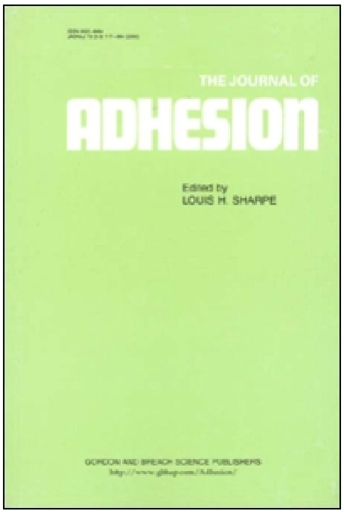

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ION REDISTRIBUTION NEAR THE POLAR GROUPS IN THE LANGMUIR WETTING PROCESS

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The theoretical analysis of electrostatic interactions and ion redistribution in the close vicinity of the three-phase contact line shows their important role in the Langmuir wetting process. To provide a sufficient rate for the ion transfer, which is intended to neutralize the interfacial charge, the concentration and potential distributions deviate from the equilibrium. As a consequence, during the deposition process the adhesion work, and hence the contact angle, are defined by the local ionic concentrations near the three-phase contact line. The concentration profiles and the electro-diffusion ion fluxes induced during the Langmuir wetting process are strongly dependent on the subphase composition and on the monolayer properties. The results of the analysis are in a good agreement with the experiments.

Keywords: Langmuir-Blodgett films; Contact angles; Adhesion work; Deposition rate; Electrostatic interactions; Ion transfer

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INTRODUCTION

The dynamic contact angle (DCA) between a floating monolayer and a substrate surface is an important parameter of the Langmuir wetting process. During the process, the dynamic contact angle should be sufficiently large to allow a rapid expelling of water during the monolayer deposition ("zipper angle" according to Langmuir [1]). When the dynamic contact angle becomes zero, a thin water layer is entrained between the monolayer and the substrate surface [2, 3]. In such a case the deposition of monolayers in the Langmuir-Blodgett (LB) film becomes unstable.

It is important that the DCA is a decreasing function of the substrate velocity. Accordingly, at a certain substrate velocity the DCA becomes sufficiently small to entrain water between the monolayers and hence to destabilize the deposition process. Thus, stable LB films can be obtained provided the substrate velocity does not exceed a certain limiting value, which is referred to as the maximum deposition rate [3]. The maximum deposition rate is an important parameter of the LB process [2]. Obtaining this parameter is a necessary precondition for the mathematical modeling of the process.

According to the hydrodynamic model [4], the maximum deposition rate is an increasing function of the equilibrium contact angle (ECA), which is observed when the deposition process is conducted with an infinitesimal velocity. Consequently, the ECA can be considered as a thermodynamic parameter of the system. The ECA is expressed through the work of adhesion attributed to deposition of the monolayer onto the substrate surface [5, 6]. Accordingly, the maximum substrate velocity can be also expressed by the adhesion work. Since the ECA increases with the adhesion work, the maximum deposition rate increases with the adhesion work as well.

The adhesion work, and hence the maximum deposition rate, depend on the parameters responsible for the equilibrium interaction between the monolayers. Considering the deposition of charged monolayers, it is necessary to take into account an additional contribution from the electrostatic interaction. The electrostatic contribution to adhesion work depends on the nature of the ionizable groups in the monolayer and on the ionic composition of the subphase (*e.g.*, pH, counterion concentration in the bulk, etc.).

Recently, it was shown [7, 8], that due to charge transfer effects the LB deposition of charged monolayers is accompanied by local changes in the subphase composition near the contact line. Such changes strongly affect both the electrostatic contribution to the adhesion work and the maximum deposition rate. In our previous article [8]; such an effect was considered for the case of monolayers, which are formed by molecules of a dissociating fatty acid, being in contact with a subphase containing bivalent counterions. In the present study we will analyse the maximum deposition rate for the same monolayer type, but for the substrate containing monovalent counterions and an indifferent (nonsurface-charge-affecting) electrolyte.

CONCENTRATION POLARIZATION IN THE THREE-PHASE CONTACT REGION

A floating monolayer and the adjacent diffuse layer (DL) form a totally electroneutral electrical double layer, where the interfacial charge of the ionized surface groups is completely compensated by the opposite charge, which is spread out within the diffuse layer. Thus, in the electrical, double layer, the positive and negative charges are macroscopically separated. For a 0.001 M solution, the mean distance of the separation for the charges (the Debye length) takes a value on the order of 10 nm. Such a macroscopic charge separation does not exist in the case of the deposited monolayer because it is formed by electroneutral molecules. During the deposition process, the counterions, which are distributed within the DL, are continuously transported to the interface where they recombine with the ionizable groups. The corresponding relaxation time for such a process depends on the length of the diffuse layer. This behavior will be considered in more detail below.

In close vicinity to the three-phase contact line, the electrical double layers formed at the monolayer and the substrate surface overlap (Figure 1). For the case of small contact angles, the overlapping region can be relatively large. Because of the overlapping, both the interfacial potentials and the counterion concentrations increase. Consequently, the adsorption of the potential-determining counterions (binding by the ionizable groups) becomes larger. The latter results in a decrease in the surface charge density. Thus, toward the three-phase contact line [9] the surface potential gradually increases, whereas the surface charge density decreases. During the deposition process the monolayer passes through this region, “captures” counterions, and removes them away from the solution. Close to the three-phase contact line, the monolayer charge approaches zero. This is a necessary condition for good adhesion of the monolayer to the substrate surface on which it is deposited.

Since the potential-determining counterions are continuously removed with the monolayer from the meniscus region, they should be

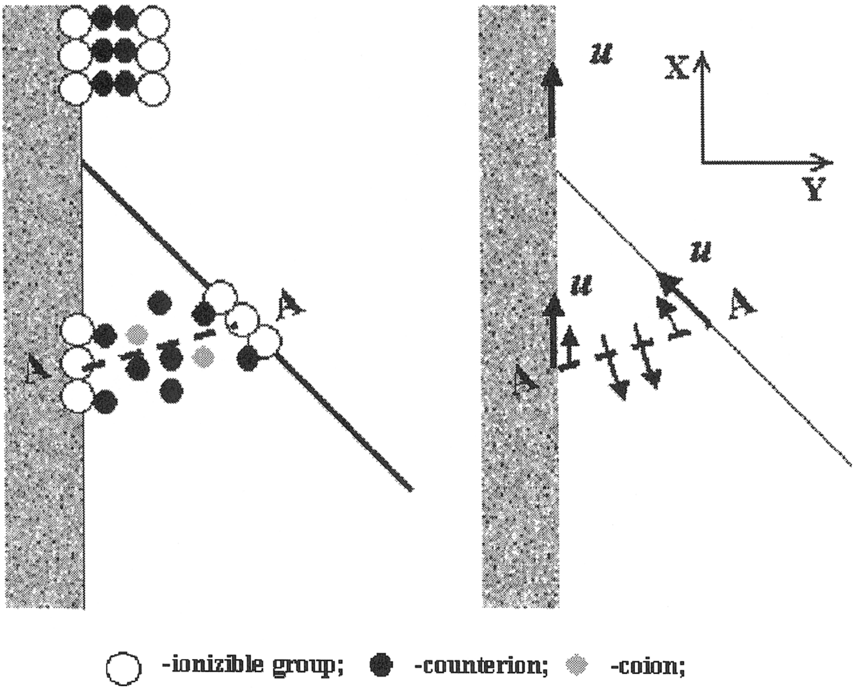


FIGURE 1 Ion distributions and velocity distribution in vicinity of the three-phase contact line.

transferred from the bulk solution toward this region sufficiently quickly to maintain neutrality. Such transfer is realized *via* bulk convection, diffusion, and electro-migration. At stationary conditions, for complete neutralization of the surface charge the flux of the potential-determining counterions in each crosssection of the solution should be the same as the surface flux of oppositely charged ionizable groups. However, pure convective transfer cannot provide the required fluxes of the potential-determining counterions. This failure occurs because in the diffuse layer overlapping region only the counterions, which are located close to the interface, move in the same direction as the monolayer (Figure 1). Due to the solution back flow (when the solvent is expelled from the contact zone), the counterions located in the intermediate part of the film move in the opposite direction. Thus, to satisfy the continuity condition for steady-state fluxes, the redistributions of electric field and counterion concentration are induced in the system. Such redistributions lead to electro-diffusional fluxes of counterions, which, together with convective fluxes, satisfy continuity.

Note that the deposited film does not remove ions that are not bound by the interface (coions or counterions of an indifferent electrolyte). At the same time, the convective flux of such ions through a crosssection of the film formed between the moving surfaces is not zero (Figure 1). Therefore, at stationary conditions the convective flux of such ions should be compensated by the electro-diffusion flux oppositely directed.

Thus, at the stationary deposition, in the region near the three-phase contact line, the electro-diffusion fluxes of all ions should be generated according to the following mechanism. In the first moment of the deposition process, there are no electro-diffusion fluxes because of the equilibrium distributions of all ions in the solution. As convective fluxes themselve do not provide continuity of ionic fluxes, during a certain transition time profiles of the electric potential and concentration are developed in the meniscus region. These profiles change with time until the stationary regime is reached. Thus, the electro-diffusion fluxes provide the conservation of ions within the region under consideration. Formation of such concentration profiles is typical for systems with selective transfer of ions (for example, membranes or electrode systems) and is referred to as *concentration polarization* [10, 11].

A faster deposition process requires stronger electro-diffusion fluxes. However, the electro-diffusion fluxes cannot increase without bound. If the velocity of the substrate motion becomes larger than a critical value, then a stationary monolayer deposition is impossible and the meniscus becomes unstable [7, 8].

Consider a fatty acid monolayer whose ionization is described by the reaction

$$\mathrm{RH} \leftrightarrow \mathrm{R}^{-} + \mathrm{H}^{+}. \tag{1}$$

We assume that the monolayer is in contact with a solution of an inorganic acid and an added indifferent electrolyte having a common anion with the acid. The acid and the indifferent electrolyte are completely dissociated, giving the cations, H^{+} and K^{+}, and the anion, A^{-}. The equilibrium condition for the reaction, given by Equation (1), is

$$\mathrm{X}_{\mathrm{RH}} = \mathrm{K}\mathrm{X}_{\mathrm{R}^{-}}\mathrm{C}^{\mathrm{S}}_{\mathrm{H}^{+}}, \tag{2}$$

where $\mathrm{X}_{\mathrm{R}^{-}}$ and X_{RH} are the interfacial molar concentrations of the dissociated fatty acid (R^{-}) and nondissociated fatty acid (RH), respectively; $\mathrm{C}^{\mathrm{S}}_{\mathrm{H}^{+}}$ is the bulk molar concentration of H^{+} at the interface; and

K is the equilibrium constant. The total amount of fatty acid at the interface is

$$X_R = X_{R^-} + X_{RH}. \tag{3}$$

When the monolayer is in a close-packed condensed state, the X_R value is nearly independent of the surface pressure and of the solution pH. For such a case, one can assume that X_R is a constant value. From Equations (2) and (3), one obtains

$$X_{R^-} = \frac{X_R}{1 + KC^S_{H^+}}. \tag{4}$$

Using Equation (4), the surface charge density is expressed as

$$\sigma = -FX_{R^-} = -\frac{FX_R}{1 + KC^S_{H^+}}, \tag{5}$$

where the Faraday constant, F, equals $9.65{\cdot}10^4$ C/mol. In the bulk solution, the conservation law for the *i*th sort of ions can be written in the form

$$\frac{\partial C_i}{\partial t} = \nabla \cdot \mathbf{j}_i, \tag{6}$$

where C_i and $\mathbf{j}_i$, respectively, are the *i*th ion concentration and flux density, ∇ is the spatial gradient operator. The flux density includes the convective, diffusive, and electro-migration components. In the case of small contact angles, the *x* axis can be directed along the liquid film formed between two charged interfaces, and the *y* axis can be directed across the film (Figure 1). We will assume that both film interfaces are covered by identical monolayers. Integrating Equation (6) with respect to coordinate y from $y = 0$ to $y = h(x)$ (where h(x) is the local film thickness), one obtains

$$\frac{\partial}{\partial t}\left(\int_0^h C_i(x,y)dy\right) = -\frac{\partial}{\partial x}(J_i) + 2j_{iy}\big|_{y=0}, \tag{7}$$

where $J_i = \int_0^h j_{ix}(x,y)dy$ is the ion flux through the given cross section of the film, and $j_{iy}\big|_{y=0}$ is the flux density of the ions, which are adsorbed (desorbed) at the monolayer. We consider the *i*th ion flux,

J_i, consisting of convective and electro-diffusional components ($J_i = J_i^C + J_i^{ED}$), which are given by the equations

$$J_i^C(x) = \int_0^h v(y) C_i(x, y) dy \tag{8}$$

$$J_i^{ED}(x) = -D_i \int_0^h \frac{C_i(x, y)}{RT} \frac{\partial \mu_i^{el}}{\partial x} dy, \tag{9}$$

where v(y) is the local velocity in the solution; $\mu_i^{el} = z_i F \varphi + RT\, ln\, C_i$ is the electrochemical potential of the *i*th ion; D_i and z_i are the *i*th ion diffusion coefficient and charge, respectively; φ is the electrostatic potential; R is the gas constant; and T is the absolute temperature. At the interfaces, the balance of nondissociated fatty acid molecules (RH) is described by the equation

$$2\frac{\partial X_{RH}}{\partial t} = -\frac{\partial J_{RH}}{\partial x} - 2 j_{H^+y}\Big|_{y=0}, \tag{10}$$

where $J_{RH} = 2UX_{RH}$ is the flux of the nondissociated molecules moving with the monolayers at the interfaces, U is the monolayer velocity,and $j_{H^+y}|_{y=0}$ is the flux density of hydrogen ions adsorbing (desorbing) at the monolayer. Using Equations (7) and (10) for a film cross section, one obtains a balance equation for the hydrogen ions,

$$\frac{\partial}{\partial t}\left(\int_0^h C_{H^+}(x, y) dy\right) + 2\frac{\partial X_{RH}}{\partial t} = -\frac{\partial J_{H^+}^C}{\partial x} - \frac{\partial J_{H^+}^{ED}}{\partial x} - \frac{\partial J_{RH}}{\partial x}. \tag{11}$$

Assuming that the anions and cations of an indifferent electrolyte are not adsorbed at the interfaces, one obtains from Equation (7)

$$\frac{\partial}{\partial t}\left(\int_0^h C_{A^-}(x, y) dy\right) = -\frac{\partial J_{A^-}^C}{\partial x} - \frac{\partial J_{A^-}^{ED}}{\partial x}, \tag{12}$$

$$\frac{\partial}{\partial t}\left(\int_0^h C_{K^+}(x, y) dy\right) = -\frac{\partial J_{K^+}^C}{\partial x} - \frac{\partial J_{K^+}^{ED}}{\partial x}. \tag{13}$$

Initially, the equilibrium distributions of the ion concentrations and the potential hold, and the electro-diffusion fluxes, are absent. The convective fluxes, however, are not zero and are different for different cross sections. They are different because of the nonuniformity in the ion concentration distributions in the overlapping region of the diffuse layers. Therefore, according to Equations (11)–(13), the concentrations begin to change with time. The concentration changes induce changes in the potential distribution of this region. The electro-diffusion fluxes, produced because of these changes, increase gradually with time until a stationary (or quasi-stationary) regime establishes itself and the time derivatives in Equations (11)–(13) become zero. After stopping the deposition process the convective fluxes disappear and the gradual relaxation to equilibrium begins with ion transfer by electro-diffusion.

For a stationary regime one obtains from Equation (11)

$$J^{C}_{H^+}(x) + J^{ED}_{H^+}(x) + J_{RH}(x) = \text{const} = 2UX_R, \tag{14}$$

where the constant is determined as the flux of H^+ ions removed with the deposited monolayers. Substituting $J_{RH} = 2UX_{RH}$ in Equations (14) and taking into account Equation (3) one obtains the electro-diffusion flux of H^+ ions,

$$J^{ED}_{H^+}(x) = 2U(X_R - X_{RH}(x)) - J^{C}_{H^+}(x) = 2UX_{R^-}(x) - J^{C}_{H^+}(x). \tag{15}$$

On the right-hand side of Equation (15), the first term signifies the flux of the potential determining ions. Such a flux is required to neutralize the surface charge before the monolayer is transferred to the substrate surface. Only a part of this flux is transferred by convective flow, and the remaining part is by the electro-diffusion flux. Thus, Equation (15) can be rewritten in the form

$$T^{ED}_{H^+}(x) = 1 - T^{C}_{H^+}(x), \tag{16}$$

where $T^{ED}_{H^+} = \frac{J^{ED}_{H^+}}{2UX_{R^-}}$ and $T^{C}_{H^+} = \frac{J^{C}_{H^+}}{2UX_{R^-}}$ are the relative parts of total H^+ ions flux transferred by electro-diffusion and convection mechanisms, respectively. By analogy with electrochemistry they can be denoted as the transfer numbers.

Since the ions of an indifferent electrolyte are not removed with the deposited monolayer, one obtains the electro-diffusion fluxes of anions and cations of the indifferent electrolyte in a stationary regime using Equations (12) and (13);

$$J^{ED}_{A^-}(x) = -J^{C}_{A^-}(x) \tag{17}$$

$$J^{ED}_{K^+}(x) = -J^{C}_{K^+}(x) \tag{18}$$

The convective ion fluxes can be obtained from Equation (8) after substituting in expressions for the velocity and concentrations distributions. For small contact angles, using the lubrication approximation [4], which is widely accepted for thin films, the velocity can be represented as

$$\mathrm{v(y)} = \mathrm{U}\left(-\frac{1}{2}+6\left(\frac{\mathrm{y}}{\mathrm{h}}-\frac{1}{2}\right)^{2}\right). \tag{19}$$

In the film, the distributions of ion concentrations and electric potential can be considered as a sum of the equilibrium values and a perturbation, denoted as $\mathrm{C_i(x,y)} = \mathrm{C_i^{eq}(x,y)} + \delta\mathrm{C_i(x,y)}$ and $\varphi(\mathrm{x,y}) = \varphi^{\mathrm{eq}}(\mathrm{x,y}) + \delta\varphi(\mathrm{x,y})$, respectively. The perturbation increases with the velocity but, for sufficiently small velocities, perturbations can be neglected in comparison with the equilibrium values. In the present study, we consider only a linear approximation with respect to the velocity U, *i.e.*, we neglect the deviations of the ion concentrations and the electric potential from equilibrium for obtaining the convective and electro-diffusion ion fluxes. For this approximation, the ion transfer numbers, $\mathrm{T^{C}_{H^+}}$ and $\mathrm{T^{ED}_{H^+}}$, are independent of the velocity and can be considered as local transport characteristics of the film. In the case of very small contact angles, the concentrations and the potential distributions can be obtained using a quasi-flat film approximation (see Appendix). The ion concentrations can be represented using the Boltzmann distribution,

$$\mathrm{C_i(x,y)} = \mathrm{C_i^0 e^{-z_i\varphi(x,y)}}, \tag{20}$$

where $\mathrm{C_i^0}$ is the *i*th ion concentration in the bulk solution and φ(x,y) is the dimensionless potential distribution within the quasi-flat film (see Appendix).

Substituting Equations (19) and (20) into Equation (8) permits the convective fluxes to be written as

$$\mathrm{J_i^C} = \mathrm{UC_i^0}\int\limits_0^{\mathrm{h}}\left(-\frac{1}{2}+6\left(\frac{\mathrm{y}}{\mathrm{h}}-\frac{1}{2}\right)^{2}\right)e^{-z_i\varphi(\mathrm{x,y})}\mathrm{dy}. \tag{21}$$

For given convective fluxes, the corresponding electro-diffusion fluxes can be easily obtained using Equations (15), (17), and (18). Combining Equations (4) and (20), the surface concentration, $\mathrm{X_{R^-}}$, is represented as

$$\mathrm{X_{R^-}} = \frac{\mathrm{X_R}}{1+\mathrm{KC^0_{HA}e^{-\varphi_s(\mathit{x})}}}, \tag{22}$$

where $\mathrm{C^0_{HA}}$ is the acid concentration in the bulk solution and φ_s(x) is the dimensionless surface potential, which is negative for the system under consideration.

Thus, the ion fluxes depend on the distance between the charged interfaces, h, on the bulk concentration, C^0_{HA} and C^0_{KA}, of acid and indifferent electrolyte, respectively, and on the equilibrium constant, K. When the distance h is much larger than the Debye length, the diffuse layers do not overlap. Accordingly, many ions move with the interfaces, and the convective transfer of ions is large. If the local distance between the monolayers, h, is small, then overlapping of the diffuse layer is strong. Accordingly, the convective transfer of ions is small because the direct flux of ions near the interfaces is compensated by their back flux in the middle part of the film. This can be seen from Equation (21) where, for a strong overlap of the diffuse layer, the electric potential is approximately constant within the film cross section. For such a case, the exponent can be taken out of the integral, and the remaining integral tends to zero. The discussion given above shows that the convective ion transfer decreases toward the three-phase contact line.

The effect of the diffuse layer thickness is the opposite. If at a given film thickness, h, the DL thickness increases, the overlap of the diffuse layer increases and the convective transfer decreases. The DL thickness is determined by the electrolyte concentrations in the bulk solution. However, the electrolyte concentrations affect the interfacial charge and potential as well [7, 9]. When the surface potential increases, the diffuse layers become more compressed, *i.e.*, the counterions are located very close to the interfaces and therefore the convective transfer increases. Thus, the effect of electrolyte concentrations is complex and is very different for potential determining and indifferent electrolyte. These effects will be considered in the next section.

RESULTS AND DISCUSSION

In Figure 2, the surface potential, φ_s, the potential in the symmetry plane, φ_0, (absolute values) and the surface concentration of the charged groups, X_{R^-}, are shown as functions of the film thickness, h. The curves were obtained for different pH values, for a fixed bulk concentration of indifferent electrolyte ($C^0_{KA} = 10^{-4}\,M$) and for an equilibrium constant which is typical for carboxylic groups in aqueous solutions ($K = 65.4\,m^3/mol$). For all calculations the value $X_R = 8.3 \cdot 10^{-6}\,mol/m^2$ was used. The latter is typical for fatty acid monolayers. It is seen that toward the three-phase contact line (*i.e.*, toward smaller film thickness), the surface potential increases, whereas the concentration of the charged groups at the surfaces decreases. At small thickness, the potential in the symmetry plane,

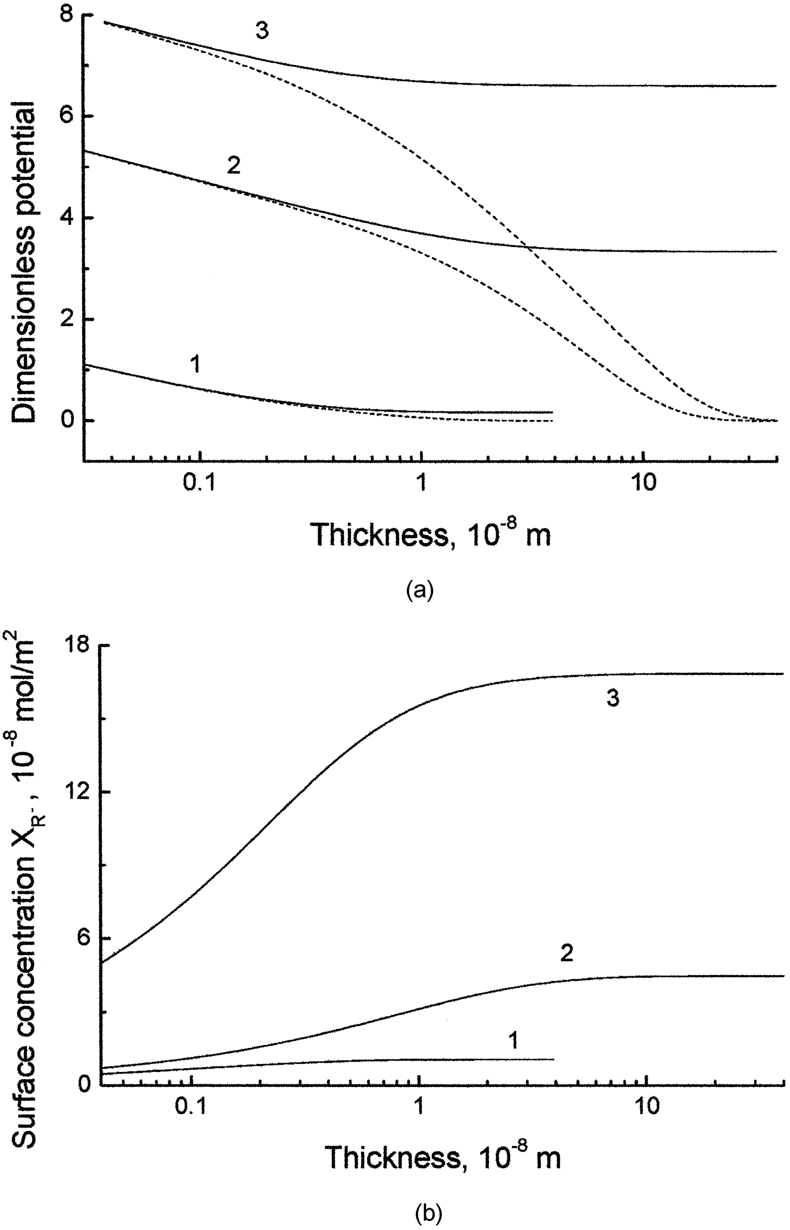


FIGURE 2 Dimensionless surface potential (continuous lines, Figure 2a), potential in the plane of symmetry (dashed lines, Figure 2a) and the surface concentration of charged groups, X_{R^-}, (Figure 2b) for $C^0_{KA} = 10^{-4}$ M, $K = 65.4\,m^3/mol$, and different pH values in the solution: pH = 2 (1), pH = 4 (2), and pH = 6 (3).

φ_0, approaches the surface potential, φ_s, as a consequence of the strong overlap of the diffuse layers. At large thickness, when the diffuse layers do not overlap, the potential in the symmetry plane approaches zero. The concentration of the potential-determining ions decreases as the solution pH increases. This results in a higher degree of the monolayer ionization and, consequently, in an increase of both the surface charge density and the surface potential. Simultaneously, due to the decrease in the electrolyte concentration at higher pH, the Debye length increases and, therefore, the overlap of the diffuse layers becomes stronger.

The curves in Figure 3 illustrate the behavior of the electro-diffusion transfer number of the potential-determining ions, $T_{H^+}^{ED}$, under the same conditions as those used to obtain the curves in Figure 2. It is seen that the transfer number increases dramatically with increasing pH value. As the pH value increases from 2 to 4 the increase in the transfer number, $T_{H^+}^{ED}$, can be explained by the stronger overlap of the diffuse layers. In this case, the Debye length increases approximately by a factor of 10 (*cf*. Figure 2). The stronger DL overlap results in a decrease of the convective flux of H^+ ions (relative to the flux of the surface-charged groups) and, according to Equation (16), in an increase in the electro-diffusion transfer number (curves 1 and 2 in Figure 3). When pH increases from 4 to 6, the Debye length increases

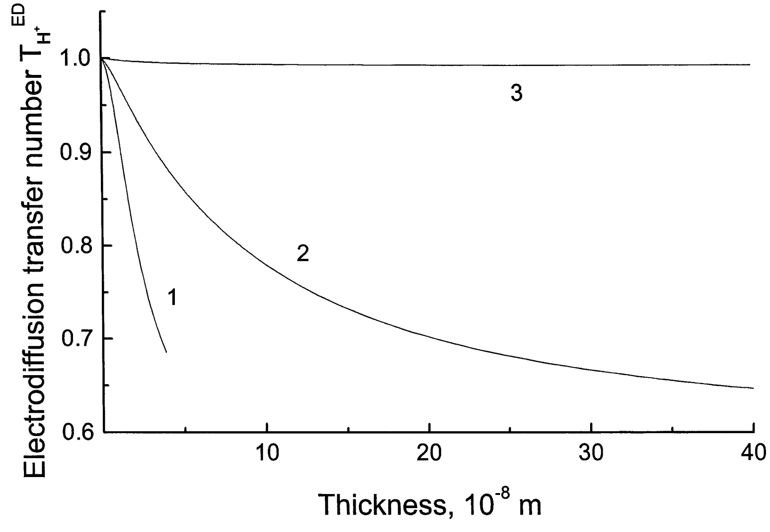
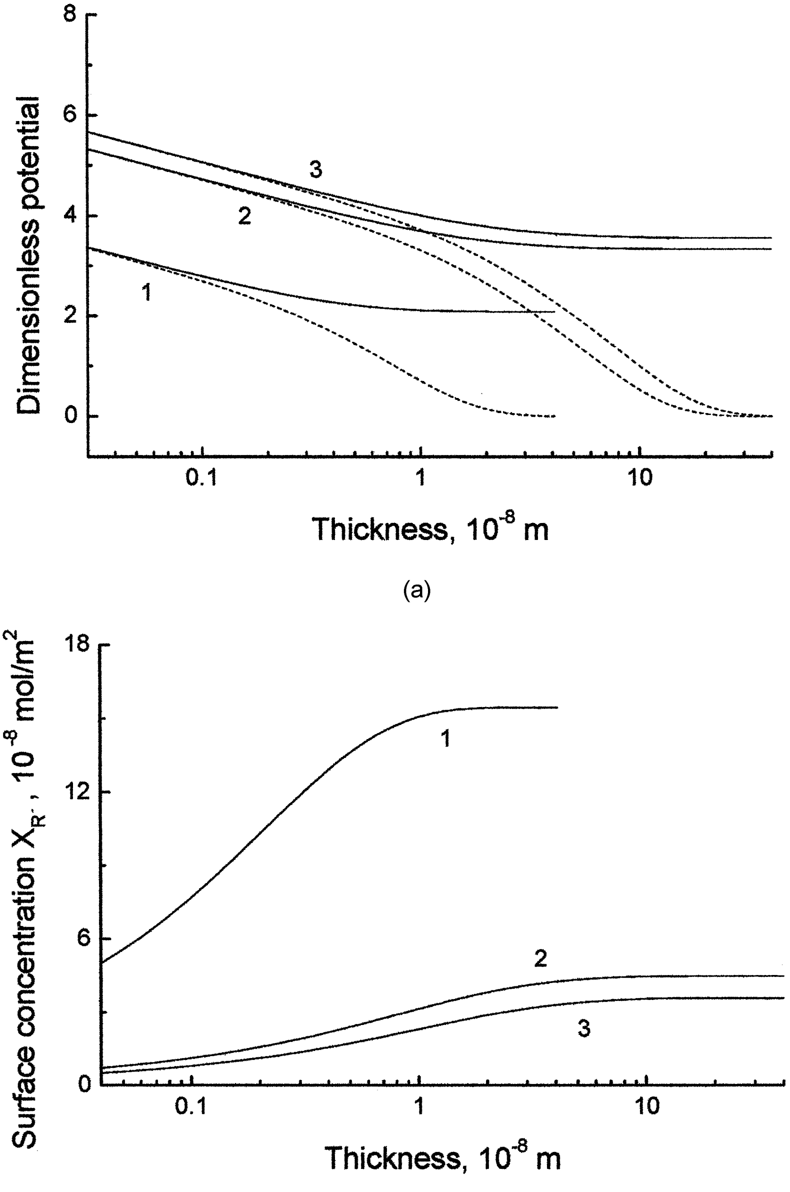


FIGURE 3 Electro-diffusion transfer number of potential-determining ions, $T_{H^+}^{ED}$, for $C_{KA}^0 = 10^{-4}$ M, $K = 65.4\,m^3/mol$, and different pH values in the solution: pH = 2 (1), pH = 4 (2), and pH = 6 (3).

more weakly, because, in this case, it is mainly defined by the indifferent electrolyte concentration. However, at these pH values, the concentration of the potential-determining ions H^+ is much lower than the concentration of cations of the indifferent electrolyte. Thus, in the diffuse layer, the H^+ ions are replaced by the cations K^+, and the convective flux of H^+ ions decreases. The convective transfer becomes much smaller than that required for surface charge neutralization (note that the surface charge also increases). Hence, the electro-diffusion transfer of potential-determining ions strongly increases (curve 3 in Figure 3).

The strong increase in the electro-diffusion transfer number of potential-determining ions, $T_{H^+}^{ED}$, which is observed at higher pH, means that very large concentration gradients of these ions are formed near the three-phase contact line. These gradients increase with the velocity of the monolayer motion. Therefore, even at small velocities, the concentration of H^+ ions near the three-phase contact line decreases and acquires such small values that a further increase of their electro-diffusion transfer becomes impossible. This means that, at higher pH values, the maximum deposition rate should be very small. Such a conclusion is in a very good agreement with the experimental observations [3].

The influence of the indifferent electrolyte concentration, C_{KA}^0, is illustrated by the curves in Figures 4 and 5. A decrease in the indifferent electrolyte concentration results in an increase in the Debye length. Accordingly, the overlap of the diffuse layers becomes stronger and the potential at the surfaces increases. According to Equation (22), the increasing surface potential leads to a decrease in the surface charge (Figure 4). The influence of the indifferent electrolyte concentration, C_{KA}^0, on the electro-diffusion transfer number of the potential-determining ions, $T_{H^+}^{ED}$, is opposite to that predicted for C_{HA}^0 (Figure 5). At small C_{KA}^0, the H^+ ions prevail in the diffuse layers and the surface charge is small. Therefore, the convective flux of H^+ ions is sufficiently large, whereas the electro-diffusion transfer remains small (curve 3 in Figure 5). At large C_{KA}^0, significantly more cations K^+ form the diffuse layers, substituting themselves for the H^+ ions. For this case, the convective flux of H^+ ions is very small, and much larger electro-diffusion transfer is required for compensating the surface charge (curve 1 in Figure 5). Thus, although an increase in the indifferent electrolyte concentration reduces the overlap of the diffuse layers, it results in an increase of electro-diffusion transfer of potential-determining ions. Consequently, the maximum deposition rate decreases as the indifferent electrolyte concentration increases. Such a result is in agreement with the experimental data



(a)

(b)

FIGURE 4 Dimensionless surface potential (continuous lines, Figure 4a), potential in the plane of symmetry (dashed lines, Figure 4a) and the surface concentration of charged groups, X_{R^-}, (Figure 4b) for $pH = 4, K = 65.4$ m^3/mol, and different concentrations of indifferent electrolyte in the solution: $C^0_{KA} = 10^{-2}$ M (1), $C^0_{KA} = 10^{-4}$ M (2), and $C^0_{KA} = 10^{-6}$ M (3).

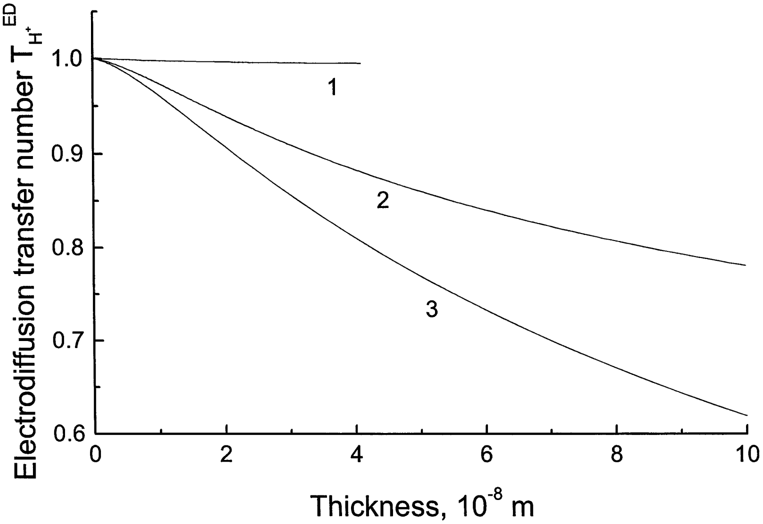


FIGURE 5 Electro-diffusion transfer number of potential-determining ions, $T_{H^+}^{ED}$, for $pH=4, K=65.4\,m^3/mol$, and different concentrations of indifferent electrolyte in the solution: $C_{KA}^0=10^{-2}M$ (1), $C_{KA}^0=10^{-4}M$ (2), and $C_{KA}^0=10^{-6}M$ (3).

[3], where, at high indifferent electrolyte concentrations, very small maximum deposition rates are observed.

Figures 6 and 7 show the effect of the equilibrium constant, K. The degree of dissociation of ionized groups increases as the constant K decreases and, therefore, the surface potential increases as well (Figure 6). The Debye length is independent of K. However, the diffuse layer becomes more dense as the surface potential increases, and the counterions are located closer to the charged interfaces. This gives rise to an increase of the convective transfer of the potential-determining ions and of a corresponding decrease of the electro-diffusion transfer number, $T_{H^+}^{ED}$ (Figure 7). It should be noted, however, that for dense diffuse layers, the more general Stern model should be used instead of the Gouy-Chapman model [12].

Thus, the presented results show that, in the case of charged monolayer deposition, the electro-diffusion ionic fluxes are inevitably induced in the vicinity of the three-phase contact line. These fluxes are necessary to support the ionic balances in this region. Depending on the experimental conditions (*e.g.*, bulk concentrations, type of the ionized groups) the effect can change within very large limits. The electro-diffusion ion fluxes are produced due to the local concentration and potential changes that are formed because of the initial

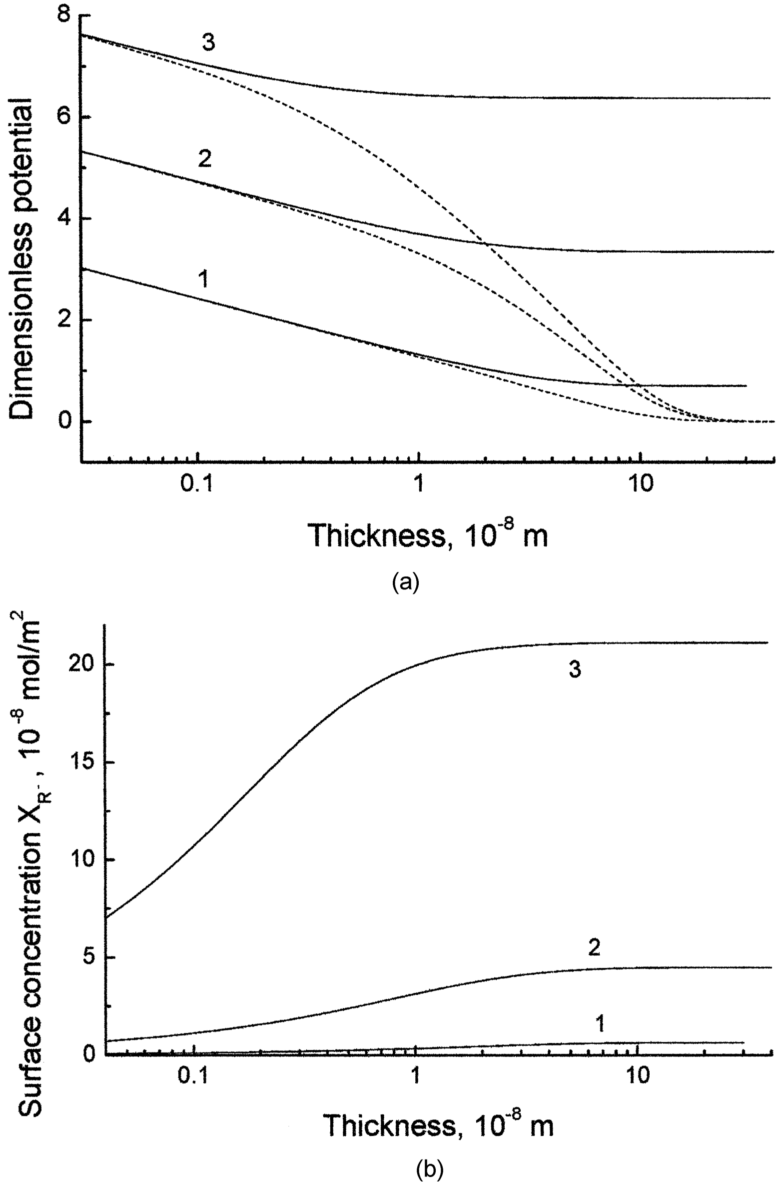


FIGURE 6 Dimensionless surface potential (continuous lines, Figure 6a), potential in the plane of symmetry (dashed lines, Figure 6a) and the surface concentration of charged groups, X_{R^-}, (Figure 6b) for pH = 4, $C^0_{KA} = 10^{-4}$ M, and different equilibrium constants: $K = 6540\,m^3/mol$ (1), $K = 65.4\,m^3/mol$ (2), and $K = 0.654\,m^3/mol$ (3).

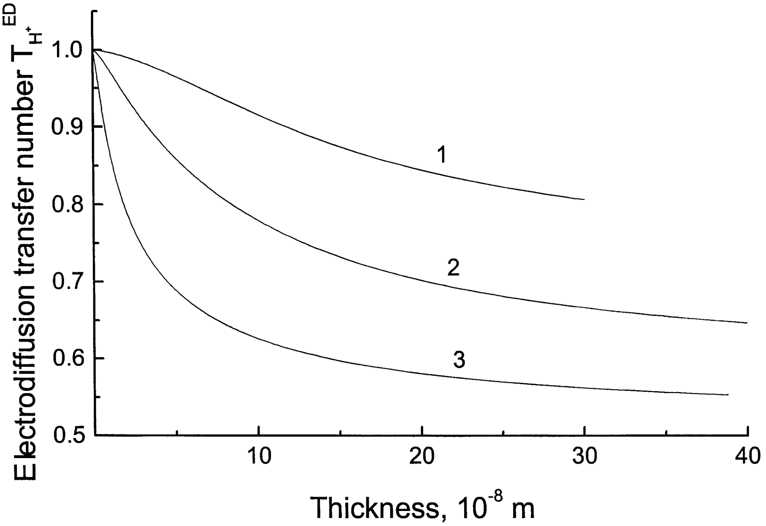


FIGURE 7 Electro-diffusion transfer number of potential-determining ions, $T_{H^+}^{ED}$, for $pH = 4$, $C_{KA}^0 = 10^{-4}$ M, and different equilibrium constants: $K = 6540\,m^3/mol$ (1), $K = 65.4\,m^3/mol$ (2), and $K = 0.654\,m^3/mol$ (3).

misbalance of the ion fluxes. The larger the electro-diffusion fluxes, the larger the concentration profiles producing these fluxes. The local changes in the solution composition give rise to changes in the monolayer state (charge and composition), thereby influencing the interaction energy between the monolayers. The most important effect is the deficit of the potential-determining ions near the three-phase contact line. As a result, the degree of monolayer ionization and the surface-charge density increases, while the contact angle and monolayer adhesion decrease.

It is obvious that, in case of smaller contact angles, the concentration polarization is stronger because the ionic transport to the three-phase contact line is more hindered. Thus, there is a positive feedback in the system that, at certain conditions, can lead to meniscus instability. When the contact angle decreases toward zero, water film entrainment begins and a stable LB film is not formed. The effect is defined by the deposition rate of the monolayer. The larger the monolayer velocity, the larger the ionic fluxes and the larger the deviations of the concentration and potential distributions from the equilibrium. At a certain critical monolayer velocity the deviations from the equilibrium become so large that the meniscus becomes unstable and the monolayer deposition becomes impossible.

As demonstrated above, the electro-diffusion ion fluxes and the deviations from the equilibrium distributions strongly depend on the properties of the monolayer and solution. When the electro-diffusion transfer number, $\mathrm{T}_{\mathrm{H}^+}^{\mathrm{ED}}$, is large, it can be expected that the deviations from the equilibrium distributions will increase faster as the velocity increases and therefore the critical deposition rate will be smaller. For example, it can be concluded from the presented results that, at small pH, the critical deposition rate will be large. The critical deposition rate will be very small at large indifferent electrolyte concentrations. These predictions are in good agreement with the experimental data [3].

CONCLUSIONS

Considering the deposition of an ionized Langmuir monolayer onto a solid substrate surface, one should take into account the effects of electrostatic interactions and the redistribution of ions in the close vicinity of the three-phase contact line. The counterions distributed within the overlapping diffuse layers should neutralize the surface charge before the monolayer deposition. To provide a sufficient rate of ion transfer, which is intended to neutralize the interfacial charge, the concentration and potential distributions deviate from equilibrium. As a consequence, during the deposition process the adhesion work and, hence, the contact angle are defined by the local ionic concentrations near the three-phase contact line. These concentrations depend on the substrate velocity and can substantially deviate from that under equilibrium conditions.

The concentration profiles and the electro-diffusion ions fluxes induced during the Langmuir wetting process are strongly dependent on the subphase composition and the monolayer properties. The effect of concentration polarization is more significant at large pH values or large indifferent electrolyte concentrations in the solution. For this case, the maximum deposition rate is smaller. For small pH and small indifferent electrolyte concentration, the effect is small, and therefore the maximum deposition rate is larger. The concentration polarization depends also on the type of ionized groups. For smaller equilibrium constants, it is always smaller.

The conclusions concerning the maximum deposition rate are supported by the experimental observations [2, 3]. Very large relaxation times, which are usually observed after stopping the deposition process, correlate with the proposed mechanism as well [6, 13, 14]. Thus, the presented analysis is in a good agreement with experiments.

REFERENCES

[1] Langmuir, I., *Science* **87**, 493–500 (1938).

[2] Roberts, G. G. (Ed.), *Langmuir-Blodgett Films* (Plenum Press, New York, 1990).

[3] Petrov, J. G., Kuhn, H., and Möbius, D., *J. Colloid Interface Sci.* **73,** 66–75 (1980).

[4] De Gennes, P. G., *Colloid Polymer Sci.* **264**, 463–465 (1986).

[5] Clint, J. H. and Walker, T., *J. Colloid Interface Sci.* **47**, 172–185 (1974).

[6] Petrov, J. G. and Angelova, A., *Langmuir* **8**, 3109–3115 (1992).

[7] Kovalchuk, V. I., Bondarenko, M. P., Zholkovskij, E. K., and Vollhardt, D., *J. Phys. Chem. B* **107**, 3486–3495 (2003).

[8] Kovalchuk, V. I., Zholkovskij, E. K., Bondarenko, M. P., and Vollhardt, D., *J. Phys. Chem. B* (2004) accepted.

[9] Kovalchuk, V. I., Zholkovskij, E. K., Bondarenko, M. P., and Vollhardt, D., *J. Phys. Chem. B* **105**, 9254–9265 (2001).

[10] Levich, V. G., *Physicochemical Hydrodynamics* (Prentice Hall, Englewood Cliffs, NY, 1962).

[11] Lakshminarayanaiah, N., *Transport Phenomena in Membranes* (Academic Press, New York, 1969).

[12] Israelachvili J. N., *Intermolecular and Surface Forces* (Academic Press, London, 1997).

[13] Gaines, G. L., Jr., *J. Colloid Interface Sci.* **59**, 438–446 (1977).

[14] Aveyard, R., Binks, B. P., Fletcher, P. D. I., and Ye, X., *Colloids Surf. A* **94**, 279–289 (1995).

APPENDIX

In the case of 1-1 electrolytes, the potential distribution within a liquid film with symmetrically charged interfaces is given by the equation [12]

$$\kappa\left|y-\frac{h}{2}\right| = \int_{\varphi}^{\varphi_0} \frac{d\varphi'}{\sqrt{2(\cosh\varphi' - \cosh\varphi_0)}}, \qquad \text{(A1)}$$

where φ_0 is the dimensionless electric potential in the symmetry plane ($y = h/2$) and $\kappa = \sqrt{\frac{2F^2\left(C^0_{HA}+C^0_{KA}\right)}{\varepsilon_0\varepsilon RT}}$ is the inverse Debye length. From Equation (A1) the potential can be presented in the form

$$\varphi = \varphi_0 + 2\ \ln\left\{\mathrm{sn}\left[\widetilde{K}(k) - \frac{\kappa}{2}\left|\frac{h}{2} - y\right| exp\left(-\frac{\varphi_0}{2}\right), k\right]\right\}, \qquad \text{(A2)}$$

where sn(t, k) is the elliptic function with the modulus $k = \exp\varphi_0$, $\widetilde{K}(k)$ is the quarter period of the elliptic function. The dimensionless interfacial potential (φ_S) is

$$\varphi_S = \varphi_0 + 2\ \ln\left\{\mathrm{sn}\left[\widetilde{K}(k) - \frac{\kappa h}{4}\ exp\left(-\frac{\varphi_0}{2}\right), k\right]\right\}. \qquad \text{(A3)}$$

The surface charge density (σ) is [12]

$$\sigma = -\left[4\varepsilon_0\varepsilon \mathrm{RT}\left(\mathrm{C}^0_{\mathrm{HA}} + \mathrm{C}^0_{\mathrm{KA}}\right)(cosh\,\varphi_S - cosh\,\varphi_0)\right]^{\frac{1}{2}}. \tag{A4}$$

On the other hand, from Equation (22) one obtains

$$\sigma = -\frac{\mathrm{FX_R}}{1 + \mathrm{KC}^0_{\mathrm{HA}}\mathrm{e}^{-\varphi_{\mathrm{S}}}}. \tag{A5}$$

The set of Equations (A3)–(A5) can be solved with respect to interfacial potential (φ_{S}), charge density (σ), and potential at the symmetry plane (φ_0) for the given film thickness, h, and the bulk concentrations $\mathrm{C}^0_{\mathrm{HA}}$ and $\mathrm{C}^0_{\mathrm{KA}}$. The obtained potentials, φ_{S} and φ_0 are substituted into Equations (A2) and (22) and, then, the potential distribution, φ(x,y) is substituted into Equation (21) to calculate the ions fluxes.