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Concentration Polarization During Langmuir–Blodgett Films' Deposition

M. P. Bondarenko[1], V. I. Kovalchuk[1], Yu. B. Borkovska[1],
E. K. Zholkovskiy[1], and D. Vollhardt[2]

[1]F. D. Ovcharenko Institute of Biocolloidal Chemistry, N.A.S. of Ukraine,
42, Academician Vernadsky Blvd.,
UA-03142 Kyiv, Ukraine
[2]Max-Planck-Institute of Colloids and Interfaces,
D-14424 Potsdam/Golm, Germany

New functional interfaces with controlled heterogeneity having a lateral resolution in the nanometre range are of great importance for many promising applications. One of the easiest ways to produce such patterned interfaces is the deposition of insoluble amphiphilic monolayers on the substrate surface, according to the well-known approach developed by Langmuir and Blodgett. Under some specific conditions, deposited monolayers can form not homogeneous layers, but well-controlled structured films. Such structured films are a result of monolayer interaction with the substrate surface and instabilities developed within the receding menisci. In particular, regular stripe patterns can be obtained by deposition of charged fatty acid monolayers, which are formed due to contact line auto-oscillations during the deposition process. In the previous studies, symmetrical systems were considered, where the monolayer is deposited onto substrate surface already covered by the previously deposited similar monolayer. In this article, we consider asymmetrical configurations, where the monolayer is deposited onto a bare substrate surface. As shown, the similar mechanism of structure formation is realized also in this case, but for significantly larger deposition rates.

Нові функціональні інтерфейси з контрольованою неоднорідністю, що мають бічну роздільчу здатність у нанометровому діяпазоні, мають велике значення для багатьох перспективних застосувань. Одним з найпростіших способів одержання таких візерункових інтерфейсів є нанесення нерозчинних амфіфільних моношарів на поверхню підкладинки, згідно з добре відомим підходом, розробленим Ленґмюром і Блоджетт. За певних умов нанесені моношари можуть утворювати не однорідні шари, а добре контрольовані структуровані плівки. Такі структуровані плівки є результатом одношарової взаємодії з поверхнею підкладинки та нестабільности, що розвивається в межах відступаючих менісків. Зокрема, реґулярні смугові малюнки можна одержати шляхом осадження заряджених моношарів жирних кислот, які утворюються внаслідок автоколивань контактної лінії в процесі осадження. У попередніх дослідженнях розглядалися симетричні системи, де моношар наноситься на поверхню підкладинки, вже покриту попередньо нанесеним подібним моношаром. У цій статті ми розглядаємо асиметричні конфіґурації, коли моношар наноситься на голу поверхню підкладинки. Показано, що подібний механізм формування структури реалізовано і в цьому випадку, але для значно більших швидкостей осадження.

Key words: Langmuir–Blodgett films, charged amphiphilic monolayers, nanostructured coatings, concentration polarization, patterned films, meniscus instability, lateral resolution.

Ключові слова: плівки Ленґмюра–Блоджетт, заряджені амфіфільні моношари, наноструктуровані покриття, концентраційна поляризація, візерункові плівки, нестійкість меніска, бічна роздільча здатність.

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1. INTRODUCTION

Monolayer and multilayer coatings obtained by the transfer of films of insoluble ionic surfactants or polymers by the Langmuir-Blodgett method are widely used: from optical lens coating, to nanostructured coatings for various applications [1, 2]. It was shown recently that the Langmuir–Blodgett method is a convenient way for the fast and cheap production of regular nanostructured coatings with a lateral resolution in the nanometer length scale over macroscopic surfaces [3, 4].

During the fabrication of such films by deposition of charged monolayers, the ions transfer processes between the bulk solution and the three-phase contact line region play an important role [5–9]. In particular, insufficient rate of such ions transfer sets a limit for the maximum possible rate, at which a stable homogeneous film is deposited on the substrate surface [2, 8, 9].

In Refs. [8, 9], we performed a detailed simulation of the process of a film transfer to the surface of a substrate covered with a previously transferred monolayer. The presence of an already deposited monolayer at the substrate surface allowed assuming the charges of both meniscus surfaces to be the same, and the potential distribution to be symmetrical relative to the meniscus middle plane. This reduced the number of independent parameters and, thus, facilitated qualitative analysis of the results. Nevertheless, even for multilayer coatings, it is important to find the conditions for obtaining a homogeneous first layer, since defects (heterogeneity) of the first layer can affect the formation of subsequent layers, causing heterogeneities of the deposited film as a whole. In the case of the first monolayer deposition, it is necessary to deal with the meniscus, where the liquid–gas interface and liquid–solid interface have substantially different charges. Based on the above, here, we focus on the redistribution of ions in the meniscus with different surfaces during the transfer of a Langmuir monolayer (Langmuir wetting process).

2. MATHEMATICAL MODEL

The considered here system is schematically shown in Fig. 1, *a*. The amphiphilic monolayer film preformed on the aqueous subphase (electrolyte solution) is transferred to a clean hydrophilic substrate surface that moves uniformly out of the solution with a speed v_0. If the transfer ratio is close to unity, the monolayer at the subphase surface moves towards the contact line with an approximately same speed. At the contact line, the molecules forming the film attach by their hydrophilic groups to the hydrophilic substrate surface. The liquid meniscus forms a contact angle θ with the substrate surface ('zipper angle' [10]), which decreases with the increasing speed.

The insoluble ionogenic surfactant molecules interacting with water can dissociate on the surface-active ions remaining at the solution surface and the counterions forming a diffuse layer near the surface. The partially dissociated ionogenic groups of the surfactant form a charged film on the solution surface with a surface charge density σ. The magnitude of this charge is determined by the specific dissociation-recombination reactions, which depend on the ionic composition of the

Fig. 1. Scheme of the monolayer transfer by the Langmuir–Blodgett method: Fig. 1, *a* (left)—the monolayer is deposited over the bare substrate surface (asymmetrical configuration); Fig. 1, *b* (right)—the monolayer is deposited over the previous monolayer (symmetrical configuration).

electrolyte solution close to the surface.

We assume here that the substrate surface remains not charged being in contact with the solution, *i.e.*, only one meniscus surface is charged. This situation is different from the previously considered case [8, 9] of symmetrically charged meniscus surfaces shown in Fig. 1, *b*, where the substrate surface is covered by a similar amphiphilic monolayer film with the same surface charge density.

Let us consider in more detail the mechanism of charge formation on the example of a film of arachidic acid on the surface of a mixed electrolyte solution of $CdCl_2$ and HCl. The solution contacting with the film contains hydrogen cations H^+, cadmium cations Cd^{2+}, and chlorine anions Cl^-. Hydrogen ions can bind to free carboxylic groups of arachidic acid anions A^-, forming neutral molecules of undissociated acid H*A*. The corresponding equilibrium reaction equation is

$$X_{\mathrm{H}A} = K_{\mathrm{H}} X_{A^-} C^S_{\mathrm{H}^+} . \tag{1}$$

Here, X_{A^-} and $X_{\mathrm{H}A}$ are the surface densities of dissociated and non-dissociated ionogenic groups, respectively, $C^S_{\mathrm{H}^+}$ is the concentration of hydrogen ions in the solution immediately adjacent to the film, K_{H} is the binding constant of hydrogen ions, which further below is assumed to be equal to 65.4 m^3/mole [11].

Two possible assumptions about the stoichiometry of complexes formed by bivalent (*e.g.*, cadmium) cations with fatty acid molecules can be made according to the literature [6, 11]. In the first type of complexes, one cadmium ion can bind with one ionogenic group at the surface, forming a positively charged complex, according to the equation

$$X_{\mathrm{Cd}A^+} = K_{\mathrm{Cd1}} X_{A^-} C^S_{\mathrm{Cd}^{2+}} , \tag{2}$$

where $X_{\mathrm{Cd}A^+}$ is the surface density of the positively charged complexes, $C^S_{Cd^{2+}}$ is the local concentration of cadmium ions in the solution immediately near the film, $K_{\mathrm{Cd1}} = 0.0155$ m^3/mole is the corresponding reaction constant. In the second case, one cadmium ion can bind to two dissociated groups, forming a neutral complex

$$X_{\mathrm{Cd}A_2} = K_{\mathrm{Cd2}} \left(X_{A^-} \right)^2 C^S_{\mathrm{Cd}^{2+}} , \tag{3}$$

where $X_{\mathrm{Cd}A_2}$ is the surface density of the neutral complexes, and the corresponding reaction constant is $K_{\mathrm{Cd2}} = 25000$ $\mathrm{m}^5/\mathrm{mole}^2$. We will consider here the both possibilities separately. One can also assume that charged complexes (Eq. (2)) and uncharged ones (Eq. (3)) are formed simultaneously. However, the results under this assumption differ insignificantly from those accounting only for the positively charged complexes, and they are not considered here. We assume that the chemical reactions at the monolayer surface are sufficiently fast, so that Eqs. (1)–(3) are applicable also under dynamic conditions.

In our model, we assumed also that in the process of film deposition, the total number of the surfactant groups (both the free ones and those included in complexes of different nature), $X_a = 8.3\cdot10^{-6}$ mole/m^2, does not change [11], that is,

$$X_a = X_{A^-} + X_{\mathrm{HA}} + 2X_{\mathrm{Cd}A_2} + X_{\mathrm{Cd}A^+} . \tag{4}$$

Since some of the surfactant ionogenic groups are in a charged state, the surface has a charge whose density σ is equal to

$$\sigma = F\left(X_{\mathrm{Cd}A^+} - X_{A^-}\right), \tag{5}$$

where $F = 96486.7$ C/mole is the Faraday constant. Due to the interaction with the charged film, the actual concentrations of ions near the surface are different from their concentrations in the bulk solution $C_{\mathrm{Cd}^{2+}}$, C_{H^+} and C_{Cl^-}, where the electroneutrality condition holds

$$C_{\mathrm{Cl}^-} = C_{\mathrm{H}^+} + 2C_{\mathrm{Cd}^{2+}} . \tag{6}$$

During the film deposition process, the distributions of ions deviate from their distributions under equilibrium conditions, and the ion flows occur in the system. However, if the contact angle θ is small, the local thickness of the meniscus near the contact line is much smaller than its height. Therefore, at real deposition rates, the local equilibrium in each meniscus cross-section establishes much faster than along it. This allows us to model each segment of the meniscus as a locally flat and being in a state of local quasi-equilibrium [12]. This quasi-equilibrium can be characterized by the concentrations $C_{\mathrm{Cd}^{2+}}$, C_{H^+} and C_{Cl^-} of the ions in an imaginary (virtual) electroneutral solution that might be in equilibrium with the given point of the real solution. Thus, the virtual ion concentrations remain constant in each meniscus cross-section, although they vary along the thin solution film formed between the substrate surface and the surfactant monolayer (Fig. 1). In this case, the actual ion concentrations are determined from the quasi-equilibrium relationships [12]

$$\tilde{C}_i = C_i \exp\left(-z_i F\phi/(RT)\right), \tag{7}$$

where z_i is the ion charge, φ is the quasi-equilibrium electric potential, $R = 8.31434$ J/(K·mole) is the universal gas constant, and T is the absolute temperature, assumed here to be 298.15 K for the purpose of modelling. In the equilibrium state (before the substrate begins to move), the virtual concentrations of all ions in the meniscus are equal to the specified concentration of ions in the bulk solution. For the model calculations, we chose the bulk concentration of cadmium $C_{\mathrm{Cd}^{2+}} = 0.25$ mM/dm^3 and hydrogen $C_{\mathrm{H}^+} = 0.0025$ mM/dm^3 that corresponds to pH = 5.6. This is close to the experimental conditions, for which the stripe patterns formation was observed in [13].

The distribution of quasi-equilibrium potential ϕ in each meniscus cross-section is described by the Poisson–Boltzmann equation

$$\frac{d^2\phi}{dx^2} = -\frac{F}{\varepsilon\varepsilon_0}\left(2C_{\mathrm{Cd}^{2+}}e^{-\frac{2F\phi}{RT}} + C_{\mathrm{H}^+}e^{-\frac{F\phi}{RT}} - C_{\mathrm{Cl}^-}e^{\frac{F\phi}{RT}}\right). \tag{8}$$

The surface charge density, Eq. (5), determines the derivative of the potential at the boundary of the meniscus with the surfactant film

$$\left.\frac{d\phi}{dx}\right|_{x=2h} = \frac{\sigma}{\varepsilon\varepsilon_0}, \tag{9}$$

where x is the coordinate across the meniscus, h is the local half-thickness of the meniscus ($0 \le x \le 2h$, Fig. 1). Equation (9) is a boundary condition for Eq. (8). The second boundary condition should be written for the clean substrate surface, which is not charged:

$$\left.\frac{d\phi}{dx}\right|_{x=0} = 0. \tag{10}$$

During the deposition process, the surfactant monolayer and the substrate surface move with approximately same speed towards the contact line, producing a hydrodynamic flow in the solution. The deposited film is dry, *i.e.*, water is practically not removed from the solution by the moving substrate. Therefore, in a steady deposition process, a counter-flow of the solution should occur in the middle part of the meniscus between the substrate and solution surface. In lubrication approximation, such hydrodynamic flow can be described by the equation

$$v = v_0\left[1 + \frac{3x(x-2h)}{2h^2}\right]. \tag{11}$$

According to this equation, the fluid velocity is equal to v_0 at the substrate surface ($x = 0$) and at the solution surface ($x = 2h$). In addition, the average volume flow through the meniscus cross-section is zero.

This hydrodynamic flow produces a convective transfer of the ions, which are non-uniformly distributed within the diffusion layer at the meniscus surface. Because of non-uniformity of the ions' distributions, the purely convective transfer of the ions cannot provide the continuity of the ion fluxes within the solution near the contact line under steady-state conditions. Therefore, diffusion and electromigration components of the ion fluxes appear in the solution to ensure the required continuity of the total fluxes for all ions. This is accompanied by appearance of gradients of quasi-equilibrium concentrations in the system, as discussed above.

Thus, the equations for the total ion fluxes through each meniscus cross-section can be written as

$$J_{\mathrm{Cl}^-} = C_{\mathrm{Cl}^-}\int_0^{2h} v(x)e^{\frac{F\phi}{RT}}dx - D_{\mathrm{Cl}^-}\frac{dC_{\mathrm{Cl}^-}}{dy}\int_0^{2h} e^{\frac{F\phi}{RT}}dx + \frac{FD_{\mathrm{Cl}^-}C_{\mathrm{Cl}^-}}{RT}\frac{d\psi}{dy}\int_0^{2h} e^{\frac{F\phi}{RT}}dx, \quad (12)$$

$$J_{\mathrm{H}^+} =$$

$$= v_0X_{\mathrm{HA}} + C_{\mathrm{H}^+}\int_0^{2h} v(x)e^{-\frac{F\phi}{RT}}dx - D_{\mathrm{H}^+}\frac{dC_{\mathrm{H}^+}}{dy}\int_0^{2h} e^{-\frac{F\phi}{RT}}dx - \frac{FD_{\mathrm{H}^+}C_{\mathrm{H}^+}}{RT}\frac{d\psi}{dy}\int_0^{2h} e^{-\frac{F\phi}{RT}}dx, \quad (13)$$

$$\begin{aligned} J_{\mathrm{Cd}^{2+}} &= v_0\left(X_{\mathrm{CdA}^+} + X_{\mathrm{CdA}_2}\right) + C_{\mathrm{Cd}^{2+}}\int_0^{2h} v(x)e^{-\frac{2F\phi}{RT}}dx - \\ &-D_{\mathrm{Cd}^{2+}}\frac{dC_{\mathrm{Cd}^{2+}}}{dy}\int_0^{2h} e^{-\frac{2F\phi}{RT}}dx - \frac{2FD_{\mathrm{Cd}^{2+}}C_{\mathrm{Cd}^{2+}}}{RT}\frac{d\psi}{dy}\int_0^{2h} e^{-\frac{2F\phi}{RT}}dx, \end{aligned} \quad (14)$$

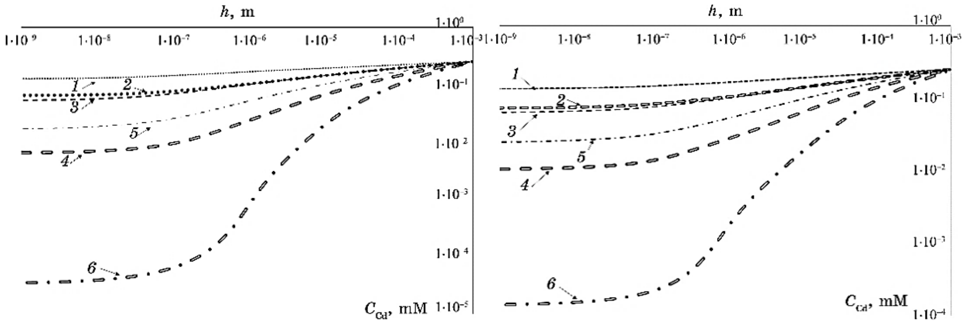
where ψ is the difference between the actual electric potential and the quasi-equilibrium potential ϕ. The diffusion coefficients in Eqs. (12)–(14) are assumed to be as follow: $D_{\mathrm{Cl}^-} = 2.04\cdot10^{-9}$ m^2/s, $D_{\mathrm{H}^+} = 9.34\cdot10^{-9}$ m^2/s, $D_{\mathrm{Cd}^{2+}} = 0.72\cdot10^{-9}$ m^2/s.

In a stationary deposition process, the total ion fluxes should be constant in each meniscus cross-section. Their values are determined by the film composition at the contact line ($h \to 0$): $J_{\mathrm{Cl}^-} = 0$, $J_{\mathrm{H}^+} = v_0X_{\mathrm{HA}}$, and $J_{\mathrm{Cd}^{2+}} = v_0\left(X_{\mathrm{CdA}^+} + X_{\mathrm{CdA}_2}\right)$. At the opposite side of the meniscus (where it turns in the bulk solution), we assume the concentrations of ions to be equal to those in the bulk solution. We assume that, far from the contact line, the mixing in the solution is sufficient to ensure the uniformity of concentrations.

3. RESULTS AND DISCUSSION

It is important that the surfactant film is deposited on the substrate surface in an electroneutral state. This condition is fulfilled due to adsorption of counterions ($C_{\mathrm{Cd}^{2+}}$ and $C_{\mathrm{H}^{+}}$) at the negatively charged surfactant groups in a close vicinity of the contact line (where the surface potential increases) [11, 12]. This means that the deposited film continuously removes the counterions from the solution, what leads to a decrease of their concentrations around the contact line and formation of concentration profiles in this region. This process is usually called concentration polarization. The higher is the substrate velocity (or the lower is the contact angle), the more pronounced is the concentration polarization in the meniscus, as discussed below.

Figures 2 and 3 show the stationary ion concentration profiles calculated for different deposition rates (*i.e.*, different v_0). The cadmium ions profiles are shown in Fig. 2, whereas those of hydrogen ions are presented in Fig. 3 (Figs. 2, *a* and 3, *a* are for the case of charged cadmium complexes, Eq. (2); and Figs. 2, *b* and 3, *b* are for neutral cadmium complexes, Eq. (3)). The results for asymmetrically charged meniscus surfaces are compared with those for symmetrically charged surfaces. The ion concentrations are presented as a function of the meniscus half-thickness h, which is proportional to the vertical coordinate y. For small contact angles θ, the ions fluxes are proportional to v_0 / θ, therefore, the ion concentration profiles were calculated for different ratios v_0 / θ. For $v_0 = 0$, the ion concentrations are constant through-



a *b*

Fig. 2. Quasi-equilibrium concentrations of cadmium ions as a function of the local half-thickness h at different ratios: $v_0/\theta = 0.005$ m/sec (curves *1*, *2*), 0.01 m/sec (curves *3*, *4*), and 0.015 m/sec (curves *5*, *6*). The results for asymmetrically and symmetrically charged meniscus surfaces are shown by single lines (curves *1*, *3*, *5*) and by double lines (curves *2*, *4*, *6*), respectively. Fig. 2, *a*—a charged complex of one cadmium ion with one surfactant group; Fig. 2, *b*—a neutral complex of one cadmium ion with two surfactant groups.

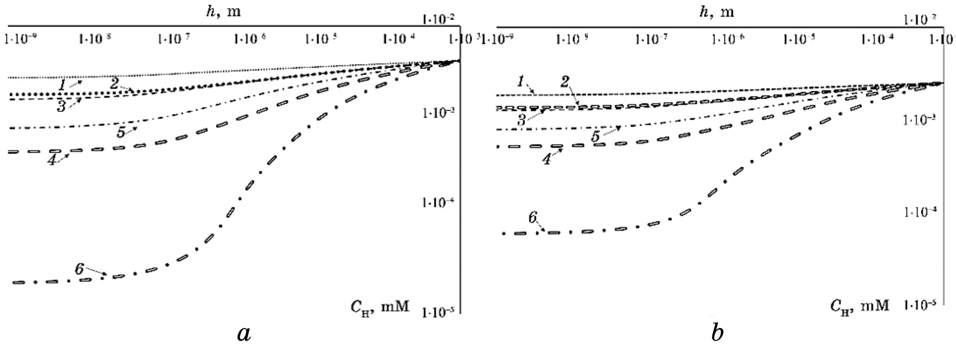


Fig. 3. Quasi-equilibrium concentrations of hydrogen ions as a function of the local half-thickness h at different ratios: $v_0/\theta = 0.005$ m/sec (curves *1*, *2*), 0.01 m/sec (curves *3*, *4*), and 0.015 m/sec (curves *5*, *6*). The results for asymmetrically and symmetrically charged meniscus surfaces are shown by single lines (curves *1*, *3*, *5*) and by double lines (curves *2*, *4*, *6*), respectively. Fig. 3, *a*—a charged complex of one cadmium ion with one surfactant group; Fig. 3, *b*—a neutral complex of one cadmium ion with two surfactant groups.

out the meniscus and are equal to those in the bulk solution. When the substrate moves, the concentrations decrease towards the contact line, while they remained fixed at the outer boundary of the meniscus.

For a stationary film deposition, it is necessary to ensure that the number of cations supplied from the bulk solution to the contact line corresponds to the number of negatively charged ionogenic surfactant groups, which should be neutralized before their transfer to the substrate surface. The purely convective ion transport is not sufficient for this. Indeed, since the average fluid flow through the meniscus cross-section is zero, the convective flux of each ion type appears due to deviations of the local concentrations from the average concentrations. However, the flux of the cations advected towards the contact line near the interface is partially compensated by the cations advected back from the contact line in the middle part of the meniscus. Therefore, the averaged convective flux of the cations in each meniscus cross-section is smaller than the flux of negatively charged ionogenic surfactant groups at the surface. Anions, unlike cations, are not included in the complexes of the film (and are not adsorbed on the substrate surface). However, their concentration is higher in the middle part of the meniscus. Thus, the cross-section averaged convective flux of anions is directed away from the contact line.

There is a significant difference between the cases of symmetrically and asymmetrically charged meniscus surfaces. In the cases of symmetrically charged surfaces, the maximums of the cations concentrations coincide with the maximums of the fluid velocity at the surfaces, and the minimums of the cations concentrations coincide with the velocity maximum of the back fluid flow in the middle part of the meniscus cross-section. For anions, we have just opposite situation, as their concentration increases with the distance to negatively charged surfaces. For asymmetrically charged meniscus surfaces, the minimums of the cations concentrations and the maximum of the anions concentration are located near the substrate surface, which is uncharged and moves towards the contact line. Therefore, the convective ions fluxes (given by the integrals from the products $C_i v$ in Eqs. (12)–(14)) are much smaller for asymmetrically charged meniscus surfaces than for symmetrically charged surfaces. It is clear that the convective ions fluxes for symmetrical configuration will be the upper boundary, whereas those for asymmetrical configuration will be the bottom boundary for any other configuration, where the charge of the substrate surface is intermediate between zero and the charge of the surfactant monolayer.

As discussed above, the purely convective transport of the cations is not sufficient to compensate completely the negative charge of ionogenic surfactant groups in the deposited monolayer under stationary conditions. This leads to a decrease of their quasi-equilibrium concentrations near the contact line (Figs. 2 and 3). On the other hand, the convective flux of anions is directed away from the contact line; therefore, their quasi-equilibrium concentration also decreases near the contact line. The change in local ions concentrations leads to appearance of additional diffusion fluxes, which supply the cations that are necessary to form electroneutral deposited film and compensate for the anions removed by the convective flux from the contact line region. Additionally, the gradient of the electric potential along the substrate and monolayer surfaces becomes different from that in static situation. This gradient is necessary to maintain local electroneutrality for each meniscus cross-section. Thus, the concentration polarization leads to appearance of additional diffusion and electromigration ion fluxes, which contribute to the total ion fluxes (Eqs. (12)–(14)). Upon reaching certain changes in concentrations and electric potential, a steady-state regime is set in the system, when all components of the ions fluxes are balanced. As the transferred film does not carry a charge, the total electric current consisting of partial currents of ions is zero for each meniscus cross-section

$$I = F\left(J_{\mathrm{H^+}} + 2J_{\mathrm{Cd^{2+}}} - J_{\mathrm{Cl^-}}\right) = 0\,. \tag{15}$$

The decrease of the quasi-equilibrium concentrations of the cations at the contact line ($h \to 0$) is determined by the film deposition rate, as it is seen in Fig. 4. For the same deposition rate, the decrease of the ion concentrations is less significant for asymmetrically charged meniscus surfaces than for symmetrically charged surfaces.

The results presented in Fig. 4 show that the counterion concentra-

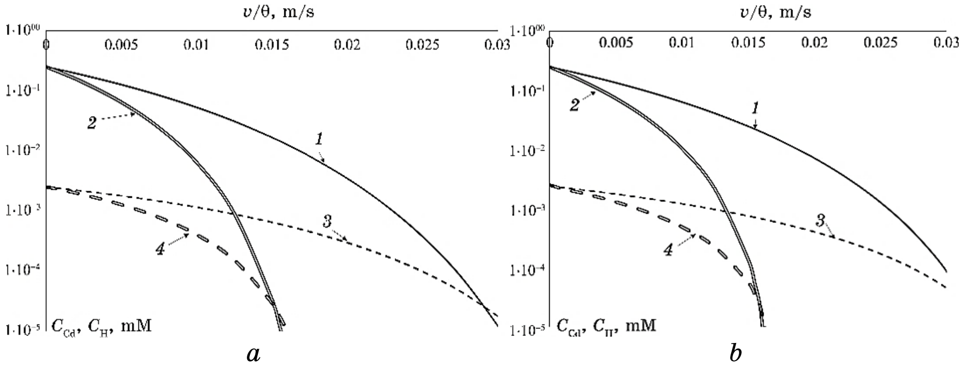


Fig. 4. Quasi-equilibrium concentrations of cadmium (curves *1*, *2*) and hydrogen (curves *3*, *4*) ions at the contact line as a function of the transfer rate. The results for asymmetrically and symmetrically charged meniscus surfaces are shown by single lines (curves *1*, *3*) and by double lines (curves *2*, *4*), respectively. Fig. 4, *a*—a charged complex of one cadmium ion with one surfactant group; Fig. 4, *b*—a neutral complex of one cadmium ion with two surfactant groups.

tions at the contact line fall down by several orders of magnitude. Remarkably, the concentration of cadmium ions decreases faster than for hydrogen ions. With decreasing counterions concentrations, the contact angle also decreases [2, 12]. This complicates the transport of counterions towards the contact line, because the ratio v_0/θ increases. That means a positive feedback in the system. For certain critical transfer rate, the adhesion of the surfactant film to the substrate surface becomes not sufficient to expel water from the contact line, and the water film is entrained by the deposited surfactant film. A strong dependence of the critical transfer rate on the pH and the bivalent counterion concentration in the subphase confirms this mechanism [2, 12].

The ratio of cadmium and hydrogen ions in the deposited film depends not only on the ratio of their concentrations in the bulk solutions but also on the transfer rate. For certain conditions, the composition of the deposited film can change from the preferably cadmium form to hydrogen form. If the concentration of hydrogen ions becomes very small, then, accumulation of hydroxyl ions becomes possible near the contact line because of the fast removal of hydrogen ions with the deposited film. This leads to an increase of the local charge density at the surfactant film and to violation of the adhesion conditions of the film to the substrate surface. In this case, the meniscus becomes unstable, and further stationary film deposition becomes impossible. The experimental data presented in [13] show that the meniscus oscillations are observed during the deposition of arachidic acid monolayers at a specific ratio of cadmium and hydrogen ions in the subphase, which are close to those in the present study. The experiments also show that under this conditions the deposited films have not a uniform composition but are composed of alternating stripes of cadmium arachidate and arachidic acid. This effect can be used for obtaining patterned substrates with the lateral resolution in the nanometer scale length.

Figures 4, *a*, *b* show that for asymmetrically charged meniscus surfaces the critical transfer rate should be approximately two times larger than for symmetrically charged surfaces. It is also seen that, in the case of the formation of neutral complex of one cadmium ion with two surfactant groups, the concentration dependence on the velocity is slightly lower (and the maximum velocity is slightly higher) than for charged complex of one cadmium ion with one surfactant group. It is likely depends on the specific reaction constants.

In Figure 5, the variation of the surface potential with the distance between the meniscus surfaces is shown for different transfer rates. Far from the contact line, the distance between the meniscus surfaces is much larger than the length of the Debye screening, and the electrical double layer formed near the charged surface is not perturbed by the second surface. However, when the thickness of the meniscus decreases and becomes comparable to the screening length, the surface potential increases (and the surface charge decreases). The potential increases slower in the case of asymmetrically charged surfaces. With decreasing meniscus thickness, the potentials at two meniscus surfaces become closer to each other and become nearly identical, when the distance between the surfaces is much smaller than the screening dis-

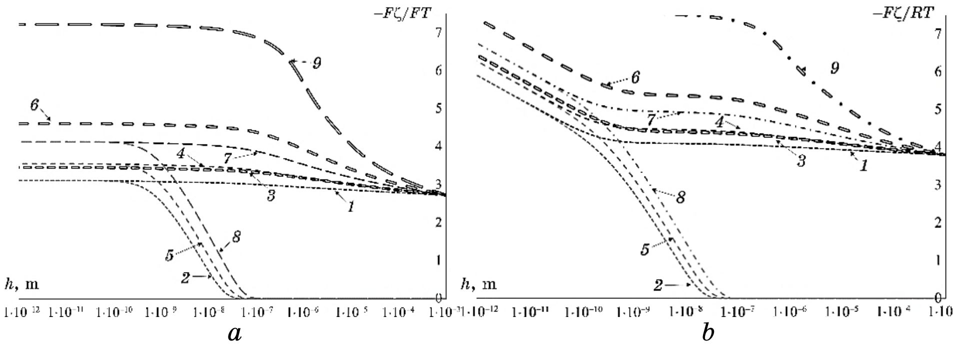


Fig. 5. Dimensionless surface potential as a function of the local half-thickness *h* at different ratios: $v_0/\theta = 0.005$ m/sec (curves *1*, *2*, *3*), 0.01 m/sec (curves *4*, *5*, *6*), and 0.015 m/sec (curves *7*, *8*, *9*). The results for asymmetrical films are shown by single black lines (curves *1*, *4*, *7*) for the monolayer surface and by single grey lines (curves *2*, *5*, *8*) for the substrate surface, respectively; the results for symmetrical films are shown by double lines (curves *3*, *6*, *9*). Fig. 5, *a*—a charged complex of one cadmium ion with one surfactant group; Fig. 5, *b*—a neutral complex of one cadmium ion with two surfactant groups.

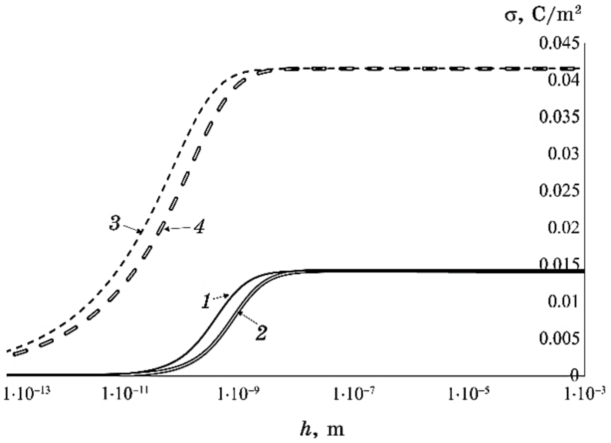


Fig. 6. Surface charge density (in C/m^2) as a function of the local half-thickness h for $\upsilon_0 = 0$. The results for asymmetrically and symmetrically charged meniscus surfaces are shown by single lines (curves *1*, *3*) and by double lines (curves *2*, *4*), respectively. A charged complex of one cadmium ion with one surfactant group (curves *1* and *2*), a neutral complex of one cadmium ion with two surfactant groups (curves *3* and *4*).

tance.

It worth noting that for charged complex of cadmium ions with surfactant groups the charge of the deposited film turns to zero at a finite value of the surface potential (Fig. 5, *a*). In contrast, for neutral complex of cadmium ions with surfactant groups, the surface potential should infinitely increase to provide the necessary zero surface charge (Fig. 5, *b*). The increasing surface potential promotes the counterions binding to the ionized monolayer groups; therefore, the surface charge density decreases near the contact line approaching to zero (Fig. 6).

4. CONCLUSIONS

In this study, we considered the specifics of transferring a Langmuir–Blodgett film to a clean uncharged substrate surface, which is compared to the results for the substrate surface bearing the same charge as the surfactant monolayer. The counterions that are necessary to form an electroneutral film are supplied from the bulk solution to the contact line due to convection, diffusion, and electrical migration mechanisms. The analysis shows that, in the deposition process, a concentration polarization is observed within the meniscus. A decrease of the quasi-equilibrium concentration of ions near the contact line can complicate the homogeneous film deposition and can result in a patterned film formation. However, in the case of deposition to an uncharged surface, such concentration polarization is less pronounced, than in the case of deposition to a charged surface, and the transfer of the film is possible with a higher rate.

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