



Electrical and dielectric properties of water

Propriedades elétrica e dielétrica da água

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A água é uma das substâncias mais importantes do planeta. É composta por hidrogênio e oxigênio, ambos de grande importância química e para vida humana. Embora na literatura científica existam vários estudos sobre as propriedades físicas e químicas da água, muito ainda pode ser estudado sobre essa substância. Neste estudo, descreveremos as propriedades elétrica e dielétrica da água na fase líquida, assim como, a impedância, constante dielétrica, polarização molar e momento dipolo em função da frequência (1-20 kHz) na faixa de temperatura entre 288 e 314 K. As medidas de constante dielétrica e impedância foram realizadas com auxílio de um analisador de impedância. Ademais, foi utilizado um sistema capacitivo de placas paralelas, todo experimento foi blindado para minimizar os efeitos de interferência eletromagnética (ruído) e conectado ao aterramento da rede elétrica do laboratório. Os valores de momento de dipolo foram estimados aplicando a teoria de Kirkwood com base na definição de campo local de Onsager para líquidos polares.

Palavras-chave: Propriedades elétrica e dielétrica, Polarização molar e momento de dipolo, Teoria de Kirkwood.

Water is one of the most important substances on planet. It's constituted by hydrogen and oxygen elements, both of great importance chemistry and fundamental to human life. Although there are many studies about your physical and chemical properties in the scientific literature, much can be studied yet about this substance. In this study we report the electrical and dielectric properties of the water in liquid phase, such as impedance, dielectric permittivity and dipole moment as a function of frequency (1-20 kHz) in the temperature range between 288 and 314 K. The impedance and dielectric permittivity measurements were carried out in experimental apparatus equipped with an impedance analyzer. In addition, a capacitive system of parallel plate was and entire experiment was shielded to minimize electromagnetic interference effects (noise), and connected to the grounding of the laboratory electrical network. The dipole moment values were estimated applying the Kirkwood's theory based on the definition of Onsager's local field for polar liquids.

Key words: Electrical and dielectric properties, Molar polarization and dipole moment, Kirkwood's theory.

1. INTRODUCTION

Water is ubiquitous in nature, playing key roles in a range of fields as varied as biochemistry, earth sciences, and atmospheric chemistry. In addition, water is one of the most common polar solvents used in synthetic chemistry. The power of liquid water as a solvent stem in part from its unusual properties, often attributed to its strong hydrogen-bond network [1]. Although there are many studies about your physical and chemical properties in the scientific literature [1-3], much can be studied yet about this essential substance to life on the planet.

The idea of dipole momentum of polar molecule was first introduced by Debye (1945) [4] to explain on thermal dependence of electric permittivity. Debye used earlier orientation theory of permanent magnetic moments, given by Langevin. The frequency dependence of electric permittivity and conductivity for the gas and dilute solution also was given by Debye in 1945 [4].

Some studies about dielectric constant in liquid water are not so recent. Malmberg and Maryott (1956) [5] conducted studies on dielectric properties of water in liquid phase in the 0 to 100°C temperature range. In addition, Haggis et al. (1952) [6] carried out a study of the dielectric properties of water in solutions aqueous of ions and organic molecules. These authors observed that the water relaxation time was shortened due to the presence of positive ions and

lengthened by hydrogen bond-forming molecules. The properties of water were treated using a statistical method in which the numbers of molecules in four, three, two, one, and zero-bonded states were estimated from dielectric and latent heat data. Fair agreement with experimental data is obtained in calculating the static dielectric constant of water at the 0-370°C range, as well as Kirkwood's dielectric theory and Verwey's calculation of the dipole moment of four-bonded water molecule.

Other paper describes the dielectric permittivity of water at the interface of biological membranes considering the effect on energy coupling mechanism, at which provide solutions to the long-lasting problem of the protonmotive force in mesophilic and alkaliphilic bacteria [3]. More recently, Rusiniak (2004) [7] studied the electric properties of distilled water in 5 Hz to 13 MHz frequency range. Dielectric permittivity, conductivity and loss tangent measurements were carried out at water with non-blocking electrodes for different thicknesses of the sample and for various oscillator levels, in 20-90°C temperature range with 10°C interval. From results obtained the author concluded that the water has a stable domain structure in the studied temperature range. Such observations were summarized as follows: the dielectric constants of domains grow linearly with increase of temperature; the domain relaxation time decreases as the temperature increases as a result of the water viscosity changes; the conductance dispersion grows with increasing temperature; and the domain structure changes as the oscillator level is too big.

In our study, we report the electrical and dielectric properties of water in liquid phase, such as impedance, electric conductive, dielectric permittivity, molar polarization and dipole moment as a function of low frequency (1-20 kHz) in the 288-314 K temperature range. The dipole moment values were estimated applying the Kirkwood's theory based on the definition of Onsager's local field [10,11]. The behavior of molar polarization and dipole moment of the water as a function of frequency here presented has not been evaluated by the literature to our knowledge.

2. MATERIALS AND METHODS

The temperature-dependent impedance, conductive and dielectric constant capacitance measurements on water (MiliQ) in liquid phase were carried out using an experimental apparatus composed of an impedance analyzer Sorlatron Analytical model 1260 through a dielectric interface Sorlatron Analytical 1296. In addition, a capacitive system of parallel plates was used (built by the authors) and entire experiment was shielded to minimize electromagnetic interference effects (noise), and connected to the grounding of the laboratory electrical network. Details about experimental setup can be found elsewhere [12].

All measurements presented here were performed with frequency in the 1–20 kHz range, values that can be considered to be nearly static field, according to the theory of the electric polarization [8]. To obtain the dielectric constant normalized, we measured the capacitance normalized (C/C_0) as a function of temperature, obtaining only the desired dielectric permittivity, $\epsilon(T)$. Experiments were carried out with temperature ranging from 288 to 314 K. The dipole moment of the water was taken through from the analysis of the experimental data on temperature dependence dielectric permittivity, where it is was found in the liquid state. The measurements were repeated several times to certify reproducibility. Results reported experiments were taken with a precision of 0.001.

3. RESULTS AND DISCUSSION

In Figure 1 is shown the electric impedance behavior of pure water in the liquid phase as a function of low frequency in the 1-20 kHz range for temperature region between 288 and 314 K. According to the presented curves, it is possible observe clearly that the impedance values decrease with increasing temperature. Another important aspect is linked to the fact that its behavior is very similar for all temperature values. In fact, all impedance curves show that the values decrease very rapidly for frequency around 0 Hz and, for values above, they are

practically constant at all temperatures. It is worth note that the experiments were performed in a frequency range considered low and in a short temperature range, characteristic of high purity water essential for analysis of trace in the environmental chemistry, medical and pharmaceutical areas [13].

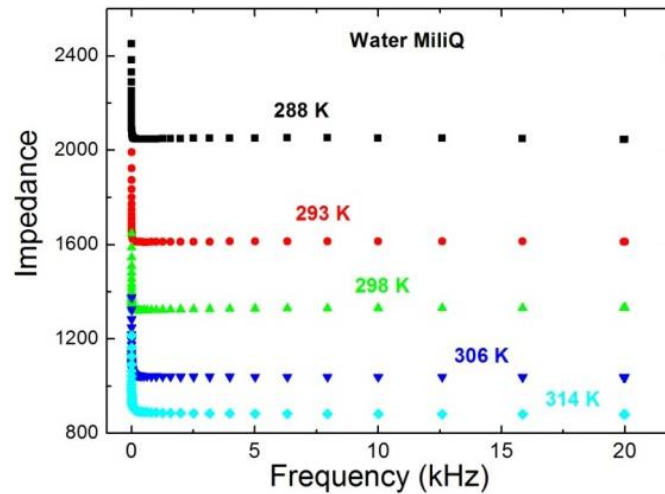


Figure 1. Impedance as a function of frequency in the 288 to 314 K temperature range.

The effect of temperature on electrical conductivity, which was measured as a function of frequency is shown in Figure 2. From the results, we can see that the behavior of the conductivity is completely inverted at comparison to the impedance, even when the temperature is increased. These values were measured in the same intervals of frequency (1-20 kHz) and temperature (288-314 K).

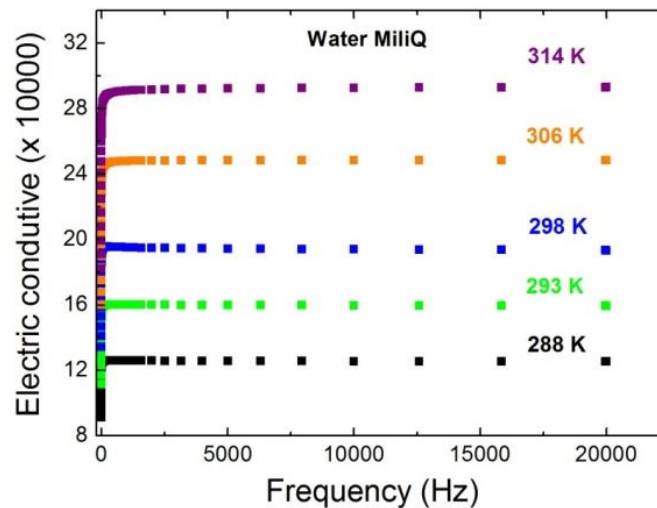


Figure 2. Electric conductive as a function of frequency in the 288-314 K temperature range.

From the results, we observe that there was no significant change in the behavior of the impedance and of the conductive with variation of both frequency and temperature (see Figures 1 and 2). Such results showed to be at good agreement with others already published in the literature [14,15].

In Figure 3 we can be see the dielectric constant as a function of frequency in the following 288-314 K temperature region. From the values of dielectric constants obtained at different temperatures to 15 points in sequence, the plots of Figure 4 were made. In which it can be clearly observed that its behavior with the temperature variation is linear.

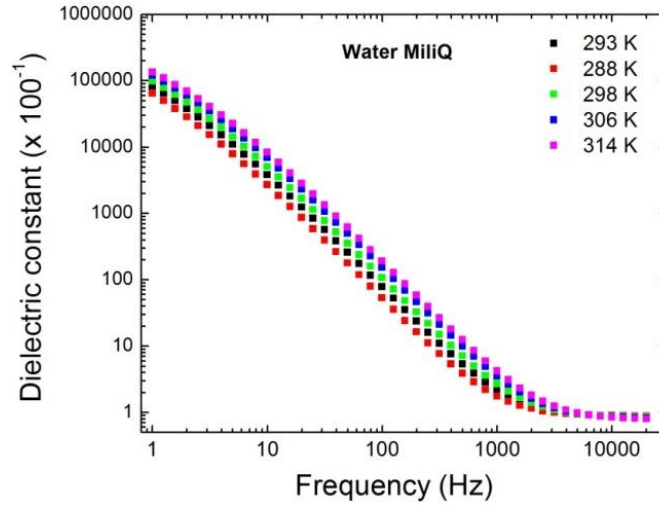


Figure 3. Dielectric constant as a function of frequency in the 288-314 K temperature range.

It is important to note that the curves of $\varepsilon(T)$ have different inclinations as well as different angular coefficients. Such results are in good agreement with data already published in literature [14]. The linear regression of these plots allowed define the linear and angular coefficients of the curve, which are associated with the average molecular polarizability and the dipole moment of the water in liquid phase, respectively. The molar polarization values can be obtained by mean of the values of dielectric permittivity, molar mass and molar density of pure water and can be described according to Kirkwood's theory [11]. Its temperature dependent behavior is analyzed as a linear function of reciprocal of the absolute temperature.

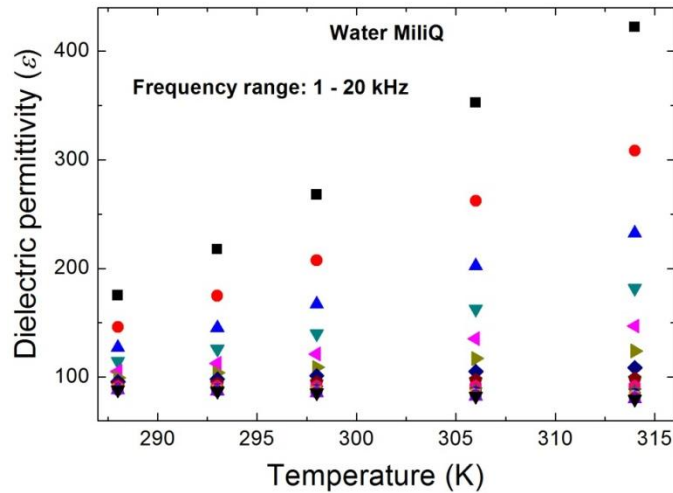


Figure 4. Dielectric constant as a function of temperature in frequency range from 1 to 20 kHz.

In Table 1 are summarized the experimental results obtained for molar polarizations (MP) as a function of absolute temperature which can be calculated from the Kirkwood-Fröhlich's equation [9,11]

$$MP = \frac{(\varepsilon - 1)(2\varepsilon + 1)}{9\varepsilon} \left(\frac{M}{\rho} \right) = \frac{N_A}{3} \left[\alpha + \frac{(\mu)^2}{3\varepsilon_0 k_B T} \right] \quad (3),$$

where ε is the dielectric permittivity, M is the molecular mass, ρ is molecular density, N_A is the Avogrado's number, α is the molecular polarizability (polarizability volume) of the molecule, μ is the dipole moment, ε_0 is the electrical permittivity in vacuum, T is the absolute temperature,

and k_B is the Boltzmann's constant. The Equation (3) is associated with a function (molar polarization) of the type $y = a + bx$, where $a = N_A\alpha/3$ is the linear coefficient, $b = N_A(\mu)^2/9\epsilon_0k_B$ is angular coefficient and $x = 1/T$. The behavior of the molar polarization is a function of the inverse absolute temperature, $1/T$.

The dipole moment values were estimated applying the Kirkwood's theory [8-11] and their values are given in Table 1, which we can observe that the molar polarization and the dipole moment have certain dependence with frequency. Also in this table, it can be seen that the molar polarization values are different at each column, which decrease with increasing frequency. On the other hand, their values increase with increasing temperature.

Is notable the behavior of the dipole moment at function of the frequency, being the maximum value (1.42 D) to 20 kHz while that at 7.9 kHz is closed 0.81 D. For frequency values below of ~ 7 kHz, the values of the dipole moment are minor than zero, suggesting that occurred an inversion of polarity in the water molecule, which are not presented in table. It is important to note also an increase in the dipole moment with the increase of the frequency.

Table 1 - Molar polarization and dipole moment of the water depending on the reciprocal of the absolute temperature and of the frequency.

Temp. (K ⁻¹)	MP* at 1kHz	MP at 5.0 kHz	MP at 6.3 kHz	MP at 7.9 kHz
3.47	699.12	369.29	361.86	357.97
3.41	868.77	374.26	363.23	357.99
3.35	1069.90	378.84	364.03	355.81
3.26	1408.18	386.69	363.29	350.63
3.18	1686.48	392.56	363.73	347.43
DM [†]	-----	-----	-----	0.81D
Temp. (K ⁻¹)	MP at 10kHz	MP at 12.6kHz	MP at 15.8 kHz	MP at 20 kHz
3.47	355.82	353.16	351.64	350.89
3.41	353.02	349.65	347.62	346.16
3.35	349.66	345.07	341.73	339.95
3.26	341.44	334.55	329.89	326.86
3.18	335.05	326.33	320.59	316.65
DM	1.11 D	1.26D	1.36D	1.42D

*MP: Molar Polarization for Kirkwood's model

†DM: Dipole moment, 1 D = 3.328×10^{-30} C.m

Such behavior of the dipole moment at low frequencies ($< \sim 7$ kHz), it indicates that can be occurring an alignment of the μ on a spherical (cavity) neighboring molecules compared to the central one in a configuration antiparallel. This causes a lowering in the dipole moments to the values inferior, achieving negative values.

4. CONCLUSIONS

From the results we were able to observe that the impedance, conductive and dielectric permittivity of the liquid water not undergo significant changes with variation of the frequency and the temperature. While the molar polarization and the dipole moment showed certain dependence in a small ratio of the low frequency region, principally. We showed that experimental results of the electrical and dielectric properties of the water are in good agreement with data already published in literature. The dipole moments of the water as a function of the low frequency presented here are reported at first time at our knowledge. All their values were determined using Kirkwood's theory, which use the definition of Onsager's local field.

5. ACKNOWLEDGMENTS

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