

Ambipolar diffusion in the low frequency impedance response of electrolytic cells

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Abstract. The electrical response of an electrolytic cell to an external ac excitation is analysed by solving the equations of the Poisson–Nernst–Planck (PNP) continuum model for two ions (ambipolar) and one mobile ion diffusive systems. The theoretical predictions of the ambipolar system, formed by positive ions of mobility μ_p and negative ions of mobility μ_m , are investigated in the limit in which one of the mobilities goes to zero. The analysis reveals that these predictions correspond to the ones arising from the one mobile ion diffusive system only in the frequency range $\omega \gg \omega_D \mu_m / \mu_p$, in which ω_D is the Debye’s frequency. For very low frequencies, it shows that the physical system formed by two mobile ions, one of which has a very low mobility, is clearly distinct from the physical system in which just one of the ions is mobile. We argue that apparent deviations of the experimental spectra from the predictions of the PNP model in the low frequency region, usually interpreted as an interfacial property, may be connected with the difference in the diffusion coefficients of cations and anions.

Keywords: diffusion, surface effects, transport properties

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1. Introduction

The role of the mobile ions in the electrical impedance response of liquid materials deserved many experimental and theoretical approaches in the last decades [1–5]. The natural experimental framework to analyse it is the impedance spectroscopy technique, which is based on the linear response of the material when it is submitted to an ac voltage of small amplitude, say V_0 , and a variable frequency, $f = \omega/2\pi$, where ω is the angular frequency [6]. The response may be immediately connected with the impedance, $Z(\omega)$, by varying the frequency of the applied voltage in a wide interval. The ion influence is expected to be more pronounced in the low frequency part of the impedance spectrum, in view of the high mobility of these charges [7]. It is also expected that the whole response of the cell strongly depends on the role played by the electrodes limiting it [8–10]. Thus, in order to account for the influence of the ions on the impedance spectroscopy response, it is necessary to investigate the problem by considering appropriate boundary conditions. A successful model to describe the dynamical behaviour of the ions is the so-called Poisson–Nernst–Planck (PNP) continuous model [1], whose fundamental equations are the continuity equations, for the positive and negative ions, coupled to the equation of Poisson, for the actual electric potential across the sample. The models proposed to interpret the low frequency region of the real and imaginary parts of the spectra are mainly based on the assumption that the electric current is of diffusion origin, and responsible for a Warburg-like impedance [11, 12]. These models have been recently criticised, since in their framework the electrical current is position dependent,

and hence the usual definition of electric impedance of the cell cannot be used [13]. Some deviations of the experimental spectra frequency dependencies, from the theoretical predictions of the PNP model, have been observed mainly in the low frequency region. They are particularly significant when one insists in interpreting experimental data of a system having very different mobilities by means of a simplified version of PNP model that assumes equal mobilities. In this case, those apparent deviations of the spectra in the low frequency region could be a consequence of this difference in the diffusion coefficients of the ions, and not due to a particular weakness of the model.

The case in which only one type of ion is mobile is of some practical interest [14, 15]. It has been considered theoretically, as a limiting case, by Franceschetti and Ross Macdonald some years ago [16]. Deviations from the theoretical predictions may also be found when one interprets experimental data of systems with very different mobilities in the framework of the one ion mobile diffusive systems. Indeed, the applicability of this kind of approach becomes meaningful only for a certain part of the frequency spectra concerning high values, as we propose to analyse hereafter in detail.

The first step of our analysis is to obtain the exact solutions of the PNP equations for the system formed by positive ions of mobility μ_p and negative ions of mobility μ_m , which we call hereafter as ‘ambipolar’ system, such that $\mu_p \neq \mu_m \neq 0$ [17–19]. Then, we also obtain the solutions for the PNP equations of the one mobile ion diffusive system ($\mu_p \neq 0$ and $\mu_m = 0$). For simplicity, we restrict the subsequent analysis to the case of blocking electrodes boundary conditions, but an immediate generalisation of our approach allows us to take into account the non-ideal blocking character of the electrodes by changing the boundary conditions on the surface density of currents [9, 10]. Our goal here is to compare the theoretical predictions of both the ambipolar and the one mobile ion diffusive systems in the limit in which one of the mobilities goes to zero. Specifically, if we put $\mu_m = y\mu_p$, with $y \in [0, 1]$, a rough perturbative analysis starting from the equations of the ambipolar system reveals the apparent existence of a singular point at $y = 0$ in the limit of very low frequency. If true, this singularity would forbid the solutions to satisfy the required boundary conditions, even in the simplest case of blocking electrodes. A more rigorous mathematical analysis of the solutions permits us to conclude instead that, in the limit $y \rightarrow 0$, the impedance response of both models shows a good agreement in the ‘high’ frequency region, but a strong disagreement in the ultra low frequency region of the spectrum, indicating that the limits $y \rightarrow 0$ and $\omega \rightarrow 0$ may not commute. In this low frequency region, the physical system formed by two mobile ions, one of which has a very low mobility, is shown to be clearly distinct from the physical system in which just one of the ions is mobile. Thus, the predictions of the one mobile ion diffusive system should always be taken with care when applied to the whole frequency range covered by the experimental data. Otherwise, unreal deviations between the theoretical predictions and the experimental data, interpreted as being due to interfacial effects, arise compromising a true interpretation of real bulk properties.

The paper is organised as follows. In section 2, we solve the basic bulk equations of the ambipolar and one mobile ion diffusive systems, obtaining analytical expressions for the electrical impedance of the cell in both systems. The apparent absence of a

continuous mapping from one model to the other is faced analytically in section 3, using a rough version of the small parameter method. In the same section, a more rigorous mathematical analysis is performed, indicating that, for a given frequency, the predictions of both models coincide in the limit $y \rightarrow 0$, for a fixed frequency. In section 4, we promote a direct comparison between the predictions of the ambipolar and the one mobile ion diffusive systems, using data from a real sample, in the limit in which one of the mobilities is decreasingly small. Some conclusions are presented in section 5.

2. The mathematical problems

To formulate the mathematical problem, we assume that the charge carriers form a continuum of positive and negative charge densities in a system in the shape of a slab of thickness d . The surfaces are electrodes placed at the positions $z = \pm d/2$, where z is the Cartesian coordinate perpendicular to the surfaces, such that all quantities depend only on the coordinate z and the time t . In the absence of an external field, the sample is locally and globally neutral, and the potentials of the electrodes coincide with that of the bulk. In what follows, we consider that the sample is subjected to an external electrical difference of potential given by

$$V(d/2, t) - V(-d/2, t) = V_0 e^{i\omega t}, \quad (1)$$

in which, as mentioned before, V_0 is the amplitude, which has to be small enough to keep the linear approximation valid, and $f = \omega/(2\pi)$ is the frequency. Before applying this external potential, we assume that the bulk density of positive and negative ions, denoted, respectively, as N_p and N_m , are such that $N_p(V_0 = 0) = N_m(V_0 = 0) = n_0$, where n_0 is the bulk density of ions in the thermodynamic equilibrium.

2.1. Ambipolar diffusion

We first tackle the case in which in the presence of a $V_0 \neq 0$ both ions move in the sample, producing currents that are partially due to the diffusion and partially due to the drift. These currents are:

$$\begin{aligned} j_p &= -D_p \left[\frac{\partial N_p}{\partial z} + \frac{qN_p}{k_B T} \frac{\partial V}{\partial z} \right], \\ j_m &= -D_m \left[\frac{\partial N_m}{\partial z} - \frac{qN_m}{k_B T} \frac{\partial V}{\partial z} \right], \end{aligned} \quad (2)$$

where p stands for the sign (+) and m for the sign (-) of the charges of the ions, whose absolute value is the elementary charge, q . In equation (2), $k_B T$ is the thermal energy and $V = V(z, t)$ is the actual electrical potential. The basic equations of the problem are the equations of continuity for the two types of ions, and the equation of Poisson,

namely:

$$\frac{\partial N_{p,m}}{\partial t} = -\frac{\partial j_{p,m}}{\partial z} \quad \text{and} \quad \frac{\partial^2 V}{\partial z^2} = -\frac{q}{\varepsilon}(N_p - N_m), \quad (3)$$

in which ε is the dielectric constant of the liquid containing the ions, assumed as non-dispersive in the frequency range analysed here. A simple inspection of the set of equations (2) and (3) shows that the equations of continuity are nonlinear because of the drift terms. Since we are working in the small ac voltage limit, it is possible to assume that $N_p = n_0 + n_p$ as well as $N_m = n_0 + n_m$, such that $n_p \ll n_0$ and $n_m \ll n_0$, i.e., the resulting system will behave as linear if we always restrict the analysis to the case $V_0 \ll v_T = k_B T/q \approx 0.025$ V. This linear regime, which is required in order to keep the concept of impedance as meaningful, permits us to modify the drift term in equation (2) as

$$\frac{N_a}{v_T} \frac{\partial V}{\partial z} \approx \frac{n_0}{v_T} \frac{\partial V}{\partial z} = n_0 \frac{\partial u_v}{\partial z}, \quad \text{for } a = p, m, \quad (4)$$

in which $u_v = V/v_T$. Now, using this approximation, the set of equation (3), combined with the resulting equations from (2), produces the following equations of the PNP model:

$$\begin{aligned} \frac{\partial u_p}{\partial t} &= D_p \left[\frac{\partial^2 u_p}{\partial z^2} + \frac{\partial^2 u_v}{\partial z^2} \right], \\ \frac{\partial u_m}{\partial t} &= D_m \left[\frac{\partial^2 u_m}{\partial z^2} - \frac{\partial^2 u_v}{\partial z^2} \right], \\ \frac{\partial^2 u_v}{\partial z^2} &= -\frac{1}{L^2} (u_p - u_m), \end{aligned} \quad (5)$$

in which, for simplicity, we have introduced the reduced quantities $u_a = (n_a - n_0)/n_0$, for $a = p, m$, as above, and

$$L = \sqrt{\frac{\varepsilon k_B T}{n_0 q^2}} = \sqrt{\frac{\varepsilon v_T}{n_0 q}} \quad (6)$$

is the Debye screening length. In the presence of an applied potential, such that at the electrodes it assumes the form

$$V \left(\pm \frac{d}{2}, t \right) = \pm \frac{V_0}{2} e^{i\omega t}, \quad (7)$$

the currents of positive and negative ions towards the electrodes are unequal and have to satisfy proper boundary conditions. To simplify the mathematical analysis, we limit ourselves to consider the so-called blocking electrodes (i.e., ideally polarisable electrodes [20]) boundary conditions, i.e.,

$$j_p \left(\pm \frac{d}{2}, t \right) = 0 \quad \text{and} \quad j_m \left(\pm \frac{d}{2}, t \right) = 0. \quad (8)$$

At this point, the mathematical problem is stated in terms of well-defined boundary conditions.

To go on further, let us now sketch the search for solutions using the elementary procedure of separation of variables. For simplicity, we introduce a more compact notation by defining the quantities:

$$\Omega_p = \omega \frac{L^2}{D_p}, \quad \Omega_m = \omega \frac{L^2}{D_m}, \quad \omega_D = \frac{D_p}{L^2}, \quad \text{and} \quad x = \frac{z}{L}, \quad (9)$$

where, for future purposes, we also have introduced the Debye frequency, ω_D . Thus, the solutions we are looking for, in the presence of a harmonic excitation, may be cast in the form:

$$\begin{aligned} u_p(x, t) &= p(x)e^{i\omega t}, \\ u_m(x, t) &= m(x)e^{i\omega t}, \\ u_v(x, t) &= v(x)e^{i\omega t}. \end{aligned} \quad (10)$$

Using (9) and (10), the system formed by equation (5) reduces to:

$$\begin{aligned} i\Omega_p p(x) &= p''(x) + v''(x), \\ i\Omega_m m(x) &= m''(x) - v''(x), \\ v''(x) &= m(x) - p(x). \end{aligned} \quad (11)$$

We consider now the ‘symmetric problem’, i.e., $u(-x) = -u(x)$, $p(-x) = -p(x)$, and $m(-x) = -m(x)$. The (odd) solutions for the system (11) are easily found as

$$\begin{aligned} p(x) &= c_1 \sinh \lambda_1 x + c_2 \sinh \lambda_2 x \quad \text{and} \\ m(x) &= c_1 (1 + i\Omega_p - \lambda_1^2) \sinh \lambda_1 x + c_2 (1 + i\Omega_p - \lambda_2^2) \sinh \lambda_2 x, \end{aligned} \quad (12)$$

in which λ_i , with $i = 1, 2$, are the two positive solutions of the eigenvalues equation

$$\lambda^4 - (2 + i\Omega_p + i\Omega_m)\lambda^2 + [(1 + i\Omega_p)(1 + i\Omega_m) - 1] = 0, \quad (13)$$

because replacing λ_i with $-\lambda_i$ does not alter the solutions (12), in the sense that just the coefficients change sign. For what concerns the equation of Poisson, from equations (11) and using (12), we obtain:

$$v(x) = c_1 \left(\frac{i\Omega_p}{\lambda_1^2} - 1 \right) \sinh \lambda_1 x + c_2 \left(\frac{i\Omega_p}{\lambda_2^2} - 1 \right) \sinh \lambda_2 x + c_3 x. \quad (14)$$

The integration constants c_1 , c_2 , and c_3 may be determined by the boundary conditions. The total electric current is

$$J = q(j_p - j_m) + \varepsilon \frac{\partial E}{\partial t}, \quad (15)$$

where the last term is the displacement current. Since no charge injection occurs at the electrodes, J is position independent, and has the simple form:

$$J = \frac{\varepsilon v_T}{L^3} [D_p + D_m + i\omega L^2] e^{i\omega t}. \quad (16)$$

Finally, the impedance of the cell, defined as $Z = \Delta V/I$, may be obtained as

$$Z(\omega) = \frac{u_0 L^3}{\varepsilon S [D_p + D_m + i\omega L^2] c_3}, \quad (17)$$

in which $u_0 = V_0/v_T$ and S is the area of the electrodes. We notice that the expression of the impedance depends only on the integration constant, c_3 , connected with the linear part of the electric potential. To find it, we recall that the blocking electrodes boundary conditions stated in (8) become:

$$p'(\pm x_0) + v'(\pm x_0) = 0, \quad m'(\pm x_0) - v'(\pm x_0) = 0, \quad (18)$$

together with $v(\pm x_0) = \pm u_0/2$, in which $x_0 = d/2L$. These equations are enough to determine the integration constants of the solutions sketched above. At this point the problem is formally solved and an analytical expression for the electrical impedance of the cell in the ambipolar regime is found for the situation of blocking electrodes. Similar calculations may be done for the case of one mobile ion diffusive system, and will be addressed now.

2.2. One mobile ion diffusive system

We shall consider the case in which one type of the ions (e.g., the negative ones) has zero mobility, $\mu_m = 0$. From the Einstein–Smoluchowsky relation, this implies that $D_m = 0$. Thus, the set of equations of the PNP model reduces to only two of them:

$$\begin{aligned} \frac{\partial u_p}{\partial t} &= D_p \left[\frac{\partial^2 u_p}{\partial z^2} + \frac{\partial^2 u_v}{\partial z^2} \right] \\ \frac{\partial^2 u_v}{\partial z^2} &= -\frac{1}{L^2} u_p. \end{aligned} \quad (19)$$

Proceeding as before, in the presence of a harmonic excitation, the solutions of the spatial part of the equations above are:

$$p(z) = c'_1 \sinh \lambda x \quad \text{and} \quad v(x) = c'_2 \sinh \lambda x + c'_3 x, \quad (20)$$

where $c'_2 = -c'_1/\lambda^2$, with $\lambda^2 = 1 + i\Omega_p$. The integration constants c'_1 and c'_3 can be determined by imposing the boundary conditions (18), for blocking electrodes, which, in the case of one mobile ion diffusive system, become:

$$p'(x_0) + v'(x_0) = 0 \quad \text{and} \quad v(x_0) = \frac{u_0}{2}. \quad (21)$$

Substitution of equations (20) into (21) yields:

$$\begin{aligned} c'_1 &= -\frac{Lu_0\lambda^2}{\lambda d(\lambda^2 - 1) \cosh(\lambda d/2L) + 2L \sinh(\lambda d/2L)}, \\ c'_3 &= \frac{Lu_0\lambda(\lambda^2 - 1)}{\lambda d(\lambda^2 - 1) + 2L \tanh(\lambda d/2L)}. \end{aligned} \quad (22)$$

The current of charged particles is now simply given by $J = qj_p + \varepsilon \partial E / \partial t$, which, in this case, becomes

$$J = \frac{\varepsilon v_T}{L^3} [D_p + i\omega L^2] e^{i\omega t}, \quad (23)$$

i.e., it is constant across the cell, as for the ambipolar diffusion system, and is just equation (16), for $D_m = 0$. Likewise, the electrical impedance may be determined as

$$Z(\omega) = \frac{u_0 L^3}{\varepsilon S [D_p + i\omega L^2] c'_3}, \quad (24)$$

which would be the case $D_m = 0$ of equation (17), if $c_3 \rightarrow c'_3$. This permits us to suppose that there exists a limiting procedure by means of which the final impedance expression obtained in the ambipolar system, equation (17), should tend to the expression obtained for the case of one mobile ion diffusive system, equation (24), in a continuous manner, and this is indeed the case. However, this limiting procedure has to be taken with some care in the low frequency region, as we discuss in detail in the next section by first using rough perturbative arguments.

3. The small parameter method

To perform a perturbative analysis, in order to investigate the possibility of continuously passing from the description of the ambipolar diffusive to the description provided by the one mobile ion diffusive system, we put $D_p = D$ and redefine the rescaled quantities of equation (9) as follows:

$$D_m = yD, \quad \Omega_p = \Omega = \omega \frac{L^2}{D} = \frac{\omega}{\omega_D}, \quad \Omega_m = \frac{\Omega}{y}, \quad \omega_D = \frac{D}{L^2}, \quad (25)$$

where $y \in [0, 1]$. In terms of these quantities, the equations of the PNP model, given by the system (11), may be rewritten as:

$$\begin{aligned} i\Omega p(x) &= p''(x) + v''(x), \\ i\Omega m(x) &= y [m''(x) - v''(x)], \\ v''(x) &= -p(x) + m(x). \end{aligned} \quad (26)$$

The boundary conditions relevant for the blocking electrodes are now:

$$p'(\pm x_0) + v'(\pm x_0) = 0 \quad y [m'(\pm x_0) - v'(\pm x_0)] = 0, \quad (27)$$

in addition to $v(\pm x_0) = \pm u_0/2$.

To clarify the meaning of the limiting behaviour $y \rightarrow 0$, a simple analysis may be carried as follows. If we use the third of equation (26) in the other two equations, we easily obtain two coupled equations for $m(x)$ and $p(x)$ in the form:

$$\begin{aligned} ym''(x) - (y + i\Omega)m(x) + yp(x) &= 0 \\ p''(x) - (1 + i\Omega)p(x) + m(x) &= 0. \end{aligned} \tag{28}$$

From the first equation one deduces that for $y \rightarrow 0$, $m \rightarrow 0$, as expected. Furthermore, from the same equation we derive that y compares with Ω . Consequently, small or large values of y means $y \ll \Omega$ or $y \gg \Omega$, respectively. This corresponds to the frequency range $\omega \gg y\omega_D$ or $\omega \ll y\omega_D$, i.e., there is a reference frequency $\omega^* = y\omega_D$ that defines the meaning of high or small frequencies, as we discuss in detail in section 4.

3.1. Arbitrary frequency

To explore the limit $y \rightarrow 0$, when the frequency is free to vary from very low to very high values, we first look for solutions of (26) in the form of a small parameter expansion of the type [21]:

$$\begin{aligned} p(x) &\approx p_0(x) + yp_1(x) + y^2p_2(x) + \dots + y^n p_n(x) + \\ m(x) &\approx m_0(x) + ym_1(x) + y^2m_2(x) + \dots + y^n m_n(x) + \\ v(x) &\approx v_0(x) + yv_1(x) + y^2v_2(x) + \dots + y^n v_n(x) + \end{aligned} \tag{29}$$

Using (29) into equation (26), to the zeroth order, we obtain:

$$\begin{aligned} i\Omega p_0(x) &= p_0''(x) + v_0''(x), \\ i\Omega m_0(x) &= 0, \quad \text{and} \\ v_0''(x) &= -p_0(x) + m_0(x). \end{aligned} \tag{30}$$

The general solutions for $p_0(x)$ and $v_0(x)$ are, simply, the same as for $p(x)$ and $v(x)$ of the one mobile ion diffusive system, namely:

$$\begin{aligned} p_0(x) &= c'_1 \sinh \Lambda x, \\ m_0(x) &= 0, \\ v_0(x) &= -\frac{c'_1}{\Lambda^2} \sinh \Lambda x + c'_3 x, \end{aligned} \tag{31}$$

where, now, $\Lambda^2 = 1 + i\Omega$. The procedure is hereafter straightforward and the method may be continued to yield the solutions up to the successive orders.

Before proceeding further, it is instructive to test the applicability of the method at its lowest order, taking into account the boundary conditions to obtain c'_1 and c'_3 .

In the case of blocking electrodes, the currents j_p and j_m , defined in equation (2) and rewritten in terms of the rescaled quantities introduced in (25), become:

$$\begin{aligned} j_p(x) &= -\frac{n_0 D}{L} [p'(x) + v'(x)] e^{i\omega t}, \\ j_m(x) &= -\frac{n_0 D}{L} y [m'(x) - v'(x)] e^{i\omega t}, \end{aligned} \tag{32}$$

and have to satisfy the following conditions:

$$j_p(x_0, t) = 0 \quad \text{and} \quad j_m(x_0, t) = 0. \tag{33}$$

Since from equation (30), $m_0(x) = 0$, to the zeroth order the boundary conditions (27) yield $v'_0(x_0) = 0$ and

$$v'_0(x_0) = -p'_0(x_0) = -\Lambda c'_1 \cosh [\Lambda x_0] \neq 0, \tag{34}$$

which is evidently impossible. As pointed out before, the iterative procedure could continue to obtain higher order solutions, but it is not necessary. The simple analysis sketched above, even if restricted to the zeroth order, apparently indicates that the solutions of the ambipolar problem cannot be expanded in power series of y near to $y = 0$ in order to continuously reach the behaviour predicted for the one mobile ion diffusive system.

It is also possible to look at this delicate problem by using a slightly different perspective. Instead of dealing with second order differential equations, we may use the first and the third of the set of equation (26) to obtain

$$m(x) = [1 + i\Omega] p(x) - p''(x), \tag{35}$$

and, from the second and the third of those equations, using the previous results, we arrive at a fourth order equation for $p(x)$:

$$y p''''(x) - [2y + i\Omega(1 + y)] p''(x) + i\Omega [(1 + y) + i\Omega] p(x) = 0. \tag{36}$$

When $p(x)$ is determined by integrating (36), equation (35) yields $m(x)$. Subsequently, the third of equation (26) can be immediately integrated to obtain $v(x)$. Now, if we perform the limit $y \rightarrow 0$, the fourth order term vanishes in equation (36), which reduces to

$$p''(x) - (1 + i\Omega)p(x) = 0. \tag{37}$$

Substitution of (37) into equation (35), immediately yields $m(x) = 0$. By invoking the boundary conditions, equation (18), we arrive again at the conflicting situation for which $v'(x_0) = -p'(x_0) \neq 0$ and also $v'(x_0) = m'(x_0) = 0$. Thus, the solution of (37), which is the same as in equation (20), is apparently not able to satisfy the boundary condition of the problem. The point $y = 0$ seems to represent a singular point because the differential equation (36) changes abruptly its order, passing from fourth to second order. This rough analysis shows that the expansion with respect to a parameter connecting the

mobilities of both types of ions has to be applied with care to this class of problems [22]. Indeed, looking at the second of equation (26) we notice that the limit of very small y is meaningful when we take into account also the order of magnitude of the value of the frequency, Ω . To demonstrate that the continuous limit between the two models exists, as expected, a more rigorous mathematical analysis is needed, and has to be carried out by keeping the values of the frequency fixed.

3.2. Fixed frequency

Let us recall the solutions of the ambipolar system, stated in equations (12) and (14), after using the rescaled quantities defined in (25):

$$p(x) = c_1 \sinh \lambda_1 x + c_2 \sinh \lambda_2 x \tag{38}$$

$$m(x) = c_1 (1 + i\Omega - \lambda_1^2) \sinh \lambda_1 x + c_2 (1 + i\Omega - \lambda_2^2) \sinh \lambda_2 x \tag{39}$$

$$v(x) = c_1 (i\Omega/\lambda_1^2 - 1) \sinh \lambda_1 x + c_2 (i\Omega/\lambda_2^2 - 1) \sinh \lambda_2 x + c_3 x, \tag{40}$$

where the c_i 's are the new arbitrary constants, while the λ_i 's are now the roots of the biquadratic equation (13), reduced to:

$$\lambda^4 - \left(2 + i\Omega + \frac{i\Omega}{y}\right) \lambda^2 + \frac{i\Omega}{y} (1 + i\Omega + y) = 0,$$

that is, after elementary computations,

$$\lambda_1^2 = 1 + \frac{i\Omega}{2y} \left(1 + y + \sqrt{(1-y)^2 - \frac{4y^2}{\Omega^2}}\right),$$

$$\lambda_2^2 = 1 + \frac{i\Omega}{2y} \left(1 + y - \sqrt{(1-y)^2 - \frac{4y^2}{\Omega^2}}\right).$$

Note that for small y they behave quite differently, namely

$$\lambda_1^2 = \frac{i\Omega}{y} + 1 - \frac{iy}{\Omega} + iO(y^2) \quad \text{and} \quad \lambda_2^2 = 1 + i\Omega + \frac{iy}{\Omega} + iO(y^2),$$

as $y \rightarrow 0$. Since, as pointed out before, replacing λ_i with $-\lambda_i$ does not affect the structure of (38)–(40), on taking square roots we may choose λ_i in such a way that

$$\text{Re } \lambda_1 \sim \text{Im } \lambda_1 \sim \sqrt{\Omega/2y} \quad \text{and} \quad \lambda_2 \rightarrow \Lambda = \sqrt{1 + i\Omega}, \tag{41}$$

with $\text{Re } \Lambda > 0$, as $y \rightarrow 0$. Now, the free constants c_1 , c_2 , and c_3 must be chosen in order to match the boundary conditions (27), which leads to the linear system

$$\begin{aligned}
 c_1 \frac{i\Omega}{\lambda_1} \cosh \lambda_1 x_0 + c_2 \frac{i\Omega}{\lambda_2} \cosh \lambda_2 x_0 + c_3 &= 0, \\
 c_1 (2 - i\Omega/\lambda_1^2 + i\Omega - \lambda_1^2) \lambda_1 \cosh \lambda_1 x_0 + c_2 (2 - i\Omega/\lambda_2^2 + i\Omega - \lambda_2^2) \lambda_2 \cosh \lambda_2 x_0 - c_3 &= 0, \\
 c_1 (i\Omega/\lambda_1^2 - 1) \sinh \lambda_1 x_0 + c_2 (i\Omega/\lambda_2^2 - 1) \sinh \lambda_2 x_0 + c_3 x_0 &= u_0/2.
 \end{aligned} \tag{42}$$

This system can be inverted to yield the integration constants. To save space, we report only c_3 for the comparative purposes with c'_3 :

$$c_3 = \frac{u_0/2}{x_0 + \frac{A}{C} \tanh(\lambda_1 x_0) + \frac{B}{C} \tanh(\lambda_2 x_0)}, \tag{43}$$

where

$$\begin{aligned}
 A &= \lambda_2^3 (\Omega + i\lambda_1^2) (-2i + \Omega + i\lambda_2^2), \\
 B &= \lambda_1^3 (-i\Omega + \lambda_2^2) (-2 - i\Omega + \lambda_1^2), \\
 C &= \Omega \lambda_1 \lambda_2 (\lambda_1^2 - \lambda_2^2) [-2i + \Omega + i(\lambda_1^2 + \lambda_2^2)].
 \end{aligned} \tag{44}$$

Due to (41), when $y \rightarrow 0$ the coefficients of c_1 grow unboundedly, while those of c_2 tend to a finite limit. If we replace c_1 with the new unknown $\hat{c}_1 = c_1 \lambda_1^3 \cosh \lambda_1 x_0$, equation (42) turns into

$$\begin{aligned}
 \hat{c}_1 \frac{i\Omega}{\lambda_1^4} + c_2 \frac{i\Omega}{\lambda_2} \cosh \lambda_2 x_0 + c_3 &= 0 \\
 \hat{c}_1 (2/\lambda_1^2 - i\Omega/\lambda_1^4 + i\Omega/\lambda_1^2 - 1) + c_2 (2 - i\Omega/\lambda_2^2 + i\Omega - \lambda_2^2) \lambda_2 \cosh \lambda_2 x_0 - c_3 &= 0 \\
 \hat{c}_1 (i\Omega/\lambda_1^5 - 1/\lambda_1^3) \tanh \lambda_1 x_0 + c_2 (2 - i\Omega/\lambda_2^2 - 1) \sinh \lambda_2 x_0 + c_3 x_0 &= u_0/2
 \end{aligned} \tag{45}$$

and now, since $\tanh \lambda_1 x_0 \rightarrow 1$ as $y \rightarrow 0$, the coefficients matrix tends to a nonsingular matrix, therefore, the vector (\hat{c}_1, c_2, c_3) tends to (\hat{C}_1, C_2, C_3) , the solution of the limit system

$$\begin{aligned}
 C_2 \frac{i\Omega}{\Lambda} \cosh \Lambda x_0 + C_3 &= 0 \\
 -\hat{C}_1 + C_2 (2 - i\Omega/\Lambda^2 + i\Omega - \Lambda^2) \Lambda \cosh \Lambda x_0 - C_3 &= 0 \\
 C_2 (i\Omega/\Lambda^2 - 1) \sinh \Lambda x_0 + C_3 x_0 &= u_0/2.
 \end{aligned} \tag{46}$$

Note that the first and the third equations, which using $\Lambda^2 = 1 + i\Omega$ can be rewritten as

$$\begin{aligned}
 C_2 \frac{i\Omega}{\Lambda} \cosh \Lambda x_0 + C_3 &= 0, \\
 -C_2/\Lambda^2 \sinh \Lambda x_0 + C_3 x_0 &= u_0/2,
 \end{aligned} \tag{47}$$

allow one to compute C_2 and C_3 , after which also \hat{C}_1 can be computed using the second equation. Thus, summing up, we have

$$\hat{c}_1 \rightarrow \hat{C}_1, \quad c_2 \rightarrow C_2 \quad \text{and} \quad c_3 \rightarrow C_3 \quad \text{as } y \rightarrow 0,$$

and, in particular, recalling that $\widehat{c}_1 = c_1 \lambda_1^3 \cosh \lambda_1 x_0$, we see that

$$c_1 \sim \frac{\widehat{C}_1}{\lambda_1^3 \cosh \lambda_1 x_0} \rightarrow 0, \quad \text{as } y \rightarrow 0. \tag{48}$$

Now, plugging this expansion into (39), since

$$|\sinh \lambda_1 x| \leq e^{|\operatorname{Re} \lambda_1 x|} = e^{|x| \operatorname{Re} \lambda_1} \leq e^{\operatorname{Re} \lambda_1 x_0},$$

$\forall x \in [-x_0, x_0]$, while $|\cosh \lambda_1 x_0| \sim e^{x_0 \operatorname{Re} \lambda_1} / 2$ as $y \rightarrow 0$, and since moreover $\lambda_2^2 \rightarrow 1 + i\Omega$, we obtain that the function $m(x)$ tends to zero uniformly over $[-x_0, x_0]$, when $y \rightarrow 0$. This is no longer true for its derivative $m'(x)$: indeed, since $\lambda_2^2 \rightarrow 1 + i\Omega$, using (39) and (48) we see that

$$m'(x_0) \sim c_1 (1 + i\Omega - \lambda_1^2) \lambda_1 \cosh \lambda_1 x_0 \rightarrow -\widehat{C}_1,$$

as $y \rightarrow 0$. Arguing as for $m(x)$, one can prove that $m'(x)$ tends to zero uniformly over any closed interval $[-a, a]$, with $a < x_0$. In a similar way, from (38) and (40), one obtains that

$$\begin{aligned} p(x) &\rightarrow p_0(x) = C_2 \sinh \Lambda x, \\ v(x) &\rightarrow v_0(x) = -C_2 / \Lambda^2 \sinh \Lambda x + C_3 x, \end{aligned}$$

uniformly over $[-x_0, x_0]$ (these two functions converge together with their derivatives up to the second order). As one can easily check, $p_0(x)$ and $v_0(x)$ solve the linear system

$$i\Omega p_0(x) = p_0''(x) + v_0''(x) \quad \text{and} \quad v_0''(x) = -p_0(x), \tag{49}$$

coupled with the boundary conditions (27), which models the case where the negative ions have zero mobility (note that, writing down the boundary conditions, one obtains the linear system (47), which determines C_2 and C_3 , while the validity of (49) follows from $\Lambda^2 = 1 + i\Omega$).

A remark is in order here for what concerns the 2×2 coefficients matrix in (47). We notice that it is always invertible (therefore, also the 3×3 matrix in (46) is invertible). Indeed, letting $\xi = \Lambda x_0$, the 2×2 determinant vanishes when $\tanh \xi = -i\Omega \xi$ (note that $\xi^2 = x_0(1 + i\Omega)$, hence $\arg \xi \in (0, \pi/4)$ and $\cosh \xi \neq 0$). Then, letting $2\xi = x + iy$ with $0 < y < x$, we have

$$\left| \frac{\operatorname{Im}(\tanh \xi)}{\operatorname{Re}(\tanh \xi)} \right| = \frac{|\sin y|}{\sinh x} < \frac{y}{x} < 1,$$

while

$$\left| \frac{\operatorname{Im}(-i\Omega \xi)}{\operatorname{Re}(-i\Omega \xi)} \right| = \frac{x}{y} > 1.$$

Therefore, the equation $\tanh \xi = -i\Omega \xi$ has no solution when $\arg \xi \in (0, \pi/4)$.

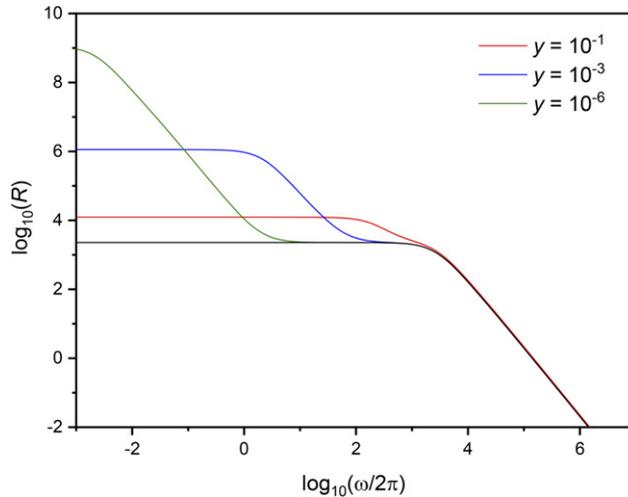


Figure 1. Frequency behaviour of $\log_{10}R$ for the one mobile ion diffusive system showing a plateau (solid black line) and for the ambipolar system: $D_m = 10^{-1}D_p$ (red), $D_m = 10^{-3}D_p$ (blue), and $D_m = 10^{-6}D_p$ (green). One observes that the first resistance plateau of the ambipolar system tends to coincide with the plateau of the one mobile ion diffusive system as y decreases. The curves have been drawn for $D_p = D \approx 10^{-9} \text{ m}^2\text{s}^{-1}$, $n_0 \approx 10^{20} \text{ m}^{-3}$, $\varepsilon = 10 \varepsilon_0$, $S \approx 10^{-4} \text{ m}^2$, and $d \approx 10^{-6} \text{ m}$, i.e., $L \approx 10^{-7} \text{ m}$ [7].

4. Two and one mobile ion diffusive system: a comparison

In this section, we shall investigate the electrical impedance response of the two models analysed in the previous sections. To do this, we use the parameter values in the experimental range of a real physical system containing ions [7]. We consider a symmetric binary electrolyte, which can be faced as a dispersion of ions in a dielectric liquid, evidencing ambipolar diffusion [23] such that the diffusion coefficients are $D_m = yD$, for $y \in [0, 1]$. From equations (17) and (24), we form the quantities $R = \text{Re } Z$ and $X = \text{Im } Z$, respectively, for the ambipolar and for the one mobile diffusive ion systems.

In figure 1, the behaviour of $\log_{10}R = \log_{10}(\text{Re } Z)$ is shown in the case of ambipolar diffusion for different values of y , together with the same quantity for the one mobile ion diffusive system. The curve corresponding to the one mobile ion diffusive system shows the existence of a single plateau in the resistance of the cell, which extends to the low frequency region of the spectrum, whose value is

$$R_1(\omega \rightarrow 0) = \frac{L^2}{2\varepsilon S D_p} \left\{ 3d - \left[6L + d \tanh\left(\frac{d}{2L}\right) \right] \tanh^2\left(\frac{d}{2L}\right) \right\}.$$

For the case of ambipolar diffusive model, a plateau appears whose value is given by

$$R_{2H} = \frac{dL^2}{\varepsilon S(D_m + D_p)} = \frac{dL^2}{\varepsilon S D(1 + y)}. \quad (50)$$

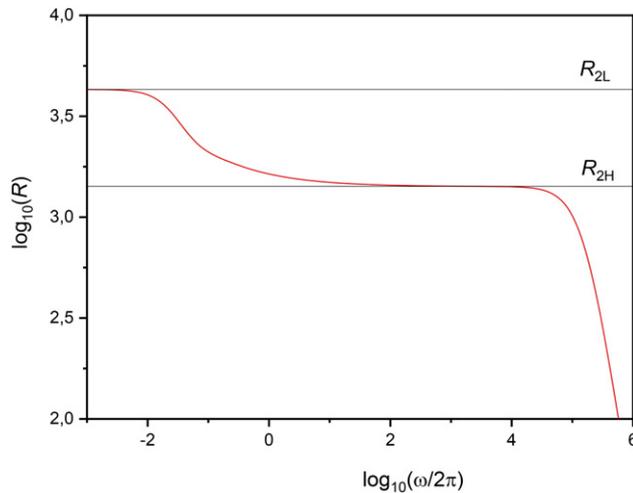


Figure 2. Frequency behaviour of $\log_{10}R$ for the ambipolar system when $D_m = 10^{-1}D_p$. The first resistance plateau of the ambipolar system, R_{2H} , is the one given by equation (50), while the value of the second, R_{2F} , is determined by equation (51). The curves have been drawn for a physical system for which $D_p = D \approx 10^{-9} \text{ m}^2\text{s}^{-1}$, $n_0 \approx 10^{23} \text{ m}^{-3}$, $\varepsilon = 80 \varepsilon_0$, $S \approx 10^{-4} \text{ m}^2$, and $d \approx 10^{-4} \text{ m}$, corresponding to $L \approx 10^{-8} \text{ m}$, i.e., $L \ll d$ [24].

In addition, a second plateau in the resistance appears in the low frequency region, whose value may be analytically determined as [23]:

$$R_{2L}(\omega \rightarrow 0) = \frac{L^2 d}{2\varepsilon D_a S} \left\{ 1 - \left(\frac{D_p - D_m}{D_p D_m} \right)^2 \frac{d^4}{480} \omega^2 \right\}, \quad (51)$$

with $D_a = 2D_p D_m / (D_p + D_m)$, if $L \ll d$, as illustrated in the case depicted in figure 2, for a different set of values of the experimental parameters.

As far as the real part of the impedance is concerned, it is worth mentioning that both models agree in the high frequency region where the free diffusion is the dominant behaviour. This is not true for the case of low frequency, as shown in figure 1, where the ambipolar curve was depicted for a value of D_m ranging from one tenth to one millionth of D_p , and the curves coincide only as we look at the low frequency region of the spectrum. This coincidence occurs for decreasingly small values of y , becoming progressively detectable as the frequency diminishes, since the high frequency resistance plateau of the ambipolar system coincides with the one of the one mobile ion diffusive system. Remarkable, we also notice that the second plateau is always present even for very small values of D_m , but can be detected only at very low, probably not experimentally accessible, frequencies. For the usual spectra, with frequencies ranging from mHz to a few MHz, the highly mobile and the highly slow ions are always responsive to low frequency stimulus and may contribute differently to the electrical impedance

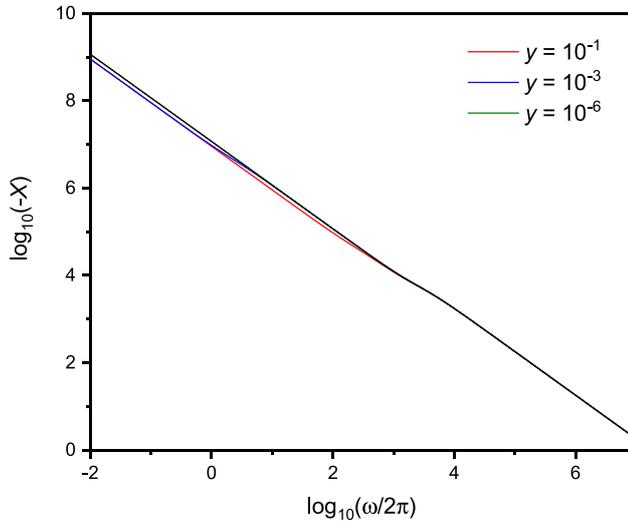


Figure 3. Frequency behaviour of $\log_{10}(-X)$ for the one mobile ion diffusive system (solid black line) and for the the ambipolar system (coloured lines), for the same values of y shown in figure 1.

as well. The different behaviour of the two systems is clearly evidenced by the resistance of the cell, which is very sensitive to the different mobilities of both types of ions.

This difference in the response of the ions is not so pronounced in the reactance of the cell, as can be deduced from figure 3, where the imaginary part of the impedance is depicted for the same different values of y as in figure 1, for experimentally relevant frequencies. From this figure, we may conclude that the predictions of both models are essentially the same, with a negligible disagreement in the very low frequency limit. This conclusion is reinforced by looking at figure 4, depicted for the same values of the parameters as in figure 2 for a wide interval of frequencies. This good agreement between the predictions of both models for the imaginary part of the impedance is expected because the mobilities in general do not influence in a conspicuous manner the reactive response of the cell, which is dominated by the displacement current.

In the analysis presented above, we have investigated the electric response of an electrolytic cell to an external difference of potential changing with the time in a simple harmonic manner. The considered medium was assumed containing two groups of ions, of opposite electric charge and different electric mobilities. In this case, the PNP model allows the analytical determination of the impedance of the cell $Z = R + iX$, in series representation. From the discussion of figures 1 and 2, the spectrum of R , related to the dissipative effects, presents two plateaus: one related to the ambipolar diffusion coefficient, $1/D_a = (1/2)(1/D_p + 1/D_m)$, in the low frequency range, and the other to the free diffusion coefficient, $D_f = (D_p + D_m)/2$, in the ‘high’ frequency range. The transitions from the first to the second plateau is continuous. The first plateau ends at the circular frequency $\omega_a = \pi^2(D_a/d^2)$. The second plateau ends at the circular frequency

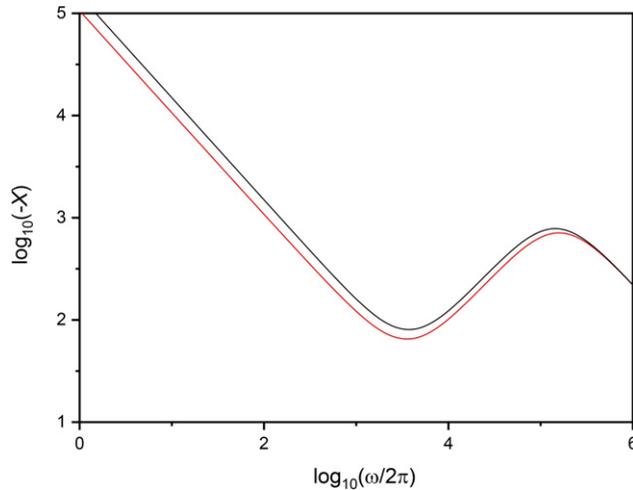


Figure 4. Frequency behaviour of $\log_{10}(-X)$ for the one mobile ion diffusive system (solid black line) and for the the ambipolar system (red line), when $D_m = 10^{-1}D$ for the same experimental values of the parameters in figure 2.

$\omega_f = D_f/(2L^2)$ [23]. In terms of the parameter y , ω_D , and x_0 these circular frequencies are given by

$$\omega_a = 2 \frac{y}{1+y} \frac{\omega_D}{x_0^2} \quad \text{and} \quad \omega_f = \frac{1+y}{2} \omega_D. \quad (52)$$

Of course, for frequencies smaller than ω_a it is meaningless to neglect the contribution of the slower ions, because in this frequency region the electric response is due to both ions present in the electrolytic solution.

We have shown in our analysis that in the case where one of the ions has a mobility small with respect to the other ion, the approximation of one mobile ion has to be applied with caution, in the sense that it is valid only for a frequency larger than a defined value, that takes into account the difference between the diffusion coefficients of ions. This circular frequency is defined by $\omega^* = y\omega_D$, large with respect to ω_a . Deviations from the experimental data of the theoretical predictions for frequencies smaller than this critical value could be due to the contribution of the slower ions to the electric response of the cell.

In the case in which the valence of the positive ions, Z_p , is different from that of the negative ions, Z_m , the analysis can be easily generalised. In this framework, a calculation similar to that presented above shows that the critical circular frequency depends on the valence of the ions and it is given by $\omega^* = Z_m y \omega_D$, where the slower ions are assumed as the negative ones and ω_D is the Debye relaxation frequency for the positive ions in the present case.

Another situation of some importance from the experimental point of view is the one in which in the electrolyte are present two groups of positive and two groups of negative ions, whose bulk density in thermodynamical equilibrium are n_1 and n_2 . In this case, limiting the analysis to the simple situation where the positive and negative ions of the

two groups have equal diffusion coefficients and are monovalent, $D_{p1} = D_{m1} = D_1$ and $D_{p2} = D_{m2} = D_2$, the equivalent ambipolar and free diffusion coefficients are [25]

$$\frac{1}{D_{II}} = \frac{N_1}{N_1 + N_2} \frac{1}{D_1} + \frac{N_2}{N_1 + N_2} \frac{1}{D_2}, \quad (53)$$

$$D_I = \frac{N_1}{N_1 + N_2} D_1 + \frac{N_2}{N_1 + N_2} D_2, \quad (54)$$

respectively. In the event in which n_2 represents a contamination for the electrolyte, and hence $n_2/n_1 \ll 1$, a criterium is necessary to know when it is possible to neglect its presence in the electrolyte. In this case the effective parameter y is defined in terms of $\xi = D_2/D_1$ by

$$y = \xi \frac{N_1 + N_2 \xi}{N_1 \xi N_2}. \quad (55)$$

It follows that the concept of small y depends on D_2 and n_2 . In particular for $n_2 \rightarrow 0$, $y \sim 1 + (n_2/n_1)\xi$, and the analysis presented above has to be performed in terms of this new parameter.

5. Concluding remarks

The frequency behaviour of the electrical impedance response of an electrolytic cell for both, an ambipolar (two ions) and one mobile ion diffusive systems, are investigated here in the limit in which one of the mobilities goes to zero, i.e., when $D_m \ll D_p$. In this limit, the predictions of both models show a coincidence only in the frequency range $\omega \gg \omega_D \mu_m / \mu_p$, while the predictions for the behaviour at high frequencies are essentially the same for the real and the imaginary parts of the impedance. To explore this limit in order to compare the descriptions provided by these two models, we first employ a rough perturbative method, focusing on the small parameter behaviour of the analytical solutions of the equations of the PNP continuum model. This procedure leads to an apparent existence of a singularity forbidding the solutions to satisfy the required boundary conditions, even in the simplest case of blocking electrodes. A more rigorous mathematical analysis is thus required to face the problem and shows that this limit has to be considered with care, being meaningful only for a fixed value of the frequency. To sum up, we show here that the predictions of the ambipolar diffusive model, when $D_m \rightarrow 0$, coincide with the ones coming from the one mobile ion diffusive system in the physically relevant frequency range only when this limit is performed for a fixed value of the frequency. This strongly indicates that, in the experimentally accessible frequency interval, the physical system formed by two mobile ions, even when one of them has a very low mobility, is clearly distinct from the physical system in which just one of the ions is mobile.

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