

Evidence of the ambipolar diffusion in the impedance spectroscopy of an electrolytic cell

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We argue that the impedance spectroscopy of an electrolytic cell in the low-frequency range can give information on the ambipolar diffusion. Our analysis is based on a theoretical investigation of the real part of the electrical impedance of an electrolytic cell. When the mobility of the positive ions differs from that of the negative ions, a second plateau of the resistance of the cell, in series representation, is expected close to the dc limit of the applied voltage. The effective diffusion coefficient, related to the measured resistance of the cell, in the dc limit, coincides with the ambipolar diffusion coefficient. The associated relaxation time corresponds to the ambipolar diffusion, and it is proportional to the square of the thickness of the sample. In the high-frequency range, the relaxation time coincides with the Debye relaxation time, connected to the free diffusion coefficient, and it is independent of the thickness of the sample. Finally, we propose a method to calculate the diffusion coefficients of the individual ions from the impedance spectrum and we discuss the implications of ambipolar diffusion in impedance measurements and interpretation of experimental quantities.

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I. INTRODUCTION

The impedance spectroscopy technique is widely used to characterize condensed matter from a dielectric point of view [1]. According to this technique, a sample of the material under investigation is submitted to an external voltage depending on time in sinusoidal manner, $\Delta V(t; \omega) = V_0 \exp(i\omega t)$. The current I flowing in the circuit containing the cell is measured by changing the circular frequency $\omega = 2\pi f$, of the applied voltage. For small enough amplitude of the applied voltage V_0 , the behavior of the sample can be considered linear and the generalized Ohm's law valid [2,3]. Knowing the applied voltage and the corresponding current, it is possible to determine the electrical impedance $Z = \Delta V/I$. From the analysis of $Z = Z(\omega)$, or of its real and imaginary parts $R(\omega)$, $X(\omega)$, it is possible to describe the electrical behavior of the sample and to obtain information on the molecular mechanisms responsible for the electrical properties of the sample [4].

In the present paper we are interested in the electrical properties of a symmetric binary electrolyte, which, in a first approximation, can be considered as a dispersion of ions in a dielectric liquid. We consider a sample in the shape of a slab and assume that the number density of ions, N , in thermodynamic equilibrium [5] is $N \ll N_0$, where N_0 is the number density of the atoms forming the liquid in which the ions are dispersed. In this framework the collisions between the ions may be neglected with respect to the collisions of the ions with the neutral atoms. Therefore, the recombination effect does not play any role in the diffusion process. Under these conditions the diffusion of positive and negative ions is not independent, because the charge separation resulting from the diffusion gives rise to an electric field that opposes further charge separation. This effect is called ambipolar diffusion in plasma physics [6,7].

Although the theory of neutral electrolytes is very well developed, the influence of ambipolar diffusion on the impedance of an electrolyte has not been considered so far. Our aim is to show that the frequency dependence of the real part of the electrical impedance can give information on the ambipolar and free diffusion coefficients of the ions, which are different when the positive and negative ions have different diffusivities. Consequently, from the impedance spectrum it is possible to obtain the diffusion coefficients of the positive and negative ions.

The paper is organized as follows. In Sec. II is presented for orientation the derivation of the ambipolar diffusion coefficient. The analysis of the impedance spectroscopy of an electrolytic cell is presented in Sec. III. There, the influence of the difference between the diffusion coefficients of the positive and negative ions on the frequency dependence of the real part of the electrical impedance of the cell is discussed. In particular, we show that the equivalent electrical resistance of the cell, in series representation, versus the frequency of the applied difference of potential presents two plateaus. The one in the low-frequency range is related to the ambipolar diffusion, whereas the one in the high-frequency range is connected to the free diffusion, where the effective diffusion coefficient is the arithmetical average of the diffusion coefficients of the two types of ions present in the electrolyte. In Sec. IV we investigate the dependence of the relaxation frequencies on the diffusion coefficients of the positive and negative ions. We show that the relaxation phenomenon occurring in the low-frequency range is a pure diffusive phenomenon, whose relaxation time depends on the square of the thickness of the sample. On the contrary the relaxation phenomenon at higher frequency is a pure Debye relaxation phenomenon, independent of the thickness of the sample. Section V is devoted to the conclusions.

II. AMBIPOLAR DIFFUSION

Let us consider the motion of a charged particle, with electrical charge q , in an isotropic dielectric liquid in the

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presence of an electric field \mathbf{E} . The mobility μ of the charged particle is defined as the proportionality factor between the mean velocity \mathbf{v} along the local field \mathbf{E} and the electric field itself according to the relation $\mathbf{v} = \mu\mathbf{E}$. Then, the electric field is responsible for a drift current density $\mathbf{j}_{\text{drift}} = n\mathbf{v} = n\mu\mathbf{E}$, where n is the bulk number density of particles subjected to the action of \mathbf{E} . In the case where the bulk density of particles is not homogeneous, according to Fick's law, there is also a diffusion current density $\mathbf{j}_{\text{diffusion}} = -D\nabla n$, where D is the diffusion coefficient of the particles in the considered medium. In an electrolytic solution, the total mass current density of the ions is

$$\begin{aligned}\mathbf{j}_p &= -D_p\nabla n_p + \mu_p n_p \mathbf{E}, \\ \mathbf{j}_m &= -D_m\nabla n_m - \mu_m n_m \mathbf{E},\end{aligned}\quad (1)$$

where $n_p = n_p(\mathbf{r}, t)$ and $n_m = n_m(\mathbf{r}, t)$ (p stands for plus, and m stands for minus) are the local ionic number densities at \mathbf{r} , and D_p and D_m the diffusion coefficients of positive and negative ions, respectively. The time evolution for n_p and n_m is obtained by solving (i) the equations of continuity for the two types of ions,

$$\begin{aligned}\frac{\partial n_p}{\partial t} &= -\nabla \cdot \mathbf{j}_p = D_p\nabla \cdot \left(\nabla n_p - \frac{\mu_p}{D_p} n_p \mathbf{E} \right), \\ \frac{\partial n_m}{\partial t} &= -\nabla \cdot \mathbf{j}_m = D_m\nabla \cdot \left(\nabla n_m + \frac{\mu_m}{D_m} n_m \mathbf{E} \right),\end{aligned}\quad (2)$$

and (ii) the Poisson equation, relating the effective electric field with the net excess charge density,

$$\nabla \cdot \mathbf{E} = q \frac{n_p - n_m}{\varepsilon}, \quad (3)$$

where ε is the dielectric permittivity of the solvent. At equilibrium the local ionic densities $n_p(\mathbf{r})$ and $n_m(\mathbf{r})$ are given by the Maxwell-Boltzmann statistics,

$$n_p(\mathbf{r}) = \mathcal{N}_p \exp[-qV(\mathbf{r})/k_B T],$$

$$n_m(\mathbf{r}) = \mathcal{N}_m \exp[qV(\mathbf{r})/k_B T], \quad (4)$$

where \mathcal{N}_p and \mathcal{N}_m are normalization factors and $V(\mathbf{r})$ is the electrical potential. From Eqs. (2) and (4) one retrieves the Einstein-Smoluchowski relation $\mu_p/D_p = \mu_m/D_m = q/k_B T$ [8].

In thermodynamic equilibrium, in the absence of an external electric field, an electrolyte of infinite thickness is locally and globally electrically neutral. Let us consider now a situation in which during the evolution of the ionic density due to an external electric field or to adsorption phenomena at the limiting surfaces, the electrolyte remains quasineutral; i.e., the characteristic dimension of the system, d , is much larger than the Debye screening length λ [defined after the Eqs. (12) below]. This is the case for a relatively high density of ions (small Debye length). In this case, where $\lambda \ll d$, any separation of charges gives rise to a large electric field that prevents further separation and preserves the quasineutrality of the electrolyte—i.e., $n_p \sim n_m$ —at scales larger than λ . This phenomenon is known as ambipolar diffusion [7]. Since $n_p \sim n_m$, the fluxes of the positive and negative ions are the same, and hence $\mathbf{j}_p = \mathbf{j}_m$. From the latter condition and Eqs. (1) we get that the resulting electric field is

$$\mathbf{E} = \frac{D_p\nabla n_p - D_m\nabla n_m}{\mu_p n_p + \mu_m n_m}. \quad (5)$$

In the limit of quasineutrality we are considering, the current density of the positive ions is given by

$$\mathbf{j}_p = -\frac{\mu_m n_m D_p \nabla n_p + \mu_p n_p D_m \nabla n_m}{\mu_p n_p + \mu_m n_m}, \quad (6)$$

obtained by substituting Eq. (5) in the first equation of Eqs. (1).

We put $n_p = N + \delta n_p$ and $n_m = N + \delta n_m$, where δn_p and δn_m are variations of the bulk densities of the ions due to diffusion. In the limit of small variations of the ionic bulk densities in the diffusion phenomenon—i.e., when $\delta n_p/N \ll 1$ and $\delta n_m/N \ll 1$ —Eq. (6) yields

$$\mathbf{j}_p = -\frac{\mu_m D_p [1 + (\delta n_m/N)] \nabla(\delta n_p) + \mu_p D_m [1 + (\delta n_p/N)] \nabla(\delta n_m)}{\mu_p(1 + \eta_p) + \mu_m(1 + \eta_m)}, \quad (7)$$

which, at first order in δn_p and δn_m , leads to

$$\mathbf{j}_p = -\frac{\mu_m D_p \nabla(\delta n_p) + \mu_p D_m \nabla(\delta n_m)}{\mu_p + \mu_m}. \quad (8)$$

Taking into account the Einstein-Smoluchowski relation, Eq. (8) can be cast in the final form

$$\mathbf{j}_p = -\frac{D_p D_m}{D_p + D_m} \nabla(\delta n_p + \delta n_m). \quad (9)$$

Since the electrolyte is assumed quasineutral, $\delta n_p \sim \delta n_m$, Eq. (9) reads

$$\mathbf{j}_p = -D_a \nabla(\delta n_p), \quad (10)$$

where the quantity

$$D_a = 2 \frac{D_p D_m}{D_p + D_m} \quad (11)$$

is called the ambipolar diffusion coefficient [6]. From Eq. (11) it follows that for $D_p \gg D_m$, $D_a = 2D_m$. Note that Eq. (6) leads to equations analogous to Eqs. (8)–(10) for the total concentrations, since $\nabla n_p = \nabla(\delta n_p)$ and $\nabla n_m = \nabla(\delta n_m)$ and once electroneutrality is assumed.

In the case where $D_p \gg D_m$, the time evolution of the negative ions is described by a diffusion equation where the effective diffusion coefficient is $D_a = 2D_m$. To this end, let us rewrite Eqs. (2), taking into account Eq. (3). At the first order in δn_p and δn_m , Eqs. (2) can be rewritten as

$$\begin{aligned} \frac{\partial(\delta n_p)}{\partial t} &= D_p \left\{ \nabla^2(\delta n_p) - \frac{1}{2\lambda^2}(\delta n_p - \delta n_m) \right\}, \\ \frac{\partial(\delta n_m)}{\partial t} &= D_m \left\{ \nabla^2(\delta n_m) + \frac{1}{2\lambda^2}(\delta n_p - \delta n_m) \right\}, \end{aligned} \quad (12)$$

where $\lambda = \sqrt{\epsilon k_B T / (2Nq^2)}$ is the Debye length, evaluated in thermodynamic equilibrium [9]. When an external field is suddenly applied to the sample, $\nabla^2(\delta n_p) \sim \delta n / d^2$ and $\nabla^2(\delta n_m) \sim \delta n / d^2$, where δn is of the order of the maximum variation induced by the field and d is a typical dimension of the sample. Since we are considering the limit of $\lambda \ll d$, Eqs. (12) are well approximated by

$$\begin{aligned} \frac{\partial(\delta n_p)}{\partial t} &= -\frac{D_p}{2\lambda^2}(\delta n_p - \delta n_m), \\ \frac{\partial(\delta n_m)}{\partial t} &= \frac{D_m}{2\lambda^2}(\delta n_p - \delta n_m). \end{aligned} \quad (13)$$

From Eqs. (13) it follows that

$$\delta n_p(t) - \delta n_m(t) = [\delta n_p(0) - \delta n_m(0)] \exp(-t/\tau_0), \quad (14)$$

where $\tau_0 = 2\lambda^2 / (D_p + D_m) \sim 2\lambda^2 / D_p$. From Eq. (14) we derive that the local difference between δn_p and δn_m decreases exponentially with the time constant τ_0 . After this initial redistribution of ions, if $D_p \gg D_m$, the positive ions rapidly reach the equilibrium state, in which $\partial(\delta n_p) / \partial t = 0$, and hence, from the first equation of Eqs. (12), $\delta n_p - \delta n_m = 2\lambda^2 \nabla^2(\delta n_p)$. By substituting this result into the second equation of Eqs. (13), taking into account that $\nabla^2(\delta n_p) \sim \nabla^2(\delta n_m)$, we get

$$\frac{\partial(\delta n_m)}{\partial t} = 2D_m \nabla^2(\delta n_m); \quad (15)$$

i.e., the effective diffusion coefficient for the slow redistribution of the negative ions is the ambipolar diffusion coefficient.

III. ROLE OF THE AMBIPOLAR DIFFUSION ON THE IMPEDANCE SPECTROSCOPY

The analysis of the electrical behavior of an electrolytic cell subjected to an external field is usually performed, in the continuum approximation, by solving the equations of conti-

nity for the positive and negative ions and the equation of Poisson for the actual electrical potential in the cell [10]. A simple extension of the analysis presented in [10] allows one to evaluate the impedance of an electrolytic cell when it is submitted to a periodic external electrical potential of small amplitude with respect to the thermal voltage [11]. The analysis reported in [11] is valid when (i) the ions have the same diffusivity ($D_p = D_m = D$), (ii) the electrodes are perfectly blocking, (iii) the sample is in the shape of a slab of thickness d , and (iv) the impurities are completely dissociated.

The analysis also takes account of the double layers close to the electrodes due to the ions confinement induced by the external electric field. In particular, the expressions used for the evaluation of the real and imaginary parts of the electrical impedance of the cell include the influence of the double layers on the impedance spectra. The analysis presented in [11] predicts that, in the limit $\omega \rightarrow 0$, (i) the equivalent resistance of the cell tends to $R(0) = \lambda^2 d / \epsilon D S$, where S is the surface area of the electrodes, and its equivalent conductivity tends to $\sigma_{\text{eq}}(0) = \epsilon D / \lambda^2$; (ii) the equivalent capacitance of the cell tends to $C(0) = \epsilon S / (2\lambda)$, and its equivalent dielectric constant tends to $\epsilon_{\text{eq}} = \epsilon (d / 2\lambda)$; (iii) the electrical resistance is practically independent of ω up to $\omega_r = D / \lambda^2$, corresponding to the Debye relaxation time $\tau_r = \lambda^2 / D$.

In the limit $\omega \rightarrow \infty$ the equivalent resistance tends to zero and the equivalent capacitance to $\epsilon (S / d)$. This limit is easily understood because in the high-frequency regime the ions do not give any contribution to the electrical properties of the liquid in which they are dispersed.

Recently we have generalized the analysis of [11] in the case that the diffusion coefficient of the positive ions differs from the one of the negative ions [12]. We have solved the fundamental equations of the problem in the presence of a small amplitude voltage, $\Delta V(t; \omega) = V_0 \exp(i\omega t)$, applied at a sample in the shape of a slab in a Cartesian reference frame with the z axis perpendicular to the limiting surfaces, placed at $z = \pm d/2$. The electrodes are assumed blocking, and the potential at the electrodes is $V(\pm d/2, t) = \pm (V_0/2) \exp(i\omega t)$. As is shown in the Appendix, it is possible to evaluate the electrical potential across the cell, $V(z, t; \omega)$, and the corresponding electric field $E(z, t; \omega) = -\partial V(z, t; \omega) / \partial z$. Further, making use of Gauss's law, the electrical charge density on the electrodes, $Q(t; \omega)$, and hence the electrical current in the external circuit, $I(t; \omega) = dQ(t; \omega) / dt$, can be easily evaluated. Finally, from the current and the applied voltage, the real and imaginary parts of the impedance are determined, $Z(\omega) = \Delta V(t; \omega) / I(t; \omega) = R(\omega) + iX(\omega)$. For convenience of the following analysis, we report the real part of Eq. (20) from [12] adapted to the normalization introduced in the Appendix:

$$R(\omega) = \text{Re} \left\{ \frac{2\phi(z=d/2)}{i\epsilon S \omega \phi'(z=d/2)} \right\}. \quad (16)$$

The function $\phi(z)$ is the amplitude of the potential normalized by the thermal voltage $V_{th} = k_B T / q$ where q is the modulus of the elementary electric charge—i.e.,

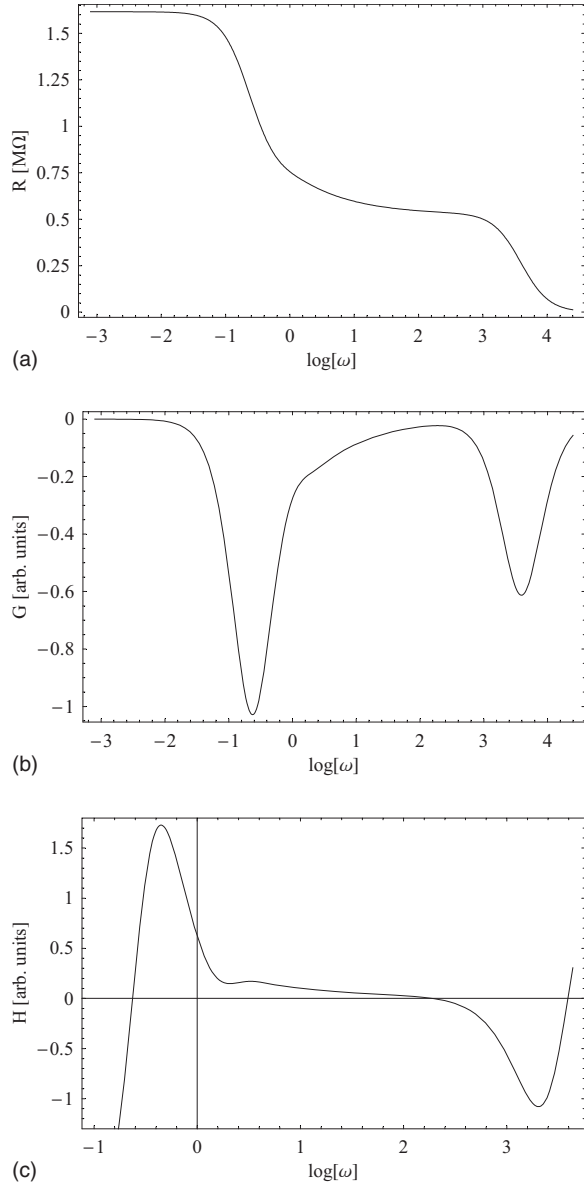


FIG. 1. Plot of the frequency dependence of $R=R(\omega)$ for $y=D_m/D_p=0.1$. Note the presence of two plateaus in the low- and high-frequency regions (a). $G=dR/d\omega$ vs $\log_{10}[\omega]$, presenting two peaks in correspondence of the two relaxation frequencies (b). $H=d^2R/d\omega^2$ vs $\log_{10}[\omega]$. The condition $H(\omega)=0$ determines the relaxation frequencies (c).

$$\frac{V(z,t)}{V_{th}} = \phi(z)\exp(i\omega t). \quad (17)$$

The analysis of the above expression for $R(\omega)$, presented in [12], shows that when $D_p \neq D_m$ the frequency dependence of $R=R(\omega)$ presents two well-defined plateaus [see Fig. 1(a)]. The problem admits an analytical solution, but the equations are rather complicated. For this reason, a numerical investigation of the formulas is rather attractive.

By expanding the full expressions for $R(\omega)$ and $X(\omega)$ reported in [12], in power series in ω around $\omega=0$, we obtain in the limit of $\lambda \ll d$

$$R(\omega \rightarrow 0) = \frac{\lambda^2 d}{\epsilon D_a S} \left\{ 1 - \left(\frac{D_p - D_m}{D_p D_m} \right)^2 \frac{d^2}{480} \omega^2 \right\},$$

$$X(\omega \rightarrow 0) = -\frac{2\lambda}{\epsilon S \omega} \left\{ 1 + \left(\frac{D_p - D_m}{D_p D_m} \right)^2 \frac{\lambda d^3}{96} \omega^2 \right\}, \quad (18)$$

where D_a is the ambipolar diffusion coefficient introduced in Eq. (11). It follows that for $\omega \rightarrow 0$ the resistance $R(\omega)$ and the capacitance $C(\omega) = -1/\omega X(\omega)$ tend to $R(0) = \lambda^2 d / \epsilon D_a S$ and $C(0) = \epsilon S / 2\lambda$. Thus, the equivalent conductivity and dielectric constant in this limit are $\sigma_{eq} = D_a \epsilon / \lambda^2$ and $\epsilon_{eq} = \epsilon d / 2\lambda$. From the expression for σ_{eq} we conclude that in the low-frequency range the conduction is connected with the ambipolar diffusion.

Increasing the frequency beyond the first relaxation frequency defining the plateau in the low-frequency range, the resistance decreases and then presents a new plateau, characterized by $R' = \lambda^2 d / \epsilon D_f S$, where $D_f = (D_p + D_m) / 2$ is the diffusion coefficient for the free diffusion phenomenon [13]. The equivalent conductivity connected to R' is $\sigma'_{eq} = D_f \epsilon / \lambda^2$; i.e., in this frequency range, the diffusion of the ions is the free diffusion.

In the limit of $\omega \rightarrow \infty$, $R(\omega)$ and $X(\omega)$ can be expanded in power series of $1/\omega$ as

$$R(\omega \rightarrow \infty) = \frac{D_f d}{\epsilon \lambda^2 S} \frac{1}{\omega^2} - \frac{D_p^{3/2} + D_m^{3/2}}{\sqrt{2\epsilon} \lambda^2 S} \frac{1}{\omega^{5/2}},$$

$$X(\omega \rightarrow \infty) = -\frac{d}{\epsilon S \omega} + \frac{D_p^{3/2} + D_m^{3/2}}{\sqrt{2\epsilon} \lambda^2 S} \frac{1}{\omega^{5/2}}. \quad (19)$$

From these equations it follows that in the high-frequency range, the electrical resistance of the cell, in the series representation, tends to zero and the equivalent dielectric constant tends to ϵ , as expected.

IV. RELAXATION FREQUENCIES ω_l AND ω_h

Using the analytical expression of $R(\omega)$, we investigate the dependence of the relaxation frequencies defining the two plateaus of $R=R(\omega)$ on the individual diffusion coefficients of the ions. Unfortunately, the explicit expression for $R=R(\omega)$ cannot be solved for the relaxation frequencies ω_l and ω_h defining the two plateaus. For this reason we show first how the frequencies ω_l and ω_h can be evaluated from $R=R(\omega)$ by use of numerical minimization. Further, we investigate the dependences of ω_l and ω_h on the ratio of the ions diffusion coefficients $y=D_m/D_p$, the thickness of the cell d , and the bulk number density of ions, N .

For the numerical calculations of $R=R(\omega)$ we assume that the ions are monovalent, $q=1.6 \times 10^{-19}$ A s, with number density $N=4 \times 10^{20}$ m⁻³ and $D_p=8.2 \times 10^{-11}$ m²/s, corresponding to a commercial liquid crystal [14]. The geometrical parameters of the cell are $d=25$ μm and $S=2 \times 10^{-4}$ m², typical for display technology.

As shown in Fig. 1(a), for the case $y=D_m/D_p=0.1$, the frequency dependence of $R=R(\omega)$ presents two well-defined plateaus. Figure 1(b) shows the function $G(\omega)=dR(\omega)/d\omega$

versus ω . It has the typical frequency dependence of the dissipation factor in dielectrics. The function $G=G(\omega)$ presents two well-defined minima, related to the relaxation phenomena. In the low-frequency range, the minimum is connected to the ambipolar diffusion, and in the high-frequency range, it is related to the free diffusion, as discussed above. To investigate the relaxation frequencies it is useful to analyze $H(\omega)=dG/d\omega=d^2R/d\omega^2$ versus ω , since the zeros of $H(\omega)$ define the relaxation frequencies ω_l and ω_h , as shown in Fig. 1(c).

To relate the relaxation frequencies in the low-, ω_l , and high-, ω_h , frequency regions with the physical parameters of the problem, we propose the following expressions:

$$\omega_l = k_l \frac{D_a}{d^2}, \quad \omega_h = k_h \frac{D_f}{\lambda^2}, \quad (20)$$

derived by dimensional arguments. k_l and k_h are dimensionless coefficients to be determined.

The expression for ω_l can be understood by means of simple considerations. Using Eq. (10), the equation of continuity for the positive ions reads

$$\frac{\partial(\delta n_p)}{\partial t} = D_a \nabla^2(\delta n_p), \quad (21)$$

which has to be solved with the boundary condition $\mathbf{j}_p \cdot \mathbf{k} = 0$, where \mathbf{k} is the geometrical surface normal, outward directed, of the surface limiting the sample. This boundary condition is connected with the hypothesis that the ions cannot leave the sample (blocking electrodes). For a sample in the shape of a slab, with the surfaces placed at $z = \pm d/2$, Eq. (21) with the relevant boundary conditions can be rewritten as

$$\frac{\partial(\delta n_p)}{\partial t} = D_a \frac{\partial^2(\delta n_p)}{\partial z^2} \quad (22)$$

and

$$\frac{\partial(\delta n_p)}{\partial z} = 0, \quad \text{at } z = \pm d/2, \quad (23)$$

respectively. Simple calculations give

$$\delta n_p(z, t) = \sum_k \left\{ A_k \sin\left(k \frac{\pi}{d} z\right) + B_k \cos\left(k \frac{\pi}{d} z\right) \right\} e^{-k^2 t / \tau}, \quad (24)$$

where $\tau = D_a^{-1}(d/\pi)^2$ is the longest relaxation time and $1/\tau$ the highest relaxation frequency. The quantity $1/\tau$ coincides with ω_l when $k_l = \pi^2$.

In a similar manner, the expression for ω_h can be derived from Eq. (14), according to which the longest relaxation time connected to the decrease of $\delta n_p - \delta n_m$ is $\tau_0 = \lambda^2/D_f$. The quantity $1/\tau_0$ is the highest relaxation frequency and coincides with ω_h .

We perform, first, a numerical evaluation of the constants k_h and k_l by fitting the dependence of the relaxation frequencies on y . We keep the same values of q , N , D_p , d , and S as before, while varying D_m . Figure 2(a) shows the numerically determined (solid points) relaxation frequency $\Omega_l = \log_{10}[\omega_l]$

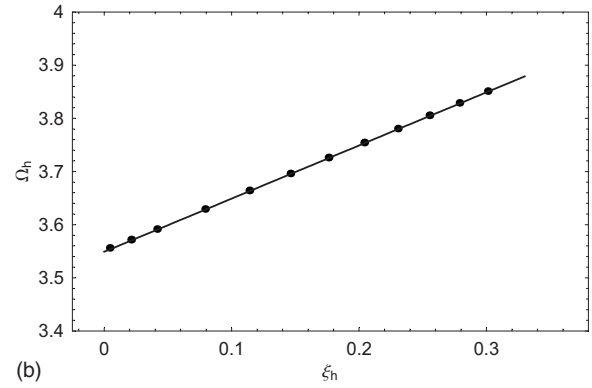
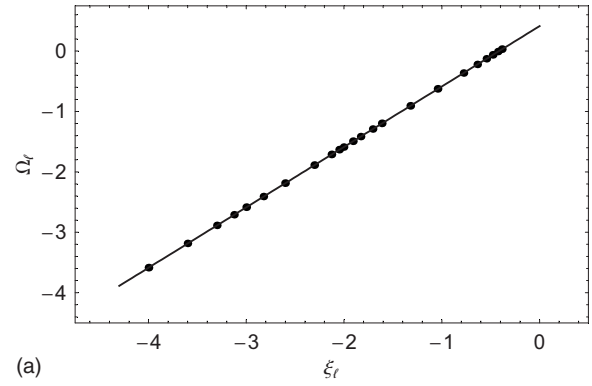


FIG. 2. $\Omega_l = \log_{10}[\omega_l]$ vs $\xi_l = \log_{10}[\frac{y}{1+y}]$ plot. ω_l is the lower relaxation frequency. The numerical results (points) show that $\Omega_l \propto \xi_l$, indicating that ω_l is related to the diffusion time for the ambipolar diffusion (a). $\Omega_h = \log_{10}[\omega_h]$ vs $\xi_h = \log_{10}[1+y]$ plot. ω_h is the higher relaxation frequency. The numerical results (points) show that $\Omega_h \propto \xi_h$, suggesting that ω_h is related to Debye's relaxation times for free diffusion.

vs $\xi_l = \log_{10}[y/(1+y)]$, whereas Fig. 2(b) shows $\Omega_h = \log_{10}[\omega_h]$ vs $\xi_h = \log_{10}[1+y]$, where $y = D_m/D_p$ varies in the range $10^{-4} \leq y \leq 1$. Fitting the numerical values of ω_l and ω_h with the scaling expressions (20), we get $k_l = \pi^2 \times 1.000\,03$ and $k_h = 0.998$. These values are essentially the theoretical ones. The agreement between the numerical values and the scaling expressions proposed above (solid lines in Fig. 2) is good over the investigated range.

The latter results reveal two distinct relaxation phenomena related to (i) the ambipolar diffusion and (ii) the free diffusion. In the low-frequency range the relaxation time depends on the square of the thickness of the slab and on the ambipolar diffusion coefficient D_a . This is a pure diffusive phenomenon. At higher frequencies, a second relaxation phenomenon appears, which originates from the free diffusion of the ions over the Debye length with a diffusion coefficient D_f [15]. In the high-frequency range the relaxation time is independent of the thickness of the sample, as in a simple Debye relaxation phenomenon. As reported in [11], when $D_p = D_m = D$ the relaxation frequency is $\omega_r = D/\lambda^2$, whereas when $D_p \neq D_m$ the higher relaxation frequency is given by $\omega_h = D_f/\lambda^2$. Therefore, the relaxation frequency in the high-frequency range depends only on $D_f = (D_p + D_m)/2$ and on the Debye length λ . From the discussion reported above it follows that the numerical values of the electrical resistance of

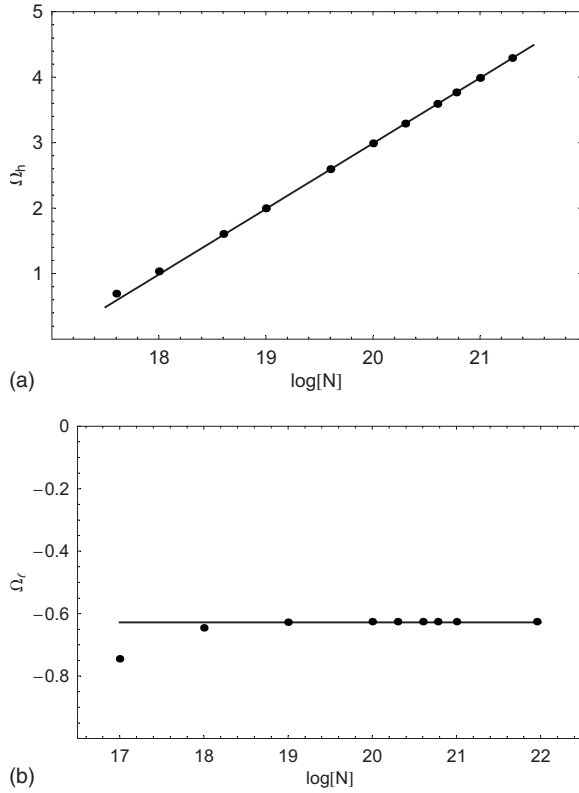


FIG. 3. $\Omega_h = \log_{10}[\omega_h]$ vs $\log_{10}[N]$ (a) and $\Omega_l = \log_{10}[\omega_l]$ vs $\log_{10}[N]$ (b) for $d = 25 \mu\text{m}$. Solid points are obtained from numerical calculations, and solid lines are calculated from the scaling relations (20). The Debye length becomes $\lambda = 6.8 \mu\text{m}$ for $N = 10^{17} \text{m}^{-3}$.

the two plateaus are related to the diffusion coefficients of the ambipolar and free diffusion phenomena. From them it is possible to determine D_a and D_f , and then the individual ionic diffusion coefficients D_p and D_m , by the relations

$$D_{p,m} = D_f \pm \sqrt{D_f(D_f - D_a)}. \quad (25)$$

Therefore, from a measurement of $R(\omega)$ for an electrolytic cell of known geometry, one may obtain the individual diffusion coefficients of the ions and their number density.

In Fig. 3 we show the plot of (a) Ω_h and (b) Ω_l vs $\log_{10} N$ while the thickness of the cell is kept constant ($d = 25 \mu\text{m}$). Solid points are the numerical values calculated from the inflection points of $R(\omega)$, and solid lines are given from the scaling relations (20). In Fig. 3(a), the slope of the solid line is unity, as can be deduced from the first equation of Eqs. (20) while ω_h does not show any dependence on N . Deviation from the scaling laws is observed in the range of N values below 10^{18}m^{-3} because in this range the Debye length starts to compare with the thickness of the cell and therefore the condition $\lambda \ll d$ is no longer fulfilled. For instance, while d is $25 \mu\text{m}$ the Debye length becomes $\lambda = 6.8 \mu\text{m}$ for $N = 10^{17} \text{m}^{-3}$.

Finally, Fig. 4 gives the plot of (a) Ω_h and (b) Ω_l vs $\log_{10} d$ while the ionic number density N is kept constant ($N = 4 \times 10^{20} \text{m}^{-3}$ corresponding to $\lambda = 0.11 \mu\text{m}$). The solid lines represent the scaling relations (20) while the solid

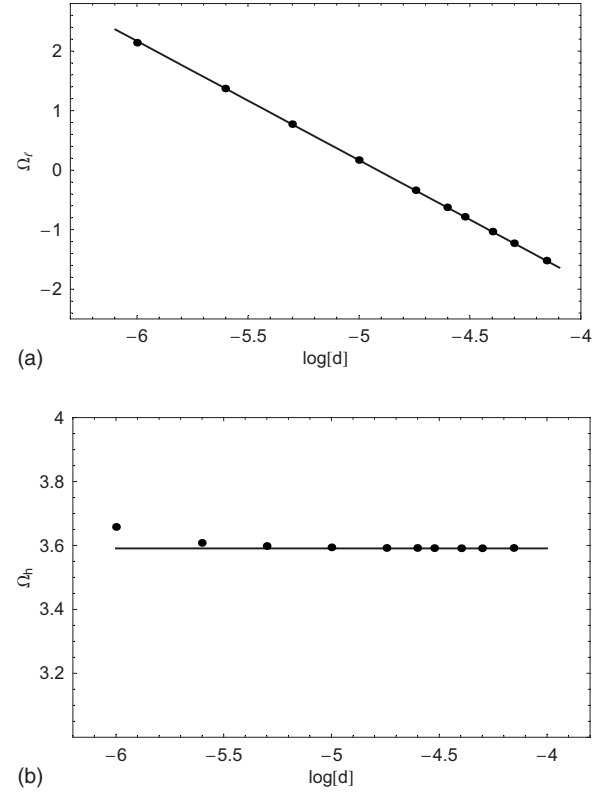


FIG. 4. $\Omega_h = \log_{10}[\omega_h]$ vs $\log_{10}[d]$ (a) and $\Omega_l = \log_{10}[\omega_l]$ vs $\log_{10}[d]$ (b) for $N = 4 \times 10^{20} \text{m}^{-3}$ corresponding to $\lambda = 0.11 \mu\text{m}$. The solid lines represent the scaling relations (20) while the solid points are computed numerically.

points result from numerical calculations. The dependence of $\Omega_l = \log_{10}[\omega_l]$ on the thickness of the cell d gives a line of slope equal to negative two in Fig. 4(b), while $\Omega_h = \log_{10}[\omega_h]$ is independent of d . Deviations from the scaling laws are observed when λ begins to compare to the cell thickness.

We conclude this section with the practical importance of the analysis presented above. The physical parameters characterizing a symmetric binary electrolyte, completely dissociated, are the diffusion coefficients of the two types of ions (D_p and D_m) and the bulk density of ions (N), which defines λ . These quantities can be determined from the impedance spectrum of the electrolytic cell in the shape of a slab of thickness d and surface area S . In fact, from the impedance spectrum, in the region $\omega \rightarrow 0$, using the relation $X(\omega \rightarrow 0) = -2\lambda/\varepsilon S\omega$, one obtains λ . After that, from the relation $R(0) = \lambda^2 d/\varepsilon D_a S$, the ambipolar diffusion coefficient is evaluated. Finally, by means of the expression $R' = \lambda^2 d/\varepsilon D_f S$, the parameter D_f is deduced. When λ , D_a , and D_f have been determined, it is possible to evaluate $\omega_l = (\pi/d)^2 D_a$ and $\omega_h = D_f/\lambda^2$ and to compare with the experimental values of these quantities to have a test of the measured parameters. However, $R(0)$ is not always easy to be measured since it requires low-frequency measurements. When $R(0)$ is not known with large accuracy, it is possible to determine λ as described above from $X(\omega \rightarrow 0) = -2\lambda/\varepsilon S\omega$, and then the diffusion coefficients from ω_l and ω_h , if the experimental resolution is good enough. In this case the test

is represented by $R(0)$ and R' . Combining both methods seems the best way to obtain D_p , D_m , and N .

V. CONCLUSIONS

We have investigated the frequency dependence of the real part of the electrical impedance of an electrolytic cell, assuming that the diffusion coefficient of the positive ions is different from that of the negative ions. Our analysis has been performed for a cell in the shape of a slab limited by perfectly blocking electrodes. According to our calculations, the plateau in the low-frequency range of the real part of the impedance, $R(\omega)$, is connected with the ambipolar diffusion, where the electrolyte is close to the quasineutral state. At higher frequency, $R(\omega)$ presents a second plateau due to the free diffusion of the ions in the presence of the electric field. The associated effective diffusion coefficient is the average between the diffusion coefficients of the two type of ions. Consequently, by the impedance spectrum of a symmetric binary electrolyte it is possible to determine the diffusion coefficients of the positive and negative ions. By analyzing the relaxation phenomena occurring in the system, we derive that the relaxation taking place at the low-frequency region is connected with the diffusion of the ions in the solution, with a diffusion coefficient equal to D_a . The frequency relaxation in the high-frequency region is connected with the Debye relaxation time for ions having a diffusion coefficient equal to D_f .

The strong variation of $R=R(\omega)$ between the two plateaus has been observed experimentally, and it is usually attributed to electrode polarization effects [16,17]. In general, circuit models neglect diffusion effects and the only characteristic times that appear are of the type RC charging time. Therefore, in order to account for diffusion effects, elements such as the Warburg element have been introduced [13]. Based on our impedance spectroscopy analysis, when individual ions have different diffusion coefficients, we argue that ambipolar diffusion should be taken into account when analyzing experimental data. Ambipolar diffusion could be simply the origin of the $R=R(\omega)$ increase or it could interfere with electrode polarization effects, ion adsorption, etc. The latter issue deserves further theoretical analysis.

It is beyond the scope of the present paper, but worth pursuing, to investigate ambipolar diffusion when the applied voltage begins to enter the nonlinear regime where (i) multiple time scales are introduced and (ii) the thin double-layer approximation may become questionable.

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APPENDIX: IMPEDANCE CALCULATION

In the following the deduction of the electrical impedance of the cell is briefly recalled [12]. The fundamental equations of the problem are Eqs. (2) and (3).

In the case of a small external electric field, when $\delta n_p \ll N$ and $\delta n_m \ll N$, Eqs. (12) can be linearized for our one-dimensional problem and they read

$$\begin{aligned} \frac{\partial(\delta n_p)}{\partial t} &= D_p \left\{ \frac{\partial^2(\delta n_p)}{\partial z^2} - \frac{1}{2\lambda^2}(\delta n_p - \delta n_m) \right\}, \\ \frac{\partial(\delta n_m)}{\partial t} &= D_m \left\{ \frac{\partial^2(\delta n_m)}{\partial z^2} + \frac{1}{2\lambda^2}(\delta n_p - \delta n_m) \right\}, \end{aligned} \quad (\text{A1})$$

while the equation of Poisson is

$$\frac{\partial^2 V}{\partial z^2} = -\frac{q}{\epsilon}(\delta n_p - \delta n_m). \quad (\text{A2})$$

The boundary conditions are $j_p=j_m=0$ at $z=\pm d/2$, connected with the hypothesis that the electrodes are blocking, and $V(\pm d/2, t) = \pm(V_0/2)\exp(i\omega t)$ due to the presence of the external power supply. The boundary conditions on the density of currents, taking into account Eq. (1), can be rewritten as

$$\begin{aligned} \frac{\partial(\delta n_p)}{\partial z} + \frac{qN}{k_B T} \frac{\partial V}{\partial z} &= 0, \\ \frac{\partial(\delta n_m)}{\partial z} - \frac{qN}{k_B T} \frac{\partial V}{\partial z} &= 0. \end{aligned} \quad (\text{A3})$$

It is useful to introduce the reduced quantities $p = \delta n_p/N$, $m = \delta n_m/N$, and $u = V/V_{th}$, representing the relative variations of the ionic densities due to the external field and the electrical potential expressed in units of the thermal potential $V_{th} = k_B T/q$. With these quantities Eqs. (A1) and (A2) and the boundary conditions (A3) and that on the potential read

$$\begin{aligned} \frac{\partial p}{\partial t} &= D_p \left\{ \frac{\partial^2 p}{\partial z^2} - \frac{1}{2\lambda^2}(p - m) \right\}, \\ \frac{\partial m}{\partial t} &= D_m \left\{ \frac{\partial^2 m}{\partial z^2} + \frac{1}{2\lambda^2}(p - m) \right\}, \\ \frac{\partial^2 u}{\partial z^2} &= -\frac{1}{2\lambda^2}(p - m) \end{aligned} \quad (\text{A4})$$

and

$$\begin{aligned} \frac{\partial p}{\partial z} + \frac{\partial u}{\partial z} &= 0, \\ \frac{\partial m}{\partial z} - \frac{\partial u}{\partial z} &= 0, \end{aligned}$$

$$u(\pm d/2, t) = \pm(u_0/2)\exp(i\omega t), \quad (\text{A5})$$

where $u_0 = V_0/V_{th}$. Since the system of differential equations (A4) has constant coefficients, the solutions are of the type

$$p(z, t) = R_p(z)\exp(i\omega t), \quad m(z, t) = R_m(z)\exp(i\omega t),$$

$$u(z,t) = \phi(z)\exp(i\omega t). \tag{A6}$$

By substituting the above trial solutions into Eqs. (A4) and (A5) we obtain

$$R_p''(z) - \frac{1}{\ell_p^2}R_p(z) + \frac{1}{2\lambda^2}R_m(z) = 0,$$

$$R_m''(z) - \frac{1}{\ell_m^2}R_m(z) + \frac{1}{2\lambda^2}R_p(z) = 0,$$

$$\phi''(z) = -\frac{1}{2\lambda^2}[R_p(z) - R_m(z)] \tag{A7}$$

and

$$R_p' + \phi' = 0,$$

$$R_m' - \phi' = 0,$$

$$\phi(\pm d/2) = \pm u_0, \tag{A8}$$

where the prime means derivation with respect to z and

$$\frac{1}{\ell_p^2} = \frac{1}{2\lambda^2} \left(1 + 2i\omega \frac{\lambda^2}{D_p} \right),$$

$$\frac{1}{\ell_m^2} = \frac{1}{2\lambda^2} \left(1 + 2i\omega \frac{\lambda^2}{D_m} \right). \tag{A9}$$

The functions $R_p(z)$, $R_m(z)$, and $\phi(z)$, solutions of Eqs. (A7) with the boundary conditions (A8) are

$$R_p(z) = C_1 \sinh(\gamma_1 z) + C_2 \sinh(\gamma_2 z),$$

$$R_m(z) = k_1 C_1 \sinh(\gamma_1 z) + k_2 C_2 \sinh(\gamma_2 z),$$

$$\phi(z) = -\frac{1}{2\lambda^2} \left\{ \frac{1-k_1}{\gamma_1^2} C_1 \sinh(\gamma_1 z) + \frac{1-k_2}{\gamma_2^2} C_2 \sinh(\gamma_2 z) \right\} + Az, \tag{A10}$$

where

$$\gamma_{1,2} = \frac{1}{2\lambda^2} \left\{ 1 + i\omega \lambda^2 \frac{D_p + D_m}{D_p D_m} \pm \sqrt{1 + \left(i\omega \lambda^2 \frac{D_m - D_p}{D_m D_p} \right)^2} \right\},$$

$$k_{1,2} = \left\{ i\omega \lambda^2 \frac{D_p - D_m}{D_p D_m} \pm \sqrt{1 + \left(i\omega \lambda^2 \frac{D_m - D_p}{D_m D_p} \right)^2} \right\}. \tag{A11}$$

Integration the constants C_1 , C_2 , and A is determined by the boundary conditions (A8), which in the present case are

$$\gamma_1 \left(1 - \frac{1-k_1}{2\lambda^2 \gamma_1^2} \right) C_1 \cosh(\gamma_1 d/2) + \gamma_2 \left(1 - \frac{1-k_2}{2\lambda^2 \gamma_2^2} \right) C_2 \cosh(\gamma_2 d/2) + \frac{A}{2} = 0,$$

$$\gamma_1 \left(k_1 + \frac{1-k_1}{2\lambda^2 \gamma_1^2} \right) C_1 \cosh(\gamma_1 d/2) + \gamma_2 \left(k_2 + \frac{1-k_2}{2\lambda^2 \gamma_2^2} \right) C_2 \cosh(\gamma_2 d/2) - \frac{A}{2} = 0,$$

$$-\frac{1}{2\lambda^2} \left\{ \frac{1-k_1}{\gamma_1^2} C_1 \sinh(\gamma_1 d/2) + \frac{1-k_2}{\gamma_2^2} C_2 \sinh(\gamma_2 d/2) \right\} + A \frac{d}{2} = \frac{u_0}{2}. \tag{A12}$$

A simple calculation gives

$$C_1 = \frac{\gamma_1^2 \gamma_2^3 (1+k_2) \lambda^2 B_2}{\mathcal{D}} u_0, \quad C_2 = -\frac{\gamma_1^3 \gamma_2^2 (1+k_1) \lambda^2 B_1}{\mathcal{D}} u_0 \tag{A13}$$

and

$$A = \frac{\gamma_1 \gamma_2 \{ -\gamma_2^2 (-1+k_1)(1+k_2) + \gamma_1^2 [(1+k_1)(-1+k_2) + 2\gamma_2^2 (k_1-k_2)\lambda^2] \} B_1 B_2}{\mathcal{D}} u_0, \tag{A14}$$

where

$$\mathcal{D} = \gamma_2^3 (-1+k_1)(1+k_2) B_2 S_1 + \gamma_1 B_1 \{ \gamma_2 d [-\gamma_2^2 (-1+k_1)(1+k_2) + \gamma_1^2 [(1+k_1)(-1+k_2) + 2\gamma_2^2 (k_1-k_2)\lambda^2] \} B_2 - \gamma_1^2 (1+k_1)(-1+k_2) S_2 \}, \tag{A15}$$

$B_1 = \cosh(\gamma_1 d/2)$, $B_2 = \cosh(\gamma_2 d/2)$, $S_1 = \sinh(\gamma_1 d/2)$, and $S_2 = \sinh(\gamma_2 d/2)$.

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