

Impedance Spectroscopy of Water Solutions: The Role of Ions at the Liquid–Electrode Interface

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We discuss the influence of the ions dissolved in a liquid on the impedance spectroscopy of a cell. Our analysis is performed in the small-voltage regime, where the actual bulk density of ions is only slightly perturbed by the external electric field. In this framework, we show that the presence of the ions can be taken into account by a surface density of charge. The agreement between the theoretical prediction, on the basis of the assumption that the ionic mobility is frequency independent, and the experimental data for the real and imaginary parts of the impedance is fairly good for frequencies larger than 100 Hz. In the low-frequency range, the agreement of the theory with the experiment is rather poor. In this region, the experimental data can be successfully fitted by introducing the impedance of the metal–electrolyte interface, which is accurately represented by $Z_i = w(i\omega)^{-\nu}$, where w and ν are two constants, with $0 < \nu < 1$. From the analysis of the experimental data, we determine w and ν . The theoretical predictions of our model are in good agreement with the experimental data in the investigated frequency range.

I. Introduction

The impedance spectroscopy technique is widely used to have information on the dielectric properties of a medium.¹ In particular, it is very useful to investigate the relaxation processes in liquids. However, in the low-frequency range, the measurements are difficult to interpret because of the ions, which always can be present in the liquid. In this paper, we analyze the influence of the ions on the impedance of a cell submitted to a periodic external voltage of low amplitude. According to our model, this assumption implies that the bulk density of ions does not change very much with respect to the one in thermodynamical equilibrium in the absence of external voltage. In the following, this approximation will be called “small surface charge density approximation”. We propose a model according to which the presence of the ions is taken into account by means of two surface densities of charge due to the drift of ions induced by the effective electric field present in the bulk. Furthermore, from the analysis of the experimental data in the low-frequency region, we characterize the impedance of the metal–electrolyte interface at the electrodes. The agreement between the theoretical predictions of our model and the experimental data is fairly good in the full range of frequencies explored by us.

Our paper is organized as follows. In Section II, we present the theoretical model. Section III is devoted to the evaluation of the impedance of the cell, and in Section IV, the theoretical predictions are derived. The experimental determination of the impedance of a cell of water containing KCl is described in Section V, where we compare the theoretical predictions with the experimental data by taking into account also the impedance of the interface metal–electrolyte. In this section, it is also

shown that, in our experimental situation, the small surface charge approximation works well. The conclusions are reported in Section VI.

II. Model

We consider a sample in the shape of a slab of thickness d . The Cartesian reference frame used in the description has the z -axis perpendicular to the bounding surfaces located at $\pm d/2$. We assume that all physical quantities affecting the problem depend only on the z -coordinate. The sample is a low-conducting liquid limited by two perfectly blocking electrodes. This means that there is no charge emission from the electrodes to the liquid. We suppose that the liquid contains, in thermodynamical equilibrium and in the absence of an external electric field, a density n_0 of positive and negative ions. In this situation, the liquid is globally and locally neutral. In our analysis, the recombination effect is neglected. When an external electric field is applied to the sample, there is a drift of ions under the bulk electric field. In the steady state, the drift continues until the diffusion current balances the drift current.² Scalerandi et al.³ have considered the ion redistribution in the presence of an electric field, by taking into account the current of drift and of diffusion, to investigate the influence of the ions on the optical properties of a nematic liquid crystal cell. In ref 3, it is shown that, in the presence of an external field, the ions give rise to a net electric charge localized in two surface layers of mesoscopic thickness, which is smaller than the length of Debye.⁴ On the contrary, in the bulk, the net electric charge density vanishes. Moving from this observation, Pagliusi et al.⁵ analyzed the same problem by assuming that the presence of the ions can be described by a surface density of charge only by neglecting the continuum distribution across the sample of the bulk density of positive and negative ions. The agreement between the theory and the experiment presented in ref 5 suggests that it is realistic to assume that, in the presence of the electric field, the ions

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can be described by a surface density. Of course, according to this approach, the diffusion current has not been taken into account because in the bulk the densities of positive and negative ions are homogeneous and equal, and a localized surface density of ions is introduced to the limiting surfaces.

In this paper, we consider the influence of the ions on the impedance of a cell filled with a conducting liquid by extending the model developed in ref 5. The ions are supposed to be monovalent and similar from the geometrical point of view. In this framework, the adsorption energies for the two types of ions are comparable, and hence there is no selective ion adsorption.⁶ Consequently, the problems connected with the ζ potential can be neglected.^{7,8} We assume that the sample can be considered to be formed by three layers. Two layers of thickness L , on the electrodes, are formed by the ions (the surface layers of Stern⁹). The relevant dielectric constant is indicated by ϵ_s . The remaining layer is the liquid, of thickness d and dielectric constant ϵ_B . When an external voltage V is applied to the sample, the surface densities of charge sent by the power supply on the electrodes are indicated by $\pm\Sigma q$, and the charge densities due to the charge separation induced by the presence of the electric field by $\mp\sigma q$, where q is the unit charge and $\pm\Sigma, \mp\sigma$ are the relevant carrier surface densities. We assume that, in the bulk, the liquid remains locally neutral, and that the presence of the external field is responsible for the migration of the ions close to the surfaces. In this framework, the electric field in the surface layers and in the bulk are given by $E_s = q\Sigma/\epsilon_s$ and $E_B = q(\Sigma - \sigma)/\epsilon_B$, respectively. By taking into account that the difference of potential applied to the sample by means of the external power supply is V , it follows that $V = 2E_s L + E_B d$. Consequently, Σ , σ , and V are related by the equation

$$q\Sigma = \gamma \frac{\epsilon_B}{d} \left(V + q \frac{\sigma}{\epsilon_B} d \right), \quad (1)$$

where $1/\gamma = 1 + 2(L\epsilon_B)/(d\epsilon_s)$ is a parameter depending on the dielectric properties of the system. In our approximation, where the electric charge of ionic origin is approximated by a surface density of charge, the bulk electric field $E_B = q(\Sigma - \sigma)/\epsilon_B$, taking into account eq 1, can be rewritten as

$$E_B = \gamma \left(\frac{V}{d} - 2q \frac{\sigma}{\epsilon_s} \frac{L}{d} \right). \quad (2)$$

The electric field E_B gives rise to a drift current $J = 2\mu n q E_B$, where μ is the mobility of the ions and n the bulk density of ions. Because of the conservation of the number of particles, $nd + \sigma = n_0 d$. Consequently, the actual bulk density of ions, n , is related to the initial one, n_0 , by $n = n_0 - \sigma/d$. The ions are pushed to the limiting surfaces by the electric field. The increasing of the surface density of ions is connected to the drift current by $d\sigma = 2\mu n E_B dt$, that for the discussion reported above is equivalent to

$$\frac{d\sigma}{dt} = 2\mu \gamma \left(n_0 - \frac{\sigma}{d} \right) \left(\frac{V}{d} - 2q \frac{\sigma}{\epsilon_s} \frac{L}{d} \right). \quad (3)$$

Equation 3, giving the time evolution of σ , is not linear. Consequently, if $V(t) = V_0 \exp(i\omega t)$, $\sigma(t)$ is not simply harmonic. However, because we are interested in the linear response of the sample to a harmonic signal, we limit our investigation to the case of $\sigma/d \ll n_0$, called above small surface charge approximation. In other words, we solve the problem under the assumption that the density of particles in the bulk only slightly

deviates from the initial value n_0 .¹⁰ In this case, eq 3 reads

$$\frac{d\sigma}{dt} = 2\mu \gamma n_0 \left(\frac{V}{d} - 2q \frac{\sigma}{\epsilon_s} \frac{L}{d} \right), \quad (4)$$

which is now linear with constant coefficients.

III. Impedance of the Cell

We indicate by $Q_e = q\Sigma A$ and $Q_i = q\sigma A$, where A is the surface of the electrodes, the total external and ionic charge, respectively, and rewrite eqs 1 and 4 as

$$Q_e = \gamma(C_B V + Q_i) \quad (5)$$

and

$$\frac{dQ_i}{dt} = \frac{1}{\beta} \left(\frac{1}{2} C_s V - Q_i \right), \quad (6)$$

where $C_B = \epsilon_B A/d$ is the electrical capacitance of the condenser represented by the bulk, $C_s = \epsilon_s A/L$ the capacitance of the surface layer, and

$$\beta = \frac{\epsilon_s d}{4\mu \gamma q n_0 L} \quad (7)$$

a parameter depending on the concentration of ions. From eq 5, it follows that the total current in the external circuit is

$$I = \frac{dQ_e}{dt} = \gamma C_B \frac{dV}{dt} + \gamma \frac{dQ_i}{dt}. \quad (8)$$

The first contribution to I represents the usual displacement current, present in an ideal condenser. The second one is connected with the presence of the ions dissolved in the liquid.

From eq 6, in the case in which $V = V_0 \exp(i\omega t)$, we derive that $Q_i = Q_{i0} \exp(i\omega t)$, with Q_{i0} keeping the phase information of the ionic charge Q_i with respect to the applied voltage V_0 :

$$Q_{i0} = \frac{C_s}{2(1 + i\omega\beta)} V_0. \quad (9)$$

A simple inspection shows that eq 9 is reasonable. For $\omega \rightarrow 0$, it gives $Q_{i0}(\omega = 0) = (1/2)C_s V_0$, which is the expected result. In fact, in this limit and for a small external electric field, the sample behaves as a conductor. Consequently, the ions move until the electric field in the bulk vanishes. The condition $E_B = 0$ gives $\sigma = \Sigma$. In this situation, all the drops of potential are localized on the surface layers, and hence, the equivalent capacitance is the one of two identical condensers of capacitance C_s , in agreement with the expression written above for $Q_{i0}(\omega = 0)$.

The total current is easily found from eq 8 in the harmonic case. Simple calculations give for the admittance $\mathcal{Y}(\omega) = I(\omega)/V(\omega)$ the expression

$$\mathcal{Y}(\omega) = i\omega \gamma \left\{ C_B + \frac{C_s}{2(1 + i\omega\beta)} \right\}. \quad (10)$$

The real and imaginary part of the cell electrical impedance $\mathcal{Z}(\omega) = 1/\mathcal{Y}(\omega) = \mathcal{R}(\omega) + i\mathcal{X}(\omega)$ are then

$$\begin{aligned}\mathcal{R}(\omega) &= \frac{\beta C_S}{2\gamma[(\omega\beta C_B)^2 + (C_B + C_S/2)^2]} \\ \mathcal{X}(\omega) &= -\frac{(\omega\beta)^2 C_B + C_B + C_S/2}{\omega\gamma[(\omega\beta C_B)^2 + (C_B + C_S/2)^2]}\end{aligned}\quad (11)$$

In the particular case in which $n_0 \rightarrow 0$, from eq 7 it follows that $\beta \rightarrow \infty$. Consequently, from eq 11 we get

$$\mathcal{R}(\omega) \rightarrow 0, \quad \text{and} \quad \mathcal{X}(\omega) \rightarrow -\frac{1}{\omega\gamma C_B}. \quad (12)$$

The first limit is expected. The second one shows that, in the case in which the sample can be considered a perfect insulator, the equivalent electrical capacitance is such that $1/C_{eq} = 1/(\gamma C_B)$. Thus, taking into account the definition of γ , $1/C_{eq}$ can be rewritten as

$$\frac{1}{C_{eq}} = \frac{1}{C_B} + \frac{2}{C_S} \quad (13)$$

as expected because, in this case, the system is equivalent to a series of three condensers: one of capacitance C_B and two of capacitance C_S . The other limit that deserves consideration is $\lim_{\omega \rightarrow 0} \mathcal{R}(\omega)$. Taking into account the definition of $C_S/2$, β , γ , and C_B reported above, by eq 11 we find

$$\lim_{\omega \rightarrow 0} \mathcal{R}(\omega) = \frac{d}{2\mu q n_0 A}. \quad (14)$$

In this limit, we derive that the conductivity, defined by means of the relation $\mathcal{R} = (1/\sigma_{eq})(d/A)$, is such that

$$\lim_{\omega \rightarrow 0} \sigma_{eq} = 2\mu n_0 q \quad (15)$$

as well-known from elementary electrodynamics.

IV. Theoretical Predictions

By means of the formulas reported in the previous section, it is possible to study the frequency dependence of the impedance of the cell under investigation. From eq 11 simple calculations show that in the limit of $\omega \rightarrow 0$

$$\begin{aligned}\mathcal{R}(\omega) &= \frac{\beta C_S}{2\gamma(C_B + C_S/2)^2} \left\{ 1 - \left(\frac{\beta C_B}{C_B + C_S/2} \right)^2 \omega^2 \right\} + \mathcal{O}(\omega^4) \\ \mathcal{X}(\omega) &= -\frac{1}{\gamma(C_B + C_S/2)} \omega^{-1} + \mathcal{O}(\omega^0).\end{aligned}\quad (16)$$

By taking into account that $C_S \gg C_B$ and the definitions of C_S , C_B , β , eq 16 can be rewritten as

$$\begin{aligned}\mathcal{R}(\omega) &= \frac{d}{\epsilon_B A \omega_r} \left\{ 1 - \left(\frac{\omega}{\omega_r} \right)^2 \right\} + \mathcal{O}(\omega^4) \\ \mathcal{X}(\omega) &= -\frac{2L}{\epsilon_S A \omega} + \mathcal{O}(\omega^0)\end{aligned}\quad (17)$$

where

$$\omega_r = \frac{2\mu n_0 q}{\epsilon_B} \quad (18)$$

is a typical cutoff frequency of the problem under investigation,

as it will be shown in the following. In the opposite limit of $\omega \rightarrow \infty$ we get

$$\begin{aligned}\mathcal{R}(\omega) &= \frac{C_S}{2\gamma\beta C_B} \omega^{-2} + \mathcal{O}(\omega^{-4}) \\ \mathcal{X}(\omega) &= -\frac{1}{\gamma C_B} \omega^{-1} + \mathcal{O}(\omega^{-2})\end{aligned}\quad (19)$$

that, as done for eq 16, can be rewritten in the approximated form

$$\begin{aligned}\mathcal{R}(\omega) &= \frac{d}{\epsilon_B A \omega_r^2} + \mathcal{O}(\omega^{-4}) \\ \mathcal{X}(\omega) &= -\frac{d}{\epsilon_B A \omega} + \mathcal{O}(\omega^{-2}).\end{aligned}\quad (20)$$

The critical frequency, ω_c , separating the low-frequency range from the high-frequency range, is obtained by eq 11 by putting $(\omega_c\beta C_B)^2 \sim (C_B + C_S/2)^2$, and it is found to be

$$\omega_c = \frac{1}{\beta} \left(1 + \frac{C_S}{2C_B} \right) \sim \omega_r. \quad (21)$$

Furthermore, from eq 11, it follows that $\mathcal{R}(\omega)$ is a monotonic decreasing function, whereas $\mathcal{X}(\omega)$ has two extrema in

$$\begin{aligned}\omega_{M,m} &= \frac{1}{\sqrt{2}\beta C_B} \{ (C_S/2)^2 - C_B(C_S/2) - 2C_B^2 \\ &\quad \mp [C_S/2 + C_B] \sqrt{C_S/2[C_S/2 - 8C_B]} \}^{1/2}\end{aligned}\quad (22)$$

whose approximated values are

$$\begin{aligned}\omega_M &\sim \sqrt{\frac{1-\gamma}{\gamma}} \omega_r \\ \omega_m &\sim \omega_r.\end{aligned}\quad (23)$$

A simple investigation shows that $\mathcal{X}(\omega)$ exhibits a maximum for $\omega = \omega_M$, and a minimum for $\omega = \omega_m$.

To get numerical values for the real and imaginary part of the impedance, we have to define the liquid under investigation. We suppose that the liquid is water doped with a salt like KCl. According to the model described above, the thickness L is in the molecular scale, in the sense that it is comparable with the size of the ions dissolved in the liquid. Of course, in the case in which the solvent is formed by polar molecules, such as water, it is necessary to take into account that the ions are hydrated, and hence L will be on the order of double linear size of one molecule of water. Beyond this surface layer, the diffuse layer will extend into the solution bulk. The thickness of this layer is comparable with the length of Debye, and it depends on the applied voltage. In a first approximation, we neglect this diffuse layer because our experimental data relevant to the impedance are independent of the applied voltage.

For the numerical calculations, we assume that the physical parameters entering in the model are

- $-n_0 = 6 \times 10^{-4}$ mole/dm³, density of ions in thermodynamical equilibrium;
- $-\epsilon_B = 80 \times \epsilon_0$, dielectric constant of the solvent;
- $-\epsilon_S = 10 \times \epsilon_0$, dielectric constant of the surface layer;
- $-\mu = 7.92 \times 10^{-8}$ m²/(V s), mobility of both positive and negative ions;¹¹

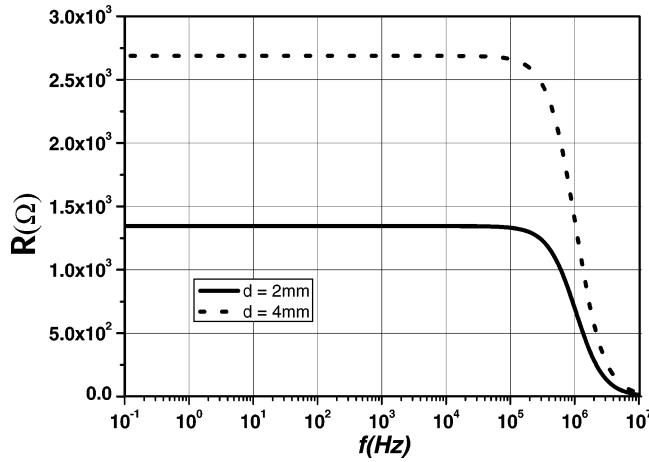


Figure 1. Real parts of the impedances of two cells \mathcal{R}_1 and \mathcal{R}_2 vs f . The thicknesses of the samples are $d_1 = 2$ mm and $d_2 = 4$ mm. The physical parameters used for the curves are the ones reported in the text.

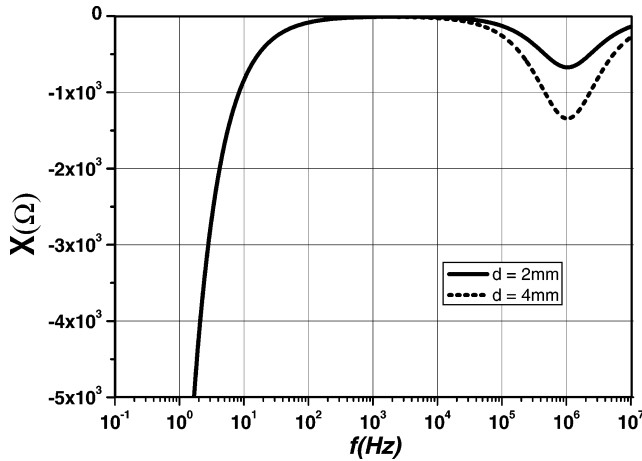


Figure 2. Imaginary parts of the impedances of two cells \mathcal{X}_1 and \mathcal{X}_2 vs f . The thicknesses of the samples are $d_1 = 2$ mm and $d_2 = 4$ mm. The physical parameters used for the curves are the ones reported in the text.

$-r = 1.5 \times 10^{-10}$ m, linear size of both positive and negative ions;¹¹

$-l = 2.75 \times 10^{-10}$ m, linear size of a water molecule;¹¹

$-L = 2/r + r = 7.5 \times 10^{-10}$ m, thickness of the surface layer.

Note that for ϵ_s we have supposed a value well below ϵ_B . This is not absurd. In fact, in the bulk, the dipolar moment of the molecules of water gives a large contribution to the polarizability. On the contrary, in the surface layer, the molecules of water are strongly stuck at the surface, and the presence of an external field cannot orient the molecular dipoles as in the bulk. Consequently, in the surface layer, the dipolar contribution to the dielectric constant is smaller than in the bulk.

In Figure 1, we show the dependence of \mathcal{R} on ω in semilogarithmic scale, relevant to two samples, one with a thickness $d_1 = 2$ mm and the other with a thickness $d_2 = 2d_1$. $\mathcal{R}(\omega)$ shows a large plateau in the low- and middle-frequency range, and tends to zero for large ω .

In Figure 2, it is reported \mathcal{X} vs ω , again in semilogarithmic scale for the same two values of the sample thickness. $\mathcal{X}(\omega)$ diverges for $\omega \rightarrow 0$, after that it presents a maximum, then a minimum, and finally it tends to zero in the limit of large frequency. The positions and the values of the \mathcal{X} extrema strongly depend on the density of ions n_0 . The position of the

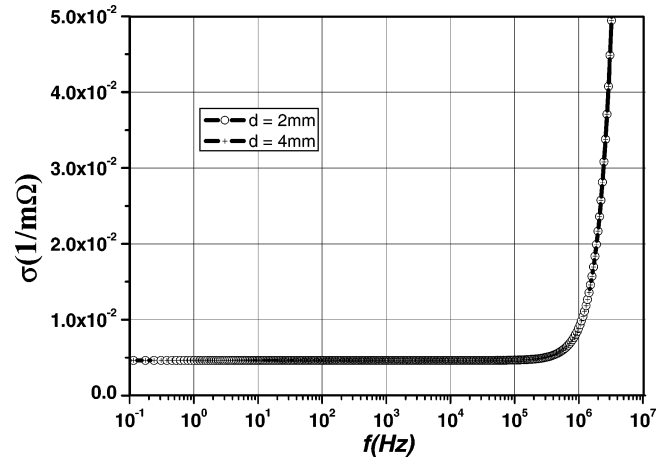


Figure 3. σ_{eq} vs f . The thicknesses of the samples are $d_1 = 2$ mm and $d_2 = 4$ mm. The physical parameters used for the curves are the ones reported in the text.

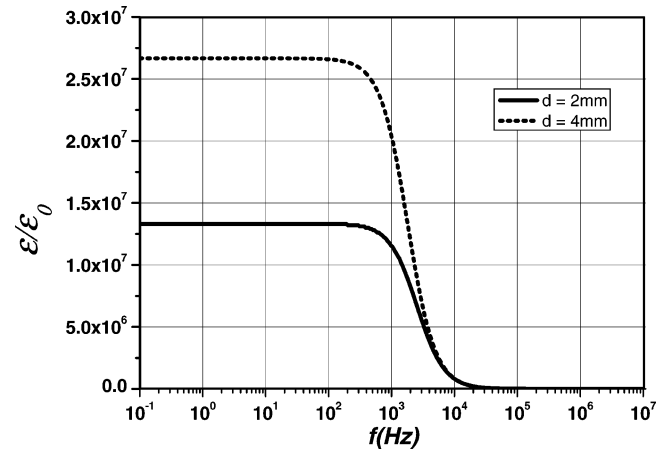


Figure 4. ϵ_{eq} vs f . The thicknesses of the samples are $d_1 = 2$ mm and $d_2 = 4$ mm. The physical parameters used for the curves are the ones reported in the text.

maximum and of the minimum numerically found agree with ω_M and ω_m given by (23).

By means of the expressions reported above for \mathcal{R} and \mathcal{X} , by taking into account that $\mathcal{R} = (1/\sigma_{eq})(d/A)$ and $\mathcal{X} = -1/(\omega C_{eq})$, where $C_{eq} = \epsilon_{eq}A/d$, we get for the equivalent electrical conductivity σ_{eq} and equivalent dielectric constant of the cell filled by the liquid-containing ions, the formulas

$$\sigma_{eq}(\omega) = \frac{d}{\mathcal{R}(\omega)A}, \text{ and } \epsilon_{eq} = -\frac{d}{\omega \mathcal{X}(\omega)A}. \quad (24)$$

In Figures 3 and 4, we show the frequency dependence of σ_{eq} and ϵ_{eq} for the two samples with $d_2 = 2d_1$. As it is evident from Figure 3, $\sigma_{eq}(\omega)$ practically do not depend on the thickness of the sample on all the range of frequency. On the contrary, $\epsilon_{eq}(\omega)$ is such that, for $\omega \rightarrow 0$, it is proportional to d . In the opposite limit of $\omega \rightarrow \infty$, on the contrary, the dielectric constant of the equivalent capacitor is thickness independent. These results are, obviously, in agreement with the formulas 17 and 20 reported above.

V. Experiment

In Figures 5 and 6, we present the experimental data relevant to the cells of thickness $d_1 = 2.03$ mm, $d_2 = 4.03$ mm, and $A = 3.21 \times 10^{-4}$ m² of KCl in water. The cell box, designed by us and constructed by the workshop MISTRAL (Cercenasco),

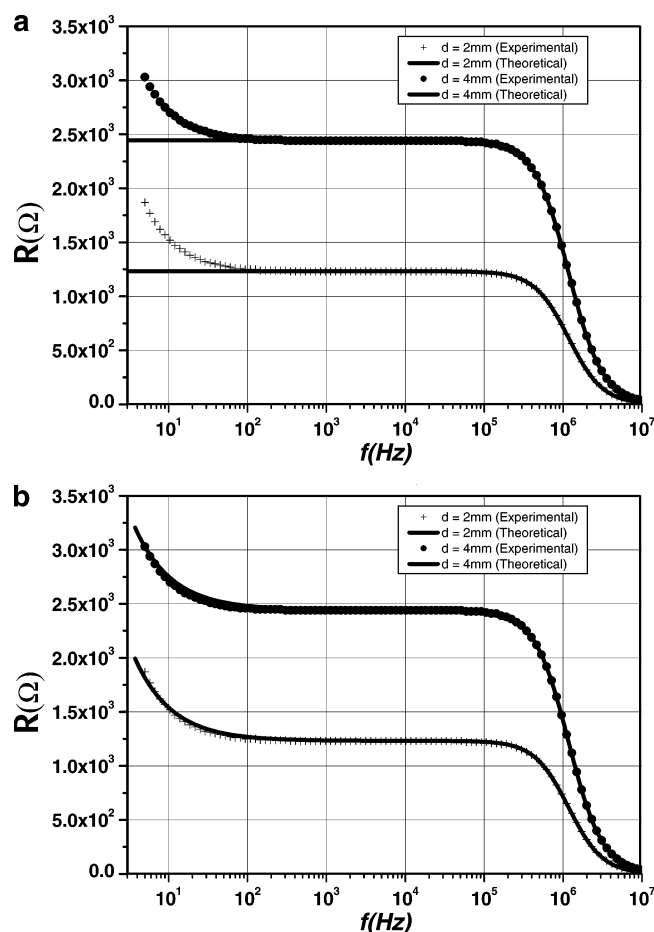


Figure 5. Experimental data relevant to two samples containing water and KCl; real part of the impedance. Dashed curve $d_1 = 2.03$ mm, dotted curve $d_2 = 4.03$ mm. Continuum curve theoretical predictions of the model: (a) by neglecting the impedance of the metal–electrolyte interface; (b) by taking into account the impedance of the metal–electrolyte interface.

is characterized by a core comprising a capacitor immersed in a vessel filled with the liquid sample under investigation.¹² The condenser is built by two golden electrodes up, electrochemically deposited onto the circular bases of two stainless steel cylinders clamped by rigid plastic supports. One of the two supports is fixed to the box, whereas the other can be positioned with its electrode at a certain preselectable distance in front of the first one. The reference electrode possesses a guard ring. The position of the moveable electrode can be adjusted along its axis by means of a micrometrical screw with a sensitivity of $1 \mu\text{m}$ and an accuracy of $10 \mu\text{m}$. The condenser has been designed for four-wire measurements, and the cell box is electrically screened. The HP4192A impedance meter in the series mode has been used, giving $\mathcal{R}(\omega)$, $\mathcal{X}(\omega)$ of the cell. A single scanning run from 5 Hz until 10 MHz typically takes 5 min. The measuring setup has been placed in a thermally controlled room, allowing a maximum temperature drift of ± 0.5 °C/day. The amplitude of the applied voltage is 200 mV. The data here assumed for elaboration are the average of five consecutive scanning runs.

The electrodes subjected to an AC voltage of 200 mV can be considered as blocking. In fact, we have measured the DC resistance of the cell, finding the asymptotic value of $20 \text{ M}\Omega$, very large with respect to the low-frequency real part of the cell impedance. This result is in agreement with the experimental data reported in refs 13 and 14 on a similar system with blocking electrodes, where the AC voltage applied to the cell was 250 mV.

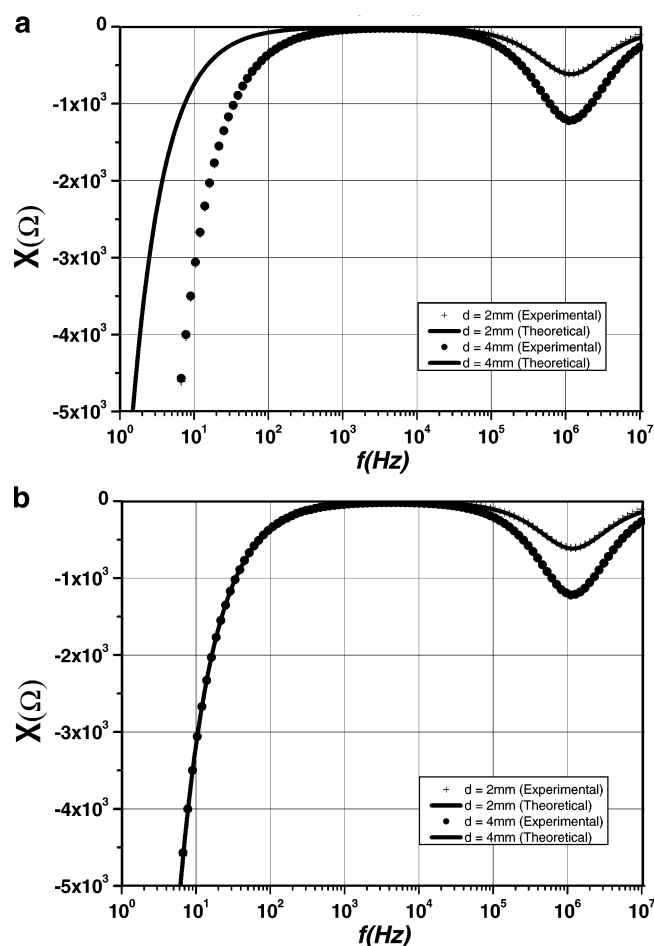


Figure 6. Experimental data relevant to two samples containing water and KCl; imaginary part of the impedance. Dashed curve $d_1 = 2.03$ mm, dotted curve $d_2 = 4.03$ mm. Continuum curve theoretical predictions of the model: (a) by neglecting the impedance of the metal–electrolyte interface; (b) by taking into account the impedance of the metal–electrolyte interface.

By assuming $\mu = 7.92 \times 10^{-8} \text{ m}^2/\text{V s}$, and $\epsilon_B = 78.5 \times \epsilon_0$,¹¹ the parameters of the best fit are obtained as: $n_0 = 20.2 \times 10^{22} \text{ m}^{-3}$, and $\epsilon_S/L = 0.133 \text{ F/m}^2$. Considering $L = 10 \times 10^{-10} \text{ m}$, on the order of the thickness of Stern,⁴ ϵ_S is found to be $15 \times \epsilon_0$. The value of n_0 determined by means of the best fit, compares well with the one directly measured, which is $n_0 = 6 \times 10^{-4} \text{ mol/dm}^3 = 36 \times 10^{22} \text{ m}^{-3}$. Using the parameters of the best fit, the approximation of the small surface density is satisfied up to 500 mV as it can be easily verified by a numerical integration of eq 3.

As is evident from Figures 5a and 6a, the agreement is rather good for $f = \omega/(2\pi) \geq 10^2$ Hz. On the contrary, for what concerns the equivalent resistance, the model and the theory do not agree in the low-frequency range, smaller than 100 Hz. According to our model, on the basis of the hypothesis that the mobility of the ion is independent of the frequency, the resistance has to tend to a constant value given by $\mathcal{R} = (1/2\mu n_0 q)(d/A)$, whereas the experimental data shows an increasing of \mathcal{R} for $\omega \rightarrow 0$. Even considering the possibility of a parasite resistance in parallel to the sample $R_{\parallel} \sim 1 \text{ M}\Omega$, the quality of the fit does not improve too much. In particular, the presence of R_{\parallel} introduces an increasing of the equivalent resistance of the system only at a very low frequency (≤ 10 Hz).

The increasing of $\mathcal{R} = \text{Re}(\mathcal{Z})$ of chemical cells with blocking electrodes for $\omega \rightarrow 0$ is usually interpreted by introducing the concept of impedance of the metal–electrolyte

interface \mathcal{Z}_i , resulting from a random distribution of local impedances onto the electrode surfaces. According to¹⁵ $\mathcal{Z}_i = w(i\omega)^{-\nu}$, where w and ν are constants depending on the metal and the electrolyte, and $\nu < 1$. The impedance of the interface \mathcal{Z}_i contributes to the total resistance of the cell with a term, $\mathcal{R}_i = \text{Re}(\mathcal{Z}_i) = w\omega^{-\nu} \cos(\nu\pi/2)$, which is frequency dependent. In particular, it diverges for $\omega \rightarrow 0$. In the same manner, it gives a contribution to the total imaginary part of the type $\mathcal{X}_i = \text{Im}(\mathcal{Z}_i) = -w\omega^{-\nu} \sin(\nu\pi/2)$. Also this contribution diverges for $\omega \rightarrow 0$, as $\omega^{-\nu}$. According to Levie,¹⁶ ν depends on the roughness of the electrodes. However, Bates et al.¹⁷ have found no correlation between ν and the fractal dimension of the surface of a rough electrode.

By introducing the impedance of the interface metal–electrolyte, the total impedance of the cell is $\mathcal{Z}_t = \mathcal{Z}_i + \mathcal{Z}$. Consequently, $\mathcal{R}_t = \mathcal{R}_i + \mathcal{R}$ and $\mathcal{X}_t = \mathcal{X}_i + \mathcal{X}$. In Figures 5b and 6b, we show the best fit of the experimental data with the model in which the impedance of the interface metal–electrolyte is taken into account. The parameters of the best fit relevant to \mathcal{Z}_i are, in the units of International System (SI), $w = 1.1 \times 10^5$ and $\nu = 0.92$ for the cells with the two gaps investigated by us. As is evident from the quoted figures, the agreement of the experimental data with the theoretical predictions is good on the entire frequency range.

VI. Conclusion

We have proposed a model to investigate the influence of the ions on the impedance spectroscopy of a liquid. In our analysis, we have assumed that the electrodes are perfectly blocking and the presence of the ions can be taken into account by means of two surface density of charged particles, according to the model of Stern. The time evolution of the surface densities of ions in the sample is deduced in the limit of small applied voltage. In this framework, the actual bulk density of ions only slightly differs from the bulk density of ions in thermodynamical equilibrium in the absence of an external electric field. We have shown that the ions contribute to the electric current in the external circuit. By assuming that the external voltage depends on time in a sinusoidal manner, we have determined the impedance of the cell and investigated the frequency dependence of its real and imaginary parts. The theoretical model, on the

basis of the hypothesis that the mobility is frequency independent, is in reasonable agreement with our experimental data relevant to a cell filled with water doped with KCl for frequencies larger than 100 Hz. In the low-frequency range (<100 Hz), the impedance of the metal–electrolyte interface, modeled as $\mathcal{Z}_i = w(i\omega)^{-\nu}$, plays a fundamental role. By means of the analysis of the frequency dependence of the real and imaginary part of the total impedance of the two cells investigated by us, we have determined w and ν . As expected, they are independent of the thickness of the cell and depend only on the interface metal–electrolyte.

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References and Notes

- (1) Macdonald, J. R.; Johnson, W. B. in *Impedance Spectroscopy*; John Wiley & Sons: New York, 1987; Chapter 1.
- (2) Lyklema, J. *Fundamentals of Interface and Colloid Sciences*; Academic Press: London, 1993.
- (3) Scalerandi, M.; Pagliusi, P.; Cipparrone, G.; Barbero, G. *Phys. Rev. E* **2004**, *69*, 051708.
- (4) Israelachvili, J. *Intermolecular Forces*; Academic Press: London, 1985; Chapter 12.
- (5) Pagliusi, P.; Zappone, B.; Cipparrone, G.; Barbero, G. *J. Appl. Phys.* **2004**, *96*, 218.
- (6) Barbero, G.; Evangelista, L. R.; Zvezdin, A. K. *Phys. Rev. E* **1999**, *59*, 1846.
- (7) Scott, M.; Paul, R.; Kaler, V. I. S. *J. Colloid Interface Sci.* **2000**, *230*, 377.
- (8) Scott, M.; Paul, R.; Kaler, V. I. S. *J. Colloid Interface Sci.* **2000**, *230*, 388.
- (9) Raistrick, I. D.; Macdonald, J. R.; Franceschetti, D. R. in *Impedance Spectroscopy*; John Wiley & Sons: New York, 1987; Chapter 2.
- (10) Cirkel, P. A.; van der Ploeg, J. P. M.; Koper, G. J. M. *Physica A* **1997**, *235*, 269.
- (11) Bockris, J. O.; Reddy, A. K. N.; Gamboa-Aldeco, M. *Modern Electrochemistry: Ionics*; Plenum Publishing, New York: 1998.
- (12) Becchi, M.; Callegaro, L.; Durbiano, F.; Strigazzi, A. *Impedance Cell for Low Conducting Liquids*. In preparation.
- (13) Hollingsworth, A. D.; Seville, D. A. *J. Colloid Interface Sci.* **2003**, *257*, 65.
- (14) Hollingsworth, A. D.; Seville, D. A. *J. Colloid Interface Sci.* **2004**, *280*, 279.
- (15) Bottleberghs, P. H.; Broers, G. H. J. *J. Electroanal. Chem.* **1976**, *67*, 155.
- (16) de Levie, R. *Electrochim. Acta* **1965**, *10*, 113.
- (17) Bates, J. B.; Chu, Y. T.; Stribling, W. T. *Phys. Rev. Lett.* **1988**, *60*, 627.