SnO_2 \mid RFc\text{- } RFF_9Val \left| \begin{array}{c} \text{Investigated} \\ \text{pH- buffer} \\ \text{sotution} \end{array} \right| \begin{array}{c} \text{Glass membrane} \\ \text{with} \\ H^+\text{- function} \end{array} \left| 0.1n\ HCl,\ \underline{AgCl} \right| Ag \qquad (III)$$

Galvanic cell (IV) was used as an electrode of the second kind, reversible to Val-anion:

$$Ag \left| \underline{AgCl}, KCl_{(sat)} \right| \left| \begin{array}{c} \text{Ivestigated} \\ KF_9Val(x) \\ \text{solution} \end{array} \right| FcF_9Val \left| SnO_2 \right| Ga \left| Ag \right. \qquad (IV)$$

4. RESULTS AND DISCUSSION

Surface pressure-area isotherms of R_IFc, $R_{II}Fc$, $R_{III}Fc$ were measured for the LBF formation. Compression isotherms of these ferrocene derivatives on the aqueous subphase (pH=6.2) are presented in Fig. 2 , The most appropriate substances for the LBF formation are R_IFc and $R_{II}Fc$ because their monolayers have greater elasticity in comparison with $R_{III}Fc$ substance. Moreover, R_IFc and $R_{II}Fc$ are more hydrophilic then $R_{III}Fc$ due to oxygen atoms. Therefore, one can expect that their monolayers will be easily obtained on solid substrate. In fact monolayers containing R_IFc and $R_{II}Fc$ substances were not only transferred on the glass surface covered with SnO_2, but LBF containing 10 monolayers were obtained. Later, after electrochemical oxidation of the derived structures that are essential for redox systems creation it showed R_IFc and $R_{II}Fc$ electrode systems potentials to be unstable. This fact may be explained with the side chain elimination from ferrocene core in R_IFc and $R_{II}Fc$ in electrochemical oxidation. It was impossible to transfer $R_{III}Fc$ monolayers at current pH.

Compression isotherm of $R_{III}Fc$ were measured at pH=4 (Fig. 3) for the investigation of monolayers transfer on solid subphase. There is a break on compression isotherm at pressure 10.5 mN/m, after which monolayer obtained elasticity harshly decreases. This break may be an evidence of the ferrocene fragment regrouping in $R_{III}Fc$ monolayer. Also at pH=4 higher collapse pressure (21.5 mN/m) is observed in comparison with 14 mN/m at pH=4. Therefore $R_{III}Fc$ monolayer transfer on solid subphase is more effective at pH=4. Monolayer transfer of ferrocene derivatives on a firm substrate was controlled by AFM (Fig. 4)
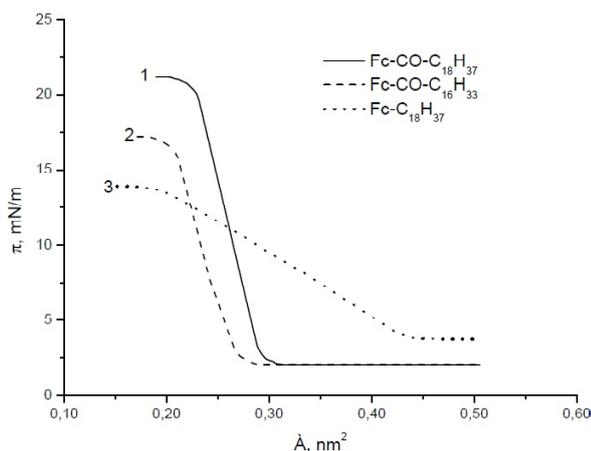
Fig. 2. Surface pressure-area isotherms of: 1 octodeconoylforrocene $COC_{18}H_{37}Fc$ [R_1Fc], 2- hexadeconoylforrocene $COC_{16}H_{33}Fc$ [R_2Fc], 3- octadecylferrocene $C_{18}H_{37}Fc$ [R_3Fc] (pH=6.2).
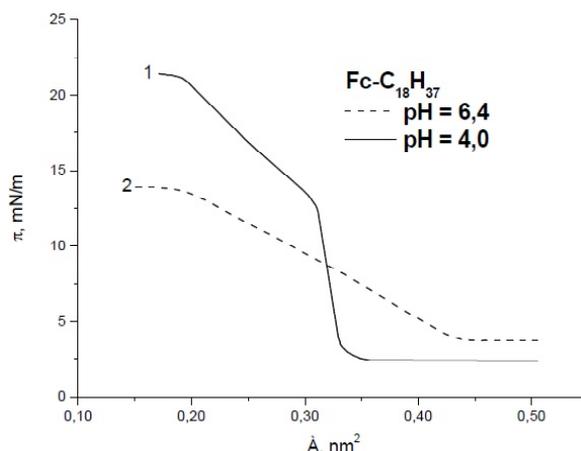
Fig. 3. Surface pressure-area isotherms of octadecylferrocene $C_{18}H_{37}Fc$ [R_3Fc]: 1-pH =4, 2-pH=6.2.

Electrochemical reaction on SnO_2 surface at passing of current from a SnO_2 plate in water solution consists in one-electron oxidation of $R_{III}Fc$ in $R_{III}Fc^+$ cation:
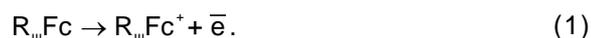
$$R_{III}Fc \rightarrow R_{III}Fc^+ + \overline{e}. \tag{1}$$

$R_{III}Fc^+$ cation then react with A^- (where A^- = St^-, F_9Val^-) leading to RFcA formation. The overall process is

$$R_{III}Fc + A^- \rightarrow R_{III}FcA + \overline{e}. \tag{2}$$
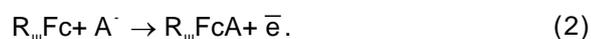
Stearin acid HSt is almost insoluble that allows to use $R_{III}Fc$-$R_{III}FcSt$ redox-system in the form of the LBF on a SnO_2 surface as comparison electrodes during electrometric measurements.

Calibration curves of the glass pH electrode in buffer solutions is shown on Fig. 5. Silver chloride electrode (Fig. 5, galvanic cell I, curve 1) and SnO_2| $R_{III}Fc$ - $R_{III}FcSt$ electrode system (galvanic cell II, curve 2) were used as reference electrodes.

Electromotive force of Galvanic cells I, II, and III is $E_{I(II,III)} = E^0_{I(II,III)} + q \lg a_{H+}$, where q = 0.058 V at 20 °C. The value $dE_{I(II,III)}/d\lg a_{H+} = (0.057\pm0.003)$ V corresponds theoretical and allows to use $R_{III}Fc$- $R_{III}FcSt$ and $R_{III}Fc$ - $R_{III}FcF_9Val$ electrode systems as reference electrode systems.

Standard electrode potential E^0 was calculated for the electrode system stabilized by isonanofluorovalerian acid. The area occupied by one octadecylferrocene molecule in a monolayer was calculated from the compression isotherms (Fig. 3) which is 0.34 nm^2. Using the electrode area and electricity amount which spent for the octadecylferrocene oxidation, we find the part of the
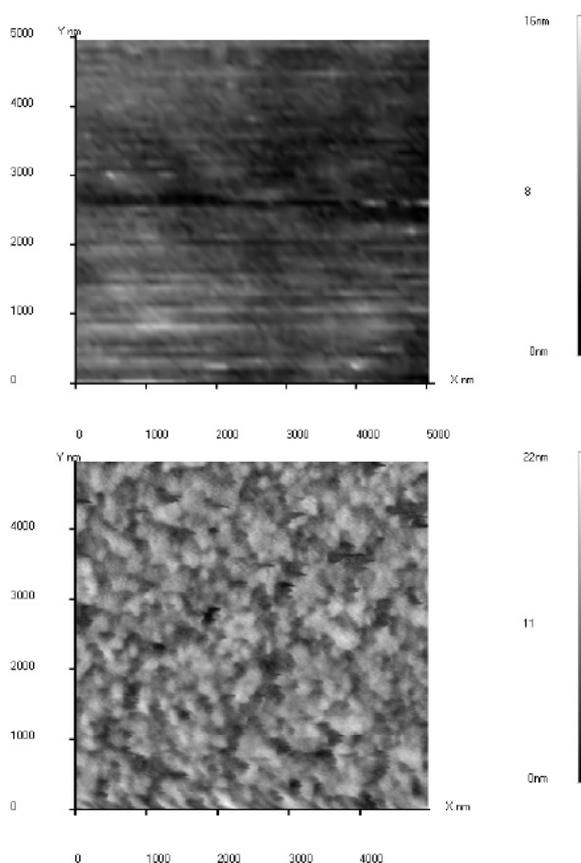

Fig. 4. AFM (a) pure surface glass with SnO_2 (b) surface with monolayer octadecylferrocene $C_{18}H_{37}Fc$ [$R_{III}Fc$] .

oxidized form of ferrocene derivative. In our experiment this part is equal 0.1.

From Eq. (3)

$$E = \varphi^0_{glass\ el.} + \theta \lg a_{H^-} - \varphi^0_{ferr\ el.} - \theta \lg \alpha', \tag{3}$$

where $\alpha' = [R_{III}Fc^+] / [R_{III}Fc]$, standard electrode potential of $R_{III}Fc$- $R_{III}FcF_9Val$ system was calculated, it is equal to 0.360±5 V.
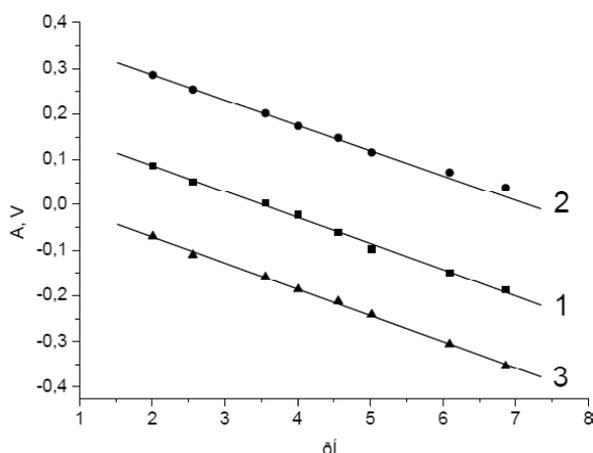
Fig. 5. Calibration curves of the glass pH electrode. Reference electrodes 1- Silver chloride electrode, 2- $R_{III}Fc$ - $R_{III}FcSt$ electrode system, 3- $R_{III}Fc$ - $R_{III}FcF_9Val$ electrode system.

For the $R_{III}Fc$- $R_{III}FcSt$ system it was impossible to calculated the standard electrode potential because of almost full insolubility of stearin acid film. It should be noted that using this electrode in solutions with pH>6 the deviation from a linear fragment on a calibration curve is observed (Fig. 5, curve 2). This is obviously connected with hydrolytic destruction of the ferrocene cations. Despite this lack use of SnO_2 | $R_{III}Fc$ - $R_{III}FcSt$ electrode system as reference electrode has a number of advantages in comparison with other reference electrodes as silver chloride electrode. When using an offered reference electrode (cell II) uncertainty in e.m.f. measurements are smaller in galvanic cells with the transfer, connected with a diffusive potential. Besides, solution studied doesn't become soiled by substances which are present at an electrolyte key, for example KCl as for an electrode I.
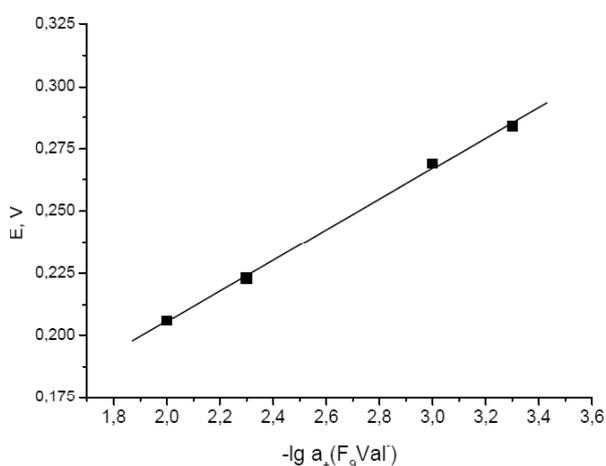

Fig. 6. Dependence of the galvanic cell IV e.m.f. on a F_9Val activity logarithm.

Realization possibility for the electrodes of the II kind on the basis of received LBF was investigated on the example of electrode system SnO_2| $R_{III}Fc$ - $R_{III}FcF_9Val$, F_9Val^- anion is the anion of strong acid HF_9Val and therefore salt KF_9Val is dissociated completely in aqueous solutions.

Dependence of the galvanic cell IV e.m.f. on a F_9Val activity logarithm is presented in Fig. 6. E.m.f. of the galvanic cell IV is

$$E_{IV} = E^0 - \theta \lg a_{\pm}\left(KF_9Val\right). \qquad (4)$$

The value of $dE_{IV}/\lg a_{\pm}(KF_9Val)$ on the linear fragment is equal to 0.059±0.002 V that corresponds to the theoretical value.

5. CONCLUSION

Thus, the possibility of receiving LBF with ferrocene-containing substances is shown. The subsequent electrochemical oxidation of these LBF is stabilized by anion SAS that allows to develop reference electrode systems and electrodes of the II kind, reversible by SAS anion.

REFERENCES

[1] *Langmuir-Blodgett Films*, ed. by G.G. Roberts (Plenum Press, New York. 1990).

[2] L.M. Blinov // *Physics Uspekhi* **155** (1988) 443, in Russian.

[3] L.M. Lanberg // *Uspekhi khimii* **12** (1997) 1141, in Russian.

[4] T. Ogi, H. Ohkita, S. Ito and M. Yamamoto // *Thin Solid Films* **415** (2002) 228.

[5] A. Osuka, S. Marumo, N. Mataga, S. Taniguchi, T. Okada, I. Yamazaki, Y. Nishimura, T. Ohno and K. Nozaki // *J. Am. Chem. Soc.* **118** (1996) 155.

[6] Osuka, N. Mataga and T. Okada // *Pure Appl. Chem.* **69** (1997) 797.

[7] Y. Nishikata, A. Morikawa, M. Kakimoto, Y. Imai, K. Nishiyama and M. Fujihira // *Polym. J.* **22** (1990) 593.

[8] Y. Morishima, K. Saegusa and M. Kamach // *J. Phys. Chem.* **99** (1995) 4512.

[9] K. Aramata, M. Kamachi, M. Takahashi and A. Yamagishi // *Langmuir* 13 (1997) 5161.

[10] F. Feng, M. Mitsuishi, T. Miyashita, I. Okura, K. Asai and Y. Amano // *Langmuir* **15** (1999) 8673.

[11] P.Y. Chow, J. Ding, X.Z. Wang, C.H. Chew and L.M. Gan // *Phys. Status Solidi A* **180** (2000) 547.

[12] S. Vaucher, M. Li and S. Mann // *Angew. Chem.* **39** (2000) 1793.

[13] S. Vaucher, J. Fielden, M. Li, E. Dujardin and S. Mann // *Nano Lett.* **2** (2002) 225.

[14] L. Catala, T. Gacoin, J.-P. Boilot, E. Riviere, C. Paulsen, E. Lhotel and T. Mallah // *Ad. Mater.* **15** (2003) 826.

[15] M. Yamada-Sasano, M. Arai, M. Kurihara, M. Sakamoto and M. Miyake // *J. Am. Chem. Soc.* **126** (2003) 9482.

[16] M. Arai, M. Miyake and M. Yamada // *J. Phys. Chem.* **112** (2008) 1953.

[17] T. Uemura and S. Kitawaga // *J. Am. Chem. Soc.* **125** (2003) 7814.

[18] T. Uemura, M. Ohba and S. Kitagawa // *Inorg. Chem.* **43** (2004) 7339.

[19] T. Uemura and S. Kitawaga // *Chem. Lett.* **34** (2005) 132.

[20] L.Catala, C. Mathoniere, A.O. Gloter, T. Stephan, J.-P. Gacoin, T. Boilot and T. Mallah // *Chem. Commun. (Cambridge, U.K.)* **6** (2005) 746.

[21] Q. Kong, X.G. Chen and J.L. Yao // *Nanotechnology* **16** (2005) 164.

[22] Y. Guari, J. Larionova, K. Molvinger, B. Folch and C. Guerin // *Chem. Commun. (Cambridge, U.K.)* (2006) 2613.

[23] D. Brinzei, L. Catala, C. Mathoniere, W. Wernsdorfer, A. Gloter, O. Stephan and T. Mallah // *J. Am. Chem. Soc.* **129** (2007) 3778.

[24] J. M. Dominguez-Vera and E. Colacio // *Inorg. Chem.* **42** (2003) 6983.

[25] N. Galvez, P. Sanchez and J.M. Dominguez-Vera // *Dalton Trans.* **15** (2005) 2492.

[26] J.G. Moore, E.J. Lochner, C. Ramsey, N.S. Dalal and A.E. Stiegman // *Angew. Chem., Int. Ed.* **43** (2003) 2741.

[27] G. Clavel, Y. Guari, J. Larionova and C. Guerin // *New J. Chem.* **29** (2005) 275.

[28] B. Folch, Y. Guari, J. Larionova, C. Luna, C. Sangregorio, C. Innocenti, A. Caneschi and C. Guerin // *New J. Chem.* **32** (2008) 273.

[29] P.H. Zhou, D.S. Xue, H.Q. Luo and X.G. Chen // *Nano Lett.* **2** (2002) 845.

[30] G. Clavel, J. Larionova, Y. Guari and C. Guerin // *Chem. Eur. J.* **12** (2006) 3798.

[31] A.P. Baioni, M. Vidotti, P.A. Fiorito, E.A. Ponzio and S.I.C. de Torresi // *Langmuir* **23** (2007) 6796.

[32] D. Brinzei, L. Catala, N. Louvain, G. Rogez, O. Stephan, A. Gloter and T. Mallah // *J. Mater. Chem.* **16** (2006) 2593.

[33] G. Romualdo-Torres, B. Agricole, C. Mingotaud, S. Ravaine and P. Delhaes, // *Langmuir* **19** (2003) 4688.

[34] N. Bagkar, C.A. Betty, P.A. Hassan, K. Kahali, J.R. Bellare and J.V. Yakhmi // *Thin Solid Films* **497** (2006) 259.

[35] H. Ohnuki, T. Saiki, A. Kusakari, H. Endo, M. Ichihara and M. Izumi // *Langmuir* **23** (2007) 4675.

[36] F. Yang, X.L. Cui, Y.N. Li, J.L. Zhang, G.R. Ren and Y.J. Wu // *Tetrahedron* **63** (2007) 1963.

[37] B. Mu, T.S. Li, J.Y. Li and Y.J. Wu // *J. Organomet. Chem.* **693** (2008) 1243.

[38] K. Fukuda and H. Nakahara // *Colloids Surf. A: Physicochem. Eng. Asp.* **102** (1995) 57.