Dielectric Dispersion of Water in the Frequency Range from 10 mHz to 30 MHz

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We investigate the dielectric dispersion of water, specially in the low-frequency range, by using the impedance spectroscopy technique. The frequency dependencies of the real R and imaginary χ parts of the impedance could not be explained by means of the usual description of the dielectric properties of the water as an insulating liquid containing ions. This is due to the incomplete knowledge of the parameters entering in the fundamental equations describing the evolution of the system, and on the mechanisms regulating the exchange of charge of the cell with the external circuit. We propose a simple description of our experimental data based on the model of Debye, by invoking a dc conductivity of the cell, related to the nonblocking character of the electrodes. A discussion on the electric circuits able to simulate the cell under investigation, based on bulk and surface elements, is also reported. We find that the simple circuit formed by a series of two parallels of resistance and capacitance is able to reproduce the experimental data concerning the real and imaginary part of the electrical impedance of the cell for frequency larger than 1 Hz. According to this description, one of the parallels takes into account the electrical properties of interface between the electrode and water, and the other of the bulk. For frequency lower than 1 Hz, a good agreement with the experimental data is obtained by simulating the electrical properties of the interface by means of the constant phase element.

I. Introduction

The theory for the ionic contribution to the electrical impedance of an electrolytic cell was developed long ago by Macdonald.[1] In Macdonald's model, the fundamental equations of the problem are the equation of continuity for the positive and negative ions, and the equation of Poisson for the actual potential across the sample. The model of Macdonald has been extended to consider different experimental situations.[2–7] When there is only one group of ions, and they have the same diffusion coefficient, a simple calculation[8,9] predicts that the real part of the impedance $R(f)$, where f is the frequency of the applied voltage, presents a large plateau ending at the frequency of Debye, f_D. For $f > f_D$, R tends to zero as f^{-2}. On the contrary, the imaginary part χ diverges in the dc limit as f^{-1}. The same frequency dependence is valid in the high-frequency limit, where the ions do not participate any longer to the conduction.

The increasing of $R(f)$ in the low-frequency range can be a signature of (1) ionic adsorption on the electrodes,[10] (2) ambipolar and free diffusion related to the difference of the diffusion coefficients of the positive and negative ions,[11] (3) the ohmic characteristic of the electrodes,[12,13] and (4) the presence of two groups of ions.[14]

From this brief introduction it follows that, in the dc limit, several mechanisms can be responsible for the increase of R in the low-frequency limit.

A simple system that can be used to investigate these phenomena, specially in the low-frequency range, is the Milli-Q water. It refers to water that has been purified and deionized to a high degree by a water purification system manufactured by Millipore Corp. It is usually employed in many laboratories

around the world for different purposes. The advantage of this system is its reliability and easy way to obtain in a reproducible manner. In the literature, only a small number of papers deal with the behavior of the impedance of water in a wide range of frequencies. A few aspects of the dielectric behavior of water as a function of f were reported in ref 15. In ref 16 the authors performed measurements of the water impedance in the frequency range from 0.01 to 10^5 Hz. Their results were analyzed in terms of equivalent circuits, without any more elaborate physical mechanism proposed.

As we will see in the following, the frequency dependencies of R and χ of water could not be fully understood by means of the usual description of its dielectric properties as an insulating liquid containing ions, based on the continuity equations of the positive and negative ions, and on the equation of Poisson for the actual potential across the sample. This is due to the incomplete knowledge of the parameters entering in the fundamental equations describing the evolution of the system, and of the mechanisms regulating the exchange of charge of the cell with the external circuit. For this reason, sometimes, an approach based on the model of Debye[17] may be used to get insights about the physics of the electric conduction in water and similar systems.[18]

Our paper is organized as follows. In section II we describe the experimental setup and the cell used in the experimental investigations. In section III the model of Debye is briefly discussed. The experimental data concerning the real and imaginary part of the electrical impedance the cell are presented in section IV. In the same section we show the best fit of the experimental data obtained by means of the model of Debye. A discussion on the standard model used for the interpretation of the electrical impedance of an electrolytic cell, based on the drift-diffusion equations and the equation of

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Poisson is also reported. From the experimental evidence that this model does not work for water, we conclude that other mechanisms play an important role in the polarization of water in the low-frequency region. The electrical circuits able to simulate the experimental data are discussed in section V. There it is shown that a simple circuit formed by the series of two parallels of a resistance and a capacitance, one of which taking into account the bulk properties, and the other the properties of the interface between the bulk and the electrode, works well for frequencies larger than 1 Hz. For frequencies smaller than 1 Hz, the agreement between this simple electrical circuit and the experimental data is rather poor. In this case, we show that, if the properties of the interface solution−electrode are described by means of the constant phase element, the agreement between the theoretical predictions and the experimental data is good. Section VI is devoted to the conclusions.

II. Experimental Section

In this work, we investigate the dielectric dispersion of water (from the Milli-Q Direct-Q3 apparatus), specially in the low-frequency range, by means of the impedance spectroscopy technique.[21] We are aware that, in the deionization process, some ionic species are still present in the sample, contributing to the conduction process. The water we have used has pH = 7.2 and resistivity ρ = 18.2 MΩ cm. Specific properties related with the purity of the deionized Milli-Q water can be found in ref 22. The measurements were performed using a Solartron SI 1296A impedance/gain phase analyzer with a 1296 dielectric interface. We used two steel electrodes of area S = 0.5 cm², spaced 0.5 mm from each other, filled with Milli-Q water at room temperature. The data were collected as a function of the frequency of the applied electric field in the range from 10^{-2} Hz to 30 MHz. The real $R(\varepsilon')$ and imaginary $\chi(\varepsilon'')$ parts of the electrical impedance (dielectric constant) were measured. The amplitude of the ac applied voltage was 20 mV. The steel electrodes were polished with alumina powder of three different diameters (3, 0.3, and 0.05 μm). After each polish, the electrodes were rinsed with pure water in ultrasonic bath for 10 min.

III. Model of Debye

We analyze our experimental data in the framework of the model of Debye, developed for linear systems.[17] In this theory, the relation between the electric displacement, $D(t)$ and the electric field, $E(t)$, in an insulating isotropic medium is

$$D(t) = \varepsilon_\infty E(t) - (\varepsilon_s - \varepsilon_\infty) \int_0^\infty \phi(\eta) E(t - \eta) \, d\eta \quad (1)$$

where ε_∞ and ε_s are the high-frequency and static dielectric constant of the medium, and ϕ is the response function of the system to the external electric field. In the case where the external field is a simple periodic function of the time $E(t) = E(\omega) \exp(i\omega t)$, in such a manner that $D(t) = D(\omega) \exp(i\omega t)$, where $D(\omega) = \varepsilon(\omega) E(\omega)$, we get

$$\varepsilon(\omega) = \varepsilon_\infty + (\varepsilon_s - \varepsilon_\infty) \int_0^\infty \phi(\eta) e^{i\omega\eta} \, d\eta \quad (2)$$

In several problems a good approximation for $\phi(t)$ is $\phi(t) = (1/\tau) \exp(-t/\tau)$, where τ is a characteristic time of the material, known as relaxation time. In this case, from eq 2 we obtain that the frequency dependence of the dielectric constant is

$$\varepsilon(\omega) = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + i\omega\tau} \quad (3)$$

A generalization of the model of Debye to the case where the system is described by means of a distribution of relaxation time has been considered by Macdonald and Brachman[19] and by Macdonald.[20] We limit our case to the situation where one relaxation time is enough for a reasonably good description of the experimental data.

In the case where the medium under consideration has a dc conductivity σ, the effective dielectric constant is

$$\varepsilon(\omega) = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + i\omega\tau} - i\frac{\sigma}{\omega} \quad (4)$$

The dielectric constant is separated in its real and imaginary parts as $\varepsilon(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)$.

Let us consider a dielectric medium, with a dc conductivity, subjected to a homogeneous electric field. In this framework, in the slab approximation, the complex capacitance is given by $C = \varepsilon(\omega)(S/d)$, where S and d are the area of the electrode surface and the thickness of the sample, respectively, and $\varepsilon(\omega)$ is given by eq 4. The electrical impedance of the sample, defined by $Z = 1/(i\omega C)$, has an equivalent resistance, R, and reactance, χ, given by

$$R = \frac{1}{\omega} \frac{\varepsilon''}{\varepsilon'^2 + \varepsilon''^2} \frac{d}{S} \quad \text{and} \quad \chi = -\frac{1}{\omega} \frac{\varepsilon'}{\varepsilon'^2 + \varepsilon''^2} \frac{d}{S} \quad (5)$$

in such a manner that $Z = R + i\chi$.

From eqs 4 and 5 it follows that in the dc limit the medium behaves as a pure conductor and, in the high-frequency limit, as a dielectric medium of dielectric constant ε_∞. In our case, ε_∞ has to be identified with the dielectric constant of the water free of ions. Since pure water presents a dispersion at a frequency of the order of 1 GHz,[23] it follows that, for the part of the spectra investigated by us, $\varepsilon_\infty \sim 80\varepsilon_0$.

IV. Results and Discussion

Figure 1 presents the experimental results of R and χ, of water. The real part of R increases when the frequency tends to zero. For frequencies larger than 1 kHz, the frequency dependencies of R and χ are the usual ones. R presents a large plateau up to the frequency of Debye, and χ has a large maximum for a frequency that depends on the thickness of the sample d, as $1/\sqrt{d}$, and a narrow minimum for a frequency independent of d.

In Figure 2 is shown the results of ε' and ε''. According to our experimental data, the real part of the dielectric constant, ε', of the cell tends to a constant ($\sim 3 \times 10^7$) for $f \rightarrow 0$, while ε'' increases in this same limit. For frequencies larger than ~ 1 kHz, $\varepsilon' \rightarrow 80\varepsilon_0$, and ε'' varies with f^{-1}, as expected. In the same figure, we compare the experimental data with the theoretical prediction based on the Debye model with one relaxation time. For the best fit we have assumed $\varepsilon_\infty = 80\varepsilon_0$, $\sigma = 15$ μS/m, $\tau = 0.9$ s, and $\varepsilon_s = 1.9 \times 10^7 \varepsilon_0$. These values are in agreement with the part of the spectrum of the dielectric constants in the high-frequency region.

From the value of ε_s we cannot estimate the bulk density of ions, N, in the water used for the experiment. In fact, as discussed in ref 8, the presence of the ions is responsible, in the case where the electrodes are perfectly blocking, for a

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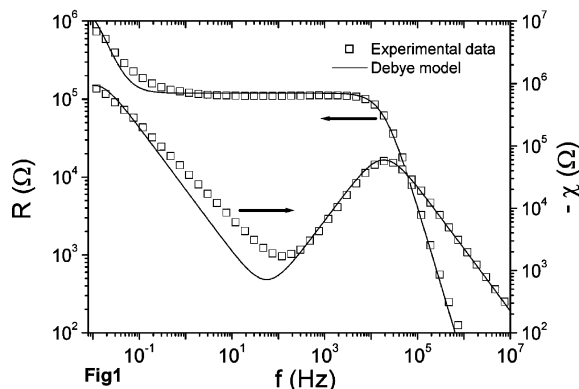
Figure 1. $R = R(f)$ and $\chi = \chi(f)$. The continuous curves are the best fit obtained with the model of Debye, where a dc conductivity is considered.
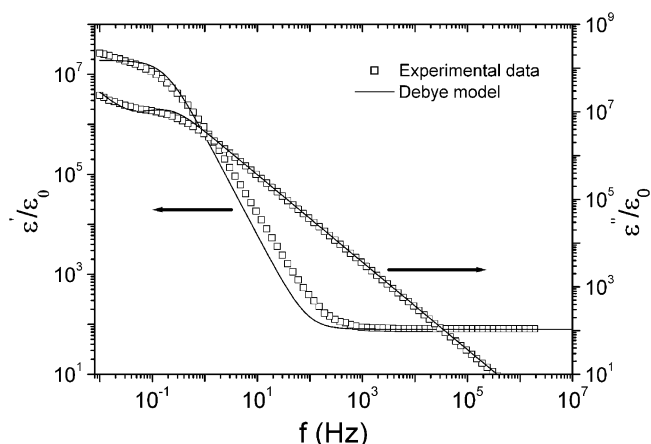
Figure 2. Real and imaginary part of the dielectric constants ε' and ε'' of Milli-Q water as a function of the frequency f. The solid curves are the fit of Debye model.

renormalization of the dc dielectric constant, independent of the diffusion coefficients and on the number of groups of ions according to $\varepsilon_s = \varepsilon(d/2\lambda)$, where ε is the dielectric constant of the liquid in the absence of ions (and in our case $\varepsilon_\infty = 80\varepsilon_0$), d the thickness of the sample, and λ the length of Debye. The length of Debye is related to the bulk density of ions by

$$\lambda = \sqrt{\frac{\varepsilon K_B T}{2Nq^2}} \qquad (6)$$

where $K_B T$ is the thermal energy (K_B is the constant of Boltzmann and T the absolute temperature), N the bulk density of ions, in thermodynamical equilibrium, and q the electrical charge of the ions, assumed identical in all the aspects, except for the sign of the charge. However, by using this expression for ε_s, despite the fact that a reasonable fit is achieved to both R and χ, an inconsistent density of ions as high as $N \sim 10^{24}$ m^{-3} is obtained, when compared to the measured pH = 7.2 of our Milli-Q water. To overcome this inconsistency, a supplementary mechanism is necessary to be considered to account for the experimental results. We have tried to fit the experimental data by taking into account the ionic adsorption on the limiting electrodes, or by means of the model where the electrodes are assumed not blocking.

In the first case the adsorption phenomenon on the electrodes has been described in the framework of the Langmuir model, that is expected to work well since we are in the limit of small

surface coverage.[10] In the second case, the current across the electrodes has been assumed proportional to the surface electric field.[12] In both cases, it is impossible to obtain a reasonable fit in the low-frequency region of the spectra when the bulk density of ions is of the order of 10^{20} ions/m^3, and the diffusion coefficient $D \sim 9 \times 10^{-9}$ m^2/s. The disagreement between the theoretical predictions of the models considered by us and the experimental data is mainly connected to the imaginary parts of the impedance. Using the expected values for the bulk density of ions and for the diffusion coefficient, the reactance of the cell in the low-frequency range is very large with respect to the experimental one. A possible explanation for this effect can be related to the actual value of the dielectric constant. In fact, in the theoretical models developed to describe the electrical behavior of an electrolytic cell, the system is described as a dispersion of ions in a dielectric liquid. The dielectric constant of the liquid is assumed to be identical to that of the liquid free of ions. This approximation works well until the density of ions is negligibly small with respect to the density of the liquid in which they are dispersed. However, in the low-frequency region, the ions are confined to a surface layer whose thickness is of the order of the length of Debye. In the limit of small applied voltage, where the system behaves in a linear manner, the bulk electric field is very small, and the system can be approximated as two surface condensers, of thickness of the order of the length of Debye. In this case the density of ions in the surface layer can be important, and actual dielectric constant depends on the ion density.[24] To evaluate the dependence of the actual dielectric constant on the density of ions when it cannot be treated as a perturbation is not an easy task.[17] The work is in progress, and a reanalysis of the experimental data will be published elsewhere. For this reason, we limited the analysis of the experimental data in the framework of the model of Debye. The solid lines in Figure 1 are the best fits obtained with the Debye model (eqs 5), with the same values of ε_∞, ε_s, and τ as before.

We are aware that the model of Debye is based on the assumption that the electric field in the sample is position independent, and hence it is not valid in the presence of ionic contamination. However, for a reasonably good agreement between the experimental data and the theoretical prediction of the model we can conclude the following:

(1) in pure water the spatial inhomogeneities of the electric field due to the ions is negligible;

(2) the dielectric constant of the water in the "high" frequency region, ε_∞ ($\sim$1 MHz) coincides with $80\varepsilon_0$;

(3) the electrical conductivity, σ, takes into account the nonblocking character of the electrodes, and of the conductivity of the water;

(4) the static dielectric constant, ε_s, is rather large and it is not due only the ionic renormalization.

As discussed in refs 19 and 20, a generalization of the model of Debye to the case of several relaxation times is possible. A physical justification for this generalization is related to the presence of several groups of ions, with different mobilities in the water under investigation. As discussed in ref 8, when only one group of ions is present, and the positive and negative ions have the same mobility, the frequency dependencies of the real and imaginary parts of the dielectric constant can be described by a model of Debye, where the relaxation time depends on the diffusion coefficient and the length of Debye. A generalization to the case of several groups of ions is not simple, but it works. Of course, from the distribution of the relaxation time is not possible to characterize the different groups of ions.
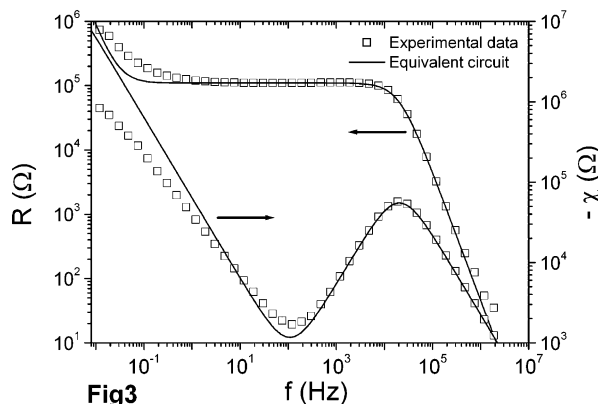
Figure 3. $R = R(f)$ and $\chi = \chi(f)$. The continuous curves are the best fit obtained with the equivalent circuit formed by the series of two parallels of a resistance and a capacitance. One of the parallels describes the bulk properties and the other the properties of the interface water electrode.

V. Analysis of the Data by Means of Equivalent Electrical Circuits

For practical purposes, our experimental data can be interpreted by means of equivalent electrical circuits. By assuming that the bulk and surface layer are equivalent to a parallel of a resistance R_B and a capacitance C_B, and R_S and C_S, respectively, in series, the equivalent impedance of the sample is $Z = Z_B + Z_S$, where

$$Z_B = \frac{-iR_B\chi_B}{R_B - i\chi_B} \quad \text{and} \quad Z_S = \frac{-iR_S\chi_S}{R_S - i\chi_S} \quad (7)$$

with $\chi_B = 1/(\omega C_B)$ and $\chi_S = 1/(\omega C_S)$. The values of R_B can be easily determined by the experimental data, and it is $R_B \sim 10^5 \Omega$. On the contrary, C_B can be evaluated knowing the value of the dielectric constant and of the geometrical characteristics of the cell, and it is found to be $C_B = 80\varepsilon_0 S/d \sim 7.08 \times 10^{-11}$ F. The bulk part of the cell is responsible for the part of the spectra in the high-frequency region. The values for R_S and C_S can be deduced by means of a best fit procedure of the experimental data on the whole spectra. A simple calculation gives $R_S = 5 \times 10^7 \Omega$ and $C_S \sim 2.5 \times 10^{-6}$ F. The fit of $R = R(f)$ and $\chi = \chi(f)$ is shown in Figure 3. The agreement is reasonably good, taking into account the simplicity of the model. Of course, the physical interpretation of R_S and C_S is not simple. One can states that R_S and C_S are related to the presence of the electrodes, responsible for an ionic confinement, or for a change of the physical properties of the water. However, the reason of these change are difficult to model.

Another possibility to fit the data is by means of the constant phase element.[25,26] According to this approach, from the electrical point of view the interface between the bulk and the electrodes is described by a surface impedance

$$Z_{nt} = A(i\omega)^{-\nu} \quad (8)$$

where A and ν are two phenomenological parameters characteristics for the electrodes and the solution (in our case water). For a discussion on Z_{int} see refs 21 and 26. In this case, the total impedance of the sample is $Z = Z_B + Z_{int}$. In this framework, using for R_B and C_B the values reported above, it is possible to determine A and ν by the best fit of the
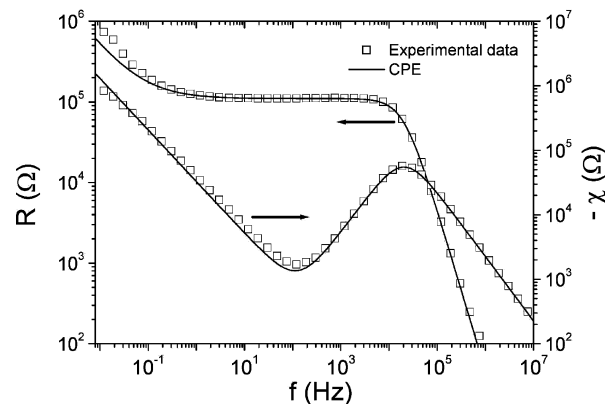
Figure 4. $R = R(f)$ and $\chi = \chi(f)$. The continuous curves are the best fit obtained with a electrical circuit where the electrical properties of the interface are described by means of the CPE.

experimental data. Using our experimental data, we get $A = 1.5 \times 10^5$, in SI units, and $\nu = 0.8$, which are reasonable values.[27] The comparison between the experimental data and the model based on the CPE is shown in Figure 4.

Also in this case, the physical interpretation of A and ν is far from being evident. As R_S and C_S they are related to the parameters entering in the description of Debye, but it is not clear how.

VI. Conclusion

In conclusion, we have investigated the dielectric dispersion of Milli-Q water in a wide frequency range using the impedance spectroscopy technique. Our experimental data is described by the model of Debye, by invoking a dc conductivity of the cell, related to the nonblocking character of the electrodes. Other models allow a description of the experimental data, but at the moment they are equivalent to the model of Debye.[28,29] For practical purposes, the sample can be modeled as a series of two parallels, formed by a resistance and a capacitance, describing the electrical properties of the bulk and the surface layer. The agreement between the experimental data and theoretical predictions is reasonably good, taking into account the simplicity of the model. We have considered also a model where the surface layer is described by means of the constant phase element (CPE). Also in this case, the agreement of the experimental data and the model is good.

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