Anomalous Dependence on the Diffusion Coefficients of the Ionic Relaxation Time in Electrolytes

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We show, by using a numerical analysis, that the dynamic toward equilibrium for an electrolytic cell subject to a step-like external electric field is a multirelaxation process when the diffusion coefficients of positive and negative ions are different. By assuming that the diffusion coefficient of positive ions is constant, we observe that the number of involved relaxation processes increases when the diffusion coefficient of the negative ions diminishes. Furthermore, two of the relaxation times depend nonmonotonically on the ratio of the diffusion coefficients. This result is unexpected, because the ionic drift velocity, by means of which the ions move to reach the equilibrium distribution, increases with increasing ionic mobility.

I. Introduction

Ambipolar diffusion is the simultaneous diffusion of positive and negative ions in the presence of their own space-charge fields.[1] In the standard analysis of this phenomenon, diffusive ions interact through their mutual electrostatic attraction, which is taken into account by assuming that the electrostatic forces are sufficient to maintain the electrical neutrality of the electrolytic solution in each point.[2] In the following, we assume that the mobility of the positive ions (D_p) is greater than that of the negative ions (D_m). In this case, positive ions are moving more rapidly than negative ions, which, as a result, sense a stronger electric field which makes them travel more rapidly than they would otherwise do. The opposite happens for positive ions, slowed down by the slow motion of negative ions. It follows that the process is governed (in time) by values for the group diffusivity and group mobility of the excess-carrier concentration distribution which is intermediate between the corresponding inherent positive and negative ion transport coefficients.[3]

This mutual interaction has important effects on the redistribution of ions as a consequence of an applied external field. In particular, the system relaxes toward the equilibrium with a decay time different from that expected when the ions have the same diffusion coefficients. In the latter case, that is, when the diffusion coefficients (and mobilities) are the same for positive and negative ions, it has been shown that a single relaxation process (with a corresponding relaxation time) is sufficient to describe the evolution of the system.[4–6] On the contrary, the dynamics of a system of ions subject to an external field is in general a multirelaxation process. Recently,[7] we have shown that even when the ratio of the diffusion coefficients, $\xi = D_m/D_p$, is close to 1, the phenomenon must be at least considered as a birelaxation process.

In this paper, we consider the case in which $D_m \ll D_p$. We show that the number of relaxation processes involved increases with decreasing ξ, with non-trivial consequences on the relaxation times of the system. The most important is that, for low ξ, the fastest relaxation time changes non-monotonically with ξ, and for some values of ξ, it increases with increasing the mobility of the negative ions. This result is absolutely unexpected, because the ions' mobility (and consequently the drift velocity) increases also when increasing D. Although the theory of ambipolar diffusion has been investigated extensively, to our knowledge, this anomalous dependence of the relaxation time on the diffusion coefficients has not yet been reported elsewhere.

The dependence on ξ of the relaxation times has practical importance to determine parameters and properties relevant for liquid crystals and other electrolytic solutions.[8,9] For instance, often, the density of ions is determined from relaxation-time measurements, on the basis of models of the system accounting for a single ion species with the same mobility for negative and positive ions. It follows that such predictions may be far from being accurate whenever ions with different diffusivities are present. The same applies to the interpretation of impedance spectroscopy results[10,11] or to 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.[12,13]

II. Theory

In this contributuion, we consider a symmetric binary electrolyte, equivalent to a dispersion of ions in a dielectric liquid. The sample is in the shape of a slab of thickness d. We use the following notation: N, bulk density of ions in thermodynamical equilibrium; N_0, bulk density of the liquid in which the ions are dispersed; D_p and D_m, diffusion coefficients of the positive and negative ions, respectively; q, modulus of the ions' charge; and ε, liquid dielectric constant. We also assume $N \ll N_0$. In this case, the effective dielectric constant of the solution coincides with ε.[14] Furthermore, from the assumption $N \ll N_0$, it follows that recombination phenomena can be neglected and the electrolyte may be considered as completely dissociated.[1] The solution is locally neutral if ions are not adsorbed by the surfaces limiting the cell, as we assume here. When the cell is subjected to an external electric field, ions are redistributed in the sample with a final non-uniform distribution. In the presence of an external field, the solution is locally charged.

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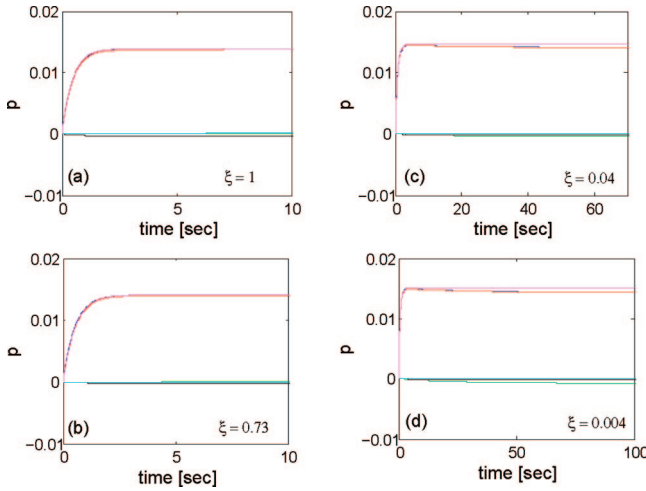
Figure 1. Temporal evolution of the density of positive ions in $z = -12.4\ \mu m$ for different values of the ratio of diffusion coefficients, ξ. Blue, numerical data; red, fitting with four exponentials; violet, green, black, and cyan, contributions of the four exponential terms corresponding to the four decay times $\tau_i (i = 1-4)$.
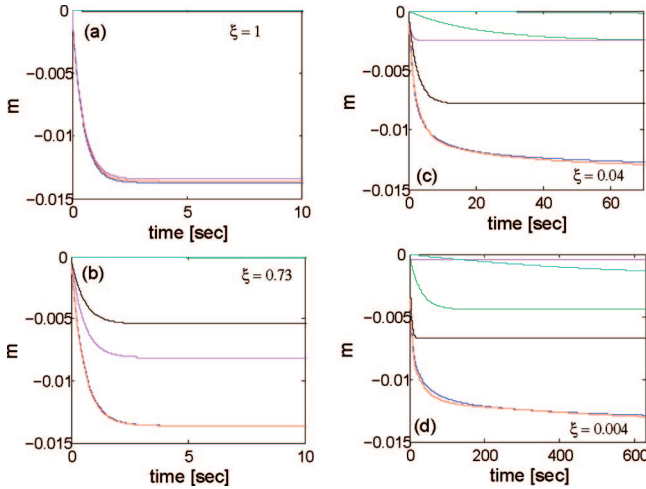
Figure 2. Temporal evolution of the density of negative ions in $z = -12.4\ \mu m$ for different values of the ratio of diffusion coefficients, ξ. Blue, numerical data; red, fitting with four exponentials; violet, green, black, and cyan, contributions of the four exponential terms corresponding to the four decay times $\tau_i (i = 1-4)$.

A. Equations of the Problem. The equations of the problem investigated are the continuity equations for the positive and negative ions, $n_{p,t} = -\nabla \cdot \mathbf{j}_p$ and $n_{m,t} = -\nabla \cdot \mathbf{j}_m$, where $F_{,t} = \partial F/\partial t$, and the Poisson equation $\nabla \cdot \mathbf{E} = (q/\varepsilon)(n_p - n_m)$, which defines the electric field as a function of the bulk density of charge. In these expressions, n_p and n_m are the actual densities of positive and negative ions, respectively; $\mathbf{j}_p = -D_p[\nabla n_p - (qn_p/K_BT)\mathbf{E}]$ and $\mathbf{j}_m = -D_m[\nabla n_p + (qn_m/K_BT)\mathbf{E}]$ are the current densities.[4] In our description, we use a Cartesian reference frame with the z-axis perpendicular to the limiting surfaces. The electrodes are assumed perfectly blocking at $z = \pm d/2$. The fundamental equations of the problem become

$$n_{p,t} = D_p[n_{p,z} + (qn_p/K_BT)V_{,z}]_{,z}$$
$$n_{m,t} = D_m[n_{m,z} + (qn_m/K_BT)V_{,z}]_{,z}$$
$$V_{,zz} = -(q/\varepsilon)(n_p - n_m) \tag{1}$$

where V is the electrical potential, defined by $E = -\nabla V$. Equations 1 have to be solved with the boundary conditions

$$n_{p,z} + (qn_p/K_BT)V_{,z} = 0$$
$$n_{m,z} - (qn_m/K_BT)V_{,z} = 0 \tag{2}$$

at $z = \pm d/2$, which describe perfectly blocking electrodes, and $V(\pm d/2, t) = \pm V_0/2$ for $t \geq 0$, given by the external power supply. We limit our analysis to the case where the amplitude of the external voltage V_0 is so small that $|n_{p(m)} - N| \ll N$. Under such assumption, eqs 1 can be linearized as[15,16]

$$p_{,t} = D(p_{,zz} + u_{,zz})$$
$$m_{,t} = \xi D(m_{,zz} - u_{,zz})$$
$$u_{,zz} = -(p - m)/(2\lambda^2) \tag{3}$$

The boundary conditions become

$$p_{,z} + u_{,z} = 0, \quad m_{,z} - u_{,z} = 0, \quad u = \pm u_0/2 \tag{4}$$

at $z = \pm d/2$. In eqs 3 and 4, we have introduced the adimensional variables $p = (n_p - N)/N$, $m = (n_m - N)/N$, $u = qV/(K_BT)$, $u_0 = qV_0/(K_BT)$, and $\lambda = [\varepsilon K_BT/(2q^2N)]^{1/2}$, which is the Debye's length.[17] We have also defined $D_p = D$ and $D_m = \xi D$.

B. Analytical Solution in an Implicit Form. We seek a solution of eqs 3 in the form $f(z, t) = f_{eq}(z) + f_{tr}(z, t)$, where $f_{eq}(z)$ is the steady-state solution (equilibrium conditions) and $f_{tr}(z,t)$ describes the transient state. The latter component is such that $\lim_{t \to \infty} f_{tr}(z, t) = 0$;[18] the equilibrium component of the solution is not dependent on the ratio ξ of the diffusion coefficients. Because we are interested in the determination of the relaxation times, from now on, we limit our analysis to $f_{tr}(z, t)$, that we assume of the form $f_{tr}(z, t) = \psi(z) \exp(-at)$, where $a > 0$ is the inverse of the relaxation time.

Substituting this ansatz into eqs 3 and 4, we obtain

$$a\psi_p = -D(\psi_p'' + \psi_u'')$$
$$a\psi_m = -\xi D(\psi_m'' - \psi_u'')$$
$$\psi_u'' = -(1/2\lambda^2)(\psi_p - \psi_m) \tag{5}$$

where $\psi' = d\psi/dz$, and

$$\psi_p' - \psi_u' = 0$$
$$\psi_m' - \psi_u' = 0$$
$$\psi_u = 0 \tag{6}$$

at $z = \pm d/2$.

The solutions of eqs 5 with the boundary conditions in eq 6 are

$$\psi_p(z) = C_1\sinh(\mu_1 z) + C_3\sinh(\mu_3 z)$$
$$\psi_m(z) = k_1C_1\sinh(\mu_1 z) + k_3C_3\sinh(\mu_3 z)$$
$$\psi_u(z) = -\frac{1}{2\lambda^2}\left\{\frac{1 - k_1}{\mu_1^2}C_1\sinh(\mu_1 z) + \frac{1 - k_3}{\mu_3^2}C_3\sinh(\mu_3 z)\right\} + Az \tag{7}$$

where C_1, C_3, and A are integration constants. The constants $\mu_{1(3)}$ and $k_{1(3)}$ are given by

$$\mu_{1(3)}^2 = \frac{1}{2\lambda^2}\left\{1 - \frac{\xi+1}{\xi}\alpha \pm \sqrt{1 + \left(\frac{\xi-1}{\xi}\alpha\right)^2}\right\} \tag{8}$$

$$k_{1(3)} = -\left\{\frac{\xi-1}{\xi}\alpha \pm \sqrt{1 + \left(\frac{\xi-1}{\xi}\alpha\right)^2}\right\}$$

Here $\alpha = a\lambda^2/D$.

We are interested in the relaxation times, which are derived from an eigenvalues equation, as reported in ref 7:

$$A_1\left(1 - \frac{\tanh(\mu_3 d/2)}{\mu_3 d/2}\right) - A_2\left(1 - \frac{\tanh(\mu_1 d/2)}{\mu_1 d/2}\right) + A_3 = 0 \tag{9}$$

Equation 9 is obtained by substituting eqs 7 into eqs 6 and imposing that the system has a solution different from the trivial one $C_1 = C_3 = A = 0$.[6] In eq 9, we have introduced

$$A_1 = \frac{(1+k_1)(1-k_3)}{\mu_3^2} = -4\lambda^2 \frac{\xi - \sqrt{\xi^2 + \alpha^2(\xi-1)^2}}{\alpha - \xi + \alpha\xi + \sqrt{\xi^2 + \alpha^2(\xi-1)^2}}$$

$$A_2 = \frac{(1-k_1)(1+k_3)}{\mu_1^2} = -4\lambda^2 \frac{\xi + \sqrt{\xi^2 + \alpha^2(\xi-1)^2}}{\alpha - \xi + \alpha\xi - \sqrt{\xi^2 + \alpha^2(\xi-1)^2}}$$

$$A_3 = 2\lambda^2(k_3 - k_1) = 4\lambda^2 \frac{\sqrt{\xi^2 + \alpha^2(\xi-1)^2}}{\xi} \tag{10}$$

It is important to note that eq 9 cannot be solved analytically, but it has infinite solutions. Consequently, the sets of eigenfunctions (eq 7) are complete, and the solution is given by a linear superposition of terms in the form of eq 7. The coefficients must be determined by means of the boundary conditions, $f_{tr}(z, 0) = -f_{eq}(z)$.

Albeit in principle the problem has been analytically solved, it should be noted that only an implicit solution can be given. On the contrary, as we will discuss in the next section, a numerical solution is possible.

C. Theoretical Considerations. A first consideration refers to the relaxation times and has already been reported in ref 7. From simple dimensional arguments, it is possible to define several relaxation times ($\tau = 1/a$). In particular, it is possible to define two combinations of the diffusion coefficients, known as the free and ambipolar diffusion coefficients (D_1 and D_2, respectively).[18] The first one is

$$D_1 = \frac{D_p + D_m}{2} \tag{11}$$

and accounts for the fact that the diffusion of the ions is independent of the electric field because of their redistribution. The ambipolar diffusion coefficient

$$D_2 = 2\frac{D_p D_m}{D_p + D_m} \tag{12}$$

is important when we consider that the effective diffusion of the ions depends on their own space-charge field.

Given these diffusion coefficients, it is possible to define three relaxation times.[7]

$$\tau_1 = \frac{\lambda d}{2D_1}$$

$$\tau_2 = \frac{d^2}{\pi^2 D_1}$$

$$\tau_3 = \frac{\lambda d}{2D_2} \tag{13}$$

We remind here that τ_1 and τ_2 are exact solutions of eq 9, whereas τ_3 is only an approximate solution. Because $D_1 \geq D_2$ and $\lambda \ll d$, $\tau_1 < \tau_2$. In the following, τ_1 and τ_2 will be called the shortest and the longest relaxation time, respectively.

A second consideration refers to the limit $\xi \to 0$, corresponding to the situation where the negative ions are fixed in space. As evident from eqs 3, $\xi = 0$ is a singular point in the space of the parameters for the system of differential equations.[19] The case $\xi = 0$ can be solved analytically.[20] The fundamental equations reduce to $p_{,t} = D_p(p_{,zz} + u_{,zz})$ and $u_{,zz} = -p/(2\lambda^2)$, with the boundary conditions $p_{,z} + u_{,z} = 0$ and $u = \pm u_0/2$ for $z = \pm d/2$. Likewise, the eigenvalues equation becomes

$$\tanh(\mu_1 d/2) = (1 - 2\lambda^2\mu_1^2)\mu_1 d/2 \tag{14}$$

where $\mu_1 = (1-2\alpha)^{1/2}/(2^{1/2}\lambda)$. In the simple case when $x = \lambda/d \ll 1$, it is possible to solve eq 14 with a simple approximation. We look for a solution in the form $\alpha = bx$, where $b \approx 1$.[6] It follows that $\mu_1 \approx (1 - bx)/(2^{1/2}\lambda)$ and $\mu_1 d/2 \approx 1/(2 \times 2^{1/2}x) \gg 1$. Equation 14 gives $b = 2^{1/2}$. It follows that $a = 2^{1/2}D/(\lambda d)$, and we find the relaxation time $\tau_0 = \lambda d/(2^{1/2}D_p)$. It is interesting to observe that $\tau_0 = 2^{1/2}\tau$, where τ is the relaxation time when the two ions have the same mobility ($\xi = 1$).[4,5]

On the contrary, a special care is necessary to analyze the case $\xi \to 0$. In fact, the solution cannot be found perturbatively, that is, by expanding $f(z, t)$ in power series of the small parameter ξ as $f(z, t) = f_0(z, t) + \xi f_1(z, t)....$[19] Rather, it must be obtained by the general formalism presented above: expanding the eigenvalues equation in power series of ξ and taking into account that $\alpha = \alpha(\xi)$. Because in the eigenvalues equation the term $\tanh(\mu_3 d/2)/(\mu_3 d/2)$ appears, the limit of which does not exist for $\xi \to 0$, it is impossible to investigate analytically the dependence on ξ of any finite relaxation time (including the shorter relaxation time τ_1).

III. Numerical Analysis

In the previous section, we have shown that an analytical solution of the problem is possible only in an implicit form. We have also shown that the transient solutions describing the dynamics of the ions are described by a linear superposition of exponentially decaying functions:

$$p(z, t) = \sum_i P_i(z)[1 - e^{-t/\tau_i}]$$

$$m(z, t) = \sum_i M_i(z)[1 - e^{-t/\tau_i}]$$

$$u(z, t) = \sum_i U_i(z)[1 - e^{-t/\tau_i}] \tag{15}$$

where the relaxation times τ_i and amplitudes P_i, M_i, and U_i are defined by eqs 8 and 9. Also, we have introduced three relaxation times, which are solutions of the eigenvalues equation, given by eq 13. Finally, we have investigated the behavior of the relaxation times for $\xi = 0$. In such case, the relaxation time is $\lambda d/(2^{1/2}D_p)$.

To proceed further, a numerical analysis is the only viable possibility, in particular to determine how many exponential terms are needed to correctly describe the evolution of the system, which are the relevant relaxation times in the multirelaxation process, and under which conditions the three relaxation times relative to ambipolar and free diffusion processes are important. Also, a numerical analysis can provide the relative amplitudes of the relevant relaxation processes involved.

For this goal, the nonlinear equations governing the dynamics of the system have been solved numerically by using the usual finite difference approach,[21] already adopted elsewhere to determine the decay time in the case of the same diffusion coefficient for the positive and the negative ions.[22] Stability and convergence of the numerical scheme adopted have been tested
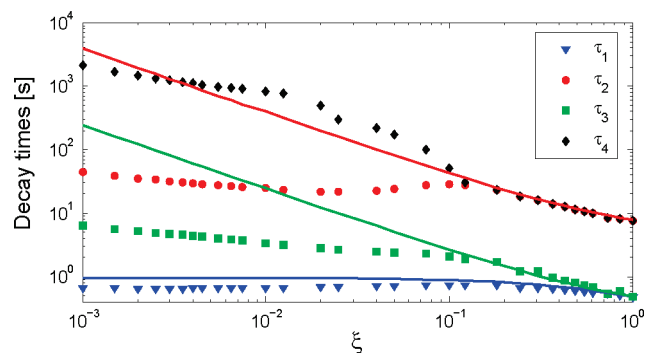
Figure 3. Dependence of the four relaxation times on the ratio of the diffusion coefficients ξ of negative and positive ions. Note the log–log scale. The solid lines correspond to the theoretically expected relaxation times (see eq 13).
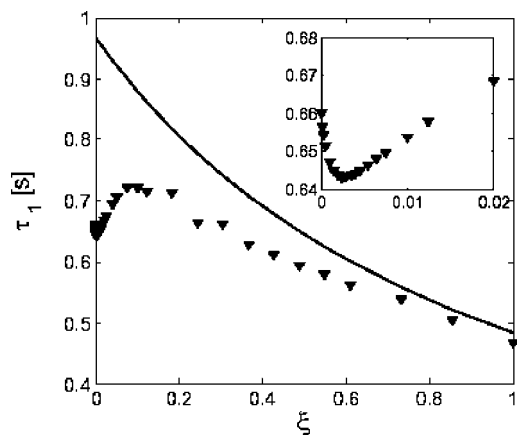
Figure 4. Dependence of τ_1 on the ratio of the diffusion coefficients, ξ, of negative and positive ions. Note the linear scale. The solid line corresponds to the theoretically expected relaxation times (see eq 13). The region for low ξ is zoomed in the inset to point out the presence of a minimum.

by comparison with the known theoretical solutions (in the case $D_p = D_m$) and by verifying the invariance of the results from the choice of time and space discretisation steps.

The analysis has been limited to the case of a small applied potential ($V_0 = 1$ mV), where the linearized solution described in the previous section is valid. We have considered parameters corresponding to a doped liquid crystal:[23] $N = 4.6 \times 10^{19}$ m^{-3}, $D_p = 8.2 \times 10^{-12}$ m^2/s, and $\varepsilon = 6.7 \times \varepsilon_0$, $d = 25$ μm. The diffusion coefficient of negative ions has been assumed to be smaller than D_p: $D_m = \xi D_p$.

In our analysis, we have studied the time evolution of the potential and density of ions in a position close to the left edge of the layer: $z^* = -d/2 + \eta$, where $\eta = 0.1$ μm.

A. Results. After an extensive numerical analysis, we have found that the temporal evolution of positive and negative ions and of the potential can be described, for any value of ξ, by a linear superposition of four exponential functions. To support our conclusion, we have also fitted the time series by using five exponential functions, and we found that for any value of ξ, at least two of the time decays obtained were approximately the same. However, even though four terms in the expansion have been found to be the minimum number, not all of them are relevant for every value of ξ, as shown in Figures 1 and 2, where the densities of positive ($p(z = z^*), t)$) and negative ($n(z = z^*), t)$) ions are reported versus time for increasing values of ξ.

When $\xi = 1$, only one exponential function is important, the amplitude of the other three being approximately zero (Figures
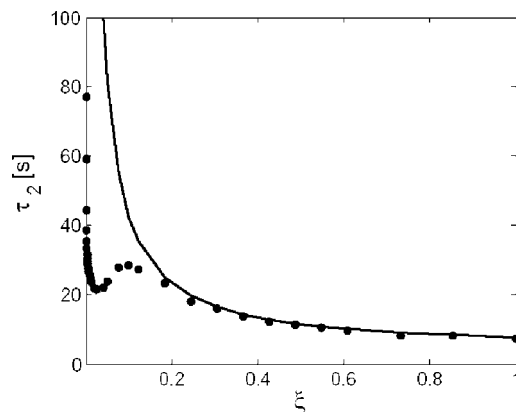
Figure 5. Dependence of τ_2 on the ratio of the diffusion coefficients, ξ, of negative and positive ions. Note the linear scale. The solid line corresponds to the theoretically expected relaxation times (see eq 13).

1a and 2a). The time decay determined ($\tau = \tau_1 = 0.48$ s) and the single relaxation process found are in good agreement with results reported elsewhere.[4,5] As soon as ξ starts diminishing, the relaxation becomes a multirelaxation process, even though it is not so clearly visible for the positive ions for which, for all values of ξ, relaxation remains in good approximation a single relaxation process. Nevertheless, already for $\xi = 0.73$ (Figures 1b and 2b), two terms have relevant amplitudes, with time decays corresponding to the relaxation times τ_1 and τ_3 (violet and black lines) approximately equivalent to those predicted by eq 13.[24] More important in this context is the behavior when ξ falls below 0.1. Already for $\xi = 0.04$ (Figures 1c and 2c), a third term in the linear superposition becomes important, particularly for the dynamics of the negative ions. Finally, a fourth term is needed to obtain a reasonable fitting of the tail when ξ falls below 0.01 (Figures 1d and 2d for $\xi = 0.004$).

Even though not reported here for brevity, conclusions similar to those for the negative ions are obtained for the evolution of the potential. Also, we stress here the good quality of the fitting obtained for every value of ξ. Finally, we remark some difficulties in fitting the curves for very low values of ξ (0.001). Here, the relaxation is very slow, and already for $\xi = 0.004$, we can observe that the equilibrium of negative ions has not yet been reached completely. Simulations for longer times, which may easily need to be as long as 10 000 s to ensure complete equilibrium, are not affordable because of the computational time. As a consequence, we cannot exclude in the region $\xi < 0.001$ the need of an additional exponential term with a very long decay time to catch adequately the tail in the relaxation.

The time decays corresponding to the four decay processes are reported in Figure 3 on a log–log scale as a function of the ratio of the diffusion coefficients. For ξ approaching 1, the first three calculated times approach well the theoretically expected values reported in eq 13 and shown as solid lines in the plot. In this region, the calculated τ_4 coincides with τ_2, and the amplitude of the corresponding exponential is absolutely negligible up to $\xi = 0.1$.

At about $\xi = 0.1$, the dependence of the time decays on the parameter is no longer as expected. Although τ_3 and τ_4 maintain a monotonous behavior with decreasing ξ, this is no longer true for both τ_1 and τ_2, as reported in Figures 4 and 5. Here, a linear scale is used to better appreciate the anomalous behavior of the two relaxation times. Both present a maximum at $\xi \approx 0.1$ and then decrease with decreasing ξ. At lower values of ξ, a
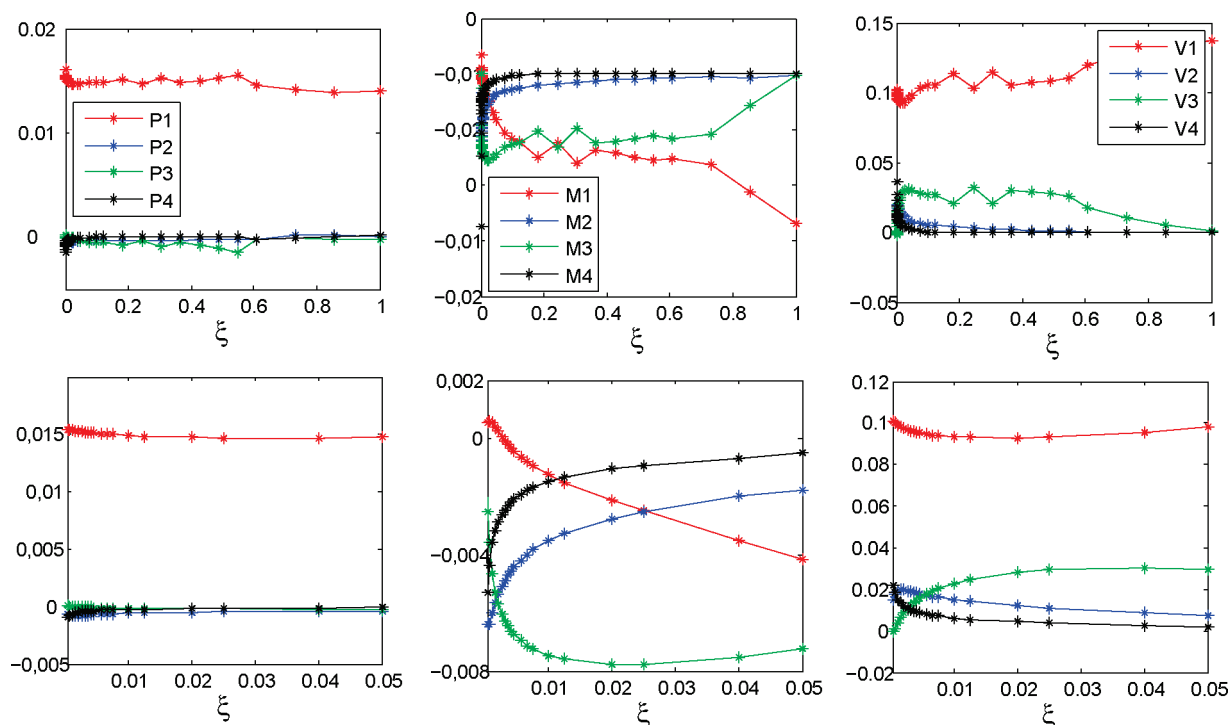
Figure 6. Dependence of the amplitudes of the four exponential terms on the ratio of the diffusion coefficients, ξ, of negative and positive ions. A zoom for low values of ξ is shown in the bottom line.

minimum can be observed, and then both start increasing again with decreasing ξ. The position of the minimum is at $\xi \approx 0.003$ for τ_1 (see inset of Figure 4) and $\xi \approx 0.02$ for τ_2. This anomalous behavior is unexpected, because a monotonous curve seems more intuitive. In fact, decreasing the parameter corresponds to decreasing the diffusivity (and therefore the mobility) of negative ions, resulting in an expected increase of the relaxation time. Finally, we remark that τ_4 presents a diverging behavior similar to the longer relaxation time predicted theoretically and reported in eq 13. τ_4 diverges very rapidly, and the contribution of the corresponding exponential term is limited to describe the tail of the temporal evolution of the corresponding variables.

We also note that the theoretical behavior of the shorter relaxation time for ξ approaching zero, reported in the previous subsection, is consistent with the findings reported here. Indeed, the shorter (and only finite) relaxation time converges to the value $\tau_1 = 0.66$ s, in agreement with the expectation $\tau_0 = 2^{1/2}\tau = 2^{1/2} \times 0.48 \approx 0.68$ s.

Finally, in Figure 6, the amplitudes corresponding to the four exponential terms in the linear superposition of eq 15 are reported versus ξ. It is confirmed that the dynamics of the positive ions is almost completely determined by the shortest relaxation process for any value of ξ. On the contrary, the role of the slower relaxation processes become more and more important for diminishing ξ for both negative ions and the potential.

B. Discussion. As shown in Figures 3–5, we have observed an anomalous behavior in the dependence of the relaxation times as a function of the ratio between the diffusivities of positive and negative ions. Indeed, besides observing an increase in the number of the relaxation processes involved in the dynamics of the system, we have found a non-monotonous behavior of two of the four decay times calculated numerically. In particular, we have found three significant discontinuities in the behavior of the smaller relaxation time (in addition to the one for $\xi = 0$, which is not relevant in this discussion and has already been analyzed). $\xi = 1$ is the only case described by a single relaxation

process. At about $\xi = 0.1$, the smaller relaxation time presents a maximum, and at about $\xi = 0.003$, the smaller relaxation time presents a minimum (see Figure 3).

To establish any correlation between the dynamics of the system and such discontinuity points, we have individuated two significant features in the temporal evolution of the positive and negative ions.

(a) For any value of ξ, except $\xi = 1$, the density of positive ions evolves to a maximum and then decays toward its equilibrium value (see Figure 7a). This is the reason why, albeit always very small, the second, third, and fourth terms in the linear superposition for the positive ions have a negative amplitude. The presence of such a maximum can be explained in physical terms as follows: positive ions, being faster than negative ones, accumulate faster close to the surfaces of the slab to compensate the applied field. At later times, the effect due to the slower motion of negative ions contributes to create an additional field, which breaks the equilibrium in a direction opposite to that originally created by the applied field. As a consequence, the positive ions feel a field of opposite sign and move back toward the center of the specimen until equilibrium is reached.

(b) For large values of ξ, the density of negative ions is monotonically decreasing, whereas for very small values of ξ, at the very initial times, the concentration of negative ions increases up to a maximum and then decreases toward its equilibrium value (see Figure 7b). From a physical point of view, we can understand the effect as follows: we are in the case in which the motion of the negative ions is very slow. In this condition, the redistribution of the positive ions rapidly leads to a concentration of the electric field in proximity of the free surfaces, that is, within less than tens of microns from the surfaces. It follows that in this region, the electric field becomes very strong, thus exerting a strong force on the negative ions despite their low mobility. Such effect is very confined to the surface and not present at a distance of 0.1 μm from the surface, where we record our data. As a consequence, negative ions flow
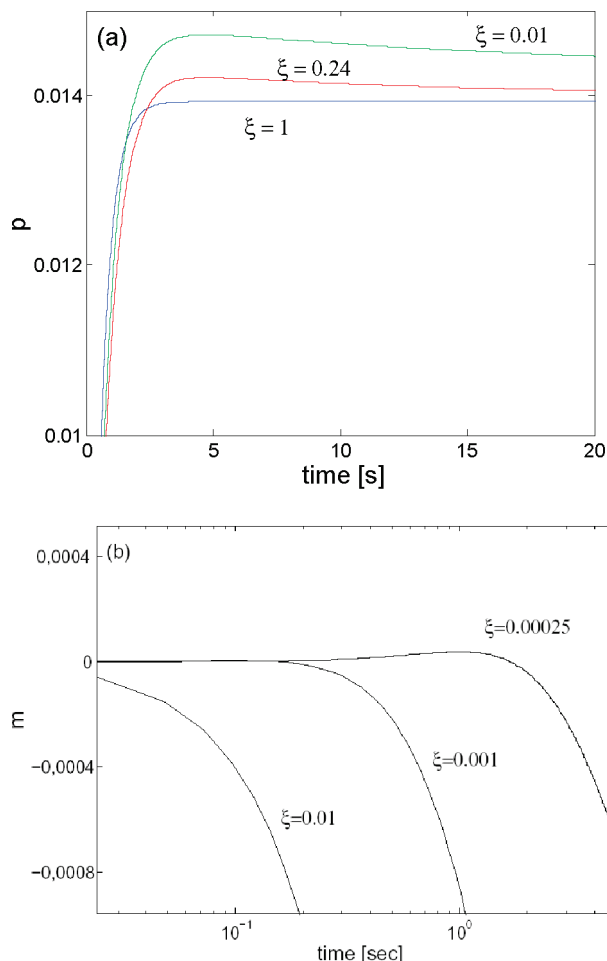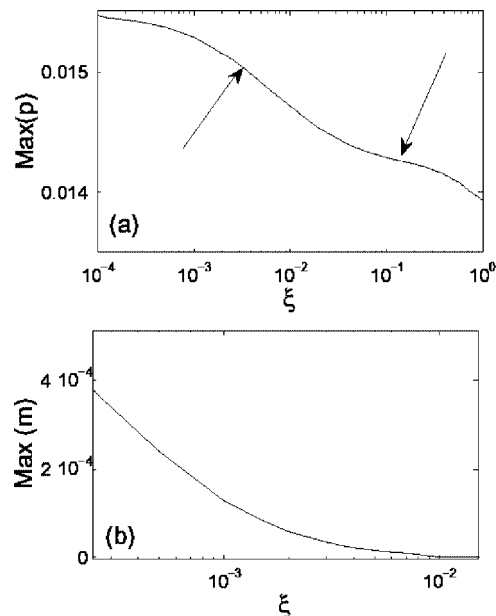
Figure 7. (a) Zoom of the initial times of the temporal evolution of the density of positive ions at $z = -12.4$ μm for different values of ξ. A non-monotonous behavior is observed for ξ different from 1. (b) Zoom of the initial times of the temporal evolution of the density of negative ions at $z = -12.4$ μm for different values of ξ. A non-monotonous behavior is observed when ξ is very small.

Figure 8. Dependence on ξ of the maximum reached by the density of positive ions (a) and by the density of negative ions (b). In the latter case, a maximum is present only when $\xi < 0.01$. Arrows in panel (a) indicate changes in concavity of the curve.

away very slowly from this latter position but flow in very rapidly because of the intense electric field to the left. In other words, the large current toward z^* is not paired with a large current away from it. As a consequence, an initial accumulation of ions may occur, leading to the observed maximum.

We have investigated the values of the maxima in the positive (Figure 8a) and negative (Figure 8b) ion densities in $z = z^*$ as a function of ξ. We found a monotonous increase of the maximum density of positive ions with decreasing ξ, as expected. Albeit variations are very small, the monotonic behavior still suggests some possible interpretation. The curve presents two changes in its concavity, marked by arrows in Figure 7a. The corresponding values of ξ correspond well to the position of the maxima and minima in the curve τ_1 versus ξ, $\xi \approx 0.1$ and $\xi \approx 0.003$. Also, the maximum in the evolution of the density of negative ions appears only for $\xi \approx 0.01$ (Figure 7b), whereas as mentioned, the negative ions decay monotonically for larger values of the parameter (no maximum appears). Again, such value approximately corresponds to the minimum of the decay time τ_2.

The discussion reported in the previous paragraph is of course only preliminary. Indeed, other observations on the behavior of the maxima in the time evolution of the ion densities can be proposed. For example, the maximum in the positive ions density stays approximately constant in the interval $0.01 < \xi$

< 0.02, values which correspond roughly to the two maxima and minima in the dependence of τ_2 on ξ.

We believe that our results are indicative of a possible correlation between the effects, which might be further investigated with a more accurate analysis of the behavior of the system in proximity of this critical values of ξ.

IV. Conclusions

We have considered the ionic redistribution in an electrolytic cell subjected to an external electric field and analyzed the relaxation processes leading to the equilibrium solution. Taking into account the drift-diffusion and Poisson equations for the ions density and electric field, respectively, we have solved numerically the system of nonlinear equations. Our analysis has shown that when the diffusion coefficients of positive and negative ions are different, a multirelaxation process governs the dynamics of the system. When the ratio between the diffusion coefficients decreases, the free diffusion and the ambipolar diffusion are no longer adequate to describe the evolution of the ions density. More relaxation processes are needed. Also, we have found that the shortest relaxation time depends non-monotonically on the diffusion coefficient of the slowest ions.

Here, the presence of adsorption phenomena at the surfaces between the electrolytic cell and the dielectric has been neglected. Likewise, we have not considered the presence of a Stern layer[17] at the interfaces. Nevertheless, we believe that including such features will not modify, at least qualitatively, the considerations reported here.

It is to be noted that the variations observed in the relaxation times as a function of the diffusion coefficient of the slowest ions are noticeable. It is therefore expected that our findings have a practical importance in several fields, whenever the relaxation times influence the observables.[8,9] Examples are 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[12,13] or the correct interpretation of impedance spectroscopy results.[10,11]

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(24) It is important to observe that in the region $0.2 < \xi < 1$, the relaxation times corresponding to τ_1 and τ_3 are very similar. It follows that in such a region, the two are not easily discernible. Indeed, as shown in ref 7, for such values of the parameters, the curves can be well fitted by using two exponential functions, one of them given by the combination of τ_1 and τ_3 into a single contribution.