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The influence of adsorption phenomena on the impedance spectroscopy of an electrolytic cell

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Abstract. In this work we investigate the influence of the adsorption of ions on the impedance spectroscopy of an electrolytic cell. We consider that the positive and negative ions present in a dielectric liquid are adsorbed in the electrode surfaces with different adsorption energies. This difference in adsorption energies causes an additional plateaux in the limit of the low-frequency range of the real part of the impedance Z. In the same frequency range, a second minimum in the imaginary part of Z is predicted. The theory is illustrated with measurements of the impedance of an electrolytic solution in the frequency range from 10^{-2} Hz to 1 KHz. A comparison between the present model and others from the literature to describe the experimental results is also made.

Introduction

The impedance spectroscopy has been shown to be a useful technique to investigate electrical properties of electrolytic systems [1]. In a typical experiment, a capacitor, filled with the fluid system to be analyzed, is subjected to a sinusoidal external voltage. The real R and imaginary part χ of the impedance Z are measured as a function of the frequency of the applied voltage. As a response to the applied electric field, the ions in the liquid migrate towards the electrodes, contributing to the electric current in the external circuit. It is well known that R presents an anomalous increasing in the low-frequency limit. Different mechanisms could account for this behavior. Among them, we may mention the Ohmic characteristic of the electrodes [2,3] and the dissociation-recombination effect [4–6]. In the last case, a detailed analysis can be found in ref. [6]. Another possible mechanism responsible for this behavior of R is the adsorption/desorption of ions in the electrode surfaces. According to this mechanism, the time dependence of the adsorbed/desorbed ions is given by a kinetic equation that contains two phenomenological parameters [7–11]. One of them is connected with the adsorption, while the other refers to the desorption of ions. It follows that, if the frequency of the external field is large with respect to the inverse of the desorption time, the impedance of the cell does not depend on the adsorption phenomenon. On the other hand, if the frequency of the applied voltage is comparable with the inverse of the desorption time, the ions contribute to the displacement current in the circuit.

In the literature, the adsorption phenomena have been classified into two types: electrostatic and specific [12]. The electrostatic adsorption is related to the ionic concentration at the electrode surface, as a response to an electric field present on it. The specific adsorption is due to an affinity between a specific ion and the electrode.

In this work, we investigate the influence of the adsorption/desorption phenomena on the impedance spectroscopy of an electrolytic cell. In our model we consider that the adsorption/desorption energies are different for the positive and negative ions. In this case, both the electrostatic and the specific adsorption studied by Pajkossy *et al.* [13–15] are implicitly considered. A theoretical analysis in this direction can be found in ref. [11] in which the author considers that the limiting surfaces have the same adsorption energies with respect to the two types of ions. An improvement of this model is done by considering the general situation in which such energies are different for the two types of ions.

In the analysis, we assume that the ions are identical, except for the sign of their electrical charge, are dimensionless and have the same mobilities. The limiting surfaces of the sample are also identical. The model will be used to analyze the experimental results obtained with electrolytic solutions of KCl.

General formalism

Let us consider an isotropic liquid containing ions, limited on both sides by two parallel surfaces of area S, separated by a distance d (slab geometry). We choose a Cartesian

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reference frame in which the z-axis is normal to the limiting surfaces, so that the problem is one-dimensional. The basic equations governing the ionic distributions in the cell are the continuity equations [5,16–25]

$$\frac{\partial n_l(z,t)}{\partial t} = -\frac{\partial J_l(z,t)}{\partial z}\,, \tag{1}$$

and the Poisson equation

$$\frac{\partial^2 V(z,t)}{\partial z^2} = -\frac{q}{\epsilon}\big[n_p(z,t) - n_m(z,t)\big], \tag{2}$$

where $n_l(z,t)$ are the density of the positive ($l = p$) and negative ($l = m$) ions, q is their electric charge and ϵ is the dielectric permittivity of the liquid. The current densities $J_l(z,t)$ in eq. (1) are given by [26,27]

$$J_l(z,t) = -D\left\{\frac{\partial n_l(z,t)}{\partial z} \pm \frac{q}{k_B T} n_l(z,t)\frac{\partial V(z,t)}{\partial z}\right\}, \tag{3}$$

where k_B is the Boltzmann constant, T is the absolute temperature, and D is the diffusion constant of the ions. In ±, the + sign is chosen for $l = p$ and − for to $l = m$. In our calculations we make the usual assumption that the dielectric permittivity ϵ and the diffusion constant D are position independent [5].

In this manner, the electrical problem can be entirely solved in the bulk. At the surfaces, a final boundary condition must be imposed. As in ref. [11], let us consider perfectly blocking electrodes (*i.e.*, charge transfer is not allowed but adsorption/desorption occur) in which the current densities are given by

$$J_l(\pm d/2,t) = \pm\frac{\mathrm{d}\sigma_l(\pm d/2,t)}{\mathrm{d}t}\,, \tag{4}$$

where $\sigma_l(\pm d/2,t)$ is the surface density of ions at the electrodes.

Static solution

Disregarding the adsorption or if the adsorption/desorption energies are the same, the density of positive and negative ions would be constant in the liquid. Assuming now different adsorption/desorption energies for the ions on the electrode surfaces, the ionic densities acquire a z dependence, even in the case in which no external voltage is applied. Let $n_l^*(z)$, $(l = p, m)$ be the density profile of positive (p) and negative (m) ions across the sample in this static situation. By imposing $J_l(z,t) = 0$ in every point of the cell, and considering that the electrodes are identical, we obtain

$$n_l^*(z) = \pm C_1 \cosh\left(\frac{z}{\lambda}\right) + C_2, \tag{5}$$

where $\lambda = \sqrt{2n_0 q^2/\epsilon k_B T}$ is the Debye length, C_1 and C_2 are integration constants. The n_0 in λ is defined by the conservation of the number of particles

$$2\sigma_l^* + \int_{-d/2}^{d/2} n_l^*(z)\mathrm{d}z = n_0 d. \tag{6}$$

From eq. (6) we can determine the constants C_1 and C_2 that are given by

$$C_1 = \gamma^{-1} d\, n_0\,(k_m\tau_m - k_p\tau_p)\,, \tag{7}$$

$$C_2 = \gamma^{-1} d\, n_0 \left[(k_m\,\tau_m + k_p\,\tau_p)\,\cosh\left(\frac{d}{2\,\lambda}\right) + 2\,\lambda\,\sinh\left(\frac{d}{2\,\lambda}\right)\right], \tag{8}$$

where

$$\gamma = \big[d\,k_m\,\tau_m + k_p\,(d + 4\,k_m\,\tau_m)\,\tau_p\big]\,\cosh\left(\frac{d}{2\,\lambda}\right) + 2\,\lambda\,(d + k_m\,\tau_m + k_p\,\tau_p)\,\sinh\left(\frac{d}{2\,\lambda}\right). \tag{9}$$

If no adsorption is considered *i.e.*, $\kappa_l = \tau_l = 0$, we can easily obtain $C_1 = 0$, $C_2 = n_0$ and $n_l^*(z) = n_0$, as expected [28]. Another relevant situation is that analysed in [11], in which $\kappa_l = \kappa$ and $\tau_l = \tau$. In this case, we obtain $C_1 = 0$, $C_2 = dn_0/(d + 2\kappa\tau)$ and $n_l^*(z) = C_2$, as reported in [11].

The static electric potential $V^*(z)$ inside the sample is obtained by applying the Poisson equation for the static densities $n_l^*(z)$ and by imposing the boundary conditions at the surfaces

$$V^*(d/2) - V^*(-d/2) = 0. \tag{10}$$

The result is

$$V^*(z) = 2\frac{q}{\epsilon}C_1\lambda^2\left[\cosh\left(\frac{d}{2\lambda}\right) - \cosh\left(\frac{z}{2\lambda}\right)\right] + V_C, \tag{11}$$

where V_C is a constant. As discussed above, if no adsorption is considered or if the adsorption energy is the same with respect to both types of ions, the constant $C_1 = 0$. Consequently, from eq. (11) we have that $V^*(z)$ has no dependence on z throughout the sample.

Dynamic solution

By deriving eq. (3) with respect to z, we obtain

$$\frac{\partial J_l(z,t)}{\partial z} = -D\left\{\frac{\partial^2 n_l(z,t)}{\partial z^2} \pm \frac{q}{k_B T}\left[n_l(z,t)\frac{\partial^2 V(z,t)}{\partial z^2} + \frac{\partial n_l(z,t)}{\partial z}\frac{\partial V(z,t)}{\partial z}\right]\right\}. \tag{12}$$

In order to solve the relevant equations analytically, let us limit our investigation to the case in which $\delta n_l(z,t) \ll n_l^*(z)$, *i.e.*, small variations of $n_l(z,t)$ throughout the sample. By considering small adsorption on the electrodes, a further approximation could be made, that is $n_l^*(z) \sim n_0$. In this case, we can disregard the second term between the brackets of eq. (12), whereas we consider the first as

$$n_l(z,t)\frac{\partial^2 V(z,t)}{\partial z^2} \approx n_0\frac{\partial^2 V(z,t)}{\partial z^2}\,.$$

Therefore, the resulting equations when an external potential is applied to the sample are given by

$$\frac{\partial \delta n_l(z,t)}{\partial t} = D\left\{\frac{\partial^2 \delta n_l(z,t)}{\partial z^2} \pm \frac{q n_0}{k_B T}\frac{\partial^2 \delta V(z,t)}{\partial z^2}\right\} \qquad (13)$$

and

$$\frac{\partial^2 \delta V(z,t)}{\partial z^2} = -\frac{q}{\epsilon}\left[\delta n_p(z) - \delta n_m(z)\right], \qquad (14)$$

where $\delta V(z,t) = V(z,t) - V^*(z)$. Simple calculations give [29]

$$\eta_l(z) = A_1 e^{\alpha z} + A_2 e^{-\alpha z} \pm A_3 e^{\beta z} \pm A_4 e^{-\beta z}, \qquad (15)$$

where

$$\beta^2 = \frac{1}{\lambda^2} + \frac{i\omega}{D}\,, \qquad (16)$$

$$\alpha^2 = \frac{i\omega}{D}\,, \qquad (17)$$

and the constants A_i, $(i = 1,\ldots,4)$ can be determined by applying the boundary conditions on the surfaces.

The electrical potential inside the sample, given by eq. (14), is obtained by integrating the equation of Poisson and by imposing the boundary conditions

$$V(d/2,t) - V(-d/2,t) = V_0/2\exp(i\omega t). \qquad (18)$$

In the steady state we can make $\delta V(z,t) = \phi(z)e^{i\omega t}$, where $\phi(z)$ is given by

$$\phi(z) = -\frac{q}{\epsilon\beta^2}\left(A_3 e^{\beta z} + A_4 e^{-\beta z}\right) + K_1 z + K_2, \qquad (19)$$

where

$$K_1 = \frac{V_0}{d} + \frac{4}{d}\frac{q}{\epsilon\beta^2}\left(A_3 - A_4\right)\sinh\left(\beta\frac{d}{2}\right), \qquad (20)$$

$$K_2 = 2\frac{q}{\epsilon\beta^2}\left(A_3 + A_4\right)\cosh\left(\beta\frac{d}{2}\right). \qquad (21)$$

The expression for the impedance Z is very extensive to be reproduced here. However, the limiting value of R and the behavior of χ for $\omega \to 0$ are useful, and are given in the following:

$$R = \frac{1}{D\,S\,\epsilon\,(2\,\lambda + \xi_m + \xi_p)^2}\Big\{2\,\lambda^2\Big[d\,\left(\xi_m^2 + \xi_p^2\right) + 2\,\lambda\,d\,(\lambda + \xi_m + \xi_p) + 2\,D\,\left(\xi_m\,\tau_m + \xi_p\,\tau_p\right)\Big]\Big\}$$

and

$$\chi = -\frac{4\,\lambda^2}{S\,\epsilon\,(2\,\lambda + \xi_m + \xi_p)\,\omega}\,, \qquad (22)$$

where $\xi_l = k_l\tau_l$ is the adsorption length [11]. It is interesting to obtain from eqs. (22) some known results for the case in which $k_l = \tau_l = 0$, that was analyzed is ref. [28]. After some calculation we can find

$$R = \frac{d\,\lambda^2}{D\,S\,\epsilon}\,, \qquad (23)$$

$$\chi = -\frac{2\,\lambda}{S\,\epsilon\,\omega}\,. \qquad (24)$$

If the zero-adsorption condition is imposed in the entire equation of Z, we obtain the impedance for completely blocking electrodes. These equations are shown in ref. [27], in which it was first reported explicitly.

Although eqs. (23) and (24) represent a limiting behavior, it is possible to show that, for small values of D and the ionic concentration, the real and imaginary parts of the impedance are well approximated by them. Moreover, these equations could also be useful in the physics of liquid crystal devices since, for these systems, D is of the order of $10^{-11}\,\mathrm{m}^2/\mathrm{s}$, $n_0 < 10^{22}\,\mathrm{m}^{-3}$ and $\lambda \sim 10^{-7}\,\mathrm{m}$ [30,31].

Adsorption/desorption of ions on the electrodes

For small adsorption/desorption rates we can consider the equation of Langmuir to describe the surface density of ions $\sigma_l(\pm d/2,t)$ at the electrodes in $z = \pm d/2$. These equation are [11,32]

$$\frac{\mathrm{d}\sigma_l(\pm d/2,t)}{\mathrm{d}t} = k_l n_l(\pm d/2,t) - \frac{1}{\tau_l}\sigma_l(\pm d/2,t), \qquad (25)$$

where τ_l is the desorption time and k_l a constant proportional to the rate of ions that are adsorbed at the electrodes.

Let us write $\sigma_l(\pm d/2,t)$ as

$$\sigma_l(\pm d/2,t) = \sigma_l^*(\pm d/2) + \delta\sigma_l(\pm d/2,t), \qquad (26)$$

where $\sigma_l^*(\pm d/2)$ is the static adsorption, given by

$$k_l n_l^*\left(\frac{d}{2}\right) - \frac{\sigma_l^*}{\tau_l^*} = 0. \qquad (27)$$

Equation (27) is obtained from eq. (25) for the static case.

The time dependent part of the adsorption, $\delta\sigma_l(t)$, is given by

$$\delta\sigma_l\left(\frac{d}{2},t\right) = \eta_l\left(\frac{d}{2}\right)\frac{k_l\tau_l}{1 + i\omega\tau_l}e^{i\omega t}. \qquad (28)$$

As $\sigma^*(\pm d/2)$ is constant, we can find A_i from eq. (4) and obtain all the quantities involved in the problem.

Simulations

In order to perform some simulations, let us consider a water solution containing ions, say $N = 6.02\times10^{23}\,\mathrm{m}^{-3}$ (10^{-3} M). We consider $S = 13.2\times10^{-4}\,\mathrm{m}^2$ and $d = 6\,\mathrm{mm}$, with $\epsilon = 78.5\epsilon_0$, where ϵ_0 is the dielectric permittivity of free space. We have used $D = 1\times10^{-9}\,\mathrm{m}^2/\mathrm{s}$, a typical diffusion constant of ions in water [33]. In fig. 1 we show results for the real part R of the impedance Z as a function of the angular frequency ω for different values of the adsorption (τ_l) and desorption (k_l) parameters. In the particular case in which $\tau_l = k_l = 0$, $R(\omega)$ presents the usual behavior with a large plateau until $\omega_r \sim D/\lambda^2$, and

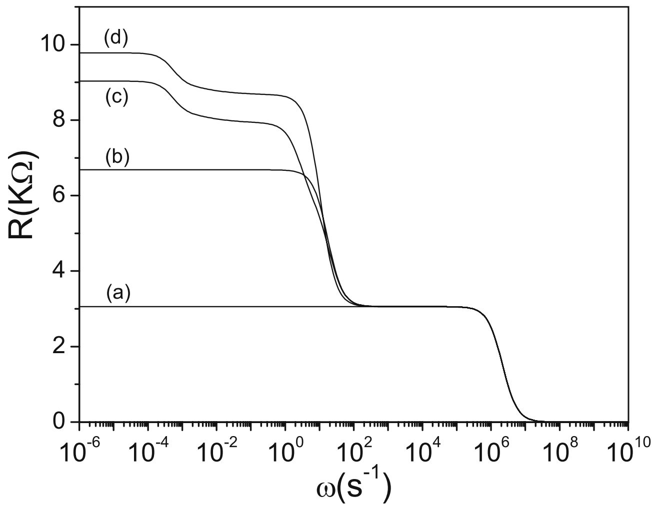

Fig. 1. The real part R of the impedance Z as a function of the angular frequency ω for various τ_l and k_l values. (a) $\tau_l = 0$ and $k_l = 0$ (no adsorption); (b) $\tau_l = 1\,\mathrm{s}$ and $k_l = 5\times10^{-7}\,\mathrm{m}^{-1}\,\mathrm{s}^{-1}$ (same energies of adsorption); (c) $\tau_l = 1\,\mathrm{s}$ and $k_p = 10^{-7}\,\mathrm{m}^{-1}\,\mathrm{s}^{-1}$, $k_m = 5k_p$; (d) $\tau_p = 0.2\,\mathrm{s}$, $\tau_m = 1\,\mathrm{s}$ and $k_l = 5 \times 10^{-7}\,\mathrm{m}^{-1}\,\mathrm{s}^{-1}$.

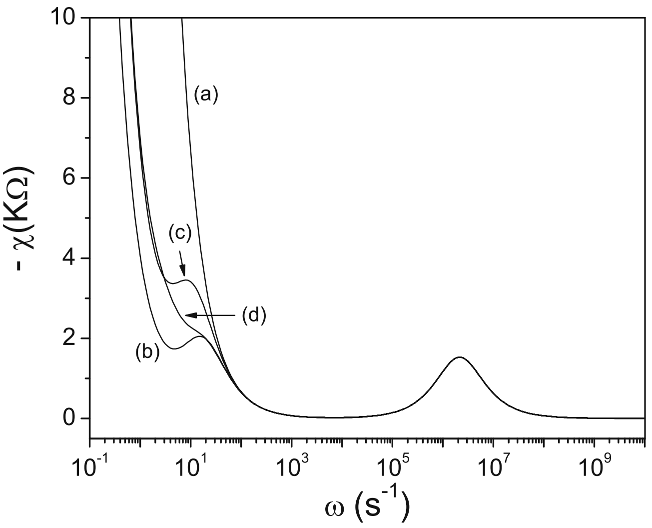

Fig. 2. The imaginary part χ of the impedance Z as a function of the angular frequency ω for various τ_l and k_l values. (a) $\tau_l = 0$ and $k_l = 0$ (no adsorption); (b) $\tau_l = 1\,\mathrm{s}$ and $k_l = 5\times10^{-7}\,\mathrm{m}^{-1}\,\mathrm{s}^{-1}$ (same energies of adsorption); (c) $\tau_l = 1\,\mathrm{s}$ and $k_p = 10^{-7}\,\mathrm{m}^{-1}\,\mathrm{s}^{-1}$, $k_m = 5k_p$; (d) $\tau_p = 0.2\,\mathrm{s}$, $\tau_m = 1\,\mathrm{s}$ and $k_l = 5 \times 10^{-7}\,\mathrm{m}^{-1}\,\mathrm{s}^{-1}$.

tends to zero in the limit of $\omega \to \infty$ (fig. 1, curve (a)). This is the situation in which no adsorption phenomena take place, and could also be obtained by using $k_l = 0$ and $\tau_l \neq 0$. This situation is similar to the one reported in [27, 28] for the case of a system with only one group of ions. In fig. 1, curve (b), we have made $\tau_l = 1\,\mathrm{s}$ and $k_l = 5 \times 10^{-7}\,\mathrm{m}^{-1}\,\mathrm{s}^{-1}$. This situation represents the case where the adsorption of the positive and negative ions has the same adsorption energy, *i.e.*, $\tau_p = \tau_m$ and $k_p = k_m$. In this case, an additional plateau appears in the low-frequency range of $R(\omega)$. This situation has already been reported in ref. [11]. In fig. 1, (curves (c) and (d)) we show R for the case in which $\tau_p \neq \tau_m$ and $k_p \neq k_m$, that represents the general situation in which the adsorption energies for the positive and negative ions are different. In this case, another plateau is obtained in $R(\omega)$ as a result of the difference in the adsorption and/or desorption constants. In fig. 2, we show the imaginary part χ of the impedance, corresponding to the same values presented in fig. 1. Further analysis should be made to understand the magnitude and position of the different plateaux that appear in the impedance spectra. It can be stressed, however, that they are strongly dependent on the adsorption/desorption physical parameters and on the geometric parameters d and S.

Experimental

To illustrate our theoretical results, we performed measurements of the impedance in solutions of water/potassium chloride (KCl from CAAL, Brazil, p.a. degree). However, due to experimental limitations, we could not decrease the angular frequency to less than $\sim 0.2\,\mathrm{s}^{-1}$. For the electrolyte preparation we used Milli-Q water from the Direct-Q3 apparatus, with a concentration of $10^{-4}\,\mathrm{M}$ of KCl. The measurements were performed by using a lock-in amplifier model SR830 from the Stanford Research System, coupled to a computer and the two electrodes. The electrodes used consist of two copper discs of area $S = 13.2\,\mathrm{cm}^2$, covered with a gold film [34]. The sides of the electrodes, not covered by gold, were involved by polyvinyl chloride (PVC) to prevent their contact with the solution. The surfaces are separated by a distance $d = 5.9\,\mathrm{mm}$ (slab geometry). The aqueous KCl solution was subjected to a sinusoidal applied electric voltage of amplitude $10\,\mathrm{mV}$ and angular frequency from $\sim 0.2\,\mathrm{s}^{-1}$ to $6280\,\mathrm{s}^{-1}$.

Results and discussion

In figs. 3 and 4 we show the experimental results of the real and imaginary parts of the impedance, together with some of the fits using some of the previous models (dashed lines: curves (a), (b) and (c)) and our theoretical fit (solid line: curve (d)).

Curve (a) represents the behavior of R and χ expected by the model of blocking electrodes [27, 28]. This model does not predict any increase in R and overestimates the imaginary part χ and, therefore, is not able to describe the experimental results in the low-frequency range. Curve (b) is the best fit performed with the model which assumes ionic adsorption/desorption, with $\tau_p = \tau_m$ and $k_p = k_m$ (equal adsorption/desorption energies). In this model, a plateau is found in the real part of the impedance in the low-frequency range and $\chi \to -\infty$ at $\omega \to 0$ [11]. This additional plateau is not observed in the experimental data in this range of frequency. As a consequence, it

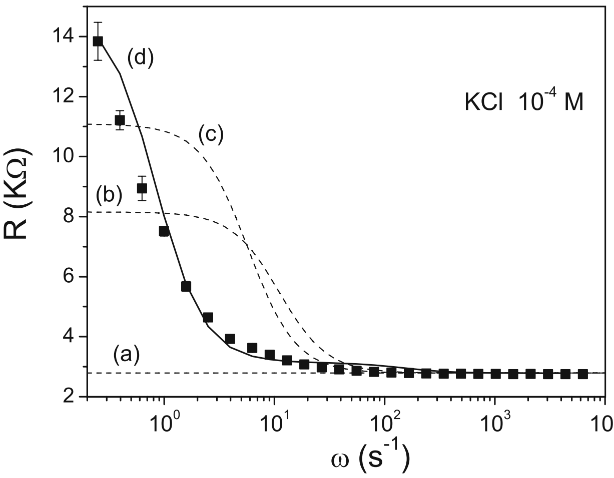

Fig. 3. The real part R of the impedance Z as a function of the angular frequency ω of aqueous solution of KCl 10^{-4} M fitted with various different models (dashed lines): (a) blocking electrodes, (b) adsorption model with the same adsorption energies, and (c) Ohmic electrodes. The curve (d) is our theoretical fit.

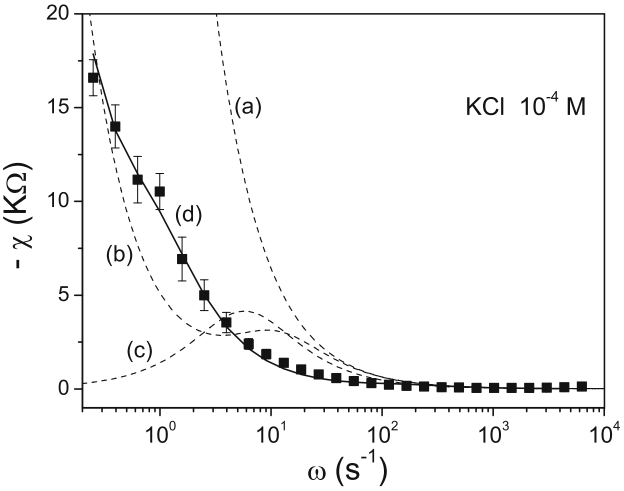

Fig. 4. The imaginary part χ of the impedance Z as a function of the angular frequency ω of aqueous solution of KCl 10^{-4} M fitted with various different models (dashed lines): (a) blocking electrodes, (b) adsorption model with the same adsorption energies, and (c) Ohmic electrodes. The curve (d) is our theoretical fit.

was not possible to fit the data by considering equal adsorption/desorption energies for the positive and negative ions. Curve (c) depicts the fit made by considering Ohmic electrodes, as described in refs. [2, 3]. In this case, particularly with respect to χ, a strong disagreement can be observed between the theoretical model and the experimental data. In the Ohmic model $\chi \to 0$ at $\omega \to 0$, *i.e.*, the system behaves like a resistor. However, this behavior was not experimentally observed in the range of frequency studied. In curve (d) we show the fit made with the model of the present work, in which we consider that the positive and negative ions are absorbed/desorbed in the electrodes with different adsorption/desorption energies. In this case, a good fit was obtained, that was not possible to obtain by considering equal adsorption/desorption energies. The obtained fitting parameters are: $\tau_p = 4.5(5)\,\mathrm{s}$, $\tau_m = 0.032(2)\,\mathrm{s}$, $k_p = 1.7(3) \times 10^{-7}\,\mathrm{m}^{-1}\,\mathrm{s}^{-1}$ and $k_m = 6.8(8) \times 10^{-6}\,\mathrm{m}^{-1}\,\mathrm{s}^{-1}$. According to these results, the mean time at which the K^+ ions remain at the surface is much higher than the time of the Cl^- ions ($\tau_p \gg \tau_m$). In the opposite, the adsorption rate of Cl^- ions is much higher than that of K^+ ($k_m \gg k_p$). If the adsorption length ξ_l is considered as a measure of the adsorption strength, we conclude that the adsorption of the K^+ is stronger than that of Cl^-, as $\xi_p/\xi_m \approx 3.5$. It must be noted, however, that the measurements were performed in a not very low-frequency region. Instead, the angular frequency as 0.1 rad/s appears to be at the beginning of the second plateau of R. It is possible that a fit made in a lower-frequency range could result in different parameters and different conclusions can be achieved about the ionic adsorption on the electrodes.

It is important to note that in all the cases, the fit of the real and imaginary parts of the impedance were made simultaneously. Although the adsorption process is very sensitive to the presence of impurities, we expect that our solution does not have a large amount of impurities (as we have used Milli-Q water and p.a. degree KCl). This eventual presence was neglected in our analysis.

Conclusion

We have analyzed the influence of the adsorption/desorption phenomena on the impedance spectroscopy on a general case in which the adsorption/desorption energies of the positive and negative ions are different. This model is able to describe the experimental results of the real and imaginary parts of the impedance in a solution of water with 10^{-4} M of KCl in the frequency range from 0.1 rad/s to 10^4 rad/s.

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List of symbols

Z	The impedance of the sample (Ω)
R	The real part of Z (Ω)
χ	The imaginary part of Z (Ω)
n_0	The density of ions (m^{-3})
p	means positive
m	means negative
$n_l(z,t)$	The density of ions of charge l ($= p, m$) (m^{-3})
$n_l^*(z)$	The time-independent density of ions (m^{-3})
d	The electrode thickness (m)
$V(z,t)$	The electric potential inside the sample (V)
V_0	The electric potential amplitude (V)

σ	The adsorption (m^{-2})
q	The modulus of the ionic charge (C)
ϵ	The electric permittivity
J	The current densities of ions ($\mathrm{m}^{-2}/\mathrm{s}$)
D	Diffusion constant (m^2/s)
k_B	The Boltzmann constant (Joule/K)
λ	The Debye length (m)
$\eta(z,t)$	The spatial part of $n(z,t)$ (m^{-3})
$V^*(z)$	The electric potential for $V_0 = 0$ (V)
V_C	The electric potential in $z = \pm d/2$ for $V_0 = 0$ (V)
$\phi(z)$	The spatial part of $V(z,t)$ (V)

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