Octadecylamine-Based Langmuir–Blodgett Films Containing Iron and Copper Hexacyanoferrates

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Abstract—Octadecylamine (ODA)-based Langmuir–Blodgett films modified with metal hexacyanoferrates are promising ion-exchange systems. The analysis of compression isotherms has led to the conclusion that iron and copper hexacyanoferrates are embedded into ODA monolayers. Optimal conditions have been determined for transferring these hybrid films onto a solid substrate by the Langmuir–Blodgett method. The optimal time required for the formation of iron and copper hexacyanoferrates in the monolayer has been established with the use of spectrophotometric measurements. The transfer of ODA monolayers modified with iron and copper hexacyanoferrates onto a conducting substrate has been confirmed by atomic force microscopy. The EMF values of galvanic cells developed based on the $ODA/Fe_4[Fe(CN)_6]_3$–KCl and $ODA/Cu_3[Fe(CN)_6]_2$–NH_4Cl systems have been shown to be close to the theoretical ones.

INTRODUCTION

The study of physicochemical properties of hybrid materials produced via the interactions of different inorganic and organic components is increasingly popular. These materials can be produced by the intercalation and/or template synthesis, sol gel method, crystallization, self-assembly, or the Langmuir–Blodgett method. The latter allows one to easily organize ions of amphiphilic organic molecules and their aggregates into regular structures. On the surface of a liquid subphase, these structures represent insoluble monomolecular layers (MLs) that can be successively transferred onto a solid substrate to form mono- or polymolecular films that are referred to as Langmuir–Blodgett films (LBFs) [1, 2].

LBFs are widely used in micro- and optoelectronics, chemical sensors, and magnetic systems and as high-resolution photo- and electron-sensitive resists, etc. [3, 4]; therefore, the investigations of novel hybrid LBFs are of great potential. Furthermore, the development of these hybrid systems may result in discovering properties that are not inherent in any of the individual components [5, 6].

The Langmuir–Blodgett method enables one to change the properties of films rather easily by varying the structure of the polar moiety of an amphiphilic molecule, the composition of an ML and a subphase, and the conditions of the transfer onto a solid substrate. All this makes it possible to produce organic film coatings with properties typical of inorganic compounds.

Metal hexacyanoferrates represent a class of inorganic polymers. The crystalline lattice of hexacyanof-errates, such as Berlin blue, $Fe_4[Fe(CN)_6]_3$, has a low negative charge [7] and a cavity size that allows water molecules and cations that are involved in redox reactions of iron to penetrate into its structure, which makes hexacyanoferrates attractive for creating electrochemical sensors.

Ion-selective membrane electrodes are often obtained via the introduction of active components into a polymeric matrix. The modification of an organic ML with metal hexacyanoferrates is attractive from the point of view of creating film electrodes with high concentrations of active sites and short response times. Moreover, such a polymeric electrochemical system is insoluble in water, which makes it applicable to technologies that require a high purity of studied solutions.

In this work, a procedure has been proposed for successive introduction of precursors into a subphase for the production of insoluble metal hexacyanoferrates in octadecylamine (ODA) MLs, the surface properties of these hybrid layers have been studied, and optimal conditions have been selected for their transfer onto solid substrates. Electrode systems based on LBFs containing iron and copper hexacyanoferrates have been obtained and investigated.

EXPERIMENTAL

Insoluble LBFs containing iron and copper hexacyanoferrates were obtained by the following procedure. A solution (1–2 mL) of ODA in hexane ($C_M = 1.5 \times 10^{-4}$ mol/L) was applied dropwise onto the surface of an aqueous subphase (a solution of potassium
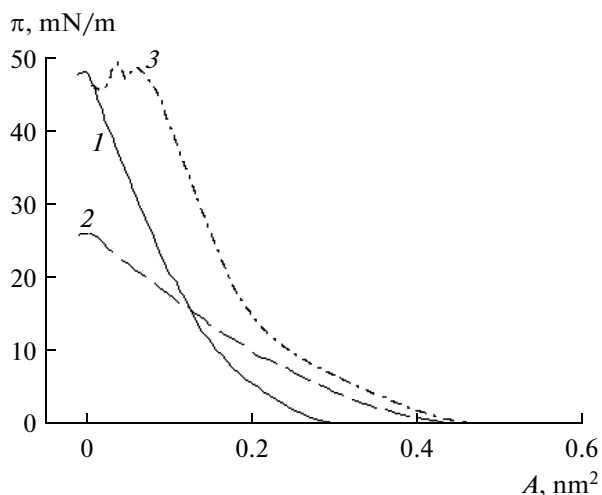
Fig. 1. Compression isotherms of ODA monolayers: (*1*) on water at pH 4.0, (*2*) on potassium hexacyanoferrate solution ($C = 10^{-4}$ mol/L), and (*3*) after formation of Berlin blue in ML.

hexacynoferrate (II) or (III)). After hexane was evaporated and an ML of the amine was formed, a solution (2 mL) of a salt that was necessary to form an insoluble hexacyanoferrate was syringed into the aqueous subphase.

The surface properties were studied by measuring compression isotherms (dependences of surface pressure π on surface area A occupied by a molecule in an ML) with the help of a conventional unit equipped with a horizontal Langmuir balance and a system for automatic recording of the isotherms [8]. This investigation allows one to gain insight into the state of sur-

factant MLs on an aqueous phase, their stability, and phase transitions occurring in them.

The structuring of an ML on the subphase surface was studied by Brewster angle microscopy using a BAM 1 microscope (Nanofilm Technology, Germany). MLs obtained by the above-described procedure were compressed to surface pressure $\pi = 30$ mN/m, and the surface was photographed in 1 and 30 min.

The spectra of the aqueous solutions of reagents with the same concentrations as those used in the Langmuir bath were measured with an SF 103 spectrophotometer (Akvilon, Russia). The absorption spectrum of water used to prepare the solutions was taken as the reference one.

A monolayer was exposed for 40–50 min, i.e., for the time required for the formation of an insoluble hexacyanoferrate (as determined from the results of kinetic experiments), and, then, it was compressed to $\pi = 30$–35 mN/m.

The hybrid MLs were transferred onto a solid substrate upon its upward movement out of the subphase in a manner such that the polar moieties of ODA molecules, along with the resulting hexacyanoferrates, were in direct contact with the substrate surface.

Film electrodes based on MLs of ODA modified with iron or copper hexacyanoferrate were prepared using glass plates, one side of which was coated with a conducting SnO_2 layer to which a silver wire was brazed with gallium. After the MLs were transferred onto the SnO_2 surface, these electrodes were used for potentiometric measurements. The EMFs (*E*) of the following galvanic cells were measured at 20°C using an I130 ionometer equipped with an EVL-1M1 standard silver-chloride reference electrode:

$$Ag|AgCl, KCl(sat)|KCl|ODA/Fe_4[Fe(CN)_6]_3|SnO_2|Ag \text{ I}$$

and

$$Ag|AgCl, KCl(sat)|NH_4Cl|ODA/Cu_3[Fe(CN)_6]_2|SnO_2|Ag. \text{ II}$$

The morphology of iron and copper hexacyanoferrate-modified ODA monolayers transferred onto the substrate was studied by means of atomic force microscopy (AFM) with a NanoEducator scanning probe microscope (NT-MDT, Russia).

RESULTS AND DISCUSSION

Figure 1 shows an isotherm of ODA monolayer compression on a water surface at pH 4.0. The isotherm has a distinctly pronounced linear region at $\pi > 14$ mN/m and a nonlinear region at lower values of the surface pressure. The surface area per molecule, as determined via the extrapolation of the linear region of the isotherm to the zero surface pressure, is 0.19 nm². The absence of the collapse and reaching of actually zero surface area per molecule testify that, at high val-

ues of π, ODA molecules are squeezed out of the ML into the subphase.

At pH < 7, the ODA monolayer is positively charged due to the protonation of amino groups. The isotherm of this ML compression on a solution of potassium hexacyanoferrate (II) (Fig. 1, curve *2*) essentially differs from that of the ODA monolayer on water. At surface pressures lower than 15 mN/m, the surface area occupied by a molecule in the ML is larger than that in ML on pure water, thereby suggesting the interaction of alkylamine with hexacyanoferrate (II) anions present in the subphase. However, there are no pronounced linear regions in the compression isotherm and the elasticity of ML is considerably lower.

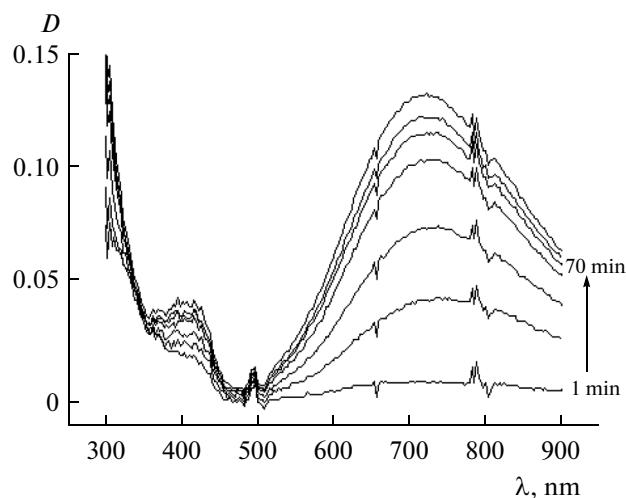After the introduction of iron(III) chloride into the subphase, the surface area per molecule increases

Fig. 2. Absorption spectra illustrating the kinetics of $Fe_4[Fe(CN)_6]_3$ formation upon mixing aqueous 10^{-4} mol/L solutions of potassium hexacyanoferrate and iron chloride.

(Fig. 1, curve *3*) compared to that for the ODA monolayer on acidified water. At $\pi > 46$ mN/m, ML collapses. The existence of two linear regions, which correspond to two-dimensional liquid crystalline and crystalline phases [9], in the isotherm leads us to suppose that ODA monolayers modified with iron hexacyanoferrate can be transferred onto a solid substrate.

To find the time required for the formation of insoluble hexacyanoferrates in MLs, the absorption spectra of corresponding mixed solutions of the reagents
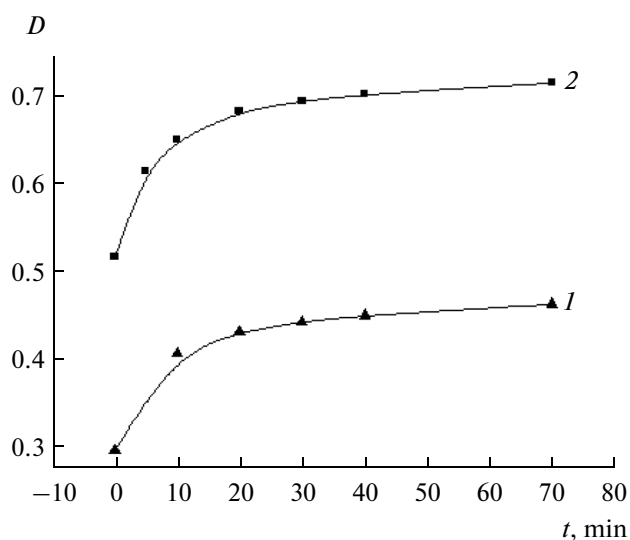

Fig. 3. Time dependences of the optical density at the absorption maximum of $Fe_4[Fe(CN)_6]_3$ measured after mixing of aqueous potassium hexacyanoferrate and iron chloride solutions with concentrations of (*1*) 5×10^{-5} and (*2*) 1×10^{-4} mol/L.
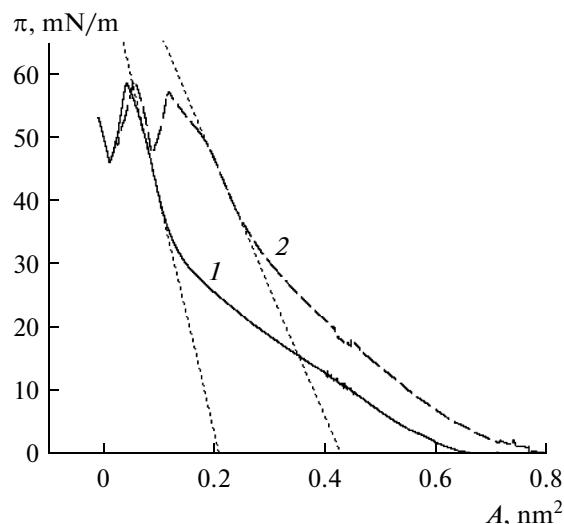

Fig. 4. Compression isotherms of ODA monolayer (*1*) on an aqueous solution of potassium hexacyanoferrate (III) and (*2*) after formation of copper hexacyanoferrate at pH 4.0.

(potassium hexacyanoferrate and iron or copper chloride) were measured at the concentrations close to those in the Langmuir bath ($5 \times 10^{-5}-10^{-4}$ mol/L). Iron hexacyanoferrate complex is blue; therefore, an increase in the intensity of the peak at 730 nm (Fig. 2) can be observed with time (1−70 min). The investigation of the time dependence of the optical density of the $Fe_4[Fe(CN)_6]_3$ solution at the absorption maximum (Fig. 3) has shown that essential changes in the system cease to be observed already in 40−50 min.

Compression isotherms illustrating the formation of copper hexacyanoferrate (III) are presented in Fig. 4. Upon the addition of copper chloride to the subphase solution, an increase in the ML area takes place at a fixed surface pressure. Two linear regions can be observed; however, the phase transition is not as pronounced as it is in the case of Berlin blue (Fig. 1). The values of extrapolated areas for the linear regions at high surface pressures amount to $A = 0.21$ nm^2 for the ML on the potassium hexacyanoferrate solution and $A = 0.43$ nm^2 after the formation of copper hexacyanoferrate (III) in the monolayer. The formation of copper hexacyanoferrate (III) enlarges the ODA monolayer at any π values.

The absorption spectra of copper hexacyanoferrate solutions are depicted in Fig. 5. The peak corresponding to the formation of this complex lies in the range of short wavelengths and is overlapped by a shoulder of the peak of iron; therefore, the formation of copper hexacyanoferrate can only be judged from a reduction in potassium hexacyanoferrate concentration. Ten minutes after the reagents are mixed, the absorption spectrum stops to vary, thereby indicating the rapid formation of insoluble copper hexacyanoferrate.
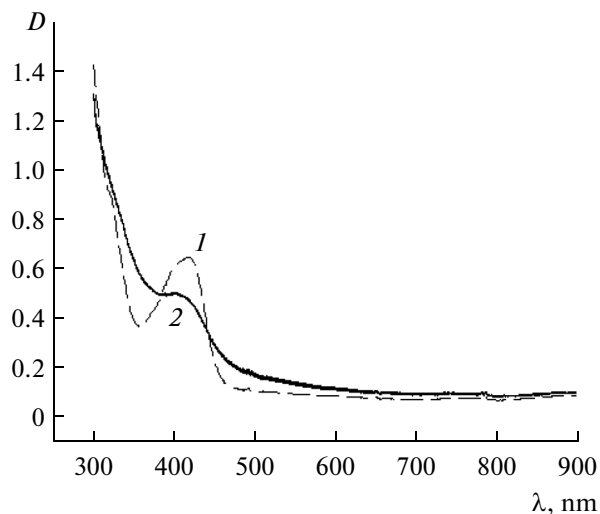
Fig. 5. Absorption spectra of aqueous solutions of (*1*) 5×10^{-4} mol/L $K_3[Fe(CN)_6]$ and (*2*) equimolar mixture of 5×10^{-4} mol/L $K_3[Fe(CN)_6]$ and $CuCl_2$.

The formation of iron and copper hexacyanoferrates in ODA monolayers was studied by Brewster microscopy. Figure 6a shows the micrographs of an ODA monolayer modified with Berlin blue, which were taken 1 and 30 min after the reagents were mixed in the subphase. It can be seen that structural formations appear on the subphase surface in 30 min and remain unchanged later on.

The micrograph taken from an ODA monolayer–copper hexacyanoferrate (III) system 30 min after mixing of the reagents in the subphase exhibits branched formations.

The next step of the study was the transfer of modified MLs onto solid substrates and their investigation by AFM. The LBF-free substrate surface is rather smooth (Fig. 7a); the roughnesses are no higher than 4 nm. The application of a Berlin blue-modified ODA monolayer onto the same substrate changes the sur-
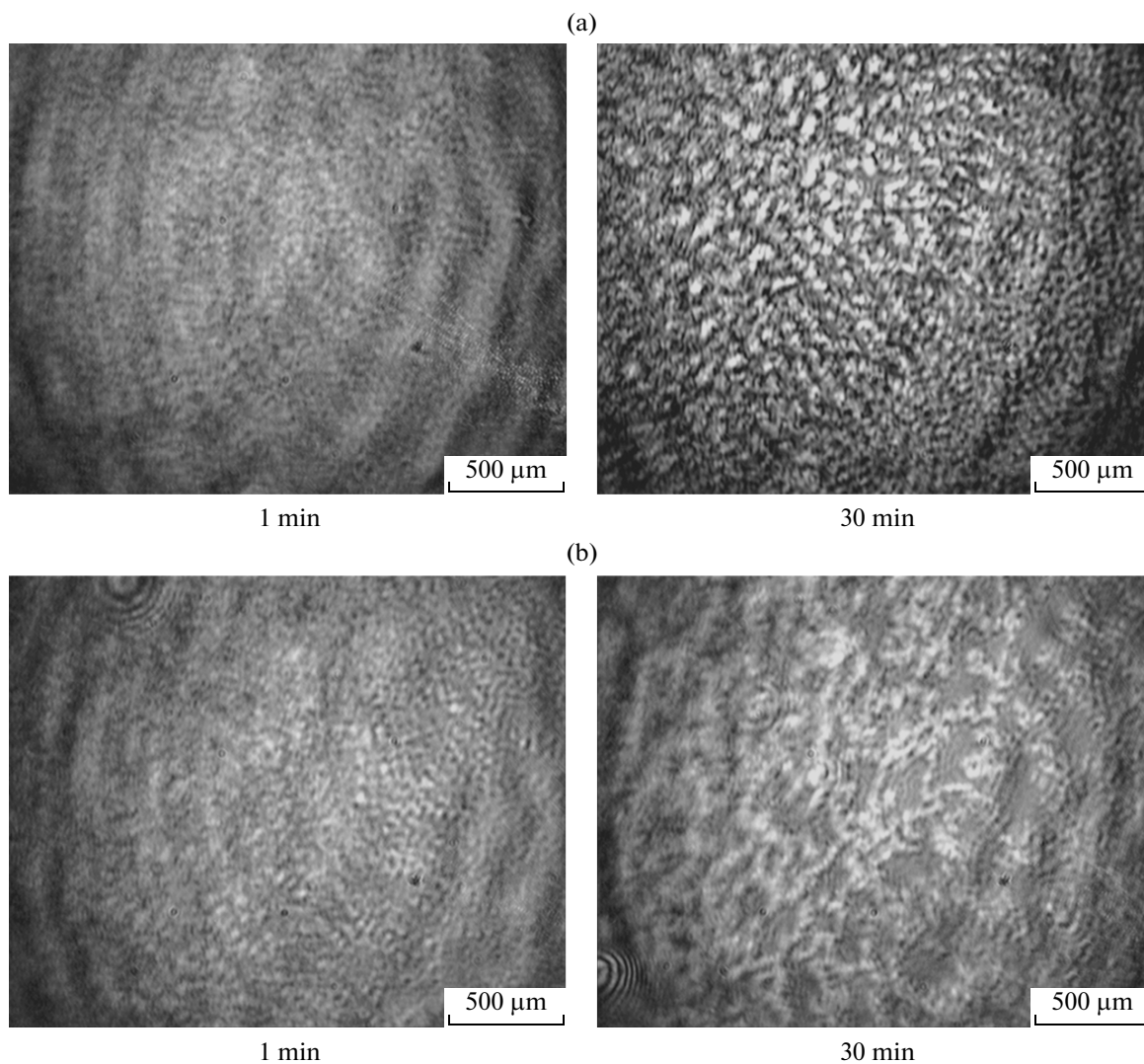
(a)

1 min

30 min

(b)

1 min

30 min

Fig. 6. Micrographs taken from (a) $ODA/Fe_4[Fe(CN)_6]_3$ and (b) $ODA/Cu_3[Fe(CN)_6]_2$ monolayers on the surface of aqueous subphase 1 and 30 min after mixing of precursor solutions.
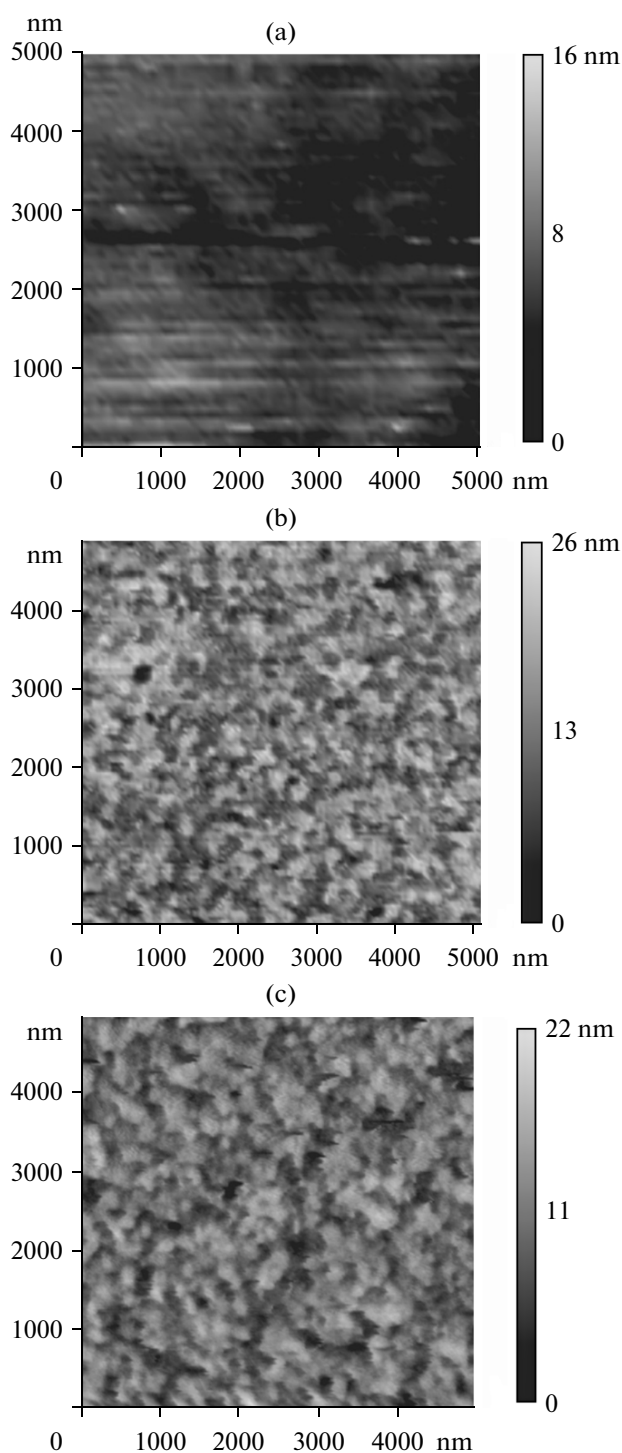
Fig. 7. AFM images of (a) LBF-free substrate, (b) ODA/Fe$_4$[Fe(CN)$_6$]$_3$ LBF, and (c) ODA/Cu$_3$[Fe(CN)$_6$]$_2$ LBF.

face topography (Fig. 7b), thereby evidencing the ML transfer. The presented AFM images testify that, unlike classical LBFs, the resulting structures are not molecularly smooth. This may be explained by the formation of hexacyanoferrate crystallites in the LBFs.
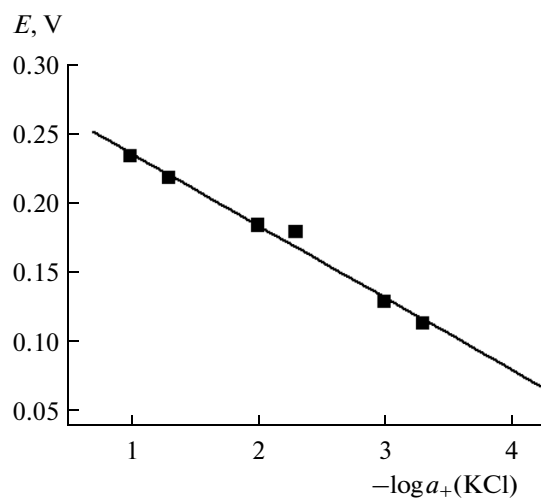

Fig. 8. Dependence of EMF of galvanic cell I on KCl activity in the aqueous solution.

The structures of films modified with iron and copper hexacyanoferrates are similar to each other (compare Figs. 7b and 7c).

For potentiometric measurements, a single monolayer of ODA modified with a hexacyanoferrate was transferred by the aforementioned method onto a glass substrate covered with SnO$_2$. The electrochemical reactions of poorly soluble Berlin blue (and its analogs) in LBFs transferred onto the electrode involve background electrolyte cations, which enter the film from a solution upon film reduction and are removed from it upon oxidation [10],

$$Fe_4^{III}[Fe^{II}(CN)_6]_3 + 4e^- + 4K^+$$
$$\rightleftharpoons K_4Fe_4^{II}[Fe^{II}(CN)_6]_3.$$
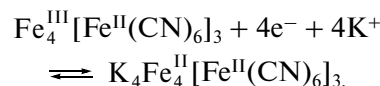
The stability of film modifications containing oxidized and reduced forms of Berlin blue makes it possible to create chemical sensors based on this film.

The results of the potentiometric measurements of the electrodes based on the ODA/Fe$_4$[Fe(CN)$_6$]$_3$ film relative to a silver-chloride electrode in KCl solutions with different concentrations are presented in Fig. 8. The potentiometric response amounts to 52 ± 3 mV/dec, which is close to the theoretical value for single-electron electrochemical process. In the case of the ODA/Cu$_3$[Fe(CN)$_6$]$_2$ film, stable values of the potential and linear dependences analogous to that presented in Fig. 8 were achieved only in ammonium chloride solutions (Fig. 9). The potentiometric response was 41 ± 3 mV/dec.

Thus, LBFs have been obtained based on MLs of octadecylamine modified with insoluble iron and copper hexacyanoferrates via sequential introduction of the reagents into the subphase. The results of our investigation are in good agreement with the literature data on the formation of inorganic compounds in MLs
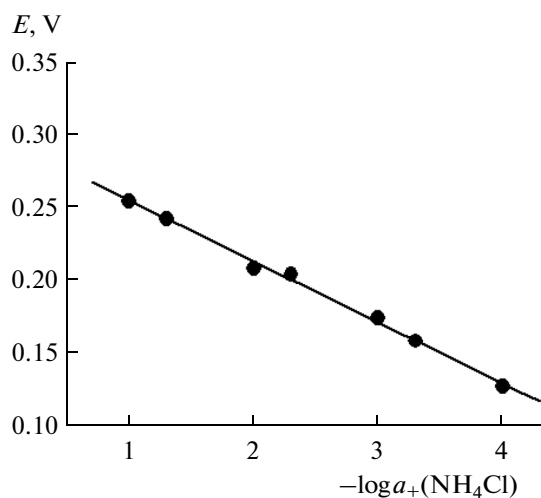
Fig. 9. Dependence of EMF of galvanic cell II on NH_4Cl activity in an aqueous solution.

[11−13]. The possibility of creating electrode systems based on the resulting LBFs has been shown.

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