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Transient effects in electrolytic cells submitted to an external electric field

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We analyse transient effects in an electrolytic cell submitted to an external voltage and determine the relaxation time of the redistribution of the ions and of the potential. We consider the case in which adsorption effects at the interface with the electrodes are present and show that the typical relaxation time, for applied voltage $V_0 \leq 25$ mV, is of the order of tens of seconds for commercial nematic liquid crystals. When $V_0 > 25$ mV the linearized analysis is no longer valid. In this case, the relaxation time depends on the applied voltage. Increasing V_0 , but still remaining in the low amplitude limit, the relaxation time starts increasing. This indicates that the reduction of the actual field in the sample, for moderate values of V_0 , plays an important role. For large values of V_0 , the relaxation time is a decreasing function of V_0 . This result is interpreted in terms of a simple model, according to which the ionic charge is localized in a surface layer whose thickness depends on the amplitude of the applied voltage.

1. Introduction

In recent years transient effects in an electrolytic cell submitted to an external voltage have received increasing attention [1] due to their potential applications in electrophoretic deposition, dielectrophoresis, self-assembly, memory recording, nematic liquid crystals and other fields [2]. Transient effects arise because the distribution of ions in the cell is perturbed by the presence of the external field. Due to a net force acting on the ions, there is a redistribution of ions close to the electrodes, which modifies the electric potential across the sample. Such redistribution follows the external field with some delay, characterized by a typical relaxation time. Therefore, to extract information about the physical parameters from measurements, the theoretical models used for the interpretation of the experimental data have to take into account correctly the transient effects occurring when the sample is submitted to an external electric potential.

In particular, when the typical time of variation of the applied potential is much shorter than the ions'

relaxation time, the latter usually play no role in the dynamics of the system [3]. It follows, for example, that the electrical impedance of an electrolytic cell may have anomalous behaviour as a function of frequency [4]. Transient times are also important for the study of the flexoelectric coefficients of a nematic liquid crystal [5], usually determined by applying a square voltage of low frequency to the nematic cell [6–8]: if the ions follow the time variation of the applied field, they give also a contribution to the actual electrical polarization [9]. Also transient charging currents in nematic liquid crystals [10–13] are due to the nematic liquid crystal reorientation and to the ion redistribution.

Such effects, at least in the case of a poorly conducting electrolytic cell, can be analysed by studying the actual distribution of ions and electrical potential, determined by solving the coupled differential equations of continuity for the ions and the Poisson equation for the electric potential, as discussed in the next section. Such a problem has already been studied reducing it to a drift-diffusion problem when the driving field can be assumed as independent of the ion redistribution [14]. Similarly, a solution of the problem for intermediate values of the applied potential has also been given in [1].

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Here we consider the case in which adsorption phenomena at the electrodes are present. Furthermore, by means of a numerical solution, the dependence of transient times on the amplitude of the applied potential is analysed for both low and large potentials, up to the order of a few volts. In our analysis, we assume that in the absence of an external electric field the ionic densities for positive and negative ions are the same, which implies that ions are identical. But we also introduce the hypotheses that both electrodes are at the potential of zero charge [15]. Furthermore, we neglect the capacitance of the surface layer [16]. Nevertheless, despite the fact that such assumptions are very strong for any practical system, we believe that the analysis presented here can be considered as a zeroth-order approximation of a real system and can stimulate further investigations in the same direction. The limits of the approximation, particularly in the case of large potentials, will be carefully discussed.

In this contribution we consider the case in which the sample is submitted to a step-like external voltage of amplitude V_0 . The solution of the linearized problem will be presented in §3, i.e. in the case of values of V_0 small (or comparable) with respect to the thermal voltage $V_T=25$ mV (for monovalent ions). Then, in §4 we compare our results with those reported in [1] and analyse the influence of adsorption. Finally, the case of large amplitude of the applied voltage is investigated, i.e. when the solution of the problem can be obtained only numerically. In the limit of large amplitude, the numerical results can be heuristically understood supposing that the ions are confined in two surface layers of thickness ℓ , which depends on V_0 . In this case, we show that the relaxation time is a decreasing function of V_0 , in agreement with the results obtained by means of the numerical analysis.

2. Fundamental equations

We consider a liquid containing ions. The sample is assumed to be in the shape of a slab of thickness d and cross section S . The cartesian reference frame has the z -axis perpendicular to the limiting surfaces at $z=\pm d/2$. All physical quantities appearing in the problem are supposed to depend only on the z -coordinate and the time t . We suppose that the ions are identical, except for the sign of the electrical charge [17, 18]. Consequently they have the same diffusion coefficient D , and the same adsorption energy with respect to the electrodes. We indicate by N the density of ions in the absence of the external field, $n_p(z, t)$ and $n_m(z, t)$ the actual density of positive and negative ions and by $V(z, t)$ the electrical potential. The density of current of the ions in the

presence of an electric field is

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

where $r=p, m$, and for $r=p$ the sign is +, whereas for $r=m$ the sign – holds. In equation(1) q is the modulus of the charge of the ion and $K_B T$ the thermal energy.

The fundamental equations of the problem are the continuity and Poisson's equations [1, 19]:

$$\begin{aligned} \frac{\partial n_r}{\partial t} &= D \frac{\partial}{\partial z} \left(\frac{\partial n_r}{\partial z} \pm \frac{q}{K_B T} n_r \frac{\partial V}{\partial z} \right) \\ \frac{\partial^2 V}{\partial z^2} &= -\frac{q}{\varepsilon} (n_p - n_m) \end{aligned} \quad (2)$$

where ε is the dielectric constant of the pure liquid.

When there is no adsorption from the surfaces and the electrodes are perfectly blocking, the current densities of positive and negative ions in $z=\pm d/2$ are null, as considered in [1]. In contrast, here:

$$j_r(\pm d/2) = \pm \frac{d\sigma_r(\pm d/2)}{dt} \quad (3)$$

where the sign is – for $z=-d/2$, and+for $z=d/2$. We also assume for the kinetic equation at the adsorbing surfaces that proposed by Langmuir [20]

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

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

$$\begin{aligned} D \left(\frac{\partial n_r}{\partial z} \pm \frac{q}{K_B T} n_r \frac{\partial V}{\partial z} \right) &= kn_r - \frac{1}{\tau} \sigma_r \\ -D \left(\frac{\partial n_r}{\partial z} \pm \frac{q}{K_B T} n_r \frac{\partial V}{\partial z} \right) &= kn_r - \frac{1}{\tau} \sigma_r \end{aligned} \quad (5)$$

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

Imposing the conservation of the number of ions:

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

we easily obtain the following initial conditions ($t=0$):

$$2 \sigma_{eq} + n_{eq} d = N d \quad (7)$$

and

$$kn_{eq} - \frac{1}{\tau} \sigma_{eq} = 0. \quad (8)$$

From equation (7) and (8), it follows that

$$\begin{aligned} \sigma_{\text{eq}} &= \frac{1}{2} N d \frac{1}{1+d/(2k\tau)} \\ n_{\text{eq}} &= N \frac{d/(2k\tau)}{1+d/(2k\tau)}. \end{aligned} \tag{9}$$

We define

$$\begin{aligned} n_r(z, t) &= n_{\text{eq}} + \delta n_r(z, t) \\ \sigma_r(t) &= \sigma_{\text{eq}} + \delta \sigma_r(t) \end{aligned} \tag{10}$$

where the quantity $\delta n_r(z, t)$ represents the perturbation of the bulk density of ions due to the presence of the applied voltage. We introduce also the reduced quantities, $r = \delta n_r/n_{\text{eq}}$, $s_r = \delta \sigma_r/n_{\text{eq}}$, and $u = V/V_T$, where $V_T = K_B T/q$ is the thermal electric potential. Equations (2) can be rewritten as

$$\begin{aligned} \frac{\partial r}{\partial t} &= D \frac{\partial}{\partial z} \left[\frac{\partial r}{\partial z} \pm (1+r) \frac{\partial u}{\partial z} \right] \\ \frac{\partial^2 u}{\partial z^2} &= -\frac{1}{2\lambda_{\text{eq}}^2} (p-m) \end{aligned} \tag{11}$$

where $\lambda_{\text{eq}} = [\epsilon K_B T / (2n_{\text{eq}} q^2)]^{1/2}$ is the Debye length [21]. We note that the equation of continuity is nonlinear for the presence of the term $r \partial u / \partial z$. In terms of the reduced quantities, the boundary conditions are given by

$$\begin{aligned} D \left[\frac{\partial r}{\partial z} \pm (1+r) \frac{\partial u}{\partial z} \right] &= kr - \frac{1}{\tau} s_r \quad z = d/2 \\ -D \left[\frac{\partial r}{\partial z} \pm (1+r) \frac{\partial u}{\partial z} \right] &= kr - \frac{1}{\tau} s_r \quad z = -d/2. \end{aligned} \tag{12}$$

3. Solution of the linearized equation

3.1. Linearized equations

We limit our considerations to the case in which $r \ll 1$. This means that the applied potential is so small that $\delta n_r \ll n_{\text{eq}}$. In this framework, where r and u are quantities both much smaller than one, it is possible to neglect the term $r \partial u / \partial z$, which is the source of the non-linearity. In this approximation, equations (11) become

$$\frac{\partial r}{\partial t} = D \frac{\partial}{\partial z} \left(\frac{\partial r}{\partial z} \pm \frac{\partial u}{\partial z} \right) \tag{13}$$

$$\frac{\partial^2 u}{\partial z^2} = -\frac{1}{2\lambda_{\text{eq}}^2} (p-m). \tag{14}$$

In the linear case the bulk differential equations (13,14) have to be solved with the boundary conditions

$$\begin{aligned} r(z, 0) &= 0 \\ D \left\{ \frac{\partial r}{\partial z} \pm \frac{\partial u}{\partial z} \right\} &= kr - \frac{1}{\tau} s_r \quad z = d/2 \\ -D \left\{ \frac{\partial r}{\partial z} \pm \frac{\partial u}{\partial z} \right\} &= kr - \frac{1}{\tau} s_r \quad z = -d/2 \\ u(\pm d/2, t) &= \pm (1/2 V_T) \Delta V(t), \end{aligned} \tag{15}$$

where $\Delta V(t)$ is the difference of potential applied to the sample by the external power supply. In our case, as stated in the Introduction, the applied potential is a step of amplitude V_0 . From the condition $u(\pm d/2, t) = \pm V_0 / (2 V_T)$, and taking into account that the ions have the same mobility, it follows that $u(z, t) = -u(-z, t)$, $p(z, t) = m(-z, t)$, and $s_r(d/2, t) = -s_r(-d/2, t)$.

In order to analyse transient effects in the cell submitted to an external electric field, we decompose the solution as $r(z, t) = r^t(z, t) + r^e(z, t)$, $s_r(\pm d/2, t) = s_r^t(\pm d/2, t) + s_r^e(\pm d/2, t)$ and $u(z, t) = u^t(z, t) + u^e(z, t)$, where the superscripts t and e refer to the transient and equilibrium components of the solution, respectively. Both components are a solution of the differential equations (13,14) with the proper boundary conditions.

The determination of the equilibrium solutions is not the goal of the present paper and will be presented elsewhere. Equilibrium solutions are well known when adsorption is absent [1]. Therefore, in the following we limit our analysis to the transient components and from now on we omit the superscript t where it is not strictly necessary.

3.2. Solution of the bulk equations for the transient components of the density of ions

Substituting equation (14) into (13), we obtain

$$\frac{1}{D} \frac{\partial r}{\partial t} = \frac{\partial^2 r}{\partial z^2} \mp \frac{1}{2\lambda_{\text{eq}}^2} (p-m). \tag{16}$$

We look for a solution of equation (16) of the form $r(z, t) = \psi_r(z) \exp(-at)$, where $a > 0$, since at the equilibrium the transient component of the solution must vanish. By substituting this expression into equation (16), we obtain

$$\psi''_{p,m}(z) - \Omega_a^2 \psi_{p,m}(z) + \Omega^2 \psi_{m,p}(z) = 0 \tag{17}$$

where $\Omega^2 = 1 / (2\lambda_{\text{eq}}^2)$ and $\Omega_a^2 = \Omega^2 - a/D$.

The solutions are then of the form $\psi_r(z) = C_r \exp(vz)$. By substituting this expression for $\psi_r(z)$ into equations (17), we obtain

$$\begin{aligned} (v^2 - \Omega_a^2) C_p + \Omega^2 C_m &= 0 \\ \Omega^2 C_p + (v^2 - \Omega_a^2) C_m &= 0. \end{aligned} \quad (18)$$

It follows that the characteristic exponents are

$$v_{1,2} = \pm \frac{1}{\lambda_{\text{eq}}} \left(1 - \frac{a}{D} \lambda_{\text{eq}}^2\right)^{\frac{1}{2}}, \quad \text{and} \quad v_{3,4} = \pm i \left(\frac{a}{D}\right)^{\frac{1}{2}}. \quad (19)$$

From equation (18) it follows that

$$\frac{C_p}{C_m} = - \frac{\Omega^2}{v^2 - \Omega_a^2}. \quad (20)$$

The solutions we are looking for are then

$$\begin{aligned} \psi_r(z) = \pm [C_{p,1} \exp(v_1 z) + C_{p,2} \exp(-v_1 z)] \\ + C_{p,3} \exp(v_3 z) + C_{p,4} \exp(-v_3 z). \end{aligned} \quad (21)$$

From equation (6) it follows that,

$$\int_{-d/2}^{d/2} \psi_r(z) dz = 0. \quad (22)$$

Therefore, $C_{p,1} = -C_{p,2} = C_1/2$, and $C_{p,3} = -C_{p,4} = C_3/2$. Consequently from (21) we obtain

$$\psi_r(z) = \pm C_1 \sinh(v_1 z) + C_3 \sinh(v_3 z). \quad (23)$$

3.3. Solution of the bulk equations for the electrical potential

The electrical potential is of the form $u(z, t) = \phi(z) \exp(-at)$, where $\phi(z)$ is the solution of the differential equation

$$\phi''(z) = - \frac{1}{2\lambda_{\text{eq}}^2} [\psi_p(z) - \psi_m(z)] \quad (24)$$

which, making use of equation (23), can be rewritten as

$$\phi''(z) = - \frac{1}{\lambda_{\text{eq}}^2} C_1 \sinh(v_1 z). \quad (25)$$

The symmetry of the problem imposes $\phi(z) = -\phi(-z)$. Consequently from equation (25) we get

$$\phi(z) = - \frac{1}{\lambda_{\text{eq}}^2 v_1^2} C_1 \sinh(v_1 z) + s z \quad (26)$$

where s is an integration constant. Transient components

of the potential must vanish at $z = \pm d/2$. Then

$$\phi(z) = \frac{1}{\lambda_{\text{eq}}^2 v_1^2} C_1 \sinh(v_1 d/2) \left[\frac{2z}{d} - \frac{\sinh(v_1 z)}{\sinh(v_1 d/2)} \right]. \quad (27)$$

3.4. Boundary conditions

Before imposing the boundary conditions, we must consider that equation (4) becomes

$$\frac{ds_r}{dt} = kr - \frac{1}{\tau} s_r, \quad \text{for} \quad z = \pm d/2 \quad (28)$$

with the following solution:

$$s_r = M_{\pm} \exp(-t/\tau) + \frac{k\tau}{1-a\tau} \psi_r \exp(-at) \quad (29)$$

in $z = \pm d/2$. The boundary conditions given by equation (15) become

$$\begin{aligned} D(\psi'_r \pm \phi') \exp(-at) &= -k \frac{a\tau}{1-a\tau} \psi_r \exp(-at) \\ &\quad - \frac{1}{\tau} M_{\pm} \exp(-t/\tau), \\ -D(\psi'_r \pm \phi') \exp(-at) &= -k \frac{a\tau}{1-a\tau} \psi_r \exp(-at) \\ &\quad - \frac{1}{\tau} M_{\pm} \exp(-t/\tau). \end{aligned} \quad (30)$$

Since equations (30) have to be valid for all t , we deduce that $M_+ = M_- = 0$.

Substituting the solutions for the density of ions and for the potential in equation (30) we obtain that equations (30) are compatible when $C_3 = 0$. In this case they reduce to

$$\left[1 - \frac{k a \tau}{D(1-a\tau)} v_1^2 \lambda_{\text{eq}}^2 \frac{d}{2} \right] \tanh\left(v_1 \frac{d}{2}\right) = \left(1 - v_1^2 \lambda_{\text{eq}}^2\right) v_1 \frac{d}{2} \quad (31)$$

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

3.5. Discussion on the transient times

3.5.1. Without adsorption effects. In this condition, $k=0$. It follows $n_{\text{eq}} = N$ and $\lambda_{\text{eq}} = \lambda = [\epsilon K_B T / (2Nq^2)]^{\frac{1}{2}}$.

When v_1 is real, i.e. for $a \leq D/\lambda^2$, one of the solution of equation (31) is $v_1 = 0$, i.e. $a = D/\lambda^2$. This first eigenvalue is however not physical, since it corresponds to no separation of ions, see (23). We seek the second relaxation time in the form $a = bD/(\lambda d)$, where b is a numerical coefficient to be determined. Simple calculations give the dimensionless form

$$\tanh\left[\frac{(1-b\gamma)^{\frac{1}{2}}}{2\gamma}\right] = \frac{1}{2} b(1-b\gamma)^{\frac{1}{2}} \quad (32)$$

where $\gamma = \lambda/d$. By taking into account that $\lambda \ll d$, we can find the solution by substituting $b = b_0 + \delta b$ and expanding in power series of δb the eigenvalue equation. It follows $b_0 = 2$ and

$$\delta b = 2(1 - 2\gamma)^{\frac{1}{2}} \frac{\tanh\left[\frac{(1 - 2\gamma)^{\frac{1}{2}}}{2\gamma}\right] - (1 - 2\gamma)^{\frac{1}{2}}}{1 - 3\gamma + (1/2) \operatorname{sech}^2\left[\frac{(1 - 2\gamma)^{\frac{1}{2}}}{2\gamma}\right]} \quad (33)$$

Consequently, the eigenvalue is $v_1 \sim (1/\lambda)[1 - 2(\lambda/d)]^{\frac{1}{2}}$. Therefore we obtain $a = bD/(\lambda d)$ and the relevant relaxation time is

$$t_d = \frac{\lambda d}{bD} \sim \frac{\lambda d}{2D} \quad (34)$$

in agreement with [1].

Note that other solutions are possible with a much shorter relaxation time when $a > D/\lambda^2$ and v_1 is imaginary. The eigenvalue equation is

$$\tan(|v_1|d/2) = (1 + \lambda^2|v_1|^2)^{\frac{1}{2}}|v_1|d/2 \quad (35)$$

where

$$|v_1| = \frac{1}{\lambda_{\text{eq}}} \left(\frac{a}{D} \lambda^2 - 1\right)^{\frac{1}{2}} \quad (36)$$

In this case we have oscillating solutions.

3.5.2. With adsorption effects. When $k \neq 0$, equation (31) 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. The first solution again is easily found to be $v_1 = 0$, that means $a = \lambda_{\text{eq}}^2/D$. However, this solution is not interesting because, as discussed above, it corresponds to a case in which there is no separation of charges.

More important are the other solutions, which can be found only numerically. Furthermore, the most interesting is that t_d is larger than τ , which is the typical time scale of the adsorption events. 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, practically, independent of V_0 .

4. Numerical analysis

The analysis presented so far suggests the existence of an infinite number of decay times. A numerical analysis is performed to evaluate which of them effectively play a role in the dynamics of a system, i.e. to evaluate the

relaxation time for the ionic charge density and the potential distribution. To this purpose, we solve numerically equations (2) with the boundary conditions (4) and (5). Details the numerical solution can be found elsewhere [22, 23].

In our analysis, we assume that the external potential is a step of amplitude V_0 , applied at $t = 0$. We consider parameters typical of a commercial liquid crystal: monovalent ions ($q = 1.6 \times 10^{-19}$ A s), $N = 4.2 \times 10^{20} \text{ m}^{-3}$, $T = 300^\circ \text{ K}$, $\epsilon = 6.7\epsilon_0$, $D = 8.2 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$, $d = 25 \mu\text{m}$ and $S = 2 \times 10^{-4} \text{ m}^2$ [24]. With these parameters, the Debye length is $\lambda \sim 0.1 \mu\text{m}$.

From a numerical point of view, we consider the evolution of the transient components of the relative variations of ions and of the potential close to the surface. In other words, we derive the decay times t_d from the plots of the quantities $p^t(t) = [n_p(z^*, t) - n_p(z^*, \infty)]/n_{\text{eq}}$ and $V^t(t) = V(z^*, t) - V(z^*, \infty)$, where $z^* = -d/2 + 0.1 \mu\text{m}$.

4.1. Estimation of the decay time in the absence of adsorption

Here we assume $k = 0$ ($n_{\text{eq}} = N$) and analyse first the case of low amplitude of the applied potential, i.e. small with respect to $V_T = K_B T/q \sim 25 \text{ mV}$. Then our numerical analysis will be used to provide indications of the relaxation times for potentials up to the order of a few volts.

4.1.1. Behaviour at low potentials. Our results suggest that only one relaxation time plays a role in the dynamic of the system. This is confirmed in figures 1 (a) and 1 (b) where we show, in semi-logarithmic scale $p^t(t)$ and $V^t(t)$. The range of applied potential is quite large and, except perhaps at the larger value of the potential ($V_0 = 25 \text{ mV}$), the straight line in the semi-log plot is an indication of a purely exponential decay. Also, the slope of the line, indicating the decay time t_d , is independent from the applied potential, in agreement with the linearized analysis presented above. In the case of $V_0 = 0.1 \text{ mV}$ the relaxation time is $t_d = 0.15 \text{ s}$, very close to the one given by equation (34). As expected from the linear analysis, the decay time is the same for both the potential and the density of ions. In figure 2, we show the relaxation time vs. the thickness of the sample, for different values of the applied potential. The relaxation time is proportional to the thickness of the sample, in agreement with equation (34) and it is independent of the amplitude of the applied voltage. Also this result is in agreement with the linearized analysis. Using for the physical parameters of the cell the ones reported above, equation (33) gives $\delta b = 0.0081$. Consequently $b = 2.0081$.

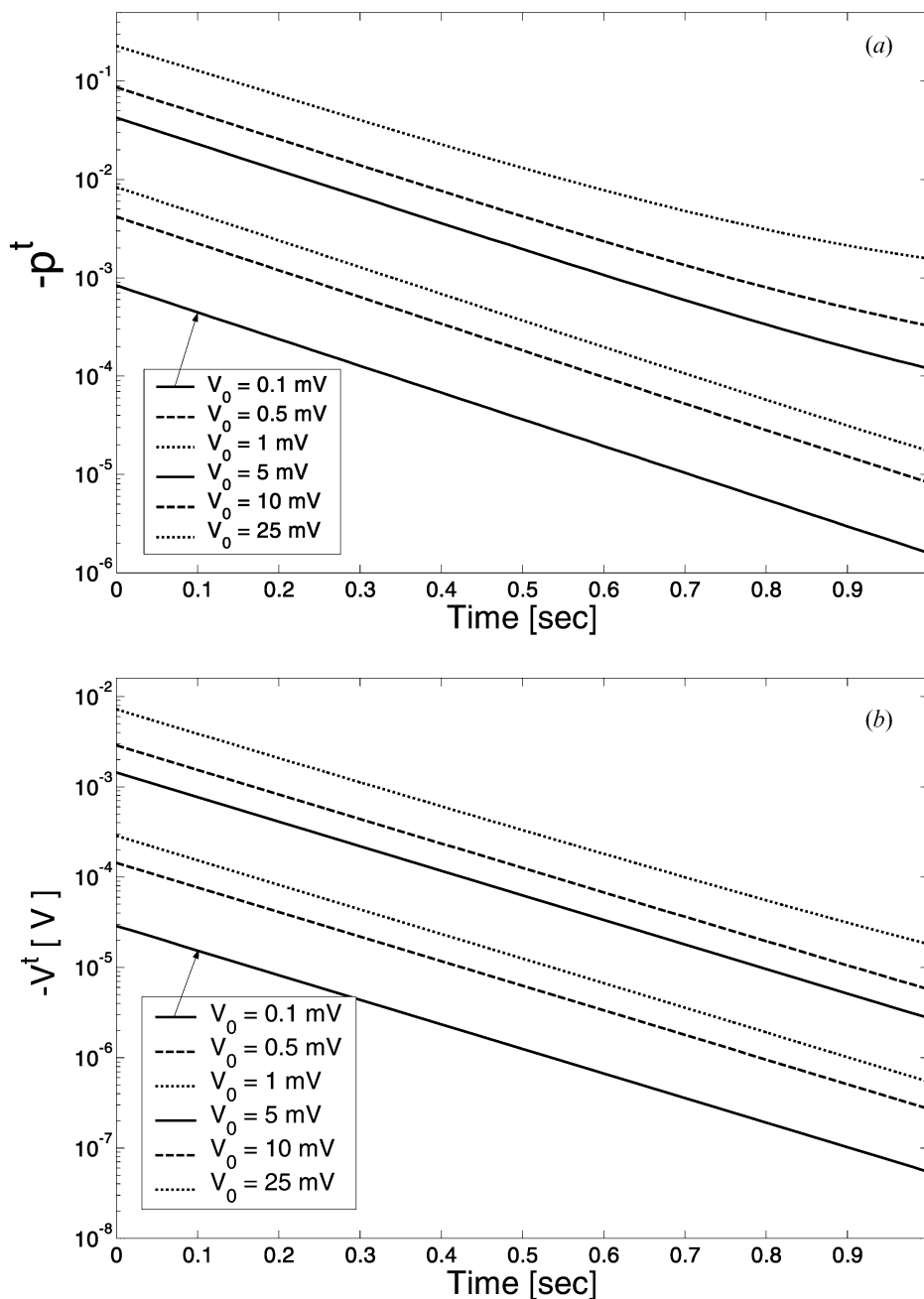


Figure 1. Transient component of the net density of positive ions (a) and of the electrical potential (b) in $z^* = -d/2 + 0.1 \mu\text{m}$ for different values of the applied potential V_0 . Lines are almost parallel up to $V_0 = 10 \text{ mV}$. Slight distortions are visible at $V_0 = 25 \text{ mV}$.

The slope of τ vs. d is $\lambda/(bD) \sim 6.4 \times 10^3 \text{ s m}^{-1}$, in good agreement with the numerical result.

4.1.2. Behaviour for large values of the applied potential. When the applied potential is large with respect to $V_T = 25 \text{ mV}$, the linearized analysis is no longer valid. In this case, the relaxation time depends on the applied voltage and, increasing V_0 the curves become more and more unlike a simple exponential

decay, and multi-relaxation becomes important. This is particularly true for what concerns the density of ions, while, although the agreement is no longer so good as for $V_0 < V_T$, the exponential function remains a reasonable approximation for the time dependence of the potential. It follows that t_d can still be interpreted as the relaxation time of the system.

Therefore, here we have extracted the decay time from the curves $v^t = V^t(t)/V_0$ vs. t . A non-trivial behavior

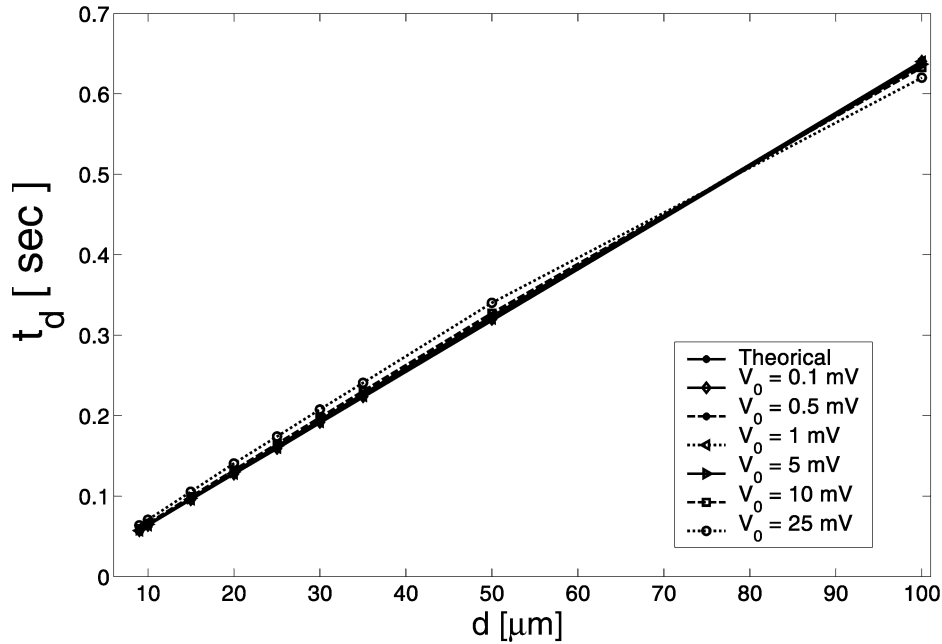


Figure 2. Decay time of the transient component of the electrical potential vs. the layer thickness d .

results as a function of the applied potential, as shown in figure (3) for different values of the thickness of the sample. Four regions may be identified in the plot.

- (1) In the limit of small amplitude of the applied voltage, t_d is, practically, independent of V_0 . Here the linearized analysis holds and the value of t_d for $V_0 \rightarrow 0$ coincides with that given by the linearised analysis.
- (2) On increasing V_0 , t_d starts to increase; this indicates that the reduction of the actual field in the sample, for moderate values of V_0 , plays an important role. Increasing the external field increases the collection of ions on the electrodes, with the consequence that the actual electric field in the sample is reduced and relaxation is much slower.
- (3) For V_0 close to the peak value (which moves to the left with decreasing specimen thickness), the relaxation time is defined only very roughly. Here, more phenomena are at play and should be further investigated.
- (4) For large values of V_0 , the relaxation time is a decreasing function of V_0 .

The dependence of the relaxation time on d and V_0 , for large V_0 , can be interpreted assuming that the ions collected close to the electrodes are confined in a surface layer of thickness $\ell \ll d$. As discussed in [25], for $V_0 \gg V_T$, we have $\ell \sim d(V_T/V_0)$. In the bulk the system remains electrically neutral. It follows that the unbalanced electrical charge in the surface layer is equivalent

to a surface density of charge $q\sigma$, responsible for a back electric field $E_c = q\sigma/\epsilon$. The net electric field in the bulk is then $E = (V_0/d) - q\sigma/\epsilon$. The ions present in the bulk are then submitted to a net force given by $F = qE$, which is responsible for an electrical current toward the electrodes $j \propto \mu n q E$, where μ is the mobility of the ions in the solution, and n the bulk density of carriers. From the conservation of the number of ions we have $n = N - \sigma/d$. By imposing that the increase of the surface density of charge per unit of time, $q d\sigma/dt$, is equal to the electrical charge coming from the bulk, $j dt$, we have the differential equation

$$\frac{d\sigma}{dt} \propto \mu \left(N - \frac{\sigma}{d} \right) \left(\frac{V_0}{d} - \frac{q\sigma}{\epsilon} \right). \quad (37)$$

From equation (37), the time evolution of the surface density of ions, and hence of the bulk density of ions and of the electrical potential, is characterized by the relaxation time [26]

$$t_d = \frac{A}{V_0 - V_c} \quad (38)$$

where $A \propto d^2/\mu$, and $V_c \sim \ell N q d/\epsilon$. Hence, for large V_0 , when $V_c \sim (d/\lambda)^2 (V_T^2/V_0)$ [25], the relaxation time is expected to be

$$t_d = \alpha \frac{d^2}{\mu \left[V_0 - \beta (d/\lambda)^2 (V_T^2/V_0) \right]} \quad (39)$$

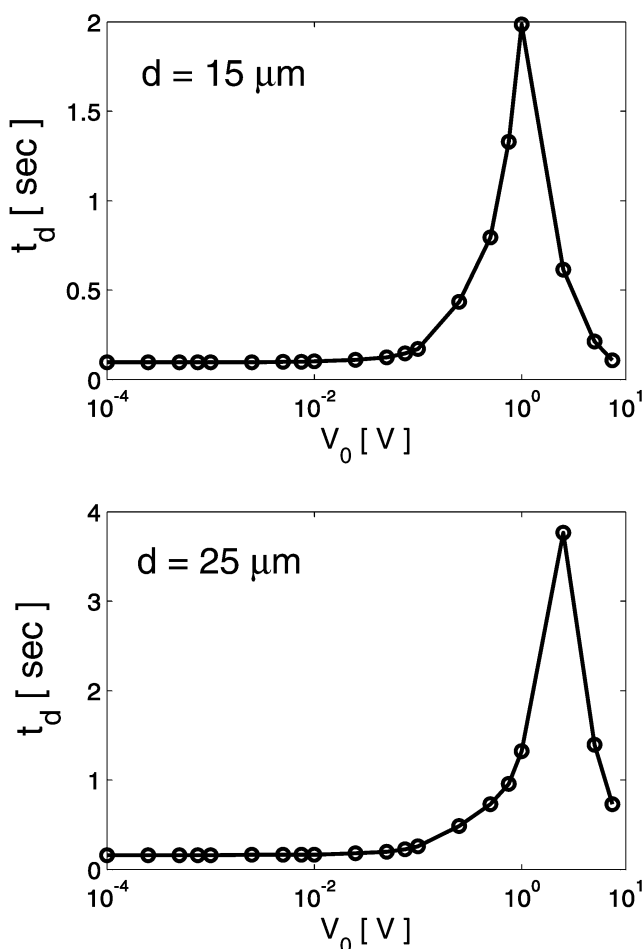


Figure 3. Decay time vs. the applied potential V_0 for different values of the thickness of the electrolytic cell d .

where α and β are two numerical constants, that cannot be determined by means of the simple model presented above. In figure 4 we show $t_d = t_d(V_0)$, in the range of $V_0 \gg V_T$. As discussed previously, t_d is determined by analysing $v'(t, z^*)$. In the same figure we show the fits of the numerical data by means of t_d given by equation (39), obtained for $\alpha=1$ and $\beta=0.5$. The agreement is reasonably good for the two thicknesses considered.

4.2. Estimation of the decay time in the presence of adsorption

The decay time t_d of the transient component as a function of the adsorption parameters k and τ is analysed in figures 5(a) and 5(b), 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 equation (31) is very good. However, already at $V_0=10$ mV, the linearized analysis stops

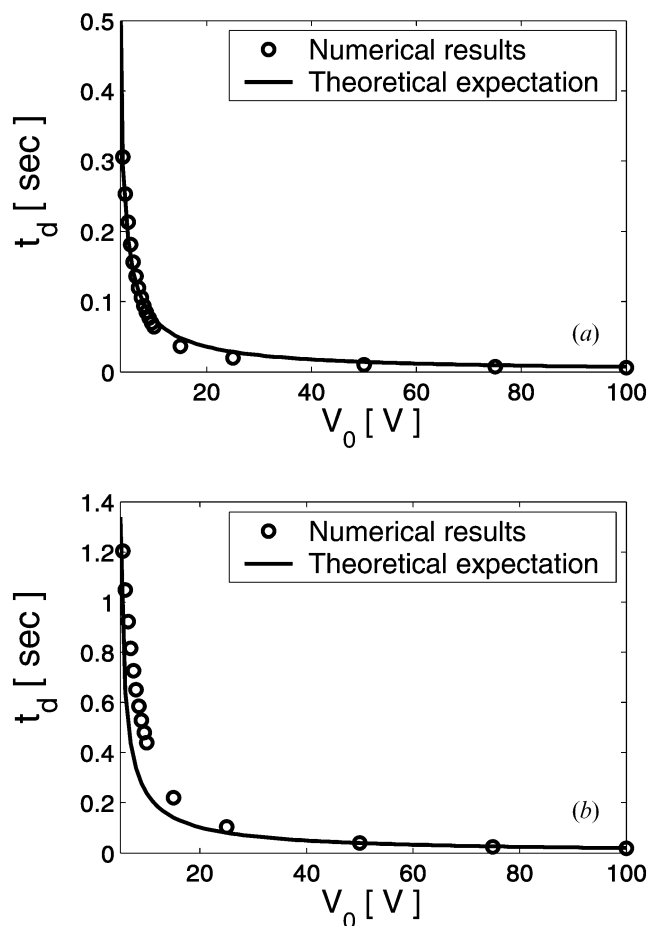


Figure 4. Decay time vs. the applied potential for large values of V_0 . Comparison of the numerical results with the theoretical expectations: (a) $d=15 \mu\text{m}$, (b) $d=25 \mu\text{m}$.

being reliable, even though the dependence of the decay time from k and τ remains qualitatively the same. Note that the decay time in the presence of adsorption phenomena is in general much larger than that expected when $k=0$.

At larger values of the applied potential the transient part of the solution is more complex than a single exponential decay, as in the absence of adsorption effects. The decay time first increases and then decreases with V_0 , as shown in figure 6. Note that the position of the peak is shifted to lower values of the applied potential when adsorption is present; compare with figure 3(b). This is compatible with the theoretical explanation given above for the behaviour at large amplitudes. In fact, adsorption leads to collection of the ions in a small layer close to the electrodes.

5. Conclusion

We have investigated the drift-diffusion problem in an electrolytic cell submitted to an external electric field in

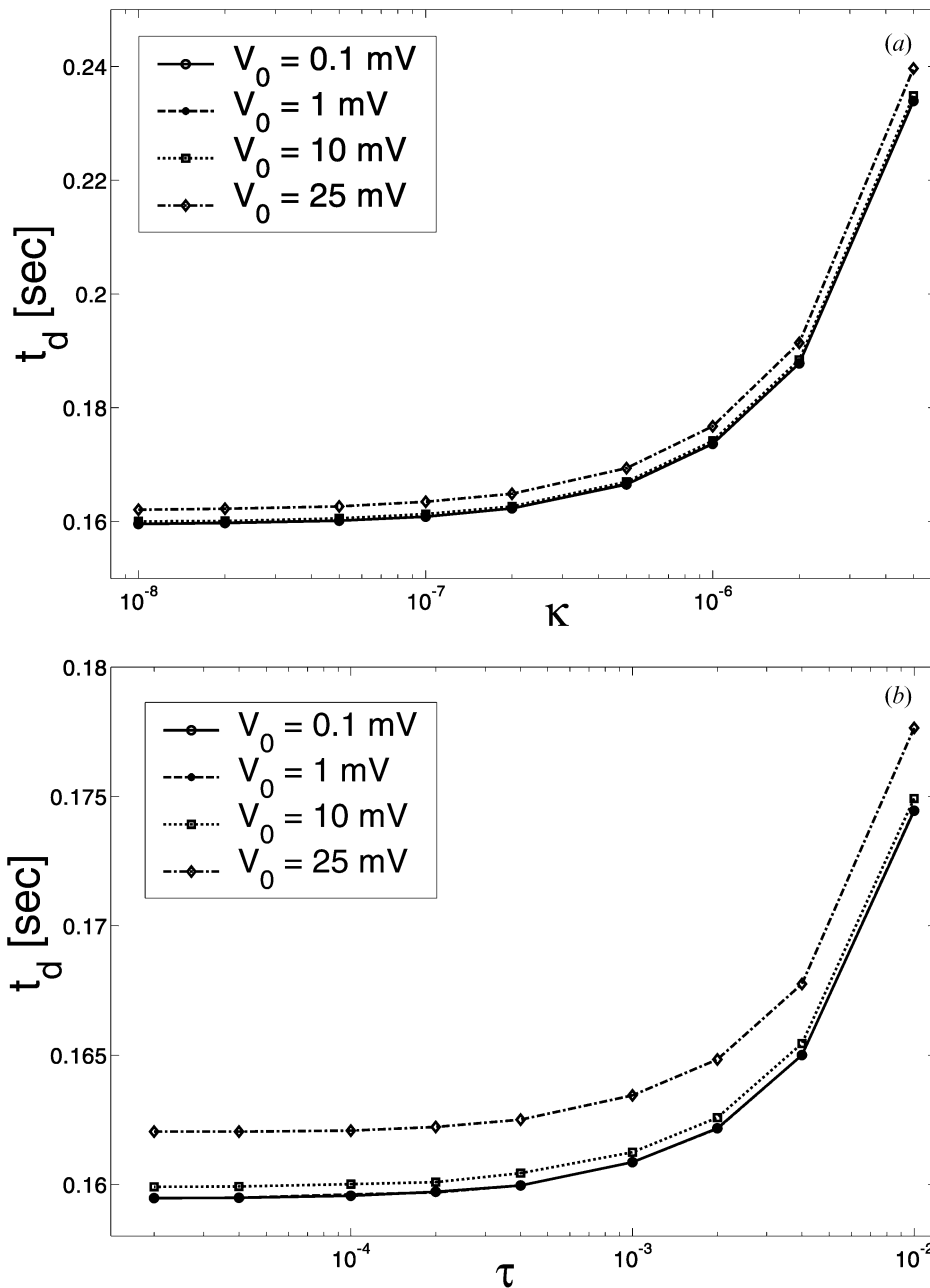


Figure 5. (a) Decay time vs. adsorption coefficient for $\tau=10^{-2}$, and (b) decay time vs. the inverse desorption coefficient for $k=10^{-6}$.

the presence of adsorption phenomena at the electrodes. We have considered an ideal system in which the electrodes are perfectly blocking, and the Stern surface layer of can be neglected. In this framework, we have taken into account the reaction field due to the separation of the ions. According to our analysis, the relaxation time of the ions in the liquid, in the low range of applied voltage and in the absence of adsorption phenomena, is close to $t_d = \lambda dl / (2D)$, that for commercial liquid crystal is of the order of 0.1 s, for $d \sim 25 \mu\text{m}$. The

decay time is larger when adsorption phenomena are present.

In the case of large amplitude of the applied voltage, a numerical analysis has been performed, showing that, in the absence of adsorption, the relaxation time is proportional to $d^2 / \mu(V_0 - V_c)$, where V_c depends on the Debye length, the thickness of the sample and on the applied voltage. A similar decrease of the decay time with V_0 is also found in the case of adsorption. Nevertheless, it should be mentioned that such results

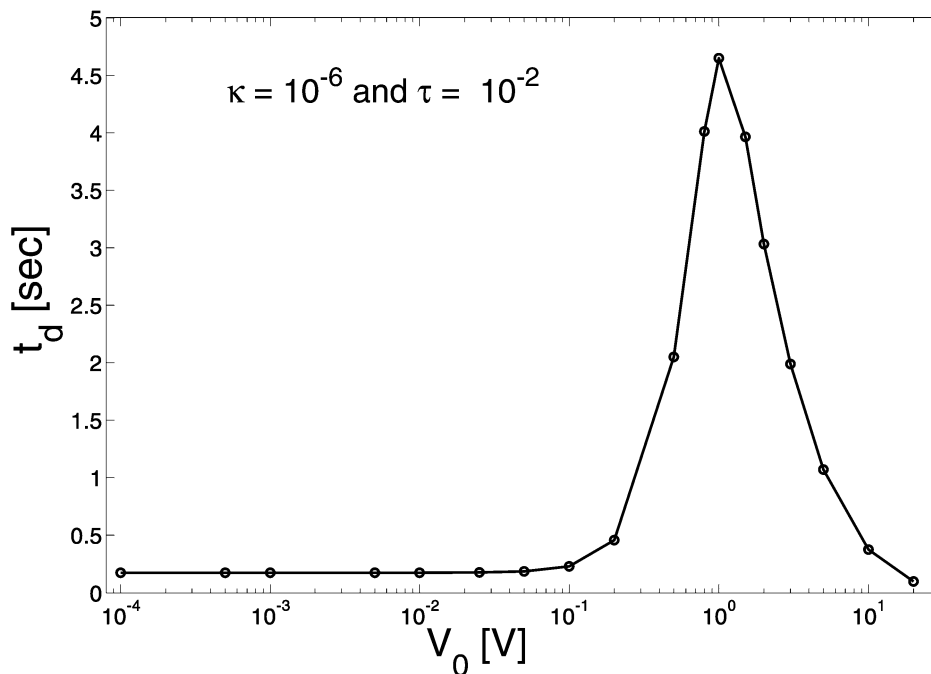


Figure 6. Decay time vs. the applied potential V_0 for different values of the potential with adsorption and $d=25\ \mu\text{m}$.

are only a preliminary indication. In fact, when the applied potential is large, ions are confined in a small space region close to the electrodes. If V_0 is sufficiently large, this region may have length comparable to that of the Stern layer (i.e. the layer of dielectric which describes the intrinsic capacity of the electrodes). Therefore, the results reported here can be considered only as a preliminary indication of the behaviour of the system, and consideration of the capacitance of the electrodes is essential to give a realistic quantitative prediction of the reduction of the decay time at large potentials.

Nevertheless, despite the strong assumptions introduced here, the analysis presented can be useful to interpret correctly the transient effects in nematic samples submitted to an external electric field. In fact, the electro-optical response of a nematic sample depends both on the elastic and viscous properties of the mesophase, and on the redistribution of the ions in the sample. The latter phenomenon is responsible for the actual electric field giving rise to the dielectric torque inducing the molecular reorientation.

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