

Relaxation Times of an Electrolytic Cell Subject to an External Electric Field: Role of Ambipolar and Free Diffusion Phenomena

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We evaluate the relaxation times for an electrolytic cell subject to a step-like external voltage, in the case in which the mobility of negative ions is different from that of positive ions. The electrodes of the cell, in the shape of a slab, are supposed to be perfectly blocking. The theoretical analysis is performed by assuming that the applied voltage is so small that the fundamental equations of the problem can be linearized. In this framework, the eigenvalues equations defining all relaxation times of the problem are deduced. In the numerical analysis, we solve the complete set of equations describing the time evolution of the system under the action of the external voltage. Two relaxation processes, connected with the ambipolar and free diffusion phenomena, are sufficient to describe the dynamics of the system, when the diffusion coefficients are of the same order of magnitude.

1. Introduction

When an electrolytic cell, in thermodynamical equilibrium, is subject to an external voltage, the ions are submitted to a net electric force pushing them close to the electrodes of opposite sign. If the external electric field is step-like, after a transient, a new equilibrium is reached, in which the diffusion current, connected with the profiles of the ionic concentration, balances the drift current, due to the actual electric field. The determination of the relaxation times of this process is important both from a theoretical point of view and for the connected applications, e.g., in liquid crystal based devices.^{1,2}

The relaxation processes occurring in an electrolytic cell are connected to the motion of ions, which is governed by nonlinear equations. The relaxation times strongly depend on the diffusion coefficients D_p and D_m of positive and negative ions. The case in which the diffusion coefficients are the same has been discussed in the limit of a low applied voltage by several authors,³ by assuming that the system behaves linearly. The cases in which a large amplitude potential is applied⁴ and/or the effects due to the presence of a Stern layer are no longer negligible⁵ have also been considered. In all cases, it has been shown that a single relaxation process (with a corresponding relaxation time) is sufficient to describe the evolution of the system.

However, in most cases the diffusion coefficient of the positive ions is different from that of the negative ions. Therefore, it is necessary to consider multirelaxation processes and the solution becomes more complex,⁶ even when the analysis is limited to the linear case, i.e., to a small amplitude step-like applied voltage,⁷ without the presence of a Stern layer and of adsorption/desorption phenomena at the interfaces cell/

electrodes. This is the case considered in this paper, limiting the analysis to physical systems in which the diffusion coefficients are of the same order of magnitude.

In the next section, we describe the physical system considered and discuss the fundamental equations of the problem and their linear approximation. In the same section, we indicate the theoretical approach to solve the linearized fundamental equations describing the dynamical evolution of the system under the action of an external electric field. In section III, we derive the equations for the transient components of the solution, deduce the eigenvalues equation, and show the existence of infinite relaxation times. Discussing the equivalent electrical circuit, we individuate two relevant times and define their dependence from the ratio of the diffusion coefficients. These two times are connected with the ambipolar diffusion and with the free diffusion of the ions dissolved in the dielectric liquid.⁶ The theoretical analysis of section III allows solutions only in an implicit form, whereas solutions of the complete nonlinear problem can be given numerically. They are reported in section IV and used to support the hypotheses that, when the ratio of the diffusion coefficients is not too small, the two relaxation processes discussed before (ambipolar and free diffusion) are dominant with respect to others and sufficient to describe the dynamics of the system. Finally, we report in the Conclusions a discussion about the role of other relaxation processes and of the inadequacy of a two-relaxation solution when the diffusion coefficients are of different orders of magnitude.

2. Theory

A. Physical System. In our analysis, we assume that the sample is in the shape of a slab of thickness d , which allows us to reduce it to a one-dimensional system. The z axis of the Cartesian reference frame used in the description is normal to the surfaces limiting the sample, located at $z = \pm d/2$. The liquid contains ions of charge q and is characterized by a dielectric constant ϵ . Since the density of ions is negligible with respect

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to that of the neutral particles of the liquid, the contribution of the ions to the effective dielectric constant can be neglected.⁸ We also neglect ionic recombination and adsorption phenomena at the cell surfaces. Furthermore, the external potential is applied to the sample through perfectly blocking electrodes limiting the cell. It follows that there is no transfer of particles (and charge) between the cell and the external circuit: the electrical current in the circuit is a displacement current, due to the time variation of the surface electric field. The external voltage is a step of amplitude V_0 , with amplitude so small that the variation in the ionic distribution is very small with respect to the bulk density of ions in thermodynamical equilibrium. In this framework, the fundamental equations describing the dynamical evolution of the system can be linearized.⁷

In the absence of an external electrical potential, the sample is locally and globally neutral, with a bulk density of ions, in thermodynamical equilibrium, indicated by N . When an external field is applied to the system, the actual potential V and the bulk densities of positive and negative ions, n_p and n_m , are expected to depend on the spatial coordinate z and the time t .

B. Equations of the System. The fundamental equations describing the dynamic of the system are the drift-diffusion equation (for the motion of ions) and the Poisson equation (for the potential across the sample)

$$\begin{aligned} n_{p,t} &= D_p [n_{p,z} + (qn_p/K_B T)V_z]_z \\ n_{m,t} &= D_m [n_{m,z} - (qn_p/K_B T)V_z]_z \\ V_{zz} &= -(q/\epsilon)(n_p - n_m) \end{aligned} \quad (1)$$

where $f_x = \partial f / \partial x$. The ions current must vanish at $z = \pm d/2$:

$$\begin{aligned} j_p &= -D_p [n_{p,z} + (qn_p/K_B T)V_z] = 0 \\ j_m &= -D_m [n_{m,z} - (qn_m/K_B T)V_z] = 0 \end{aligned} \quad (2)$$

Also, the applied potential is step like, and for $t \geq 0$, $V(\pm d/2, t) = \pm V_0/2$.

In the equations reported above D_p and D_m are the diffusion coefficients of the positive and negative ions, respectively, and the Einstein–Smoluchowski's relation between the mobility and the diffusion coefficient has been assumed valid.⁹ In our analysis, we consider the case where $D_p \neq D_m$.

As usual,⁵ we define $n_p = N + \delta n_p$, $n_m = N + \delta n_m$. Being $V_0 \ll K_B T/q$, we have $\delta n_p \ll N$ and $\delta n_m \ll N$. Introducing the reduced quantities $p = \delta n_p/N$, $m = \delta n_m/N$, and $u = qV/K_B T$, and neglecting terms of the order of $\delta n_{p,m}u$, we obtain

$$\begin{aligned} p_t &= D_p (p_{zz} + u_{zz}) \\ m_t &= D_m (m_{zz} - u_{zz}) \\ u_{zz} &= -(1/2\lambda^2)(p - m) \end{aligned} \quad (3)$$

that are the linearized equations of the problem under investigation.¹⁰ Here, the variables p and m represent the relative variation in the ionic densities due to the presence of the electric field; u is the electrical potential expressed in $K_B T/q$ units. We have also introduced the Debye's length $\lambda = [\epsilon K_B T / (2Nq^2)]^{1/2}$.¹¹ The boundary conditions at $z = \pm d/2$ are linearized as

$$\begin{aligned} p_z + u_z &= 0 \\ m_z - u_z &= 0 \\ u &= \pm u_0/2 \end{aligned} \quad (4)$$

where $u_0 = qV_0/(K_B T)$.

Furthermore, we separate p , m , and u into equilibrium and transient components: $p(z, t) = p^{\text{eq}}(z) + p^{\text{tr}}(z, t)$, $m(z, t) = m^{\text{eq}}(z) + m^{\text{tr}}(z, t)$, and $u(z, t) = u^{\text{eq}}(z) + u^{\text{tr}}(z, t)$, where $\lim_{t \rightarrow \infty} p^{\text{tr}}(z, t) = 0$, $\lim_{t \rightarrow \infty} m^{\text{tr}}(z, t) = 0$, and $\lim_{t \rightarrow \infty} u^{\text{tr}}(z, t) = 0$.

The equilibrium solutions can be easily found setting to zero the time derivatives. We obtain

$$p^{\text{eq}}(z) = -m^{\text{eq}}(z) = -\frac{u_0}{2} \frac{\sinh(z/\lambda)}{\sinh(d/2\lambda)} \quad (5)$$

$$u^{\text{eq}}(z) = \frac{u_0}{2} \frac{\sinh(z/\lambda)}{\sinh(d/2\lambda)} \quad (6)$$

As expected, the equilibrium components of the solution are independent from the diffusion coefficients.

The linearized equations to be solved for the transient components are

$$\begin{aligned} p_t^{\text{tr}} &= D_p (p_{zz}^{\text{tr}} + u_{zz}^{\text{tr}}) \\ m_t^{\text{tr}} &= D_m (m_{zz}^{\text{tr}} - u_{zz}^{\text{tr}}) \\ u_{zz}^{\text{tr}} &= -(1/2\lambda^2)(p^{\text{tr}} - m^{\text{tr}}) \end{aligned} \quad (7)$$

with boundary conditions, at $z = \pm d/2$, given as

$$\begin{aligned} p_z^{\text{tr}} + u_z^{\text{tr}} &= 0 \\ m_z^{\text{tr}} - u_z^{\text{tr}} &= 0 \\ u^{\text{tr}}(\pm d/2, t) &= 0 \end{aligned} \quad (8)$$

The third boundary condition stems from the fact that $u^{\text{eq}} = \pm u_0/2$ at the boundaries. In the following, we will consider only transient components and therefore omit the superscript tr.

C. Transient Components. As usual in the theory of transient phenomena,¹² we look for a solution in the form $p(z, t) = \psi_p(z) \exp(-at)$, $m(z, t) = \psi_m(z) \exp(-at)$, and $u(z, t) = \phi(z) \exp(-at)$, where $a > 0$. Equation 6 becomes

$$\begin{aligned} \psi_p'' + \phi'' + (a/D_p)\psi_p &= 0 \\ \psi_m'' - \phi'' + (a/D_m)\psi_m &= 0 \\ \phi'' &= -(1/2\lambda^2)(\psi_p - \psi_m) \end{aligned} \quad (9)$$

where $f' = df/dz$. Replacing ϕ'' from the third equation into the former two, we obtain

$$\begin{aligned} \psi_p'' - \Omega_p^2 \psi_p + \frac{1}{2\lambda^2} \psi_m &= 0 \\ \psi_m'' - \Omega_m^2 \psi_m + \frac{1}{2\lambda^2} \psi_p &= 0 \end{aligned} \quad (10)$$

where

$$\Omega_p^2 = \frac{1}{2\lambda^2} - \frac{a}{D_p} \text{ and } \Omega_m^2 = \frac{1}{2\lambda^2} - \frac{a}{D_m} \quad (11)$$

From eq 10, we can eliminate $\psi_m(z)$ and obtain the differential equation for $\psi_p(z)$ in the form

$$-2\lambda^2 \xi \psi_p'''' + 2 \left\{ \xi \left(1 - \frac{a}{D_p} \lambda^2 \right) - \frac{a}{D_p} \lambda^2 \right\} \psi_p'' + \frac{a}{D_p} \left\{ \xi + 1 - 2 \frac{a}{D_p} \lambda^2 \right\} \psi_p = 0 \quad (12)$$

if eq 11 is taken into account and $\xi = D_m/D_p$. It is evident from eq 12 that $\psi_p(z)$ is solution of an ordinary differential equation of fourth order. Equation 12, when $\xi = 0$, reduces to a second order differential equation. Therefore, the point $\xi = 0$ is a singular point, in the parameter space, of eq 12. For this reason, in our investigation, we assume D_p of the same order of magnitude of D_m , which is the case physically meaningful in real electrolytic solutions.⁹

We look for a solution of eq 10 in the form $\psi_p(z) = C_p \exp(\mu z)$ and $\psi_m(z) = C_m \exp(\mu z)$. By substituting these expressions into eq 10, we obtain

$$(\mu^2 - \Omega_p^2) C_p + \frac{1}{2\lambda^2} C_m = 0$$

$$\frac{1}{2\lambda^2} C_p + (\mu^2 - \Omega_m^2) C_m = 0 \quad (13)$$

A solution, different from the trivial one $C_p = C_m = 0$, exists only if

$$(\mu^2 - \Omega_p^2)(\mu^2 - \Omega_m^2) - 1/(4\lambda^4) = 0 \quad (14)$$

which gives 4 solutions μ_i resulting from

$$\mu^2 = \frac{\Omega_p^2 + \Omega_m^2}{2} \pm \sqrt{\left(\frac{\Omega_p^2 - \Omega_m^2}{2} \right)^2 + \frac{1}{4\lambda^4}} \quad (15)$$

where the sign + is for μ_1 and $\mu_2 = -\mu_1$, and the sign - for μ_3 and $\mu_4 = -\mu_3$.

From eq 13, we have $C_m/C_p = -2\lambda^2(\mu^2 - \Omega_p^2)$. Therefore

$$C_m^1/C_p^1 = C_m^2/C_p^2 = -2\lambda^2(\mu_1^2 - \Omega_p^2) = k_1$$

$$C_m^3/C_p^3 = C_m^4/C_p^4 = -2\lambda^2(\mu_3^2 - \Omega_p^2) = k_3 \quad (16)$$

The solutions we are looking for are then in the form

$$\psi_p(z) = C_p^1 e^{\mu_1 z} + C_p^2 e^{-\mu_1 z} + C_p^3 e^{\mu_3 z} + C_p^4 e^{-\mu_3 z}$$

$$\psi_m(z) = k_1(C_p^1 e^{\mu_1 z} + C_p^2 e^{-\mu_1 z}) + k_3(C_p^3 e^{\mu_3 z} + C_p^4 e^{-\mu_3 z}) \quad (17)$$

Since the electrodes are blocking, the total ionic density must remain constant

$$\int_{-d/2}^{d/2} n_p(z, t) dz = \int_{-d/2}^{d/2} n_m(z, t) dz = Nd \quad (18)$$

Therefore

$$\int_{-d/2}^{d/2} \psi_p(z) dz = \int_{-d/2}^{d/2} \psi_m(z) dz = 0 \quad (19)$$

Consequently, $C_p^1 = -C_p^2 = C_1/2$ and $C_p^3 = -C_p^4 = C_3/2$. It follows that

$$\psi_p(z) = C_1 \sinh(\mu_1 z) + C_3 \sinh(\mu_3 z)$$

$$\psi_m(z) = k_1 C_1 \sinh(\mu_1 z) + k_3 C_3 \sinh(\mu_3 z) \quad (20)$$

The electrical potential across the sample can be evaluated from the third of eq 9, with $\psi_p(z)$ and $\psi_m(z)$ given by eq 20. We obtain

$$\phi(z) = B - \frac{1}{2\lambda^2} \left\{ \frac{1-k_1}{\mu_1^2} C_1 \sinh(\mu_1 z) + \frac{1-k_3}{\mu_3^2} C_3 \sinh(\mu_3 z) + Az \right\} \quad (21)$$

where A and B are two integration constants. From the boundary conditions $V(\pm d/2, t) = 0$, it follows $B = 0$. The boundary conditions at $z = \pm d/2$ for j_p , j_m , and V give

$$\psi_p' + \phi' = 0$$

$$\psi_m' - \phi' = 0$$

$$\phi = 0 \quad (22)$$

that form a homogeneous system.

3. Relaxation Times Of The System

A. Eigenvalues Equation. Using the results reported above for ψ_p , ψ_m , and $\phi(z)$ in eqs 20 and 21, eq 22 can be rewritten as

$$\left(\mu_1 - \frac{1-k_1}{2\lambda^2 \mu_1} \right) \cosh\left(\frac{\mu_1 d}{2}\right) C_1 + \left(\mu_3 - \frac{1-k_3}{2\lambda^2 \mu_3} \right) \cosh\left(\frac{\mu_3 d}{2}\right) C_3 - \frac{A}{2\lambda^2} = 0$$

$$\left(k_1 \mu_1 + \frac{1-k_1}{2\lambda^2 \mu_1} \right) \cosh\left(\frac{\mu_1 d}{2}\right) C_1 + \left(k_3 \mu_3 + \frac{1-k_3}{2\lambda^2 \mu_3} \right) \cosh\left(\frac{\mu_3 d}{2}\right) C_3 + \frac{A}{2\lambda^2} = 0$$

$$\frac{1-k_1}{\mu_1^2} \sinh\left(\frac{\mu_1 d}{2}\right) C_1 + \frac{1-k_3}{\mu_3^2} \sinh\left(\frac{\mu_3 d}{2}\right) C_3 + A \frac{d}{2} = 0 \quad (23)$$

that, as pointed out above, form a homogeneous system in C_1 , C_3 , and A . A solution different from the trivial one exists only if the determinant of the coefficients vanishes. This condition allows to calculate the relaxation times $\tau = 1/a$ of the problem we are analyzing, which are included in the definitions of the μ_i . The eigenvalue equation of the problem, after some calculations, becomes

$$\begin{vmatrix} \mu_1 - \frac{1-k_1}{2\lambda^2 \mu_1} & \mu_3 - \frac{1-k_3}{2\lambda^2 \mu_3} & -1 \\ k_1 \mu_1 + \frac{1-k_1}{2\lambda^2 \mu_1} & k_3 \mu_3 + \frac{1-k_3}{2\lambda^2 \mu_3} & 1 \\ \frac{1-k_1}{\mu_1^2} \tanh\left(\frac{\mu_1 d}{2}\right) & \frac{1-k_3}{\mu_3^2} \tanh\left(\frac{\mu_3 d}{2}\right) & \lambda^2 d \end{vmatrix} = 0 \quad (24)$$

that generalizes the equation reported in ref 5, valid in the case where $D_p = D_m$.

B. Relaxation Times. As discussed in ref 5, when $D_p = D_m = D$, in the limit of $\lambda \ll d$, we have one relaxation time given by

$$\tau = \frac{\lambda d}{2D} \quad (25)$$

Unfortunately, the solutions of eq 23 cannot be found in the more general case. The presence of a large number of solutions, due to the presence of trigonometric tangents, is also a limit for numerical solutions of the equation (see Appendix I). Nevertheless, some considerations, stemming from properties of the equivalent electrical circuits of the cell considered, can be used to guide us in the seek of some of the relevant relaxation times of the system.

Indeed, in a recent paper, the impedance spectroscopy of an electrolytic cell has been analyzed by solving the drift-diffusion equations for the positive and negative ions and the equation of Poisson for the actual potential in the cell.¹⁰ By assuming the electrodes perfectly blocking, it has been shown that in the low-frequency range of the applied voltage ($\omega \rightarrow 0$) the equivalent electrical circuit of the cell is a series of a resistance and of a capacitance, given by $\mathcal{R} = \lambda^2 d / (\epsilon D S)$, and $\mathcal{C} = \epsilon (S / 2\lambda)$, where S is the surface area of the electrodes. Therefore, the relaxation time is expected to be $\tau = \mathcal{R}\mathcal{C}$. Using for \mathcal{R} and \mathcal{C} the expressions reported above, we obtain again eq 25, supporting the validity of the equivalent electric circuit of the cell proposed in ref 10. Changing the frequency of the external voltage, the effective resistance of the cell, $\mathcal{R} = \mathcal{R}(\omega)$, changes. It remains almost frequency independent up to the relaxation frequency, $\omega_r \sim D/\lambda^2$: for $0 \leq \omega \leq \omega_r$ we have $\mathcal{R}(\omega) \sim \mathcal{R}(\omega \rightarrow 0)$. For $\omega > \omega_r$, $\mathcal{R} = \mathcal{R}(\omega)$ decays to zero, as expected. In fact, in the high-frequency region, the ions do not follow the time variations of the external potential and the electrolyte behaves as a perfect dielectric material, in the equivalent electrical circuit.

The effect of $D_p \neq D_m$ on the impedance spectroscopy of an electrolytic cell has been discussed in ref 13. According to the authors, the difference in the diffusion coefficients of the positive and negative ions is responsible, in the low-frequency range, for a new plateau for $\mathcal{R}(\omega)$. The effective diffusion coefficient of the cell in the plateau in the low-frequency range is

$$D_2 = 2 \frac{D_p D_m}{D_p + D_m} \quad (26)$$

corresponding to the ambipolar diffusion,⁶ where the effective diffusion of the ions depends on their own space charge field. The other plateau is connected to the diffusion coefficient

$$D_1 = \frac{D_p + D_m}{2} \quad (27)$$

which refers to the free diffusion of the positive and negative ions in the dielectric liquid.⁶ In this case, the diffusion of the ions is independent from the electric field due to their redistribution.

From simple dimensional arguments, it is possible to define several relaxation times, e.g.

$$\tau_1 = h_1 \frac{\lambda d}{D_1}, \quad \tau_2 = h_2 \frac{d^2}{D_2} \quad \text{and} \quad \tau_3 = h_3 \frac{\lambda d}{D_2} \quad (28)$$

in analogy with eq 25. Indeed, as shown in Appendix I, τ_1 and τ_2 are exact solutions of eq 24, for $h_1 = 1/2$ and $h_2 = 1/\pi^2$, whereas τ_3 is an approximate solution when $h_3 = 1/2$.

C. Eigenfunctions. As discussed in the previous subsection, the eigenvalues equation allows many relaxation times. The number of solutions of eq 24 increases rapidly when ξ decreases.

It follows that, due to the linearity of eq 3, the transient components of the solution of the problem are linear combinations of the form

$$\begin{aligned} p^{\text{tr}}(z, t) &= \sum_{a_k} \psi_p(z; a_k) \exp(-a_k t) \\ m^{\text{tr}}(z, t) &= \sum_{a_k} \psi_m(z; a_k) \exp(-a_k t) \end{aligned} \quad (29)$$

where $a_k = 1/\tau_k$ are the solutions of eq 24. Of course, the relative amplitudes of the various solutions determine their importance in describing the relaxation of the system.

In the limit case $\xi \sim 1$, eq 24 has one solution, or, better, several solutions which all converge to τ_1 .¹⁵ In this case, the problem in the linear approximation can be solved. In fact, by taking into account that $p(z, t) = p^{\text{eq}}(z) + p^{\text{tr}}(z, t)$ and $m(z, t) = m^{\text{eq}}(z) + m^{\text{tr}}(z, t)$, and that $p(z, 0) = 0$, $m(z, 0) = 0$, we have

$$p^{\text{tr}}(z, 0) = -p^{\text{eq}}(z)$$

and

$$m^{\text{tr}}(z, 0) = -m^{\text{eq}}(z) \quad (30)$$

Using eqs 5 and 20, we obtain

$$C_1 \sinh(\mu_1 z) + C_3 \sinh(\mu_3 z) = \frac{u_0}{2} \frac{\sinh(z/\lambda)}{\sinh(d/2\lambda)} \quad (31)$$

$$k_1 C_1 \sinh(\mu_1 z) + k_3 C_3 \sinh(\mu_3 z) = -\frac{u_0}{2} \frac{\sinh(z/\lambda)}{\sinh(d/2\lambda)} \quad (32)$$

by means of which we can evaluate C_1 and C_3 and then the constant A appearing in the potential. When $\xi \sim 1$, $k_1 \sim -1$ and $k_3 \sim 1$. Consequently, we have $C_1 \sim (u_0/2)/[\sinh(d/2\lambda)]$ and $C_3 \sim 0$.

In the general case, to determine the amplitudes of the modes, C_{1k} and C_{3k} , it is necessary to solve the equations

$$\begin{aligned} \sum_{a_k} \{C_{1k} \sinh[\mu_1(a_k)z] + \\ C_{3k} \sinh[\mu_3(a_k)z]\} &= \frac{u_0}{2} \frac{\sinh(z/\lambda)}{\sinh(d/2\lambda)} \end{aligned} \quad (33)$$

$$\begin{aligned} \sum_{a_k} \{k_1(a_k)C_{1k} \sinh[\mu_1(a_k)z] + \\ k_3(a_k)C_{3k} \sinh[\mu_3(a_k)z]\} &= -\frac{u_0}{2} \frac{\sinh(z/\lambda)}{\sinh(d/2\lambda)} \end{aligned} \quad (34)$$

which is extremely difficult, since the eigenfunctions of the problem are not orthogonal. In this case, it is necessary to orthogonalize them by means of a proper linear transformation, before proceeding to the determination of the amplitudes of the modes, as discussed in ref 16. An explicit solution is not possible and we will determine the solution using a numerical approach, as discussed in the next section.

4. Numerical Analysis

The equations governing the dynamic of the system have been solved numerically using the usual finite difference (FD) approach,¹⁷ already adopted elsewhere to determine the decay time in the case of the same diffusion coefficient for the positive

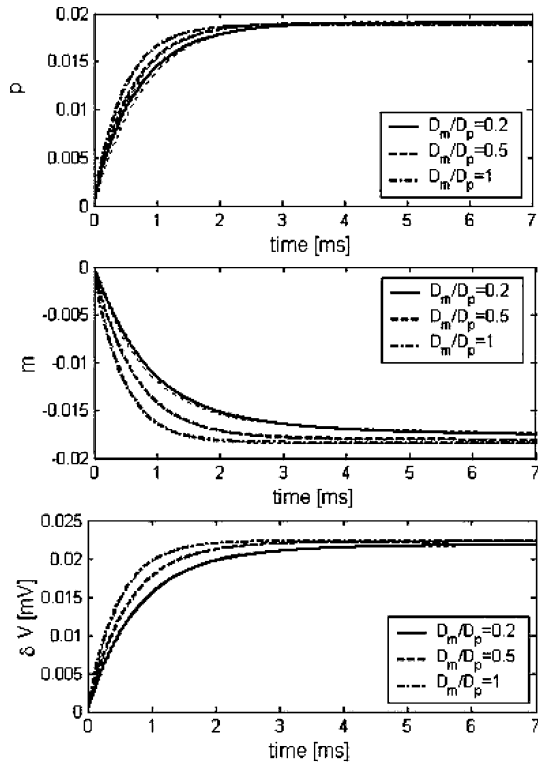


Figure 1. Temporal evolution of the relative density of positive and negative ions (p and m) and of the potential (δV) close to the electrodes surface (in $z = -d/2 + 0.0025 \mu\text{m}$) for different values of $\xi = D_m/D_p$. The thin dotted lines represent the best fitting using a two exponential decay models (eq 35). For large values of ξ , the fitting curve is completely superimposed to numerical data.

and negative ions.^{5,18} Stability and convergence of the numerical scheme adopted have been tested 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 the time and space discretisation steps.

The analysis has been limited to the case of a small applied potential ($V_0 = 1 \text{ mV}$), where the linearized solution described in the previous section is valid. We have considered parameters corresponding to a doped liquid crystal:¹⁴ $N = 4.6 \times 10^{19} \text{ m}^{-3}$, $D_p = 8.2 \times 10^{-12} \text{ m}^2/\text{s}$, $\epsilon = 6.7\epsilon_0$, $d = 25 \mu\text{m}$. With these physical parameters, the length of Debye of the electrolytic solution, in thermodynamical equilibrium, is $\lambda = 0.3 \mu\text{m}$. The diffusion coefficient of negative ions has been assumed smaller than D_p : $D_m = \xi D_p$. For the reasons mentioned above, we have limited our analysis to $0.05 \leq \xi \leq 1$. Preliminary results indicate a more complex behavior for lower values of D_m , which has still to be investigated.

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 $\eta = 0.025 \mu\text{m}$ is the space discretisation step. Simulations indicate a relaxation toward the expected equilibrium values (see ref 18) for both the relative variation of the density of positive/negative ions $p(z = z^*, t) = [n_p(z = z^*, t) - N]/N$ and $m(z = z^*, t) = [n_m(z = z^*, t) - N]/N$ and of the potential $\delta V(z = z^*, t) = (V(z = z^*, t) - V(z = z^*, 0))$. The argument $z = z^*$ will be omitted from now on for brevity. As expected the equilibrium values are independent of ξ , whereas the relaxation time increases with diminishing the negative ions diffusion coefficient. Some of the results are reported in Figure 1. Here, the slow down of the relaxation process is particularly evident for the evolution of the negative ions whose dynamic is more affected by the choice of D_m .

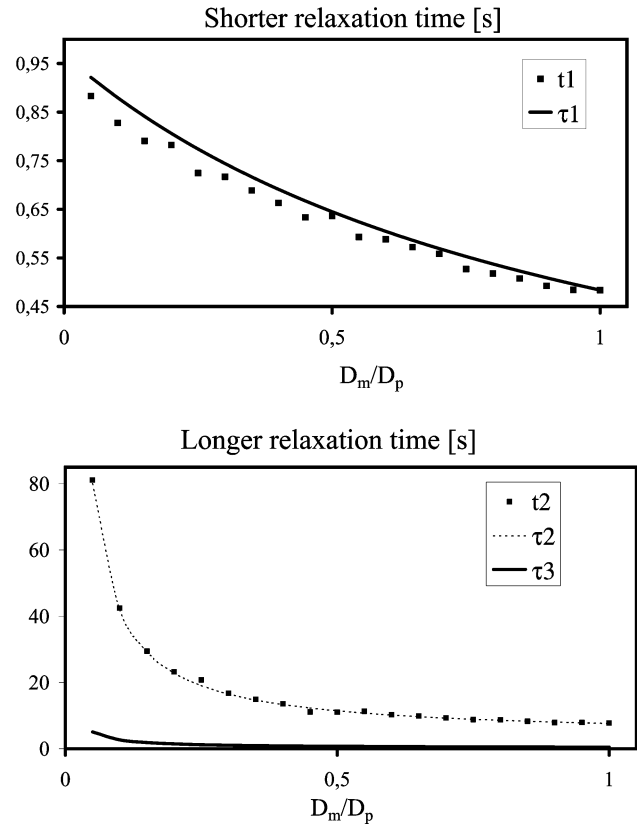


Figure 2. Longer and shorter relaxation times as a function of $\xi = D_m/D_p$: comparison between theoretical expectations from the linearized analysis (τ_1 and τ_2) and best fitting analysis of the numerical data (t_1 and t_2). The decay time τ_3 is reported for reference: it corresponds to one of the infinite (other than τ_1 and τ_2) possible relaxation times of the system, whose contribution to the solution of the system is however negligible.

The curves reported in Figure 1 cannot be interpreted as a single-exponential decay (results not reported for brevity). On the contrary, the conjecture reported in the previous section indicates that two relaxation times may be dominant, among the infinite number of solutions of the eigenvalues equation. In particular, we expect these values to be $\tau_1 = \lambda d / (2D_1)$ and $\tau_2 = d^2 / (\pi^2 D_2)$, reported in eq 28. Also, the theoretical analysis indicate that these relaxation times must be the same for the potential and for negative and positive ions, due to the linear independence of the corresponding exponential terms in eq 7.

To verify such a conclusion, we have fitted the numerical data with double exponential functions of the form

$$\begin{aligned} p(t) &= P_1(1 - \exp(-t/t_1)) + P_2(1 - \exp(-t/t_2)) \\ m(t) &= M_1(1 - \exp(-t/t_1)) + M_2(1 - \exp(-t/t_2)) \\ \delta V(t) &= V_1(1 - \exp(-t/t_1)) + V_2(1 - \exp(-t/t_2)) \end{aligned} \quad (35)$$

The eight parameters (six amplitudes P_1 , P_2 , M_1 , M_2 , V_1 , V_2 and two relaxation times t_1 and t_2) have been estimated by a minimization process in which the three variables are best fitted at the same time. In Figure 1, the fitting curves are reported and superimposed to the corresponding numerical data for a few selected cases. Results indicate that the interpretation of the redistribution processes as an exponential relaxation with two decay times is reasonable and accurate, for all of the values of ξ considered. Nevertheless, the quality of the fits decreases with decreasing ξ . This trend becomes even more evident for

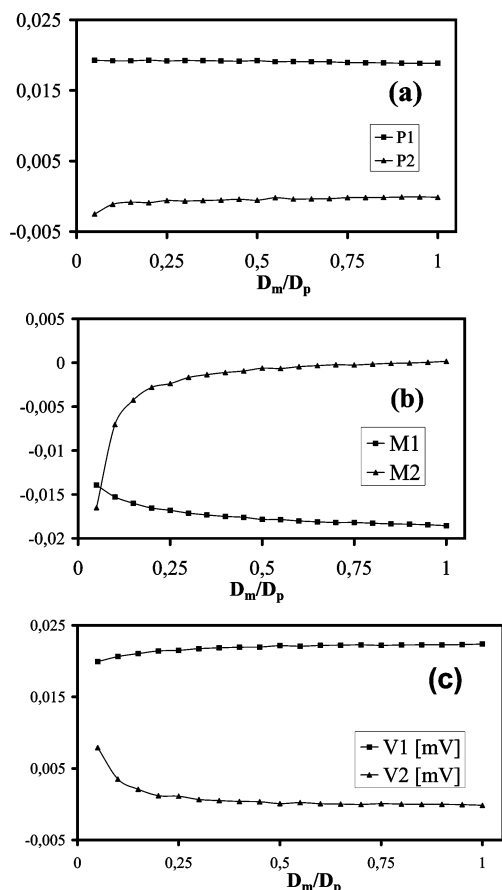


Figure 3. Amplitudes of the two exponential decays (eq 35) from the fitting of the numerical data vs $\xi = D_m/D_p$. (a) Positive ions; (b) negative ions; (c) potential.

lower values of the ratio between the diffusion coefficients, clear indication of an increasing role of other relaxation times and of the need of a more general multirelaxation process, which is not discussed here.

The fit of the numerical data also allows us to estimate the relaxation times. They are reported as a function of ξ , in Figure 2. The agreement with the expected theoretical values is very good. In Figure 2b, the relaxation time τ_3 is also reported for comparison.

Finally, we conclude our analysis with a discussion of the amplitudes relative to the two relaxation processes. They are reported in Figure 3 as a function of ξ . The variation in the diffusion coefficients of negative ions affects only very slightly the amplitudes P_1 and P_2 (see Figure 3a). Indeed, the motion of positive ions remains mostly dominated by D_1 , being always $|P_2| \ll |P_1|$. It is remarkable to observe that P_2 is always negative, indicating that positive ions, initially, move too fast toward the negative electrodes. The slow redistribution of negative ions has a counter-effect, which pushes the positive ions back toward the center. In any case, such effect is small for the values of ξ considered here, but increases with decreasing ξ .

On the contrary the amplitudes for the negative ions are strongly affected by the choice of D_m , as expected (see Figure 3b). In particular both amplitudes are negative and M_2 , which is zero for $\xi = 0$, increases rapidly with decreasing ξ . Finally, the amplitudes of the potential present an intermediate behavior: V_2 increases with decreasing ξ , but V_1 is always dominant.

It is worth mentioning that the sum of the amplitudes is constant and does not depend on ξ . In particular $P_1 + P_2 \sim$

$|M_1 + M_2| \sim 0.019$, in agreement with eq 5. Likewise $V_1 + V_2 \sim 0.022$ mV, in agreement with eq 6

5. Conclusions

We have investigated the dynamic behavior of an electrolytic cell subject to an external electric field, assuming that the positive and negative ions have different diffusion coefficients. In the linear approximation, where the fundamental equations of the problem can be linearized, we have determined the eigenvalues equation defining the relaxation times of the problem, and we have calculated some of its solutions starting from the definition of an equivalent electrical circuit.

We have also solved numerically the fundamental equations of the problem in the case of a small applied electric field. We have shown that the relaxation of the ionic bulk densities and of the electrical potential are reasonably well described by considering only two relaxation processes. We have shown that the relaxation times correspond to those determined in the analytical approach. The corresponding relaxation processes are related to ambipolar diffusion, where the diffusion of the ions strongly depends on the electric field created in the ionic separation, and free diffusion, where the ionic diffusion only depends on the averaged ionic diffusion coefficient.

The numerical calculations have been performed by considering parameters typical of a doped liquid crystal, submitted to an external electric field of small amplitude. However, results have a general validity, qualitatively independent from the chosen values of the parameters. Therefore, we expect the results obtained to have a validity beyond problems regarding doped liquid crystals. In particular, we expect our findings to be relevant for problems of general interest in electrochemistry, where the dynamics of the ionic redistribution in the presence of an external electric field plays a fundamental role.

Two directions of investigation have still to be pursued, following an approach similar to that reported here. First of all, the extension of our results to cases in which the diffusion coefficient are of different orders of magnitudes. In fact, in our theoretical analysis, we have assumed $\xi = D_m/D_p \sim 1$, i.e., $D_p \neq D_m$, but of the same order of magnitude. Of course, when ξ becomes very small, more relaxation processes are expected to take place. Indeed, our numerical results indicate the fit with two exponential decays to be less and less precise with decreasing ξ . In such cases, multirelaxation processes must be considered.

A second approximation adopted here is that we have neglected the ionic adsorption taking place at the electrodes. It is well-known, as discussed in ref 5, that the presence of the adsorption modifies the relaxation time characterizing the transient effects when the electrolytic cell is subjected to an external field of small amplitude. In fact, additional time scales are added to the problem and the dynamic of the ionic redistribution in the bulk cannot be faster than that of the adsorption on the electrodes. In ref 5, we have already analyzed the influence of adsorption mechanisms in the case $D_p = D_m$, with kinetic equations at the surfaces of the Langmuir's type, with the same adsorption-desorption coefficients for positive and negative ions. We expect to be possible to follow the same analysis reported in ref 5 also in the case $D_p \neq D_m$. Furthermore, we believe that a significant influence on the relaxation times can appear when the kinetic equations for the adsorption of positive and negative ions are not identical. We leave this analysis for future investigations.

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Appendix I

The goal of this Appendix is to show that τ_1 and τ_2 are solutions of the eigenvalues equation, eq 24. To this purpose, by taking into account eq 11, we rewrite eqs 15 and 16 as follows:

$$\mu_{1,3}^2 = \frac{1}{2\lambda^2} \left\{ 1 - \frac{\xi+1}{\xi} \alpha \pm \sqrt{1 + \left(\frac{\xi-1}{\xi} \alpha \right)^2} \right\} \quad (36)$$

$$k_{1,3} = - \left\{ \frac{\xi-1}{\xi} \alpha \pm \sqrt{1 + \left(\frac{\xi-1}{\xi} \alpha \right)^2} \right\} \quad (37)$$

where $\xi = D_m/D_p$, and $\alpha = a\lambda^2/D_p$. Furthermore, by means of simple calculations, we write eq 24 in the form

$$\frac{(1+k_1)(1-k_3)}{\mu_3^2} \left(1 - \frac{\tanh(\mu_3 d/2)}{\mu_3 d/2} \right) - \frac{(1-k_1)(1+k_3)}{\mu_1^2} \left(1 - \frac{\tanh(\mu_1 d/2)}{\mu_1 d/2} \right) + 2\lambda^2(k_3 - k_1) = 0 \quad (38)$$

From eq 36 it follows that $\mu_1^2 > \mu_3^2$ for all acceptable values of α (>0). μ_1 is real when the condition $\mu_1^2 > 0$, is satisfied, which is equivalent to $\alpha < (\xi+1)/2$, i.e.

$$a < \frac{\xi+1}{2} \frac{D_p}{\lambda^2} = \frac{D_1}{\lambda^2} \quad (39)$$

For all values of ξ and α , $\mu_3^2 < 0$ and μ_3 is imaginary. We note that $\tau = \lambda^2/D_1$ corresponds to Debye's relaxation time for free diffusion. Finally, $\mu_1^2(\alpha=0) = 1/\lambda^2$, and $\mu_3^2(\alpha=0) = 0$. It follows that for $a < D_1/\lambda^2$ the eigenvalues equation is

$$\frac{(1+k_1)(1-k_3)}{\mu_3^2} \left(1 - \frac{\tan(|\mu_3|d/2)}{|\mu_3|d/2} \right) - \frac{(1-k_1)(1+k_3)}{\mu_1^2} \left(1 - \frac{\tanh(\mu_1 d/2)}{\mu_1 d/2} \right) + 2\lambda^2(k_3 - k_1) = 0 \quad (40)$$

For $a > D_1/\lambda^2$, both μ_1 and μ_3 are complex. Therefore, we have

$$\frac{(1+k_1)(1-k_3)}{\mu_3^2} \left(1 - \frac{\tan(|\mu_3|d/2)}{|\mu_3|d/2} \right) - \frac{(1-k_1)(1+k_3)}{\mu_1^2} \left(1 - \frac{\tan(|\mu_1|d/2)}{|\mu_1|d/2} \right) + 2\lambda^2(k_3 - k_1) = 0 \quad (41)$$

Let us consider now the case where $x = \lambda/d \ll 1$ and let us define $\alpha = bx$, with α and x of the same order. By expanding in power series of x the terms in eq 38, at the first order in x we obtain

$$\frac{(\xi-1)^2}{\xi(\xi+1)} b \left(1 - \frac{\tan \Omega}{\Omega} \right) = \frac{\xi+1}{\xi} b - 4 \quad (42)$$

where

$$\Omega = \frac{1}{2} \sqrt{\frac{b}{x} \frac{\xi+1}{2\xi}} \quad (43)$$

We first consider the case in which the term $(\tan \Omega)/\Omega$ is small. By neglecting it in eq 42, we have

$$\frac{(\xi-1)^2}{\xi(\xi+1)} b = \frac{\xi+1}{\xi} b - 4 \quad (44)$$

from which we obtain $b = \xi + 1$. Consequently $a = (\xi+1)D_p/(\lambda d)$, and the corresponding relaxation time is $\tau = \tau_1 = \lambda d/(2D_1)$.

On the contrary, when $(\tan \Omega)/\Omega \gg 1$, eq 42 becomes

$$-\frac{(\xi-1)^2}{\xi(\xi+1)} b \frac{\tan \Omega}{\Omega} = \frac{\xi+1}{\xi} b - 4 \quad (45)$$

that for $\xi \neq 1$ is equivalent to

$$\frac{\tan \Omega}{\Omega} = 4\xi \frac{\xi+1}{(\xi-1)^2} \frac{1}{b} \quad (46)$$

By taking into account eq 43, the solutions of eq 46 are $\Omega \sim (2h+1)(\pi/2)$, where h is an integer. Since in the present case $\alpha = bx$, we get

$$a_h = (2h+1)^2 \pi^2 \frac{D_2}{d^2} \quad (47)$$

The smallest value is then $a_0 = D_2(\pi/d)^2$ and the longest relaxation time is $\tau_2 = (1/\pi^2)(d^2/D_2)$, as anticipated in the main text.

References and Notes

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