

Role of the Adsorption Phenomenon on the Ionic Equilibrium Distribution and on the Transient Effects in Electrolytic Cells

Giovanni Barbero,^{†,‡} Fernando C. M. Freire,^{*,†,§} Marco Scalerandi,[†] and Anca L. Alexe-Ionescu^{†,⊥}

Dipartimento di Fisica del Politecnico, Corso Duca degli Abruzzi 24, 10129 Torino, Italia, Instituto de Física, Universidade de São Paulo, P.O. Box 66318, São Paulo, 05389-970, SP, Brazil, Departamento de Física, Universidade Estadual de Maringá, Avenida Colombo 5790, 87020-900 Maringá, PR, Brazil, and Facultatea de Stiinte Aplicate, Universitatea Politehnica, din Bucuresti, Splaiul Independentei 313, RO-060042, Bucuresti, Romania

Received: April 12, 2006; In Final Form: July 26, 2006

We analyze the influence of the adsorption of ions at the interfaces on the transient phenomena occurring in an electrolytic cell submitted to a steplike external voltage. In the limit of small amplitude of the applied voltage, where the equation of the problem can be linearized, we obtain an analytical solution for the bulk and surface densities of ions and for the electrical potential. We also obtain, in this limit, the relaxation time for the transient phenomena.

I. Introduction

To extract information about the physical parameters from measurements on electrolytic cells submitted to an external electric field, the theoretical models used for the interpretation of the experimental data have to correctly take into account the occurring transient effects.^{1,2} Several studies have indeed been devoted to analyze the response of poorly conducting electrolytic cells to a steplike potential,^{3–5} in the Gouy–Chapman approximation,⁶ in which the ions are assumed to be dimensionless. Such approximation is definitely valid for nematic liquid crystals, that is, insulating materials for which the electrical conduction is mainly of ionic origin.⁷ In this case, the knowledge of the ionic distribution, both during the transient and at equilibrium, is fundamental to correctly interpret the physical results. For instance, the optical response of electrically controlled nematic liquid crystal strongly depends on the ionic charge dissolved in the liquid crystal.⁸ Furthermore, experimental evidence of the importance of the ionic charge on the anchoring energy of the interface solid substrate–nematic liquid crystal has been recently reported,⁹ suggesting an interpretation of its dependence on the sample thickness¹⁰ and on the voltage applied to the cell.¹¹ Finally, the presence of the ions can also play a role in the total electric conduction^{12,13} or in the measurements and in the theory presented in ref 14. The aim of this contribution is to extend previous analyses to take into account the adsorption phenomenon at the limiting surfaces.

To simplify the problem as much as possible, we suppose that, in the absence of an external field, the liquid is locally and globally neutral. In this case, in the absence of an applied difference of potential, the electric potential in the cell is position independent, and the electric field is zero. This hypothesis implies that the adsorption energy of the positive and negative ions with the limiting surfaces are the same. Since the adsorption

energy can be identified with the electrostatic interaction energy of a given ion with its image in the substrate, the ions are supposed to have the same electrical charge, q , and geometrical dimensions, l .^{15,16} As in ref 3, we assume furthermore that (1) the ions are dispersed in an insulating isotropic liquid whose dielectric constant is ϵ ; (2) the external voltage is a step of amplitude V_0 applied at $t = 0$; (3) the electrodes are perfectly blocking, but they can adsorb ions; (4) the ionic mobility, μ , and the diffusion coefficient, D , are not independent, and $\mu/D = q/(K_B T)$, where K_B is the Boltzmann constant and T is the absolute temperature; (5) the density of ions, in thermodynamical equilibrium and in the absence of limiting surfaces and external electric field is N .

The goal of our paper is to solve the fundamental equations governing the redistribution of the ions in a liquid submitted to an external field, and determine the relevant relaxation time in the presence of the adsorption–desorption phenomena at the limiting surfaces. This problem is of some importance from the fundamental and experimental point of view.^{17–19} One example is the determination of the frequency of a sinusoidal voltage at which the motion of ions starts to play a role in the dynamics of the system.^{20–22}

In our analysis, we assume that the adsorption–desorption process is well described by the kinetic equation following from the model of Langmuir,²³ which is based on the following hypotheses: (1) all the adsorbing sites are equivalent, (2) the surface is uniform, (3) only one monolayer of adsorbed particles is possible, and (4) the probability of a particle being adsorbed is independent of the surface density of particles already adsorbed. Assumptions 1, 2, and 3 are verified for the system considered by us. In the case in which the adsorbed particles are ions, assumption 4 is questionable. However, since we work in the limit of small applied voltage and small density of ions in thermodynamical equilibrium, in the linear analysis, the dependence of the adsorption–desorption coefficients on the surface density of adsorbed particles can be neglected. It follows that the Langmuir model for the adsorption–desorption is expected to work well for the system considered in our analysis. A more rigorous analysis, valid in the case of large

* Corresponding author. E-mail: fernando.freire@polito.it.

[†] Corso Duca degli Abruzzi 24.

[‡] Universidade de São Paulo.

[§] Universidade Estadual de Maringá.

[⊥] Universitatea Politehnica.

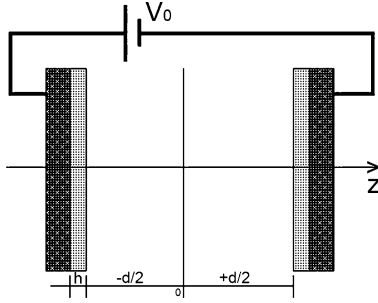


Figure 1. Schematic representation of the electrolytic cell and dielectric layers.

adsorption of ions, requires a description of the adsorption–desorption phenomenon by means of the model proposed by Temkin.²³ An analysis of the influence of an external voltage on an electrolytic cell using the Temkin model was proposed long ago by Delahay et al.,^{24–26} who, however, did not consider the influence of a dielectric layer between the electrodes and the cell.

The fundamental equations of the problem are discussed in section II. The case in which the applied potential is small with respect to the thermal voltage, $V_T = K_B T/q$, where the equations can be linearized, is considered in section III. We determine the profiles of the bulk densities of ions and of the electrical potential across the cell. In the same section, we also obtain the eigenvalue equation determining the relaxation times of the redistribution of ions under investigation. In section IV, we compare the analytical solution with the results obtained from a numerical analysis of the basic equations of the problem. The agreement between the analytical and numerical results, in the low range of applied voltage, is good. In section V, we discuss the limitation of our analysis in which the surface layer of Stern is neglected.^{1,2} There we show that, in the case in which the linearized analysis works well, there is no need to introduce the layer of Stern connected with the finite dimension of the ions. The conclusions of the paper are presented in section VI.

II. Theoretical Background

In our analysis, we assume that the sample under investigation is in the shape of a slab. The Cartesian reference frame used in the description has the z -axis normal to the bounding surfaces and the origin in the middle of the sample. In this framework the physical quantities entering in the problem depend on z and t , where t is the time. Let us consider an electrolytic cell of thickness d (with dielectric constant ϵ) bounded by two identical dielectric layers of thickness h and dielectric constant ϵ_h (see Figure 1). We indicate by n_p and n_m the bulk densities of the positive and negative ions (p stands for plus, and m stands for minus), and indicate by $\sigma_p(\pm d/2)$ and $\sigma_m(\pm d/2)$ the surface densities of positive and negative ions at the surfaces at $z = \pm d/2$.

In the absence of the external field and of the adsorbing surfaces, $n_p = n_m = N$. When the surfaces are present and the external field is absent due to the symmetries of the problem, we still have $n_p = n_m = n_{eq}$ when the equilibrium has been reached. But now, n_{eq} is different from N since a part of the ions has been adsorbed by the surfaces. In this condition, the surface densities of adsorbed ions are indicated by $\sigma_p = \sigma_m = \sigma_{eq}$.

When the external field is applied, at $t = 0$, there is a migration of ions. In this case, at equilibrium, $n_p(z, t) \rightarrow n_{p,eq}(z)$, $n_m(z, t) \rightarrow n_{m,eq}(z)$, $\sigma_p(\pm d/2, t) \rightarrow \sigma_{p,eq}(\pm d/2)$, and $\sigma_m(\pm d/2, t) \rightarrow \sigma_{m,eq}(\pm d/2)$. The phenomenon is governed by the equations of

continuity for the two types of ions and the equation of Poisson, giving the actual electric potential profile when the ions are present.

The current density of ions is

$$j_r = -D \left(\frac{\partial n_r}{\partial z} \pm \frac{q n_r}{K_B T} \frac{\partial V}{\partial z} \right) \quad (1)$$

where $r = p$ or m , and the sign is $+$ for $r = p$ and $-$ for $r = m$. The equation of continuity is

$$\frac{\partial n_r}{\partial t} = D \frac{\partial}{\partial z} \left(\frac{\partial n_r}{\partial z} \pm \frac{q}{K_B T} n_r \frac{\partial V}{\partial z} \right) \quad (2)$$

The equation of Poisson is^{3,22}

$$\frac{\partial^2 V}{\partial z^2} = -\frac{q}{\epsilon} (n_p - n_m) \quad (3)$$

We also assume for the kinetic equation at the adsorbing surfaces that proposed by Langmuir:^{27,28}

$$\frac{d\sigma_r}{dt} = k n_r - \frac{1}{\tau} \sigma_r \quad (4)$$

where k is the adsorption coefficient, and τ is a parameter, having the dimension of time, connected with the desorption phenomenon.

The boundary conditions for the ion density, in the presence of the adsorption phenomenon, are given as

$$j_r = \pm \frac{d\sigma_r}{dt} \quad (5)$$

where the sign is $-$ for $z = -d/2$ and $+$ for $z = d/2$. This equation satisfies the conservation of the number of ions:

$$\sigma_r(-d/2, t) + \sigma_r(d/2, t) + \int_{-d/2}^{d/2} n_r(z, t) dz = N d \quad (6)$$

as it follows from eq 2. Using eq 4, the boundary conditions (eq 5) become

$$D \left(\frac{\partial n_r}{\partial z} \pm \frac{q}{K_B T} n_r \frac{\partial V}{\partial z} \right) = k n_r - \frac{1}{\tau} \sigma_r$$

$$-D \left(\frac{\partial n_r}{\partial z} \pm \frac{q}{K_B T} n_r \frac{\partial V}{\partial z} \right) = k n_r - \frac{1}{\tau} \sigma_r$$

for $z = -d/2$ and $z = d/2$, respectively.

The boundary conditions for the potential should account for the presence of the dielectric layers. The potential difference at the electrodes should be equal to the applied potential V_0 . We assume that the voltage in the center of the cell is the reference voltage. Therefore $V(\pm d/2 \pm h) = \pm V_0/2$, and the electric field is directed along $-z$. In the following, we indicate this by $-E$, where $E > 0$. Furthermore, the electric field should satisfy the proper continuity equations at the cell–dielectric layer interface:

$$V_0 = -2hE_h(t) - \int_{-d/2}^{d/2} E(z, t) dz$$

$$\epsilon E(-d/2, t) = \epsilon_h E_h(t) + q\sigma \quad (7)$$

where $\sigma = \sigma_p - \sigma_m$, and $E_h(t)$ is the electric field inside the dielectric layer. Since free charges are not present within the

dielectric layers, the electric field E_h is position independent. It follows that

$$\begin{aligned} V_h(t) &= V(-d/2, t) = -V_0/2 - hE_h(t) \\ &= -\frac{V_0}{2}\gamma + q\sigma\frac{h\gamma}{\epsilon_h} + \\ &\quad q\frac{h\gamma}{d\epsilon_h} \int_{-d/2}^{d/2} dz' \int_{-d/2}^{z'} n(z'', t) dz'' \end{aligned} \quad (8)$$

where $n = n_p - n_m$ and $\gamma = d\epsilon_h/(d\epsilon_h + 2h\epsilon)$.

The initial conditions ($t = 0$) can be obtained from eqs 4 and 6:

$$2\sigma_{eq} + n_{eq}d = Nd \quad (9)$$

and

$$kn_{eq} - \frac{1}{\tau}\sigma_{eq} = 0 \quad (10)$$

From eqs 9 and 10, it follows that

$$\begin{aligned} \sigma_{eq} &= \frac{1}{2}Nd \frac{1}{1 + d/(2k\tau)} \\ n_{eq} &= N \frac{d/(2k\tau)}{1 + d/(2k\tau)} \end{aligned} \quad (11)$$

for the surface and the bulk densities of ions, in the absence of the external electric field.

III. Linear Analysis

A. Linearized Equations. We assume that the presence of a weak external electric field produces only a small perturbation on the distribution of ions (see ref 21, where the limit of such an assumption is discussed). By stating that

$$\begin{aligned} n_r(z, t) &= n_{eq} + \delta n_r(z, t) \\ \sigma_r(t) &= \sigma_{eq} + \delta\sigma_r(t) \end{aligned} \quad (12)$$

where $\delta n_r(z, t) \ll n_{eq}$, it follows that

$$\frac{q}{K_B T} n_r \frac{\partial V}{\partial z} \sim \frac{q}{K_B T} n_{eq} \frac{\partial V}{\partial z} \quad (13)$$

Therefore eqs 2 and 3 become

$$\frac{\partial(\delta n_r)}{\partial t} = D \frac{\partial}{\partial z} \left(\frac{\partial(\delta n_r)}{\partial z} \pm \frac{q}{K_B T} n_{eq} \frac{\partial V}{\partial z} \right) \quad (14)$$

$$\frac{\partial^2 V}{\partial z^2} = -\frac{q}{\epsilon} (\delta n_p - \delta n_m) \quad (15)$$

The boundary conditions simplify as

$$D \left(\frac{\partial(\delta n_r)}{\partial z} \pm \frac{q}{K_B T} n_{eq} \frac{\partial V}{\partial z} \right) = k\delta n_r(t) - \frac{1}{\tau}\delta\sigma_r \quad (16)$$

$$-D \left(\frac{\partial(\delta n_r)}{\partial z} \pm \frac{q}{K_B T} n_{eq} \frac{\partial V}{\partial z} \right) = k\delta n_r(t) - \frac{1}{\tau}\delta\sigma_r \quad (17)$$

for $z = -d/2$ and $z = d/2$, respectively.

To find the solution, we separate the unknowns of our analysis in transient and equilibrium (for $t \rightarrow \infty$) components as

$$\delta n_r(z, t) = \delta n_r^l(z, t) + \delta n_r^e(z) \quad (18)$$

$$V(z, t) = V^l(z, t) + V^e(z) \quad (19)$$

$$\delta\sigma_r(\pm d/2, t) = \delta\sigma_r^l(\pm d/2, t) + \delta\sigma_r^e(\pm d/2) \quad (20)$$

B. Equilibrium Components of the Solution. The transient components have to vanish for $t \rightarrow \infty$. Therefore, by substituting eqs 18, 19, and 20 into eqs 14/15 and 16/17, we obtain that the equilibrium components of the solution satisfy the equations

$$\frac{\partial(\delta n_r^e)}{\partial z} \pm \frac{q}{K_B T} n_{eq} \frac{\partial V^e}{\partial z} = 0 \quad (21)$$

$$\frac{\partial^2 V^e}{\partial z^2} = -\frac{q}{\epsilon} (\delta n_p^e - \delta n_m^e) \quad (22)$$

and

$$k\delta n_r^e - \frac{1}{\tau}\delta\sigma_r^e = 0 \quad (23)$$

for $z = \pm d/2$.

From eq 21, we obtain

$$\delta n_r^e(z) = \mp \frac{q}{K_B T} n_{eq} V^e(z) \quad (24)$$

By substituting eq 24 into eq 22, we get

$$\frac{d^2 V^e}{dz^2} = 2 \frac{n_{eq} q^2}{\epsilon K_B T} V^e(z) \quad (25)$$

The quantity

$$\lambda_{eq}^2 = \frac{\epsilon K_B T}{2n_{eq} q^2} \quad (26)$$

is the effective length of Debye² when the adsorption phenomenon takes place.

The solution of eq 25 is

$$V^e(z) = C_1 \sinh(z/\lambda_{eq}) \quad (27)$$

It follows that

$$\delta n_r^e(z) = \mp \frac{qn_{eq}}{K_B T} C_1 \sinh(z/\lambda_{eq}) \quad (28)$$

$$\delta\sigma_r^e = k\tau\delta n_r^e(-d/2) \quad (29)$$

Imposing the boundary conditions for the applied potential and using a perturbative solution as shown in Appendix 1, we can determine the coefficient C_1 . Note that, in the case in which $h = 0$, we have the exact solution

$$C_1(h = 0) = \frac{V_0}{2 \sinh(d/2\lambda_{eq})} \quad (30)$$

C. Relaxation of the Transient Components. Using eqs 14–17 and 18–20, we obtain for the transient components the equations

$$\frac{\partial(\delta n_r^t)}{\partial t} = D \frac{\partial}{\partial z} \left(\frac{\partial(\delta n_r^t)}{\partial z} \pm \frac{q}{K_B T} n_{eq} \frac{\partial V^t}{\partial z} \right)$$

$$\frac{\partial^2 V^t}{\partial z^2} = -\frac{q}{\epsilon} (\delta n_p^t - \delta n_m^t) \quad (31)$$

and the boundary conditions

$$D \left(\frac{\partial(\delta n_r^t)}{\partial z} \pm \frac{q}{K_B T} n_{eq} \frac{\partial V^t}{\partial z} \right) = k \delta n_r^t - \frac{1}{\tau} \delta \sigma_r^t \quad (32)$$

$$-D \left(\frac{\partial(\delta n_r^t)}{\partial z} \pm \frac{q}{K_B T} n_{eq} \frac{\partial V^t}{\partial z} \right) = k \delta n_r^t - \frac{1}{\tau} \delta \sigma_r^t \quad (33)$$

for $z = \pm d/2$.

We look for solutions of the bulk equations of the form

$$\delta n_r^t(z, t) = \psi_r(z) e^{-at}, \quad V^t(z, t) = \phi(z) e^{-at} \quad (34)$$

where $a > 0$, since we are looking for solutions vanishing for $t \rightarrow \infty$. By taking into account eq 34, from the kinetic equation at the interface

$$\frac{d\delta\sigma_r^t(t)}{dt} = k\delta n_r^t(t) - \frac{1}{\tau} \delta\sigma_r^t(t), \text{ for } z = \pm d/2 \quad (35)$$

we obtain

$$\delta\sigma_r^t(t) = M_{\pm} e^{-t/\tau} + \frac{k\tau}{1-a\tau} \psi_r(\pm d/2) e^{-at} \quad (36)$$

where M_{\pm} are integration constants to be determined by the boundary conditions. By substituting eqs 34 and 36 into eqs 32 and 33 we obtain

$$\left(\psi_r' \pm \frac{qn_{eq}}{K_B T} \phi' \right) e^{-at} = -\frac{k}{D} \frac{a\tau}{1-a\tau} \psi_r e^{-at} - \frac{1}{D\tau} M_{\pm} e^{-t/\tau}$$

$$\left(\psi_r' \pm \frac{qn_{eq}}{K_B T} \phi' \right) e^{-at} = \frac{k}{D} \frac{a\tau}{1-a\tau} \psi_r e^{-at} + \frac{1}{D\tau} M_{\pm} e^{-t/\tau} \quad (37)$$

for $z = -d/2$ and $z = d/2$, respectively. From eqs 37, which have to be valid for all t , it follows that $M_+ = M_- = 0$.

From eqs 31, by taking into account the symmetry of the problem, we get

$$\psi_r(z) = \pm B_1 \sinh(\nu_1 z) + B_3 \sinh(\nu_3 z) \quad (38)$$

$$\phi(z) = A_1 z - \frac{2q}{\epsilon \nu_1^2} B_1 \sinh(\nu_1 z) \quad (39)$$

where

$$\nu_1 = (1/\lambda_{eq}) \sqrt{1 - (a/D)\lambda_{eq}^2}, \text{ and } \nu_3 = i\sqrt{a/D} \quad (40)$$

The boundary conditions for the potential are

$$\phi(-d/2, t) e^{-at} - V^e(-d/2) = V_h(t) \quad (41)$$

Substituting eq 39 into eq 41, we obtain

$$A_1 = \frac{2B_1}{d} \left[-\frac{2q}{\epsilon \nu_1^2} X_d - \frac{2qk\tau}{1-a\tau} \frac{h\gamma}{\epsilon_h} X_d + \frac{2qh\gamma}{d\epsilon_h} \left(\frac{2X_d}{\nu_1^2} + \frac{dY_d}{\nu_1} \right) \right]$$

where $X_d = -\sinh(d/(2\lambda_{eq}))$ and $Y_d = \cosh(d/(2\lambda_{eq}))$.

By imposing the boundary conditions of eqs 37, we obtain $B_3 = 0$ and

$$\left(1 - \frac{k a \tau}{D(1-a\tau)} \nu_1^2 \lambda_{eq}^2 \frac{d}{2} + \frac{h\gamma\epsilon}{d\epsilon_h} \left(\frac{dk\tau\nu_1^2}{1-a\tau} - 2 \right) \right) =$$

$$\coth \left(-\nu_1 \frac{d}{2} \right) \left(-1 + \nu_1^2 \lambda_{eq}^2 + \frac{2h\gamma\epsilon}{d\epsilon_h} \right) \nu_1 \frac{d}{2} \quad (42)$$

which is the equation for the eigenvalues of the present problem.

D. Discussion on the Relaxation Times of the Transient Components. Equation 42 has an infinite number of solutions, corresponding to an infinite number of relaxation times of the transient component of the solution, defined as $t_d = 1/a$. However, not all of them are physically meaningful. It follows that the solution of the problem is given by the superposition of solutions in the form of eqs 34 with only the acceptable values of ν_1 .

The first solution is easily found to be $\nu_1 = 0$, that means $a = \lambda_{eq}^2/D$. However, this solution is not interesting because it corresponds to a case in which there is no separation of charges. More important are the other solutions, which can be found numerically. Note that solutions with t_d smaller than τ , which is the typical time scale of the adsorption events, are also not interesting. In fact, the transient in the bulk cannot be faster than the adsorption phenomenon at the limiting surfaces.

A general property of the solution is that, in the limit of small amplitude of the applied voltage, t_d is independent of V_0 .

IV. Results and Discussion

We consider here an electrolytic cell of thickness $d = 25 \mu\text{m}$ bounded by two dielectric layers of thickness h (varied in the numerical experiments). We assume monovalent ions are distributed in the liquid, with density $N = 4.2 \times 10^{20} \text{ m}^{-3}$ and diffusion coefficient $D = 8.2 \times 10^{-12} \text{ m}^2/\text{s}$. Temperature is considered to be $T = 300 \text{ K}$. The cell has dielectric constant $\epsilon = 6.7\epsilon_0$, while that of the dielectric layer is $\epsilon_h = 2.1\epsilon_0$. The parameters used correspond to that of a doped liquid crystal.²⁹ The results are expected to be qualitatively similar in the case of a much lower concentration of ions. Finally, we have assumed that adsorption occurs at the surfaces separating the cell from the dielectric layer, with $k = 10^{-6} \text{ (m/s)}$ and $\tau = 0.01 \text{ s}$, unless otherwise specified. Furthermore, the potential V_0 is chosen in the range from 0.1 to 25 mV.

The analytical solutions are found using the linearized analysis reported in the previous section for both the transient and equilibrium components. Since linearization is valid only when the applied potential is small, we have also performed numerical simulations to study the dynamics of the system. To this purpose we have discretized eq 2 and eq 3 using a finite difference forward scheme with space step $l = 0.05 \mu\text{m}$. The space step has been chosen to be small enough to warrant convergence of the numerical scheme. In the meantime, l is much larger than the typical size of ions, so that the assumption of dimensionless ions is reasonable. Details about the numerical solution can be found elsewhere.^{30,31}

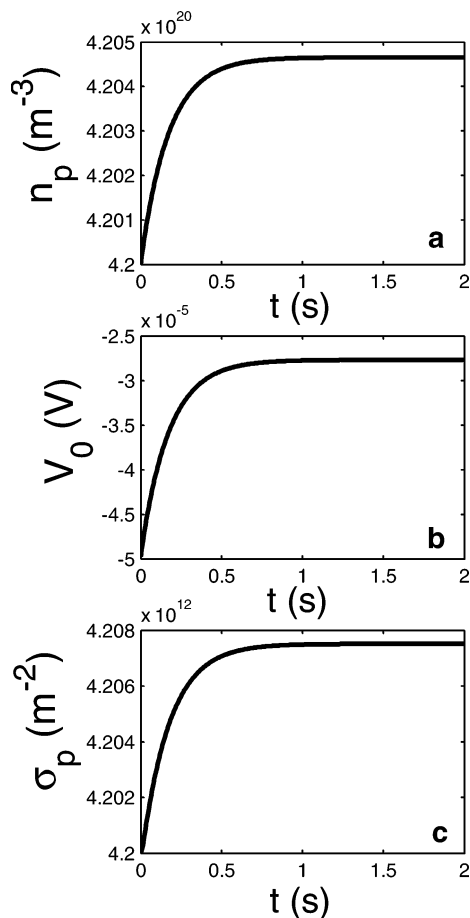


Figure 2. (a) Density of positive ions close to the surface $z = -d/2 + l/2$ vs time; (b) electrical potential close to the surface $z = -d/2 + l/2$ vs time; (c) surface density of adsorbed positive ions at the surface in $z = -d/2$.

As mentioned before, the response of the system to a steplike potential consists of a transient component that decays exponentially toward an equilibrium state, as shown as an example in Figure 2. We plot the temporal evolution of $n_p(\zeta, t)$, $V(\zeta, t)$ in $\zeta = -d/2 + l/2$ and that of $\sigma_p(-d/2, t)$, for $V_0 = 0.1$ mV and $h = 0$. The applied potential causes the accumulation of ions close to the surface, which is responsible for the generation of an electric field opposite to the applied one. As a consequence, the electrical potential in the bulk diminishes with increasing time, as expected. All quantities, after a transient (of exponential form), reach a stationary condition, with equilibrium values in agreement with the ones obtained from the linear analysis. Of course, the agreement becomes poorer upon increasing the applied potential, albeit the qualitative behavior (exponential transient followed by a stationary condition) is always the same, at least for the potential range considered here.

A. Behavior for $h = 0$. 1. Equilibrium Components. In Figure 3, we compare the analytical and numerical predictions for $\delta\sigma^e(-d/2)$ as a function of the adsorption parameters k and τ . We have considered a low voltage ($V_0 = 0.1$ mV). The agreement between the numerical and analytical solutions is very good. The equilibrium density of ions increases very rapidly upon increasing the adsorption rate and/or decreasing the desorption rate.

However, as expected, the agreement is poorer upon increasing the applied potential, being that the linear approximation no longer valid, as shown in Figure 4. Here, the net density of

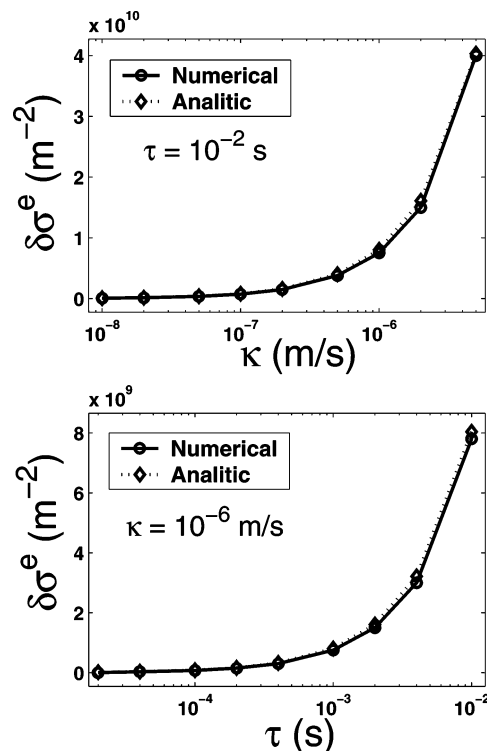


Figure 3. Analytical and numerical predictions of the net density of ions at equilibrium close to the layer surface in the case where $h = 0$. Behavior is shown as a function of the adsorption parameters.

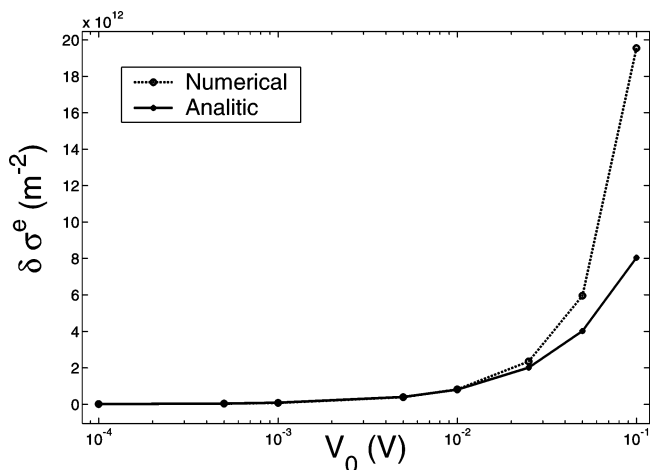


Figure 4. Analytical and numerical predictions of the net surface density of adsorbed ions at equilibrium in the case where $h = 0$. Behavior is shown as a function of the applied voltage.

ions adsorbed on the left surface of the layer ($\delta\sigma^e$) is reported as a function of the applied potential V_0 for $k = 10^{-6}$ (m/s) and $\tau = 10^{-2}$ s.

2. Transient Components. The decay time t_d of the transient components as a function of the adsorption parameters k and τ is analyzed in Figures 5 and 6, respectively, for different values of the applied potential: $V_0 = 0.1, 1, 10$ and 25 mV. As expected, for small values of V_0 , the decay time does not depend on the amplitude of the potential. In this case, the agreement with the analytical results from eq 42 is very good. However, already at $V_0 = 10$ mV, the linearized analysis stops being reliable, even though the dependence of the decay time from k and τ remains qualitatively the same. At larger values of the applied potential, the transient part of the solution is more

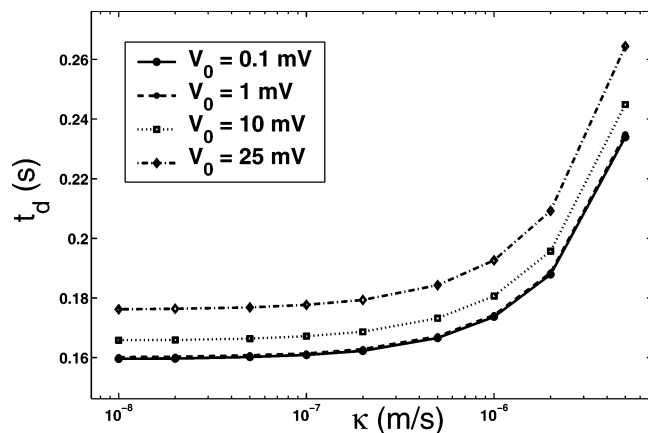


Figure 5. Decay time vs adsorption coefficient for $\tau = 10^{-2}$ s and $V_0 = 0.1, 1, 10, 25$ mV. The analytical solutions coincide perfectly with the curve at $V_0 = 0.1$ mV and do not depend on V_0 .

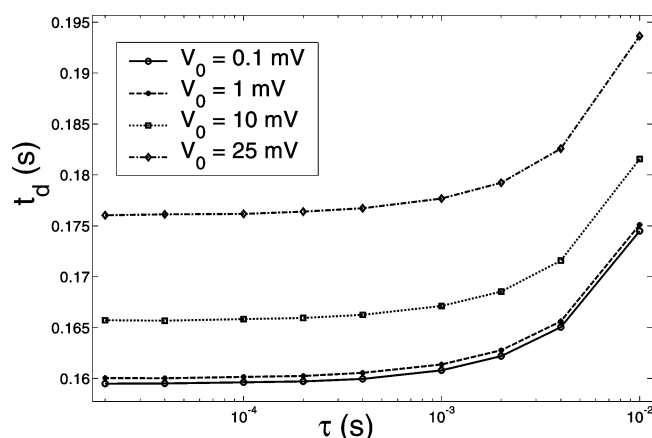


Figure 6. Decay time vs the inverse desorption coefficient with a fixed value for $k = 10^{-6}$ (m/s), and $V_0 = 0.1, 1, 10, 25$ mV.

complex than a single-exponential decay. This part will not be further investigated here, but the results are similar to those obtained in the absence of adsorption/desorption phenomena as reported in ref 4. Note that the decay time in the presence of adsorption phenomena is much larger than that expected when $k = 0$ (m/s).

B. Behavior for $h \neq 0$. 1. Equilibrium Components. As shown in Appendix 1, the analytic solution for the equilibrium components is given only in implicit form and can be calculated iteratively up to the desired accuracy. In Figure 7 we analyze the behavior of the electrical potential and of the net density of ions close to the surface ($\zeta = -d/2 + l/2$) and of the net density of adsorbed ions as a function of the thickness of the dielectric layer (h). The plot indicates that, upon increasing the number of iterations in the calculation of C_1 up to 15 iterations (Appendix 1), the agreement between the numerical and analytical solutions becomes better and better, at least for small values of h .

Upon increasing the thickness of the dielectric layer, the analytical solution, even after increasing the accuracy order in the determination of C_1 , no longer agrees well with the numerical results. Therefore, to analyze the behavior of the system for large values of h , in Figure 8 we consider only the numerical results. The plot of the density of adsorbed ions as a function of h indicates that the presence of the dielectric layer contributes to a consistent reduction of the number of ions participating to the dynamics. Indeed this is to be expected, since the presence of a dielectric layer causes a reduction in the

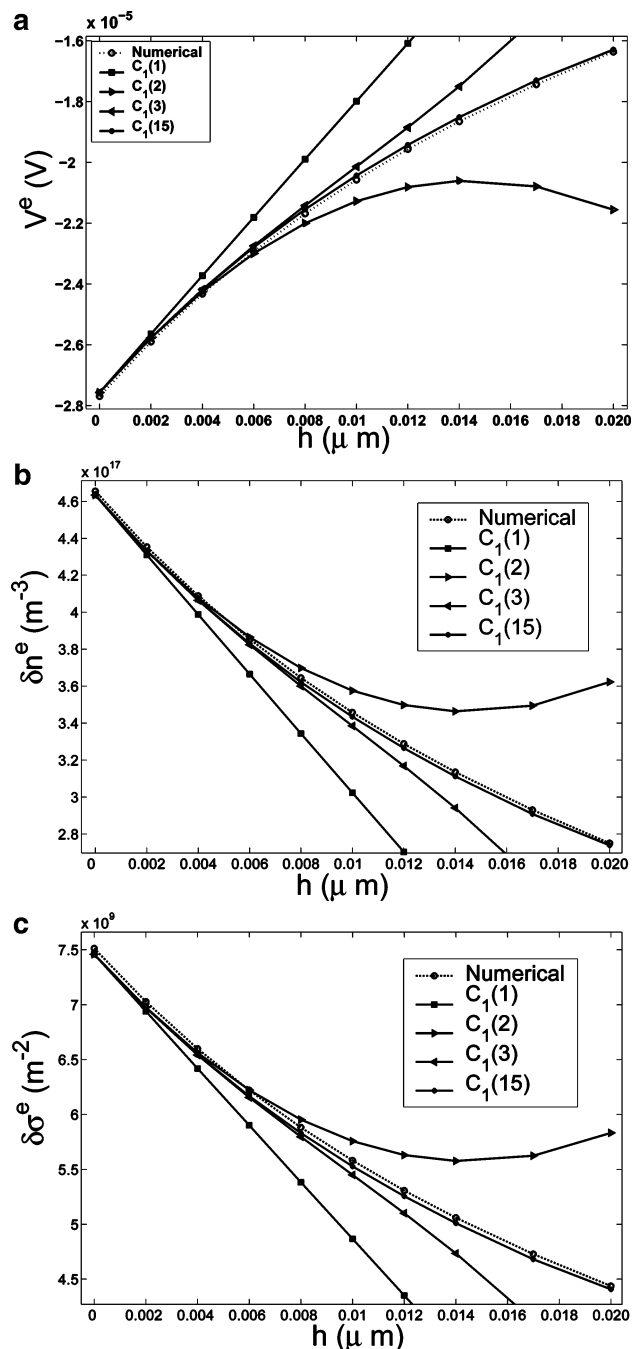


Figure 7. Numerical and analytical solutions for the equilibrium components of the electrical potential (a) and the net density of adsorbed ions (b) close to the surface as a function of h . The net density of adsorbed ions is reported in plot c. The solutions labeled with $C_1(n)$ denote the analytical solution calculated using n iterations for the determination of C_1 , here $V_0 = 0.1$ mV. Here, $k = 10^{-6}$ m/s and $\tau = 10^{-2}$ s.

amplitude of the electric field effectively applied to the electrolytic cell.

2. Transient Components. In Figure 9, we report the decay time (of both the analytical and the numerical solutions) as a function of h for different values of the applied potential and for $k = 10^{-6}$ (m/s) and $\tau = 0.01$ s. The relaxation to the equilibrium solution is faster (smaller decay time) for large values of h , in agreement with the fact that fewer ions participate in the dynamics. Likewise, the decay time increases with the amplitude of the applied potential. Also, we observe a good agreement between the analytical and numerical solutions for

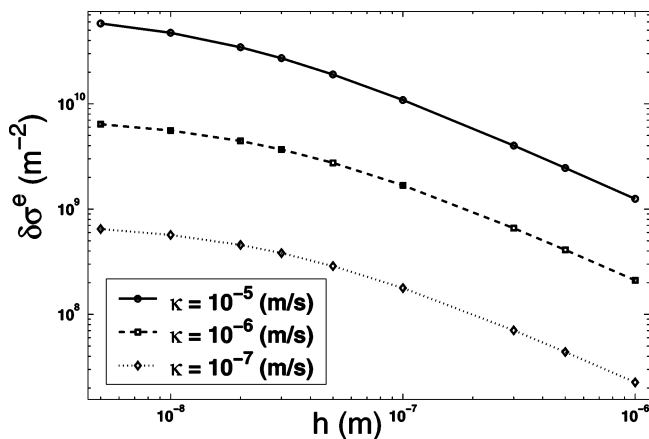


Figure 8. Numerical solution for the net density of adsorbed ions as a function of h for large values of the dielectric thickness h and different values of the adsorption coefficient k , here $V_0 = 0.1$ mV.

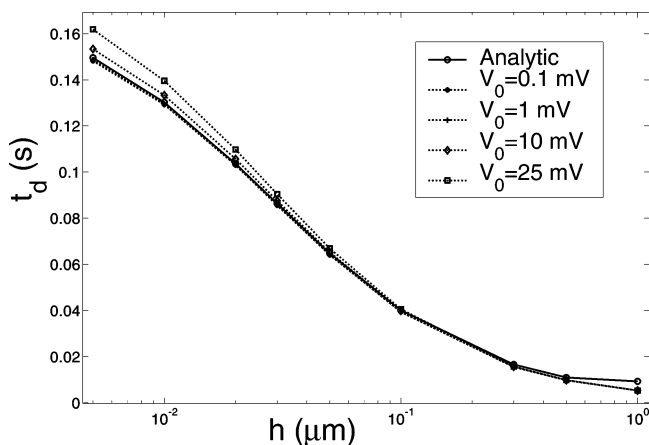


Figure 9. Decay time as a function of h for different values of the applied potential. A comparison between the analytical and numerical solutions is shown.

small amplitudes of the potential effectively applied to the cell, i.e., for small V_0 and/or for large h . On the contrary, the two solutions differ (but not in their qualitative behavior) when the potential becomes larger. For small h , discrepancies are already visible for $V_0 = 10$ mV.

Finally, in Figure 10, the decay time is reported as a function of h for $V_0 = 0.1$ mV and different values of the adsorption parameters (as reported in the plot). The decay time is sensitive to the adsorption parameters only for low values of the dielectric layer thickness. Upon increasing h , adsorption becomes less and less important for the determination of the transient solution. Also, the agreement between the numerical and the analytical solutions becomes poorer upon increasing h and/or increasing the adsorption parameters.

V. The Gouy–Chapman Approximation

As stated in the Introduction, our analysis is performed in the framework of the Gouy–Chapman model.⁶ It is therefore necessary to comment on the limit of validity of such an approximation.

According to the Gouy–Chapman model, the liquid containing ions is assumed to be a pure insulator and is described by a dielectric constant, which is constant across the sample under investigation. The electrodes are perfectly blocking, and the surfaces are assumed to adsorb the positive and negative ions with the same adsorption energy. This is introduced in the model

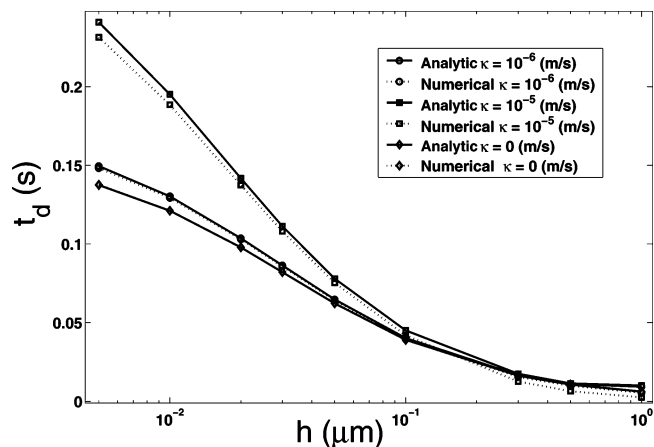


Figure 10. Decay time as a function of h for different values of the adsorption parameters. A comparison between the analytical and numerical solutions is shown. For the case where $k = 0$ and $\tau = 0$, the analytic and numerical curves coincide perfectly for small values of h . Here, $\tau = 10^{-2}$ s.

by assuming the same adsorption and desorption coefficients for the positive and negative ions. The model is built in the framework of the Poisson–Boltzmann theory. The basic assumptions of this theory are that (i) the ions can be considered dimensionless point charges; (ii) the surface charge is assumed to be uniformly smeared over the surface; and (iii) the electrolyte solution is described as a continuum with a dielectric constant equal to that of the pure liquid.

As discussed in ref 6, a serious defect of the Gouy–Chapman theory is that, in treating the ions as point charges, it can lead to absurdly high values of the charge concentration in the immediate neighborhood of the interface. This limitation is particularly important when one considers the presence of an external field. In fact, in this case, the electrical force pushes the ions close to the electrode of opposite electrical charge, and, for large electric field, the ionic bulk density of ions close to the electrodes can be larger than $n_{\max} = 1/l^3$, where l is a typical dimension of the ion, as stated above.

This results are obviously unphysical, and it is a consequence of the hypothesis that the ions are assumed to be dimensionless. However, for the case considered by us, the Gouy–Chapman approximation is a good approximation for a few reasons listed below.

First, we consider the initial conditions, that is, in the absence of the external field. The values for the physical parameters describing the adsorption–desorption phenomena are in the range of 10^{-8} – 10^{-5} m/s for k , and 10^{-5} – 10^{-2} s for τ , in agreement with the estimation reported in ref 27. It follows that $k \cdot \tau$ is small with respect to the thickness of the sample d considered in our investigation. Consequently, from eq 11 we know that $\sigma_{\text{eq}} \sim Nk\tau$ and $n_{\text{eq}} \sim N$. This means that the presence of the adsorbing surfaces only slightly perturbs the bulk density of ions near the electrodes. Furthermore, the surface density of adsorbed ions is equivalent to a bulk density of ions given by $\rho = \sigma_{\text{eq}}/l$, where l is of the order of the dimension of the ion. The condition $\rho \ll n_{\max} = 1/l^3$ gives $N \ll N_{\max} = 1/(k\tau l^2)$. By assuming that $k \cdot \tau \sim 10^{-7}$ m is the maximum value for the product of the desorption and desorption coefficients, and $l \sim 0.5 \times 10^{-9}$ m,⁶ we get $N \ll N_{\max} = 4 \times 10^{25}$ m⁻³. Since, in our analysis, we have considered for N the typical bulk density of ions in a doped liquid crystal, the condition $N \ll N_{\max}$ is satisfied. It follows that, in the absence of the external field, for the set of physical parameters used in our analysis, the Gouy–Chapman approximation works well.

In the presence of an external field, we can obtain an estimation of the surface density and of the bulk density of ions in front of the electrode. If the thickness of the surface layer is $h = 0$, we have

$$\delta n_p^e(-d/2) = \frac{1}{2} n_{eq} \frac{qV_0}{KT} \quad (43)$$

for the positive ions. In the limit of small applied voltage, where V_0 is small or comparable with $V_T = KT/q \sim 25$ mV, the perturbation of the bulk density of ions is small, and we recover again the results discussed above. The presence of the surface layers, according to eq 7, reduces the difference of potential over the electrolyte. Consequently, the Gouy–Chapman model is expected to work well up to $V_0 \sim V_T$.

A final remark on the hypothesis of ϵ being position independent, which is implicit in the Gouy–Chapman model, can be useful. When the electric field is applied, there is a movement of ions in the direction of the electrodes of opposite sign. Consequently, there is a profile of the ionic density. If we assume that the dielectric constant of the ions is ϵ_I , the dielectric constant of the solution, ϵ_S , is position dependent and given by³²

$$\epsilon(z) = \epsilon + c(z) \frac{\epsilon_I(\epsilon - \epsilon_I)}{\epsilon + \epsilon_I} \quad (44)$$

which is valid in the limit of small concentration of ions in the liquid, c . A simple calculation gives

$$c(z) = c_{eq} \left\{ 1 + \frac{\delta n_p(z)}{N} + \frac{\delta n_m(z)}{N} \right\} \quad (45)$$

where c_{eq} is the density of ions in the absence of the external electric field. In our analysis, $|\delta n_p/N| \ll 1$, and the dielectric constant enters in the problem by means of the equation of Poisson. Consequently, at the first order in $|\delta n_p/N|$, the dielectric constant can be assumed to be position independent.

VI. Conclusion

We have investigated the influence of the adsorption phenomenon at the interfaces on the transient phenomena occurring in an electrolytic cell submitted to a steplike external voltage, in the limit of small amplitude of the applied voltage. In our analysis, the cell is considered to be a slab of thickness d , and the electrodes are assumed to be covered with an insulating film of thickness h , to render blocking electrodes. We have numerically solved the fundamental equations of the problem under investigation by considering as electrolyte a doped nematic liquid crystal, and the thickness of the sample has been assumed to be $25 \mu\text{m}$, as used in display technology. Following the standard procedure, we have solved the equation of the problem, linearizing, and obtained an analytical solution for the bulk and surface densities of ions and for the electrical potential. We also obtained the relaxation time for the transient phenomena.

Our analysis has been performed in the framework of the Gouy–Chapman approximation, where the surface layer of Stern is neglected. For the set of physical parameters considered, in the limit of small applied voltage, we are far from the problems connected with the unphysical increase in the surface density of the ions close to the electrodes, requiring the introduction of the layer of Stern. Hence, our analytical predictions are expected to work well for applied voltages smaller than (or on the order of) the thermal electrical voltage.

For applied voltages larger than 0.1 V, the Gouy–Chapman model still works well for the used set of the adsorption–desorption coefficients, but the linearized analysis is no longer a good approximation of the problem.

Acknowledgment. F.C.M.F. acknowledges the financial support received from CAPES (Brazil).

VII. Appendix 1

Equations 27–29 and 8 should be solved to define the integration constant C_1 . In the zeroth order approximation, we assume that $n = n_p^e - n_m^e = 0$ and $\sigma = \sigma_p^e - \sigma_m^e = 0$. It follows that

$$C_1^{(0)} = \frac{V_0}{2} \frac{\gamma}{\sinh(d/2\lambda_{eq})}$$

Therefore,

$$n^{e(0)} = n_p^{e(0)} - n_m^{e(0)} = \frac{V_0 q}{K_B T} n_{eq} \gamma \frac{\sinh(z/\lambda_{eq})}{\sinh(-d/2\lambda_{eq})}$$

where $\gamma = d\epsilon_h/(d\epsilon_h + 2h\epsilon)$.

Introducing the zeroth order solution for the density of ions and the surface density (eq 29) into eq 8, we obtain the first-order solution

$$C_1 = -\frac{V_0 \gamma}{2X} \left[1 - \frac{h k \tau \gamma \epsilon}{\epsilon_h \lambda_{eq}^2} \right] + -\frac{V_0 h \gamma^2 \epsilon}{2\lambda_{eq} X^2 d \epsilon_h} [2\lambda_{eq} X + dY] \quad (46)$$

where $X = \sinh(-d/2\lambda_{eq})$ and $Y = \cosh(-d/2\lambda_{eq})$. Further corrections (starting from the order of h^2) can be found iteratively. As will be shown later, several iterations to determine C_1 are necessary to obtain a reasonable convergence of the solution.

References and Notes

- (1) Hunter, R. J. *Introduction to Modern Colloid Science*; Oxford Science Publications: New York, 2003.
- (2) Israelachvili, J. *Intermolecular Forces*; Academic Press: London, 1985; Chapter 12.
- (3) Bazant, M. Z.; Thornton, K.; Ajadari, A. *Phys. Rev. E* **2004**, *70*, 021506.
- (4) Alexe-Ionescu, A. L.; Barbero, G.; Freire, F. C. M.; Scalerandi, M. *Liq. Cryst.*, in press.
- (5) Barbero, G.; Evangelista, L. R. *Adsorption Phenomena and Anchoring Energy In Nematic Liquid Crystals*; Taylor and Francis Group: London, 2005.
- (6) Moore, W. J. *Physical Chemistry*; Prentice-Hall, Inc.: London, 1972.
- (7) Briere, G.; Gaspard, F.; Herino, R. *J. Chim. Phys.* **1971**, *68*, 845.
- (8) de Vleeschouwer, H.; Verschueren, A.; Bougriouva, F.; van Asselt, R.; Vermael, E.; Neyts, K.; Pauwels, H. *Jpn. J. Appl. Phys.* **2001**, *40*, 3272.
- (9) Alexe-Ionescu, A. L.; Ionescu, A. Th.; Barna, E. S.; Barna, V.; Scaramuzza, N. *J. Phys. Chem. B* **2004**, *108*, 8894.
- (10) Alexe-Ionescu, A. L.; Barbero, G.; Petrov, A. G. *Phys. Rev. E* **1993**, *48*, R1631.
- (11) Strangi, G.; Versace, C.; Scaramuzza, N. *Appl. Phys. Lett.* **2001**, *78*, 2455.
- (12) Alexe-Ionescu, A. L.; Ionescu, A. Th.; Barna, E. S.; Barna, V.; Scaramuzza, N.; Strangi, G. *J. Phys. Chem. B* **2003**, *107*, 5487.
- (13) Scaramuzza, N.; Berlic, C.; Barna, E. S.; Strangi, G.; Barna, V.; Ionescu, A. Th. *J. Phys. Chem. B* **2004**, *108*, 3207.
- (14) Ionescu, A. Th.; Scaramuzza, N.; Versace, C. *J. Phys. Chem. B* **1997**, *101*, 8438.
- (15) Scott, M.; Paul, R.; Kalert, K. V. I. S. *J. Colloid Interface Sci.* **2000**, *230*, 377.
- (16) Scott, M.; Paul, R.; Kalert, K. V. I. S. *J. Colloid Interface Sci.* **2000**, *230*, 388.
- (17) Mazzulla, A.; Ciuchi, F.; Sambles, R. *Phys. Rev. E* **2001**, *64*, 021708.

- (18) Mazzulla, A.; Ciuchi, F.; Sambles, R. *Phys. Rev. E* **2002**, 68, 023702.
- (19) Barbero G.; Evangelista, L. R. *Phys. Rev. E* **2002**, 68, 023701.
- (20) Becchi, M.; Avendano, C.; Strigazzi, A.; Barbero, G. *J. Phys. Chem. B* **2005**, 109, 23444.
- (21) Freire, F. C. M.; Barbero, G.; Scalerandi, M. *Phys. Rev. E* **2006**, 73, 051202.
- (22) Cirkel, P. A.; van der Ploeg, J. P. M.; Koper, G. J. M. *Physica A* **1997**, 235, 269.
- (23) Atkins, P. W. *Physical Chemistry*, 5th ed.; Oxford University Press: Oxford, 1994.
- (24) Delahay, P.; Mohilner, D. M. *J. Phys. Chem.* **1962**, 66, 959.
- (25) Delahay, P.; Mohilner, D. M. *J. Am. Chem. Soc.* **1962**, 84, 4247.
- (26) Delahay, P. *J. Phys. Chem.* **1963**, 67, 135.
- (27) Maximus, B.; de Ley, E.; de Meyere A.; Pauwels, H. *Ferroelectrics* **1991**, 121, 103.
- (28) Barbero, G. *Phys. Rev. E* **2005**, 71, 062201.
- (29) Sawada, A.; Tarumi, K.; Naemura, S. *Jpn. J. Appl. Phys.* **1999**, 38, 1423.
- (30) Scalerandi, M.; Pagliusi, P.; Barbero, G. *Phys. Rev. E* **2004**, 69, 051708.
- (31) Kaniadakis, G.; Delsanto, P. P.; Condat, C. A. *Math. Comput. Modell.* **1993**, 17, 31.
- (32) Landau, L. D.; Lifchitz, E. I. *Elettrodinamica dei Mezzi Continui*; Editori Riuniti: Genova, 1970.