



Dielectric spectroscopy of water at low frequencies: The existence of an isopermittive point

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ABSTRACT

We have studied the relative permittivity of water from 100 Hz to 1 MHz. We have found that there is a frequency where this parameter is independent of temperature, and called this the isopermittive point. Below this point the relative permittivity increases with temperature, above, it decreases. To understand this behavior, we may consider water as a system of two species: ions and dipoles, the first giving rise to the so-called Maxwell–Wagner–Sillars effect, the second obeying the Maxwell–Boltzmann statistics. At the isopermittive point, the effects of both mechanisms in the dielectric response compensate each other.

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1. Introduction

Water, the most abundant substance in Earth, is fundamental for life, and for this reason it has been widely studied for a long time. Due to their atomic and molecular interactions, water is an excellent solvent for many substances [1]. Water molecules not only join themselves by hydrogen bonds, but can also do the same with other molecules. Biological functions are possible only in the presence of water. It is necessary for cell dynamics and plays a relevant role in the stability and flexibility of biomolecules [2,3]. Indeed, many studies have been performed in order to understand the mechanisms of water–protein interaction. In this context, it has been always important to evaluate how the hydration level of proteins influences their conformational motions. In general, water–protein interaction takes place in two tiers: one corresponding to water molecules interacting directly with proteins and the other through weaker forces in bulk water [4,5].

One of the most powerful techniques to study the molecular response of water is dielectric spectroscopy. The macroscopic polarizability of a material can be characterized in terms of the relative permittivity (ϵ') [6]. In order to avoid the problem of ionic conduction in water, the dielectric studies are usually performed at frequencies higher than 1 GHz [7–9]. It is widely accepted that a reference value of ϵ' is 80 (at 20 °C) in the entire region of low frequencies (less than 1 GHz), and only when the temperature changes, ϵ' changes [8,10,11]. This number is crucial to explain salt solubility in water and the origin of cell functioning. In the present Letter, we experimentally revisit this subject, measuring the relative permittivity of water at low frequencies. We found that the behavior of this parameter in this regime may have an importance

not considered before. Using the dielectric spectroscopy technique, we measured the temperature dependence of ϵ' in the frequency region from 10^2 to 10^6 Hz. Contrary to the expectations, we found that ϵ' varies as a function of frequency. Moreover, we found that at a well defined frequency its value is independent of temperature. We propose to call this frequency the isopermittive point. Below this frequency ϵ' increases with temperature, above, it decreases. In order to understand this behavior, we consider that water can be seen as a system of two species: ions and dipoles at different concentrations. So, similar to the existence of an isosbestic point in reversible chemical processes, where two species exchange concentrations under a temperature change [12], at the isopermittive point the effects of both dielectric contributions compensate each other.

2. Experimental

2.1. Setup

The experimental setup used in this work is similar to the one employed in a previous study [13]. The central piece of our system is a stainless steel cylindrical capacitor with length 25 cm consisting of an inside electrode with diameter 0.47 cm separated by 0.23 cm from the outside electrode, whose wall has 0.11 cm of width. The capacitor is surrounded by cylindrical Nylon shell and all together is put inside a coil made of a copper pipe. The whole piece, in turn, is placed within an aluminum tube and fixed by two taps of the same material at the ends. The electrodes are connected with copper wires to BNC connectors located at the outside of the taps. In order to change in a controlled way the temperature of the system, water flows through the coil. The outer aluminum tube not only sets the working temperature but also acts as a Faraday cage to electrically isolate the capacitors and connectors from

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the outside environment. The temperature of the device (the aluminum tube with the copper coil and capacitor inside) is controlled using a Thermo Electron heater (Haake DC10), that pumps water continuously. Because the measurements are very sensitive to temperature fluctuations, the aluminum tube was wrapped with a roll of 7 cm fiberglass and placed inside of a closed cooler. A thermocouple is connected at the wall of the copper pipe and monitored with a multimeter and a computer. The precision in the temperature measurements was about 0.2 °C. The capacitances of the capacitor, with and without water, are measured by a LCR meter model 4284A, which operates in the range of 20 Hz–1 MHz, with an accuracy of $\pm 0.05\%$. The LCR meter has been wrapped in a wire netting to further reduce electromagnetic noise.

2.2. Methods

The capacitor is totally filled with 11.9 ml of the liquid sample to study (water of different salinity and water mixtures, see Section 3). The measurements start when the system is at 26 °C, and thereafter, the temperature increases each 2 °C until 40 °C. Every 2 °C we measure the value of the capacitance. After each temperature increment, we wait approximately 30 min to reach thermal equilibrium in the whole capacitor. Every measurement is performed in a frequency range from 100 Hz to 1 MHz, with an oscillating voltage of 1 V. Due to the fact that the capacitor is much longer than the gap between the electrodes, it is not necessary to use a guarded electrode. ϵ' in the figures shown below is directly the ratio of the measured capacitances with the capacitor filled and empty.

3. Results and discussion

Figures 1 and 2 show the frequency dependence of ϵ' of bi-distilled water (18.2 M Ω cm) measured at different temperatures, from 26 to 40 °C. We can distinguish two behaviors: on one hand we observe that ϵ' has an enormous value at 100 Hz and it reduces drastically as the frequency increases, see Figure 1. On the other hand, at high frequencies, near 1 MHz, ϵ' is almost constant, see Figure 2. Note that in each regime the temperature has inverse effects: while a temperature increment makes ϵ' to augment in the first regime, it causes a decrease in the second.

Water molecules can autodissociate forming ion pairs (H^+ and OH^-) [14–16]. If the temperature is increased, the number of ions from the separation of molecules increases too and a grad-

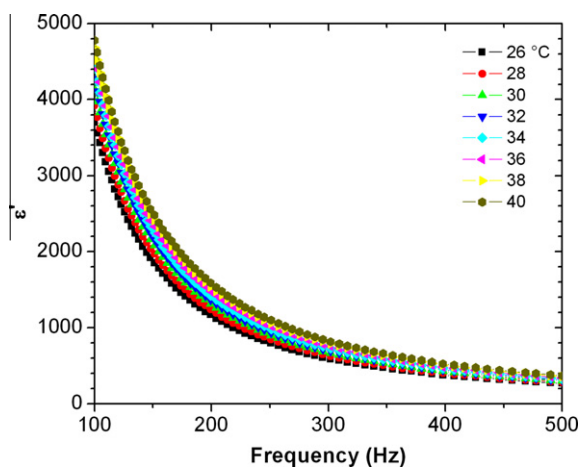


Figure 1. Relative permittivity (ϵ') of water as a function of frequency (100–500 Hz) at different temperatures. These particular plots represent a single experiment.

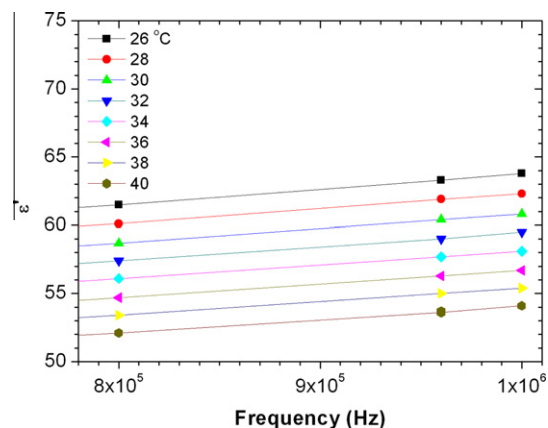


Figure 2. Relative permittivity (ϵ') of water as a function of frequency (0.8–1 MHz) at different temperatures.

ual decrease of the pH is obtained [17]. When an oscillating electric field is applied to the water sample contained in the capacitor, different dielectric processes can occur depending on the frequency of the field. At low frequencies, a phase difference appears between the electrodes as a result of two dielectric phenomena which occur simultaneously; the dipoles align in the direction of the applied field while the ionic pairs move towards the electrodes (Maxwell–Wagner–Sillars (MWS) phenomenon [18]). Even if the number of ion pairs is much lower than water molecules, the MWS phenomenon is dominant. This is the reason why, under a temperature increment, ϵ' increases. At high frequencies, the polarity of the electrodes changes so quickly that only the water dipoles are able to respond effectively, and therefore, the value of ϵ' follows the Maxwell–Boltzmann statistics. As the thermal energy is increased, it becomes more and more difficult for the dipoles to align in the direction of the field and the dielectric response decreases.

The most striking result of this work is that the observed mechanisms at low and high frequencies give rise to effects that compensate each other as the temperature is varied. In other words, at one point (frequency), ϵ' is independent of temperature, as shown in Figure 3. In the spectroscopy of reversible chemical reactions a similar phenomenon occurs when two chemical species exchange concentrations under temperature changes and their associated spectra cross at one point. This is called the isosbestic point [19,12]. Because the term means the same absorbance, it is also widely used in Raman spectroscopy [20,21]. However, in such

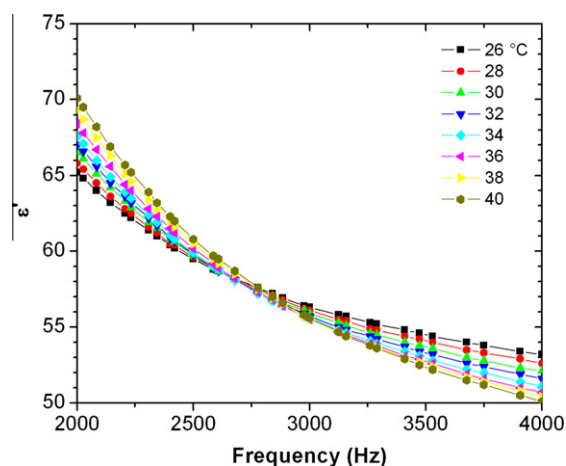


Figure 3. The existence of an isopermutive point of water: Frequency plots at different temperatures cross in a point.

a case, it would be more appropriate to call it, as in Ref. [20], isokedastic (equal scattering) point. Considering these antecedents, we name the crossing point found in our measurements in Figure 3, the isopermutive point. In this sense, water can be seen as a system of two species, ions and dipoles, and in such a point these species contribute independently in such a way that their effects compensate each other.

The frequency of the isopermutive point is more precisely located plotting ϵ' as a function of temperature for fixed values of frequencies around this point, as shown in Figure 4. One can see that the isopermutive point is where the slope is practically zero. We repeated these measurements with different bi-distilled water samples and found that this value is at 2.96 ± 0.17 kHz.

We would like to emphasize that although ϵ' below 10^9 Hz is considered to be constant [10], we have found that it is important to measure ϵ' at low frequencies. We believe that the existence of the isopermutive point may have implications in understanding biological processes because a biological cell can be seen as a capacitor where there is an exchange of ions through the membrane. We would like to remark that during cell functioning the transport of ions occurs at a frequency of the order of 1 kHz.

As we have seen above, the behavior of ϵ' at very low frequencies is governed by the presence of water ions. The higher the temperature, the greater the ionic concentration, and then, the larger ϵ' . So, what would happen if other types of ions are present? For example, ions from salts. We consider now water with different concentrations of salts: filtered and tap water. It is remarkable the difference in ϵ' for bi-distilled, filtered and tap water, as can be observed in Figure 5, where the first two are multiplied by 100 and 10, respectively. In both cases, the isopermutive point does exist (see Figure 3 and the inset of Figure 5). One can also see that in the filtered water sample the isopermutive point moves to higher frequencies (6.3 kHz). It is clear that the reason is because at this salt concentration, the effect of the dipoles appears later. Note that ϵ' is negative above the isopermutive point. We believe that this intriguing phenomenon is due to a thermodynamic instability produced by the high concentration of salt ions at the electrode surfaces. Negative dielectric responses have been measured in solid materials where conductivity is high [22,23]. On the other hand, ϵ' is so high for tap water that the isopermutive point does not show up. Indeed, for this water sample, there are not appreciable changes in ϵ' as a function of temperature. This is because the concentration of salty ions dominate over water ions, regardless the temperature.

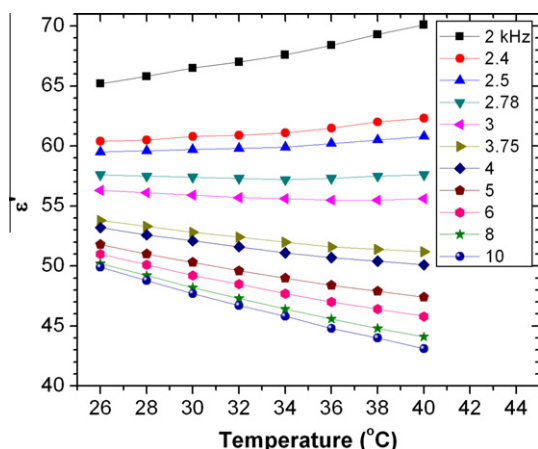


Figure 4. ϵ' as a function of temperature around the isopermutive point. The line with the slope close to zero defines the frequency of the isopermutive point.

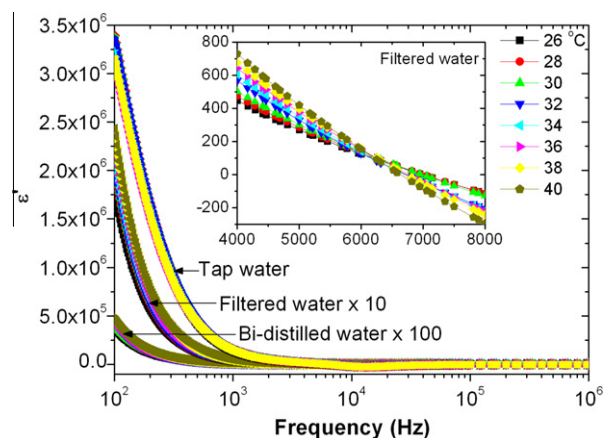


Figure 5. ϵ' as a function of frequency at different temperatures, of bi-distilled (18.2 M Ω cm), filtered (1.3 M Ω cm), and tap water (1.2 M Ω cm). The inset shows the existence of the isopermutive point in filtered water.

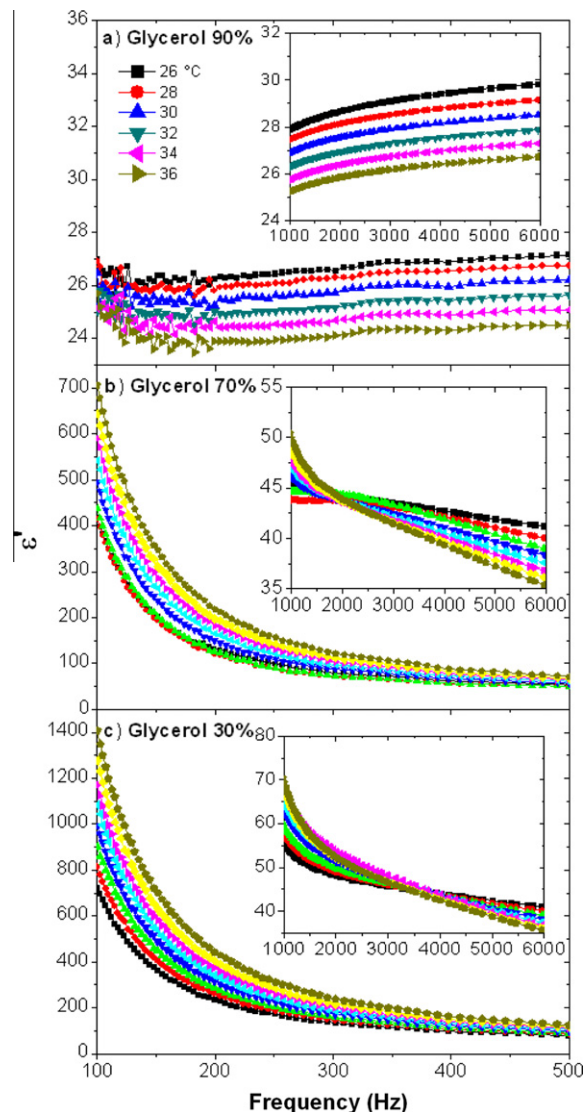


Figure 6. ϵ' of a glycerol-water mixture as a function of frequency at different temperatures. See the text for an explanation of the inset.

We have also studied a glycerol–water mixture. Figure 6 shows clear differences in ϵ' as the concentration of water is changed. One

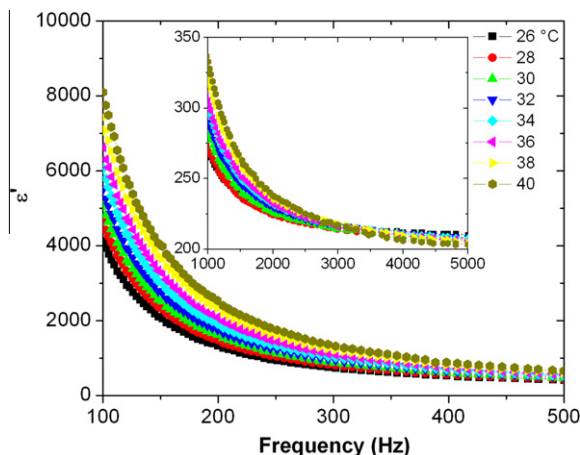


Figure 7. ϵ' of water as a function of frequency at different temperatures with a different gap between electrodes, see text. The inset shows the existence of the isopermittive point.

can see that when water is increased, the dielectric response augments. In the case of almost pure glycerol (Figure 6a) there is no MWS effect and therefore, no isopermittive point. However, upon increasing the presence of water the MWS effect shows up (Figure 6b) and the isopermittive point as well, see inset. When water is more abundant in the mixture, the MWS effect is much stronger (Figure 6c) and the isopermittive point shifts to higher frequencies (see inset) in the same fashion discussed in Figure 5.

Finally, in order to assess the effect of the gap between the electrodes in the capacitor, we varied the diameter of the inside electrode. This is illustrated in Figure 7, where ϵ' is shown at low frequencies for an inside electrode of 0.31 cm. Note the existence of the isopermittive point, see inset. It is clear that the ϵ' curves are similar to the ones described in Figure 1. Considering that the dielectric properties of water should not change with the geometry of the capacitor, it is interesting that the curves are not exactly the same. A theoretical model is needed to describe this phenomenon.

4. Conclusions

We have measured the relative permittivity of water samples between 100 Hz and 1 MHz at different temperatures. The most important result we have found is that there is a frequency where the dielectric response is independent of temperature, and called this the isopermittive point. This point adds to other physical crossing points insensitive to temperature, like in Raman spectroscopy or in chemical reactions.

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