# Electric Impedance of a Sample of Dielectric Liquid Containing Two Groups of Ions Limited by Ohmic Electrodes: A Study with Pure Water

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ABSTRACT: We present a generalization of the Poisson–Nernst–Planck model for a dielectric liquid containing two groups of ions limited by Ohmic electrodes. The theoretical results are used to interpret experimental results of impedance spectroscopy of pure water limited by electrodes of different metallic materials. The agreement between theoretical predictions of the presented model and experimental data obtained with pure water is rather good for all types of electrodes.
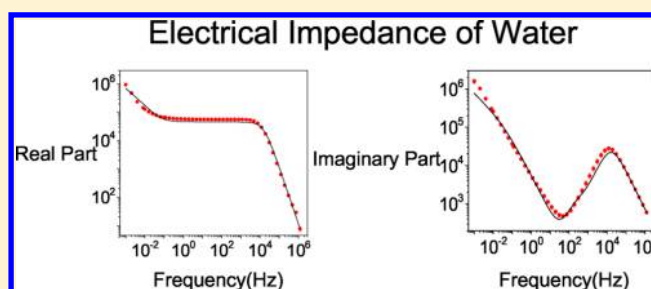
1. INTRODUCTION

The impedance spectroscopy is a powerful technique used to investigate dielectric properties of a wide class of materials.[1−11] This technique allows to have information on the dispersion of the dielectric constant, related to the molecular properties of the medium under investigation. When the medium is not dispersive, the dielectric constant is frequency-independent. In this case, the presence of ions dissolved in the medium is responsible for a special kind of dispersion, not related to molecular properties of the medium. The influence of the ions on the dielectric properties of an insulating medium can be theoretically analyzed by means of a model based on the equations of continuity for the ions and on the equation of Poisson for the electric potential. This model is known as Poisson–Nernst–Planck (PNP) model.[12] The fundamental equations are not linear, due to the coupling of the bulk density of ions with the actual potential. If the applied voltage is small enough, the bulk equations can be linearized, and the problem becomes linear.[12−14] The parameters entering in the model for the bulk are as follows: (1) the bulk density of ions in thermodynamical equilibrium, N_0; (2) the dielectric constant of the medium in which the ions are dispersed, ε; (3) the diffusion coefficient of the ions in the medium, D; (4) the electric charge of the ions, q; (5) the thermal energy $k_B T$, where k_B is the Boltzmann constant and T the absolute temperature. If the sample is in the shape of a slab, the geometrical parameters of the cell are the thickness, d, and the surface area of the electrodes, S. In its simplest version the electrodes are assumed blocking and only one group of ions is considered. In this framework, the bulk density of currents vanish on the electrodes, and the bulk differential equations of the model have to be solved by imposing that the bulk density of current vanishes on the electrode, taking into account the presence of the external power supply. If the external power supply applies

a simple harmonic difference of potential of amplitude V_0 and angular frequency $\omega = 2\pi f$ it is possible to evaluate the electric impedance, Z, of the cell. When the electrodes are blocking, $R = \text{Re}[Z]$ presents a plateau, ending at the frequency of Debye $\omega_D = D/\lambda^2$, where $\lambda = (\varepsilon K_B T/(2N_0 q^2))^{1/2}$ is the length of Debye.[13] The imaginary part $\chi = \text{Im}[Z]$ in the high frequency region tends to zero as $1/\omega$ and, in the dc limit, diverges with the same law. A simple calculation allows to show that in the dc limit the equivalent series capacitance of the cell tends to $C(0) = \varepsilon S/(2\lambda)$, whereas in the high frequency region it tends to $C(\infty) = \varepsilon S/d$. The PNP model has been generalized in several directions. The hypothesis of blocking electrodes has been removed by using several type of boundary conditions on the ionic current density on the electrodes.[15−18] We have proposed some years ago a model according to which the surface current density of ions is proportional to the surface electric field.[19] This model has been shown to be equivalent[20,21] to that used in refs 15, 16, and 18. The hypothesis of a generalization of the model to take into account the presence of several groups of ions has also been discussed.[22] Other generalizations have been proposed to take into account the ionic adsorption on the electrodes.[23−25] Also the possibility of anomalous diffusion has been explored.[26−29] All the quoted generalizations have been proposed to justify anomalous behavior of the real and imaginary parts of the electrical impedance in the low frequency region, usually discussed in terms of the constant phase element, whose physical meaning is unclear.[30]

Recently, an anomalous-diffusion approach has been proposed[31] to interpret the electrical response of water to an external periodic electric signal of small amplitude. In ref 31, a

generalization of the PNP model, discussed in refs 26 and 29, is considered in the case where the boundary conditions on the electrodes are represented by integro-differential equations of fractional order. In ref 31, a very good agreement between the proposed model and the experimental data is obtained. However it is rather difficult to relate the fractional order appearing in the boundary conditions to the physics of the adsorption–desorption phenomenon. In other words, the approach proposed by Lenzi and co-workers[31] is, actually, equivalent to a constant phase element masked by a kernel present in the boundary conditions.

Another possible generalization of the PNP model not yet performed until now is to consider a dielectric solution with two groups of ions, limited by two Ohmic electrodes. In order to apply this model to a system of practical interest, we decide to analyze pure water, as in ref 31. Despite the importance of water, there is not in the literature many information about the behavior of its impedance in the low frequency region.[31−36] Moreover, in pure water we expect to have[37] the H^+ and OH^- ions, and same residual ionic impurities. This solution, with two groups of ions, will provide us an adequate sample material to apply our model. In the present investigation we report on impedance spectroscopy measurements performed on Milli-Q water in the frequency range from 1 mHz to 1 MHz. We show that our data can be interpreted by means of a model based on the assumption that in pure water two groups of ions are present, and that the electrodes are of Ohmic type.

Our paper is organized as follows: Section 2 is devoted to the description of the experimental setup. The extension of the PNP model is described in section 3. The mathematical properties of the fundamental equations of the model are discussed in section 4, and their solution is presented in section 5. The electric impedance of the cell is evaluated in section 6. The comparison of the theoretical predictions of the model with the experimental data is discussed in section 7, and the conclusions are reported in section 8.

2. EXPERIMENTAL PART

The sample investigated is pure water, in the shape of a slab (from the Milli-Q Direct-Q3 apparatus), with measured resistivity of 18 MΩcm. The measurements of the Real - R and Imaginary - χ parts of the impedance (Z) were made with a Solartron SI 1296A impedance/gain phase analyzer, with a commercial sample holder model 12962A. Samples were confined between two disk-like electrodes of effective area $S = 3.14$ cm^2. The sample thicknesses were $d = 0.5, 1.0, 2.0, 3.0,$ and 4.0 mm. A sinusoidal voltage of amplitude $V_0 = 20$ mV was applied and the data was collected, as a function of the frequency, in the range of 1 mHz to 1 MHz.

We used electrodes made of different materials: surgical steel, titanium, gold, and platinum. The surfaces of the electrodes were polished with sandpapers until to obtain a light-reflective surface. After each burnish procedure, the electrodes were placed in ultrasonic bath for 10 min and dried for more 10 min in a stove at a temperature of 65 °C. All measurements were performed at room temperature (22 °C). During the low-frequency experiments we took care in not to let the water-sample much time between the electrodes in successive measurements. For this reason, in the very low frequency range of 10−100 mHz, the protocol for cleaning the electrodes was repeated after each measurement at a given frequency. All the measurements were done just after the burnish procedure of the electrodes. At a given frequency, several measurements were done to evaluate the averages and the standard deviations.

3. MODEL

Let us consider a sample of dielectric liquid, of dielectric constant ε, containing two groups of ions, that will be indicated as 1 and 2. The cell is assumed in the shape of a slab of thickness d and surface area S. The Cartesian reference frame used for the mathematical description has the z-axis perpendicular to the limiting surfaces, at $z = \pm d/2$, coinciding with the electrodes. We assume that the bulk density of ions is so small that the recombination phenomenon can be neglected. In this framework, we suppose complete dissociation of the impurities. The bulk densities of ions, in thermodynamical equilibrium are indicated by N_1 and N_2. The actual bulk density of ions when the sample is subjected to an external voltage are $n_{pi} = N_i + p_i$ and $n_{mi} = N_i + m_i$ for the positive and negative ions of the group $i = 1, 2$, respectively. We assume that the ions of the group 1 and of the group 2 are identical in all aspects, except for the sign of their electrical charge. In the linear limit, where $p_i, m_i \ll N_i$, the bulk differential equations describing the evolution of the bulk densities of ions, and of the effective potential, across the sample are

$$\frac{\partial p_i}{\partial t} = D_i \frac{\partial}{\partial z}\left(\frac{\partial p_i}{\partial z} + \frac{qN_i}{K_B T}\frac{\partial V}{\partial z}\right) \tag{1}$$

$$\frac{\partial m_i}{\partial t} = D_i \frac{\partial}{\partial z}\left(\frac{\partial m_i}{\partial z} - \frac{qN_i}{K_B T}\frac{\partial V}{\partial z}\right) \tag{2}$$

representing the equations of continuity for the two groups of ions, and

$$\frac{\partial^2 V}{\partial z^2} = -\frac{q}{\varepsilon}(p_1 + p_2 - m_1 - m_2) \tag{3}$$

Equation 3 is the equation of Poisson relating the actual potential to the bulk density of ionic charge. The external potential applied to the sample is assumed to be

$$V(\pm d/2, t) = \pm\frac{V_0}{2}e^{i\omega t} \tag{4}$$

where V_0 is the amplitude and $\omega = 2\pi f$ the circular frequency. Finally, the electrodes are considered partially blocking, and the exchange of charge regulated by the boundary conditions $j_{pi} = s_i E$ and $j_{mi} = -s_i E$, where s_i is characteristic constant of the electrode so that $s = \sigma q$, σ is the conductivity and E the surface electric field. In the expression written above for the boundary conditions j_{pi} and j_{mi} are the current densities of the positive and negative ions of the group i, respectively, given by

$$j_{p_i} = -D_i\left(\frac{\partial p_i}{\partial z} + \frac{qN_i}{K_B T}\frac{\partial V}{\partial z}\right) \tag{5}$$

$$j_{m_i} = -D_i\left(\frac{\partial m_i}{\partial z} - \frac{qN_i}{K_B T}\frac{\partial V}{\partial z}\right) \tag{6}$$

It follows that the boundary conditions of the present problem are

$$\frac{\partial p_i}{\partial z} + \frac{qN_i}{K_B T}\frac{\partial V}{\partial z} = -\frac{s_i}{D_i}E \tag{7}$$

$$\frac{\partial m_i}{\partial z} - \frac{qN_i}{K_B T}\frac{\partial V}{\partial z} = +\frac{s_i}{D_i}E \tag{8}$$

We note that in these equations only the ratio s_i/D_i appears. Since $E = -\partial V/\partial z$ we get that the intrinsic surface conductivity is

$$s_i^* = D_i \frac{qN_i}{K_B T}$$

Hence, large or small s means that $s_i \gg s_i^*$ or $s_i \ll s_i^*$.

4. PROPERTIES OF THE BULK DIFFERENTIAL EQUATIONS

Since the system formed by eqs 1, 2, and 3 is linear, the solutions we are looking for are of the type

$$p_i(z, t) = P_i(z)e^{i\omega t} \quad \text{and} \quad m_i(z, t) = M_i(z)e^{i\omega t} \tag{9}$$

Note that from the bulk eqs 1 and 2 it follows that

$$\frac{\partial}{\partial t}(p_i + m_i) = D_i \frac{\partial^2}{\partial z^2}(p_i + m_i) \tag{10}$$

whereas from the boundary conditions, eqs 5 and 6, we get

$$\frac{\partial}{\partial z}(p_i + m_i) = 0 \tag{11}$$

for $z = \pm d/2$. From eq 10 it is clear that $\psi_i(z,t) = p_i(z,t) + m_i(z,t)$ is solution of the pure diffusion equation, whose partial derivative with respect to z vanishes on the borders $z = \pm d/2$. From the discussion reported above $\psi(z,t) = \Psi(z) \exp(i\omega t)$, where $\Psi(z)$ is such that

$$i\omega\Psi(z) = D_i\Psi''(z) \tag{12}$$

Solution of eq 12 is

$$\Psi(z) = A_i \cosh(\xi_i z) + B_i \sinh(\xi_i z) \tag{13}$$

where $\xi_i = (\omega/(2D_i))^{1/2}(1 + i)$. By imposing the conditions $\Psi'(-d/2) = \Psi'(d/2) = 0$ we obtain $A_i = B_i = 0$, and hence $\Psi_i(z) = 0$. It follows that $P_i(z) = -M_i(z)$, and consequently, $p_i(z,t) = -m_i(z,t)$. In other words, for each group, the increasing of the density of positive ions is equal to the decreasing of the density of the negative ions. By taking into account that during the evolution $\psi_i(z,t) = p_i(z,t)+m_i(z,t) = 0$ we can limit our analysis to the positive density of ions of each group.

5. SOLUTION OF THE BULK DIFFERENTIAL EQUATIONS

The equations to be solved are then

$$\frac{\partial p_1}{\partial t} = D_1\left(\frac{\partial^2 p_1}{\partial z^2} + \frac{qN_1}{K_B T}\frac{\partial^2 V}{\partial z^2}\right) \tag{14}$$

$$\frac{\partial p_2}{\partial t} = D_2\left(\frac{\partial^2 p_2}{\partial z^2} + \frac{qN_2}{K_B T}\frac{\partial^2 V}{\partial z^2}\right) \tag{15}$$

and

$$\frac{\partial^2 V}{\partial z^2} = -2\frac{q}{\varepsilon}(p_1 + p_2) \tag{16}$$

By substituting eq 16 into eqs 14 and 15, we get

$$\frac{\partial p_1}{\partial t} = D_1\left\{\frac{\partial^2 p_1}{\partial z^2} - \frac{1}{\lambda_1^2}(p_1 + p_2)\right\} \tag{17}$$

$$\frac{\partial p_2}{\partial t} = D_2\left\{\frac{\partial^2 p_2}{\partial z^2} - \frac{1}{\lambda_2^2}(p_1 + p_2)\right\} \tag{18}$$

where

$$\lambda_1 = \sqrt{\frac{\varepsilon K_B T}{2N_1 q^2}} \quad \text{and} \quad \lambda_2 = \sqrt{\frac{\varepsilon K_B T}{2N_2 q^2}} \tag{19}$$

are the lengths of Debye related to the different groups of ions. For the linearity of the problem discussed above $p_1(z,t) = P_1(z) \exp(i\omega t)$ and $p_2(z,t) = P_2(z) \exp(i\omega t)$. By substituting this ansatz into eqs 17,18, we obtain

$$P_1'' - \frac{1}{\lambda_1^2}\left(1 + i\omega\frac{\lambda_1^2}{D_1}\right)P_1 - \frac{1}{\lambda_1^2}P_2 = 0 \tag{20}$$

$$P_2'' - \frac{1}{\lambda_2^2}\left(1 + i\omega\frac{\lambda_2^2}{D_2}\right)P_2 - \frac{1}{\lambda_2^2}P_1 = 0 \tag{21}$$

Because of the symmetry of the problem, we look for a solution of eqs 20,21 of the type

$$P_1(z) = C_1 \sinh(\mu z) \quad \text{and} \quad P_2(z) = C_2 \sinh(\mu z) \tag{22}$$

where C_1 and C_2 are constants, and μ a characteristic length defined by the system

$$\left[\mu^2 - \frac{1}{\lambda_1^2}\left(1 + i\omega\frac{\lambda_1^2}{D_1}\right)\right]C_1 - \frac{1}{\lambda_1^2}C_2 = 0 \tag{23}$$

$$-\frac{1}{\lambda_2^2}C_1 + \left[\mu^2 - \frac{1}{\lambda_2^2}\left(1 + i\omega\frac{\lambda_2^2}{D_2}\right)\right]C_2 = 0 \tag{24}$$

The system formed by eqs 23 and 24 has a solution different from the trivial one $C_1 = C_2 = 0$ only if

$$\left[\mu^2 - \frac{1}{\lambda_1^2}\left(1 + i\omega\frac{\lambda_1^2}{D_1}\right)\right]\left[\mu^2 - \frac{1}{\lambda_2^2}\left(1 + i\omega\frac{\lambda_2^2}{D_2}\right)\right]$$
$$- \frac{1}{\lambda_1^2\lambda_2^2} = 0 \tag{25}$$

that defines the characteristics lengths of the problem. Equation 25 is biquadratic. Its solutions are $\mu_1 = -\mu_3$ and $\mu_2 = -\mu_4$. From eq 23, we get

$$k = \frac{C_2}{C_1} = \lambda_1^2\left\{\mu^2 - \frac{1}{\lambda_1^2}\left(1 + i\omega\frac{\lambda_1^2}{D_1}\right)\right\} \tag{26}$$

Consequently the ratio C_2/C_1 can takes the two values given by

$$k_1 = \frac{C_{21}}{C_{11}} = \lambda_1^2\left\{\mu_1^2 - \frac{1}{\lambda_1^2}\left(1 + i\omega\frac{\lambda_1^2}{D_1}\right)\right\} \tag{27}$$

$$k_2 = \frac{C_{22}}{C_{12}} = \lambda_1^2\left\{\mu_2^2 - \frac{1}{\lambda_1^2}\left(1 + i\omega\frac{\lambda_1^2}{D_1}\right)\right\} \tag{28}$$

It follows that the solution we are looking for are given by

$$P_1(z) = C_{11} \sinh(\mu_1 z) + C_{12} \sinh(\mu_2 z) \tag{29}$$

$$P_2(z) = k_1 C_{11} \sinh(\mu_1 z) + k_2 C_{12} \sinh(\mu_2 z) \tag{30}$$
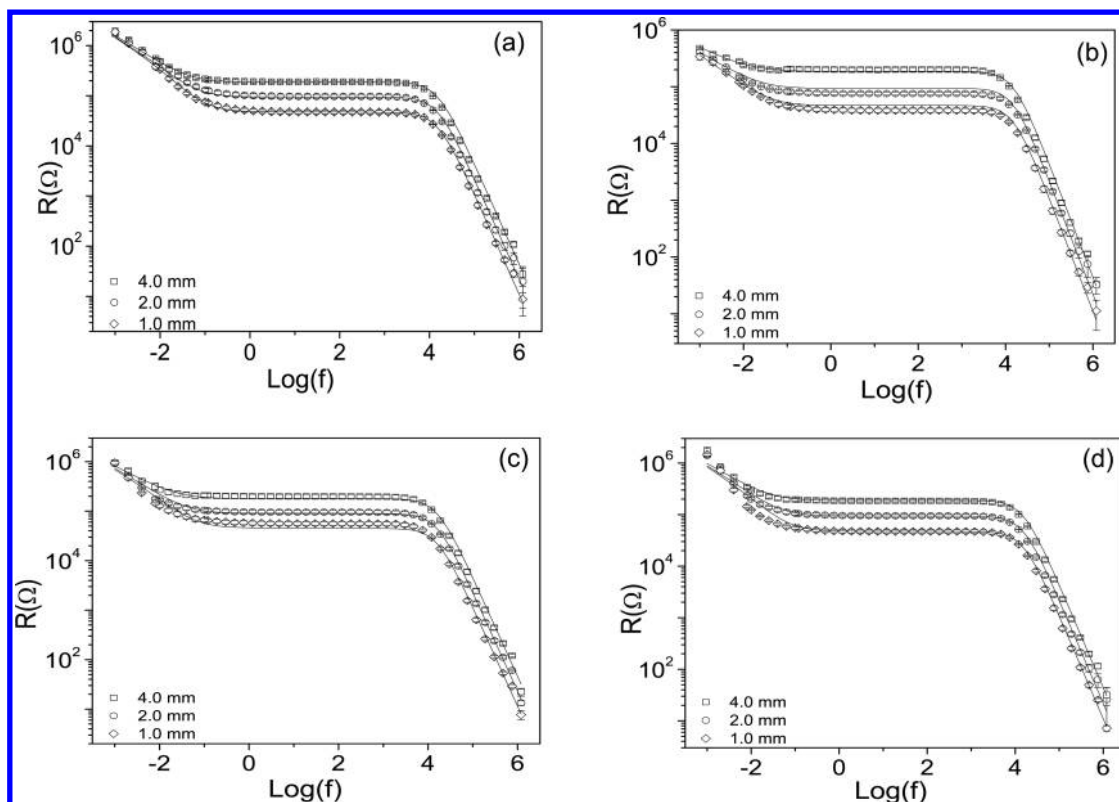
Figure 1. Real part, R, of the electric impedance, Z, of the cell with pure water versus the frequency of the applied voltage f. Sample thickness: ($\square$) 1.0 mm; ($\bigcirc$) 2.0 mm; ($\lozenge$) 4.0 mm. Electrode material: (a) gold; (b) platinum; (c) steel; (d) titanium. Solid lines represent best fits.

The actual electrical potential across the cell is given by eq 16. By putting $V(z,t) = \phi(z) \exp(i\omega t)$ and taking into account eqs 29 and 30, eq 16 can be rewritten as

$$\phi''(z) = -2\frac{q}{\varepsilon}\{(1 + k_1)C_{11} \sinh(\mu_1 z) + (1 + k_2)C_{12} \\ \sinh(\mu_2 z)\} \tag{31}$$

whose solution is

$$\phi(z) = -2\frac{q}{\varepsilon}\left\{\frac{1 + k_1}{\mu_1^2}C_{11} \sinh(\mu_1 z) + \frac{1 + k_2}{\mu_2^2}C_{12} \\ \sinh(\mu_2 z)\right\} + Az \tag{32}$$

where A is a new integration constant. The solution of the problem under consideration is given by eqs 29, 30, and 32, where the integration constants C_{11}, C_{12}, and A have to be determined by means of the boundary conditions. The boundary conditions of the problem are eqs 4, 7 and 8, related to the presence of the external power supply and to the partial blocking character of the electrodes.

6. EVALUATION OF THE IMPEDANCE OF THE CELL

From eq 32, the surface electric field

$$E_s = E(d/2, t) = -\frac{\partial V(z, t)}{\partial z} = -\phi'(d/2) \exp(i\omega t) \tag{33}$$

is found to be

$$E_s(t) = \left\{2\frac{q}{\varepsilon}\left[\frac{1 + k_1}{\mu_1}C_{11} \cosh(\mu_1 d/2) + \frac{1 + k_2}{\mu_2}C_{12} \\ \cosh(\mu_2 d/2)\right] - A\right\}e^{i\omega t} \tag{34}$$

The total current across the electrode is then

$$I(t) = \{2q(s_1 + s_2) + i\omega\varepsilon\}E_s(t)S \tag{35}$$

where S is the surface area of the electrode. The first term in eq 35 is the conduction current, related to the partial blocking character of the electrode, and the second contribution is due to the displacement current. Since the difference of potential applied to the cell is $\Delta V = V_0\exp(i\omega t)$, the impedance of the cell is given by $Z = \Delta V/I$. The parameters s_1, s_2 and the diffusion constants D_1 and D_2 are determined by fitting the model to the experimental results. The parameters μ_1 and μ_2 are obtained solving the biquadratic eqs 23 and 24.

7. RESULTS AND DISCUSSION

Figure 1 shows the Real part (R) of Z of the Milli-Q water, as a function of the frequency (f), with different electrodes and different sample thicknesses (d): (a) gold; (b) platinum; (c) steel; (d) titanium. To avoid an overcrowded of experimental points in the figure, we show only data of $d = 1.0$; 2.0 and 4.0 mm, however, the conclusions drawn refer to all the sample thicknesses investigated. The errors were evaluated taking into account the reproducibility of the experiments at a given frequency. All the measurements of R versus f present the same behavior for $f > f_D$, with $R \rightarrow 0$ as f^{-2}, and f_D independent of the thickness of the sample as well as on the nature of the
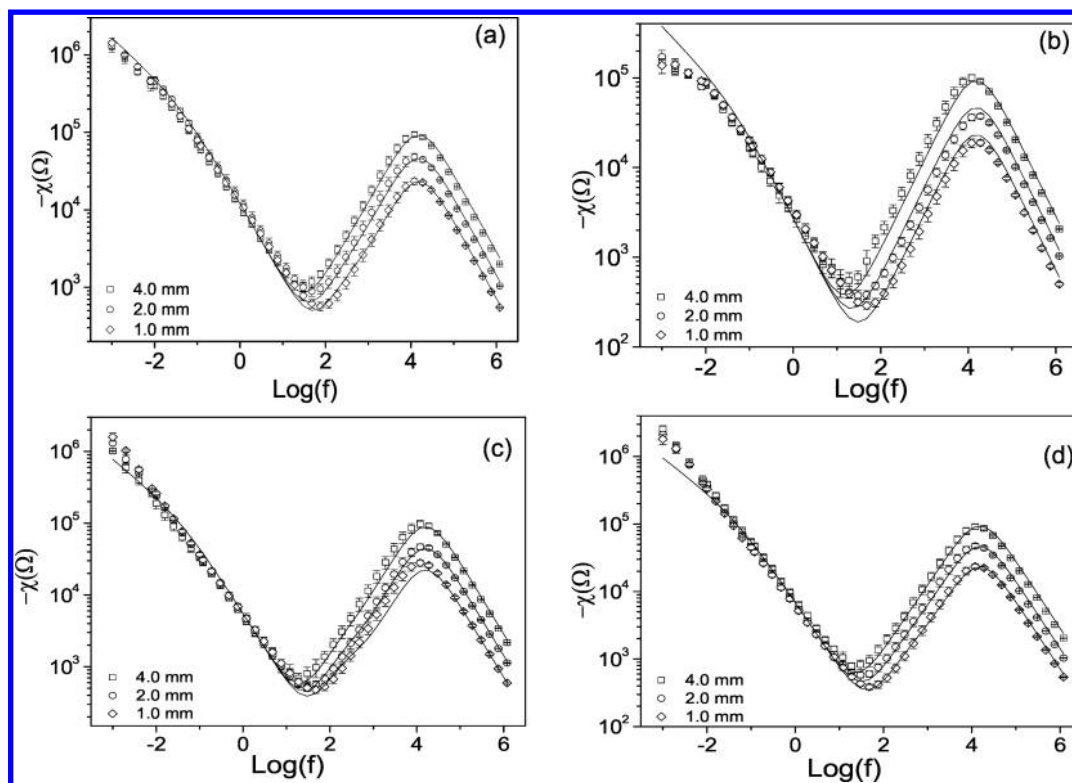
Figure 2. Imaginary part, χ, of the electric impedance, Z, of the cell with pure water versus the frequency of the applied voltage f. Sample thickness: ($\square$) 1.0 mm; ($\bigcirc$) 2.0 mm; ($\diamondsuit$) 4.0 mm. Electrode material: (a) gold; (b) platinum; (c) steel; (d) titanium. Solid lines represent best fits.

electrodes. The R versus f results also show a plateau in the region of frequencies from $\sim 10^{-1}$ Hz to f_D. We observed that the value of R in the plateau is proportional to the sample thickness d. In this region the response of the cell is independent of the electrodes, and is just a bulk property. In the low-frequency region, below $\sim 10^{-1}$ Hz, R increases when f decreases, and all the results collapse to a common value, independent of the sample thickness d. In this region, the response of the sample is dominated by the electrodes.

Figure 2 shows the results of the Imaginary part (χ) of Z as a function of the applied frequency, and the different electrodes and sample thicknesses, corresponding to the experiments shown in Figure 1. The errors were evaluated in the same way described before for R. Also in this case, the behavior of χ as a function of f is similar for all the electrodes. For $f > f_D$, $\chi \to 0$ as f^{-1} and, as before, f_D is independent of d, and the value of χ is $\propto d$. In the low-frequency region, smaller than 10 Hz, χ is thickness independent and depends on f as $\chi \propto f^{-0.8}$. The values of R and χ of steel and titanium electrodes are very near each other, except for $f < 10^{-2}$ Hz. The result for platinum electrodes, showed lower values for R compared with the other electrodes and the χ values in the region of low frequency showed a tendency to saturation.

For frequencies greater than 1 kHz, the dependencies of R and χ on f are the expected ones, and in good agreement with the predictions of the PNP model for blocking electrodes.[13,19,21,22] However, strong deviations are observed in the limit of small frequencies, e.g., lower than 10 Hz. In this frequency region the presence of several groups of ions as well as the properties of the electrodes strongly influence the electric response of the cell at the impedance level. Our numerical simulations indicate that it is not possible to fit the experimental data only (1) by assuming a partial blocking

character of the electrodes, with only one group of ions, or (2) by assuming blocking character of the electrodes and two groups of ions.

On the contrary, the experimental data can be fitted in a reasonable manner by means of the model described in the previous sections, where two groups of ions are present and the electrodes are considered Ohmic.

Equations 34 and 35 were used to derive R and χ as a function of f, for each experiment. In the fit procedure we used $N_1 = N_2 = N = 10^{21} m^{-3}$, which was independently evaluated. To evaluate this number we prepared different solutions of Milli-Q water with known amounts of KCl, and measured the sample impedance Z_{el}. We also measured the impedance of pure water Z_w, with the same electrodes and same values of thickness d and surface S. With the values of Z_{el} and Z_w, we recalculate the ionic concentrations (assuming that the electric resistance is inversely proportional to the conductivity), finding a maximum order of magnitude for N in pure water, which was $10^{21} m^{-3}$. The fitting parameters to be obtained from each experiment (i.e., fixed electrode and sample thickness) are: s_1, s_2, D_1, and D_2. The same values of these parameters must be used to fit both R and χ for a given electrode, and the different thicknesses. This was verified in our experiments. As the sample used in all the experiments is the same (pure water) we impose in the fitting procedure that the parameters which characterize the water with two groups of ions are the same for all the electrodes employed; i.e., D_1 and D_2 should be the same for all the experiments. The fitting procedure developed takes into account all the eight experimental data of R and χ versus the frequency, at the same time, for the four electrodes (at a given sample thickness), imposing that D_1 and D_2 should be the same. We obtained from the fit $D_1 = (5.50 \pm 0.12) \times 10^{-15}$ m^2/

s and $D_2 = (5.50 \pm 0.12) \times 10^{-9}$ m^2/s. Table 1 gives the fitting parameters s_1 and s_2 obtained.

Table 1. Fitting Parameters s_1 and s_2 for All the Electrodes Employed and All the Sample Thicknesses

electrode↓	s_1 $(\Omega mC)^{-1}$	s_2 $(\Omega mC)^{-1}$
Au	$(2.29 \pm 0.05) \times 10^{11}$	$(5.75 \pm 0.13) \times 10^{12}$
Ti	$(1.74 \pm 0.04) \times 10^{11}$	$(7.76 \pm 0.18) \times 10^{12}$
Pt	$(1.12 \pm 0.03) \times 10^{14}$	$(1.29 \pm 0.03) \times 10^{16}$
steel	$(0.77 \pm 0.02) \times 10^{11}$	$(4.07 \pm 0.09) \times 10^{12}$

The errors in the fitting parameters were evaluated taking into account the experimental errors in R and χ, and the convergence in the fitting procedure. The corresponding fitting curves are plotted in Figures 1 and 2. Despite the simpleness of the model, the theoretical description is remarkable good. It is important to stress, as noted before, that it was not possible to obtain a reasonable fit considering blocking electrodes ($s_1 = s_2 = 0$) for all the experiments performed. The value of D_2 is much larger than D_1. It means that the ions of the group named 1 is practically stationary in comparison to those of group 2. Nevertheless, ions of group 1 play a key role in the impedance spectroscopy results in the low frequency limit. In the case of our Milli-Q water, one of the groups of ions present (let us say, group 2) is that with the H^+ and OH^- (hydroxide), and the other (group 1), some impurity not removed by the Direct-Q3 apparatus. In this picture, D_2 refers to the H^+ and OH^- ions, and D_1 ($\ll D_2$) and to the impurity present in the water, which seems to have the property of being much less mobile than the small ions of group 2.

The results shown in Table 1 are interesting and require some discussion. As defined in the presentation of the model, s_i is a characteristic constant of the electrode so that $s_i = \sigma_i q_i$, σ_i being its conductivity for the ions of group i. So, the bigger the electrode conductivity, the bigger the value of s. Our results show that the Au, Ti and steel electrodes present comparable values of s_1 and s_2, of the order of 10^{11} and 10^{12} $(\Omega mC)^{-1}$, respectively. The Pt, on the other hand, present bigger values of these parameters, of the order of 10^{14} and 10^{16} $(\Omega mC)^{-1}$, respectively. The smallest the order of magnitude of s the more the electrode electric characteristics approach those of a blocking electrode. In the framework of our model, the Pt electrode is the one whose electric characteristics, for the groups of ions present in pure water, deviate more from those of a blocking electrode.

8. CONCLUSION

We have described impedance measurements on sample of pure water in the shape of slab, with different types of electrodes in the range from 1 mHz to 1 MHz. Our experimental data indicate that this type of measurement can give information on the role of the electrodes on the electric response of the sample to an external excitation. By performing measurements on samples with different thicknesses, we have separated the bulk from the electrode contribution to the total impedance of the cell. In the high frequency region, the electric impedance of the sample is dominated bulk property of the medium under consideration, and its real and imaginary parts are proportional to the thickness of the sample, and independent of the nature of the electrodes. On the contrary, in the low frequency region, the response of the cell is independent of the thickness of the sample, and dominated by the electrodes properties. These results can be easily interpreted by means of generalization of the PNP model by assuming that the electrodes are Ohmic and that in the water are present two group of ions, with very different diffusion coefficients. The presented model is a generalization of the PNP model, where just one group of ions is considered. In our analysis we have considered, for sake of simplicity, a situation where charges of both signs have equal mobility. The analysis could be generalized to the case where the mobilities of the ions are different without difficulty, since in the limit of small applied voltage the fundamental equations of the problem are linear. The work is in progress to compare the quality of the fit obtained with our model with that obtained by the standard PNP model where the ions have different mobilities with the boundary conditions of Ohmic type or of the Chang–Jaffe type.[38]

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Notes

The authors declare no competing financial interest.

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