Impedance spectroscopy of water in comparison with high dilutions of lithium chloride

A. R. Miranda, A. Vannucci and W. M. Pontuschka*

Comparative analyses of impedance measurements carried out on high dilutions of LiCl and reference water, in the frequency range of 1 kHz $\leqslant f \leqslant$ 13 MHz, revealed distinct differences that could not be explained by external contamination during sample production. To model the experimental data, an equivalent resistor–capacitor circuit was considered and the results corroborated the differences between the impedance values of the *15c* LiCl dilutions and the corresponding reference water for a given lot of specimen samples. The formation of clusters of water during each stage of the dynamisation process could, perhaps, be proposed as an explanation for the observed differences.

Keywords: Water, Impedance spectroscopy, High dilution, Dynamisation, LiCl

Introduction

Despite the considerable amount of well refined data available from numerous investigations into the nature of water, it is a general belief that very little is known about the properties of this vital substance.[1]

Many are the peculiar anomalies presented by water, such as the fact that water is liquid within an unexpectedly large interval of temperatures, from 0 to 100°C;[2–4] others even contest our intuition, such as when its volume is observed to increase when it is cooled below 4°C.[5]

Nowadays, statistical models based on orientational variables point towards the coexistence of different water densities in a given region of the pressure–temperature space, and because the entropy of these models is of an orientational nature, they are considered to be directly related to the hydrogen bonding dynamics.[6–8]

Interestingly, models describing the structure of liquid water under natural pressure and temperature conditions were already proposed in 1972, in which large size H_2O molecular clusters should necessarily be present.[9] However, even long before that time, many authors had imagined different configurations for the molecular organisation of water, in an attempt to justify the several macroscopic properties exhibited by water.[10]

More recently, studies carried out to investigate the electric dipole of single water molecules, or water clusters of different sizes and configurations, brought important contributions to a better understanding about the fundamental structure of liquid water.[11] In addition, systematic investigations of diluted water solutions in recent years have established a challenging area of research.[12–17] In this respect, the study of extremely diluted solutions, produced by a continuous process of dilutions and succussions (or dynamisation) has opened a very interesting door to a deeper comprehension about the nature of water and how the physical properties of water are affected when it has been in contact with another substance.[12–15]

In the present work, the real and imaginary components of the impedance parameter were measured for high dilutions of LiCl and corresponding ‘reference waters’. A great amount of repeated experimental measurements were carried out in a frequency interval of 1 kHz to 13 MHz using an impedance analyser model HP4192A. The LiCl solutions were prepared following the method of dynamisation described in the literature.[18,19] After each measurement of a chosen LiCl dilution specimen, the results were compared to the measurements obtained from the corresponding reference water, which was produced according to exactly the same process of dilutions and succussions used for obtaining the LiCl solution under analysis. In other words, after a large amount of distilled water had been manufactured (which will be called a water lot), one half of this initial water was used to produce highly diluted samples of LiCl. The sample solution concentrations decreased by 10^{-2}M after each dilution process (designated here as *1c*, *2c*, *3c*,…, *15c*, as will be explained in the sequel), and the other half of the initial distilled water was submitted to the same process above, to produce the so called reference water samples.

During the experiment, the analysis of each LiCl sample was compared to the results obtained for the corresponding water sample, produced exactly in the same manner, but with no LiCl salt whatsoever included. The authors considered this procedure to be crucially important to have reliable conditions under which the two measurements can be compared, as it will be described in more detail below. Finally, a computer

---

Physics Institute, University of São Paulo, 05508-090, SP, Brazil

*Corresponding author, email pontuska@if.usp.br

Received 28 March 2011; accepted 29 March 2011
DOI 10.1179/143307511X13109310554445

program was used to model the experimental measurements as a resistor–capacitor (RC) electric circuit.[16,20]

Experimental

It is important to stress that all of the experimental arrangement and measurement procedures were carefully performed and controlled, from an appropriately chosen type of glass used to manipulate and produce the liquid samples, to the method used to store the samples before and during measurements. Moreover, precautions were adopted to prevent possible interference from external influences, such as variations of the temperature during the sample measurements and the way that the sample holder was cleaned and refilled between measurements. We considered these controlled conditions to be important for obtaining reproducible experimental data for each set of liquid samples used in the experiment.

Preparation of samples

The concentrations (formally calculated) of the lithium chloride used in this study ranged from $2{\cdot}4\times10^{-1}$ to $2{\cdot}4\times10^{-29}$M; intermediate concentrations were obtained through hundredfold dilutions. We started the dilution process by evaluating the weight of the quantity of solute to be dissolved using a precision digital balance, and the sample preparation was carried out in a temperature and humidity controlled environment. A 99% pure LiCl salt matrix was purchased from the Sigma-Aldrich company, and the distilled water used to prepare the samples was produced in a pharmaceutical lab.

During specimen preparation, each dilution step was immediately followed by a process of succussion, in which the liquid sample was placed at the end of a mechanical shaking arm that produced successive impacts on a semi-rigid material, with controlled impact frequency and intensity. All of the dilution and succussion (dynamisation) steps were performed with flasks of 100 mL filled with 60 g of a given solution, which were succussed 100 times by the mechanical arm.

The glassware was submitted to an exhaustive cleaning process before being used, which involved bathing the glassware several times in running distilled water, washing it with 70% alcohol, and exposing it to temperatures of around 140°C for a time period of ~1 h.

The first solution was then obtained by mixing one part LiCl to 99 parts (by weight) distilled water, so that the final saline concentration was far below the saturation limit. Subsequently, the solution was submitted to a series of succussions by the mechanical arm. At the end of 100 succussions, the solution was designated *1c* of LiCl (corresponding to a concentration of $2{\cdot}4\times10^{-1}$M of the salt). The next dilution stages followed an identical procedure, that is, one part of the previous solution was mixed with 99 parts (by weight) of the initial distilled water, followed by 100 succussions, and so on, until *15c* LiCl solution was obtained. There were thus a total of 15 different LiCl specimens.

The water control samples (called here reference waters), used in the comparative analyses with the saline solutions, were produced following an identical procedure of dilution and succussion, as described above. The only difference was that no LiCl had been mixed into the distilled water. Besides this particular difference, all experiments were performed in an identical manner, to obtain the so called *1c*, *2c*,..., *15c* reference water specimens. This procedure was considered necessary to avoid any possible influence from the sample production process on the final experimental results.

Finally, proper care was also taken in storing the dynamised liquid samples before measurement. All of the samples were analysed within a relatively short period of time after they were produced (maximum of 10 days) and, during this period, the samples were cooled in a refrigerator (at ~10°C) to prevent the development of fungus and/or bacteria, which could influence the final results.

Detailing measurement protocol

For this work, the modulus $|Z|$ of the electrical impedance and the phase angle θ of both the LiCl solutions and the reference water samples were measured as functions of frequency in the range 1 kHz to 13 MHz, using a capacitor (the liquid sample holder) coupled to the HP4192A impedance analyser.

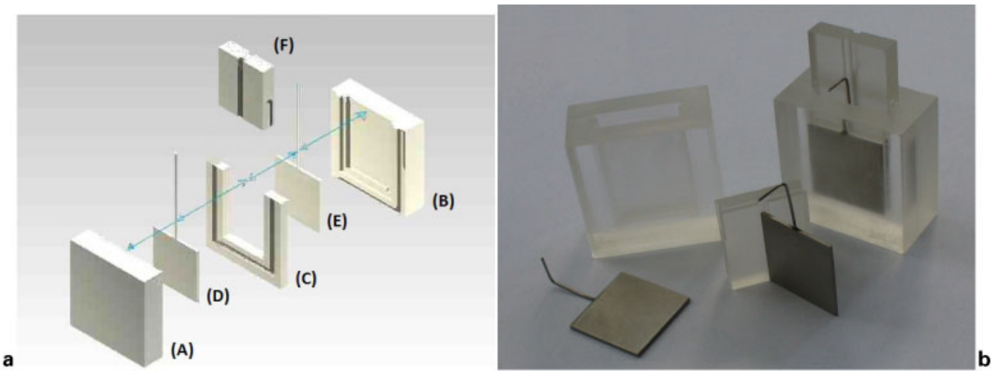
The measurements were carried out using 2 to 5 different sample holders. All of the sample holders were identically constructed to be specifically used in this study. A schematic drawing of the sample holders is shown in Fig. 1. As can be observed, a transparent Lucite cover includes the two stainless steel parallel plates of the capacitor. The metallic plates have identical areas $A=(8{\cdot}98\pm0{\cdot}04)\times10^{-4}$ m^2, and are separated by a distance $d=5{\cdot}25\pm0{\cdot}11$ mm, yielding a sample volume $V=4{\cdot}71\pm0{\cdot}10$ mL.

After a sample holder was filled with the liquid sample to be measured, it was attached to the HP4192A impedance analyser and a sequence of measurements was taken over the frequency range $1\ \text{kHz}\leqslant f\leqslant 13$ MHz. It is important to remember that possible interface effects can be excluded[21] in this frequency interval, which was experimentally confirmed by us.[22]

At the end of each measurement, the liquid solution was discarded and the sample holder was disassembled, washed three times with distilled running water, and refilled with a new liquid sample (alternating between LiCl and reference water). During this cleaning procedure, a different specimen (previously prepared) was usually under measurement with the impedance analyser. Moreover, it should be mentioned that each daily sequence of measurements was preceded by another and more rigorous cleaning stage, in which the capacitor plates were washed with acetone, alcohol and distilled water. Immediately afterwards, all dismounted parts of the sample holder were immersed in distilled water and left in an ultrasound cleansing vat for at least 30 min. Once again, everything was washed with running and de-ionised distilled water, and finally dried in a stove at 70°C for ~2 h.

For the present work, 14 different lots of LiCl and their respective reference water samples were systematically studied. Twelve of these lots were produced by one pharmaceutical lab, and two of them were prepared by two different labs for comparison. All of the measurements were carried out at ambient temperature in an acclimatised room, and the temperature conditions were monitored by taking the sample temperature at the end of each measurement.

The experimental data were analysed, separately considering the real ($Z'(f)$) and the imaginary ($Z''(f)$)



1 ***a*** **Exploded view of the sample holder (basically a parallel plate capacitor) that was constructed for this work and used to measure the real and imaginary impedance components of the tested liquid samples. Parts A, B and C form the basic structure of the liquid container. They were carefully glued together (using special acrylic solvent) so no leak was detected. Parts D, E and F (the cover) are mounted using the corresponding mortises carved in parts A, B and C, respectively;** ***b*** **photograph showing details of two of the sample holders (disassembled on the left and ready for measurement on the right) constructed for the experiment**

parts of the specimens' electrical impedances and by calculating the resistances and the capacitances of an equivalent electric circuit through simulations. Plots were then constructed with the acquired data, and the resulting curves for each of the analysed samples were obtained by averaging the values of several repeated measurements at each frequency value. This procedure was followed for all of the LiCl samples and their respective reference water samples (which were submitted, as already mentioned, to the same process of dilution and succussion – or dynamisation), using more than one sample holder in succession.

Results

The effect that dilution and succussion had on the liquid samples was investigated through comparative analysis of the observed differences (between the reference water samples and the high dilutions of LiCl) at each stage of sample production.

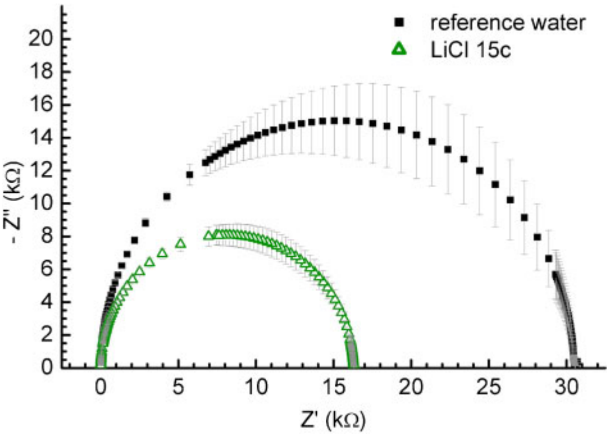
The first two LiCl dynamisations, corresponding to *1c* and *2c*, were not of any interest for our purposes because their behaviours were observed to be totally dominated by the physical presence of the ions (Li^+ and Cl^-) in the solution. For the other formally calculated concentrations, up to *15c*, the technique of impedance spectroscopy was very successful in clearly distinguishing the LiCl solutions from the reference water of the same lot, even at high dilutions of lithium chloride, as we shall demonstrate in the sequel. More thorough attention was directed towards the *15c* samples.

In Fig. 2, the $Z'(f)$ data are plotted against the $Z''(f)$ data, yielding the typical semicircular curve usually found in this kind of measurement. Figure 3 shows the typical behaviour of $Z'(f)$ and $Z''(f)$ for the *15c* LiCl solution and the corresponding reference water sample obtained for one particular lot. It is interesting to note that these resulting characteristic curves follow the same overall pattern in all of the *15c* aqueous solutions studied (both LiCl dilutions and reference water samples). The only observed discrepancies, which will be discussed bellow, are as follows:

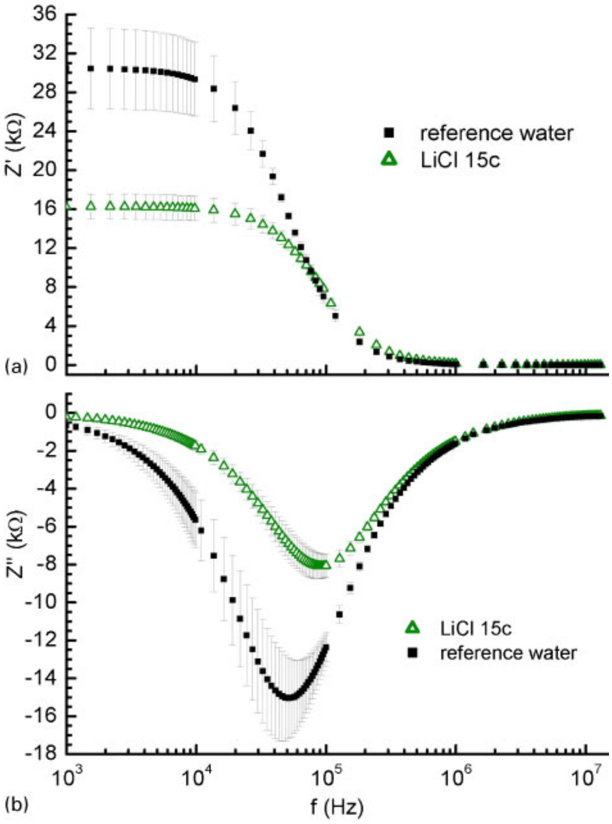
(i) the difference of the absolute values of $Z'(f)$ obtained at lower frequencies
(ii) the frequency values at which $Z'(f)$ is reduced to one half of its initial value
(iii) the absolute value and the frequency of the minimum of $Z''(f)$.

When the data acquired using samples from different lots are compared, sometimes they are observed to differ. The reason for these variations will be discussed and explained. However, it is important to mention that when the measurements of the LiCl solutions are compared to the corresponding reference water samples from a given lot, the obtained curves are always clearly separated, as shown in Fig. 3 (for *15c* specimens), despite the LiCl solution being extremely diluted. Note that the error bars of the curves presented in this figure were evaluated by taking into account several measurements carried out on each liquid sample using four different sample holders, which were dismounted and cleaned between each measurement. As can be observed in both graphs ($Z'(f)$ and $Z''(f)$), the differences between the LiCl data and reference water (*15c*) are clear.

Now, to investigate whether this observed difference between the LiCl and reference water samples could



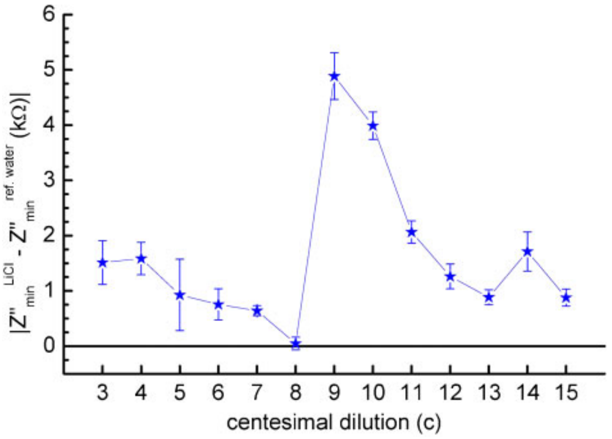
2 **Z′ plotted against Z″ at each applied frequency. The data correspond to the measurements of lot A, also shown in Fig. 3. The semicircular curves indicate that the system has only one relaxation time**



3 Average of *a* Z′ and *b* Z″ values as functions of frequency, obtained for 12 measurements of the reference water and the LiCl *15c* solution (of lot A), in the frequency interval 1 kHz to 13 MHz. The error bars calculated for each point were obtained by averaging the experimental data measured using four different sample holders

result from an unsuspected contamination during preparation of the samples, i.e. during the several stages of dilutions and successions, the difference between the minimum values of Z″(*f*) for each curve (LiCl and reference water) was calculated and plotted against the number of dilution stages, from *3c* to *15c*. The results obtained for one of the analysed lots are shown in Fig. 4. The error bars represent the mean deviation, calculated by considering the number of repeated measurements carried out for each dynamisation. As can be observed, the results do not exhibit a monotonic behaviour over the process of dynamisation, indicating that the possibility of contamination during the samples manipulation can be ruled out. That is, if some kind of contamination had occurred in any step of the dynamisation process, causing an increased impedance of the LiCl solution relative to the reference water, for example, the subsequent dynamisations of this lot would systematically yield LiCl solutions with higher impedance values. The non-monotonic curve of Fig. 4 shows that this is not the case.

Similarly, two other sets of LiCl solutions and the corresponding reference water samples from different lots were also measured from *3c* to *15c*. The non-monotonic behaviour was again confirmed in both cases, although modifications were observed in relation to which dynamisation step the LiCl solutions and the reference waters are peaked.



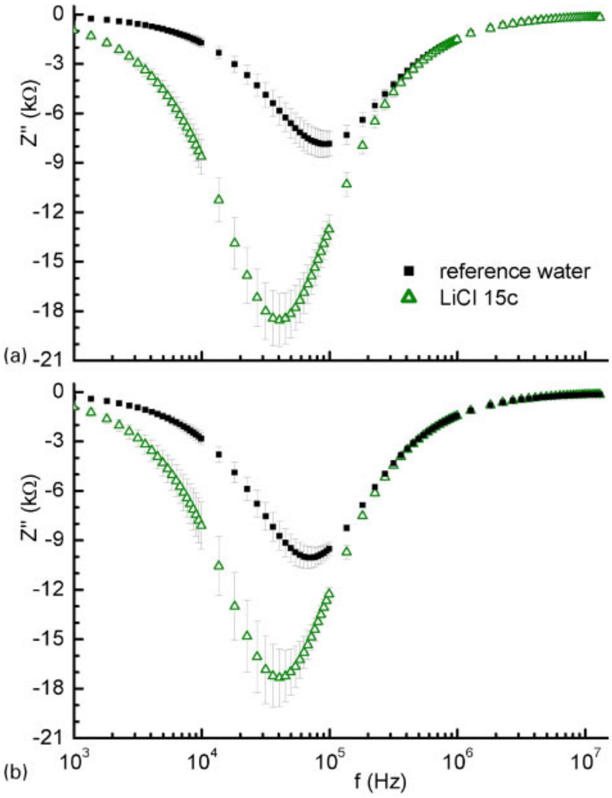
4 Modulus of the difference between the Z″$_{min}$ values of the *3c* to *15c* LiCl solutions of lot L and the corresponding reference water samples. The error bars represent the mean deviation from a number of repeated measurements carried out for each dynamisation

Now, when the experimental data of different lots are compared, variances related to the absolute values of the impedance components are often observed. This discrepancy is believed to be due to the initial physicochemical conditions of the particular distilled water lot that began the process of dynamisation. As was found later on, despite the initial precautions concerning production of the distilled water used in our experiment, water lots that were distilled at different periods of time (separated by many days or weeks), did end up exhibiting considerable differences in terms of the intrinsic electrical conductivity values and pH parameters.

Furthermore, the data obtained from the thorough study carried out on the *15c* specimens did emphasise the possibility that the physicochemical characteristics of the initial distilled water could be responsible for the variations observed in the absolute values of the impedance components of the different lots.

Figure 5 shows the imaginary component of the impedance measured for the LiCl *15c* solutions and the corresponding reference water samples from two different lots. Note that, notwithstanding the high number of experimental repetitions, routinely using two or three different sample holders for each measurement, the LiCl and reference water curves are very clearly distinguished from each other. If the absolute values of Z″ are now compared around the samples' respective minima, differences are observed due to physicochemical differences (according to our understanding) of the starting waters of the two distinct lots.

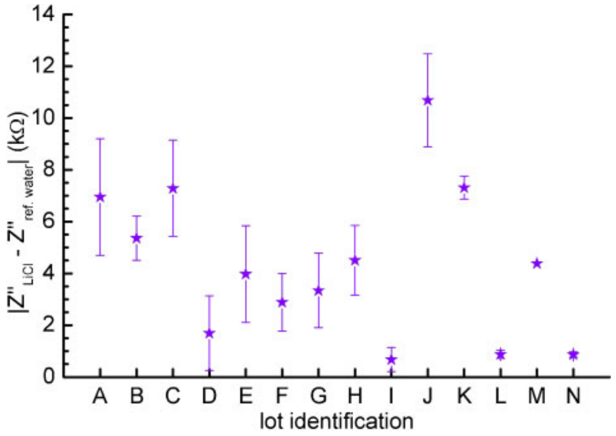
For each of the LiCl *15c* dilutions and reference waters, the corresponding Z′(*f*) and Z″(*f*) curves always exhibited differences similar to the ones shown in Fig. 3. That is, although the absolute values of Z′(*f*) and Z″(*f*) of the liquid samples differed from lot to lot, the curves constructed for the LiCl *15c* and reference water of one given lot systematically exhibited clear differences, well beyond the error bars. Interestingly, however, for some of the lots investigated, the relative positions of the Z′(*f*) and Z″(*f*) curves of the LiCl *15c* solutions and reference water samples were inverted, as can be seen for the Z″(*f*) component in comparing Fig. 3 (lot A) and Fig. 5 (lots J and C). Note that the



5 **Imaginary component of the impedance (Z″) for two lots of LiCl *15c* solutions and reference water samples (lots J and C). The specimens were measured in the frequency interval 1 kHz to 13 MHz, and the error bars were obtained *a* by averaging 27 repetitions using three distinct sample holders; *b* by averaging 6 repetitions using three distinct sample holders**

experimental points for the LiCl solution in Fig. 3 are above the values of the reference water in this particular case. This result is believed to be a consequence of the different physicochemical characteristics of the water used to produce the different lots. By means of a rough estimation, carried out by measuring the electrical conductivity of the water used in the production of the different lots, it could be confirmed that the conductivity of the distilled waters that generated the different lots that exhibited this inversion was approximately twice the value of the conductivity of the distilled water used to produce the remaining lots (though the conductivity of the starting water was below $5\ \mu\Omega\ \mathrm{cm}^{-1}$ in all of the analysed lots).

Figure 6 shows the data points obtained by calculating the modulus of the difference between the minimum values of Z″(*f*) measured for each LiCl *15c* solution and the corresponding reference water samples. In total, 14 lots were measured for this study (designated by lot A, lot B, lot C, etc.). In all cases, it was found that the moduli of these differences for the *15c* solutions indicate a clear distinction between the LiCl impedance and the corresponding reference water impedance. The larger error bars obtained for some of the measurements reflect a greater number of sample holders used during the repetitions; the measurements with the smallest error bars indicate the use of a single sample holder. The data in Fig. 6 show that the high dilution of LiCl from one lot does have different values than the corresponding reference water. It also demonstrates that this difference is not the same from lot to lot, and that this result is due to the different physicochemical characteristics of the starting water of each lot.



6 **Modulus of the difference between the minimum of the Z″ values of the LiCl *15c* solutions and the corresponding reference water samples, for all of the analysed lots**

Equivalent circuit

The experimental data taken with the impedance analyser were also used to model an equivalent circuit composed of a resistor *r* in series with a parallel RC circuit. This kind of analysis is usually performed to quantify how the measurements are affected by the experimental setup and to study the homogeneity of the liquid samples measured in this experiment.[20] For this task, a computer program was employed to calculate the desired resistances of the circuit according to the equations given below, which express the impedance (of the LiCl or the reference water) in terms of its real (Z′) and imaginary (Z″) parts[20]

$$Z = Z_r + Z_{RC} \tag{1}$$

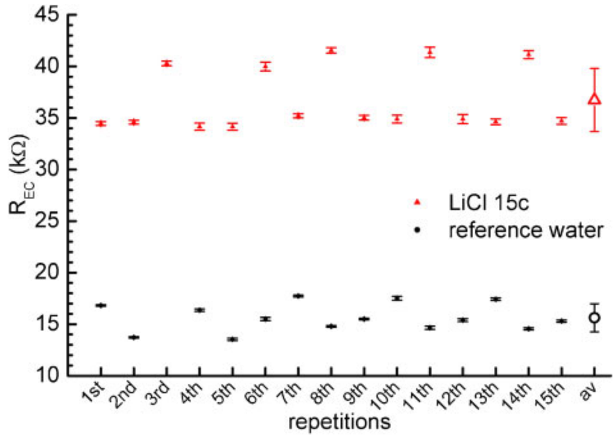
where

$$Z = r + \frac{R}{1 + i\omega RC} \tag{2}$$

and

$$Z = Z' + iZ'' = \left[r + \frac{R}{1 + (\omega RC)^2} \right] - i \left[\frac{\omega R^2 C}{1 + (\omega RC)^2} \right] \tag{3}$$

As can be seen in these equations, for low frequencies, the Z′ component tends to $r + R$, which corresponds to the sum of the resistance (*r*) intrinsic to the experimental arrangement (representing the influence of the threads and connections between the sample holder and the impedance analyser) and the cell's resistance (*R*) related to the situation when the capacitor is filled with the liquid specimen. On the other hand, for sufficient large values of ω, both Z′ and Z″ tend to zero (because *r* is typically very small). Moreover, when $\omega = 1/RC$ the Z″ function achieves a minimum, which corresponds to

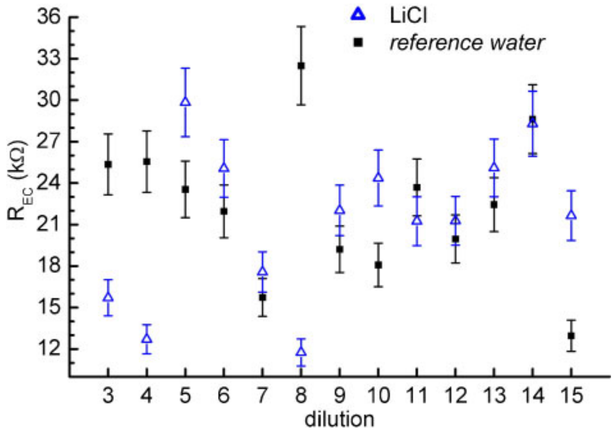


7 Equivalent resistance R_{eq} calculated for each repetition of the LiCl *15c* sample and the reference water of lot J. The error bars (for each point) are observed to be smaller than 1%. The larger bars on the right (indicated as *av*) correspond to the deviation of all of the R_{eq} for each specimen (LiCl *15c* and reference water), which are of the order of 10% in this case

the value *R*/2. Interestingly, this overall behaviour is verified for all of our results, as can be observed in Fig. 3, for example, indicating that our measurements are not influenced by the experimental arrangement and that the analysed samples can be considered homogeneous (despite the 1 V alternated voltage connected across the stainless steel capacitor plates).

The *r*, *R* and *C* values of the equivalent circuit were then calculated for each measured *15c* liquid sample from each lot. The maximum deviation obtained for the calculated parameter *r* of the equivalent circuit within each lot was 1%.

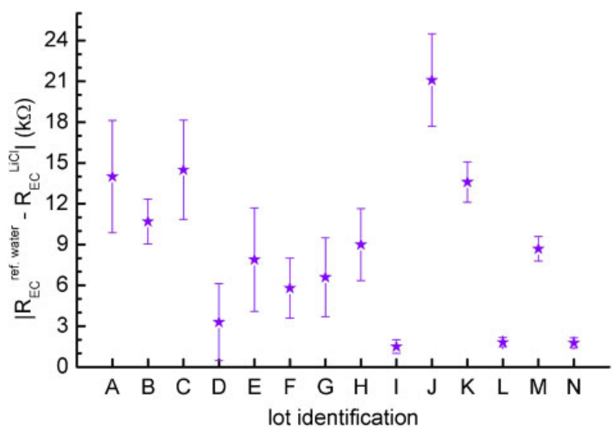
The resistance *r* was approximately constant in all of the measurements performed, and its value was much less than the value of *R* (*r* was calculated to be ~2 Ω, whereas *R* was of the order of kΩ). Now, for a given sample from a given lot, the values of the equivalent resistance *R* obtained from several repeated measurements achieved a maximum variability of only 10% around the average value, despite the use of 2 to 5 different sample holders for the measurements. This result is illustrated in Fig. 7 for the *15c* LiCl and respective reference water of lot L. After 15 repeated measurements of the same samples, the values obtained were $R_{\mathrm{LiCl}}=36{\cdot}7\pm3{\cdot}1$ kΩ and $R_{\mathrm{ref.water}}=15{\cdot}6\pm1{\cdot}4$ kΩ. The moduli of the differences between these values, calculated by modelling the RC electric circuit for all *15c* samples from all lots, are plotted in Fig. 8. Note that these findings corroborate previous results obtained (Fig. 6).



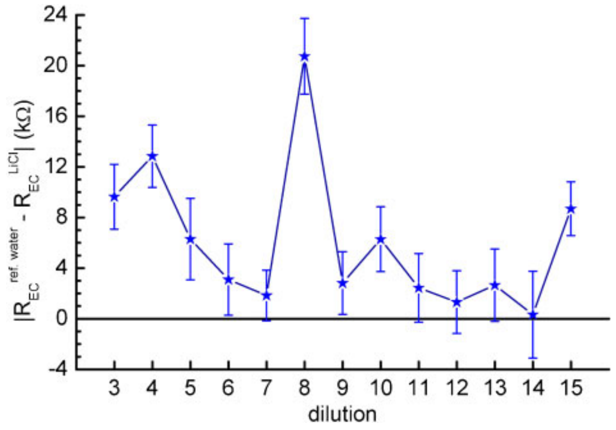
9 Equivalent resistance calculated for the reference water and LiCl solutions ranging from *3c* to *15c* for lot M. Each error bar was evaluated from several repeated measurement

Furthermore, the equivalent capacitances obtained through modelling an RC circuit for all the *15c* liquid specimens resulted in small differences relative to the theoretical values calculated by considering solely the geometric dimensions of the capacitor (sample holder). This result is in good agreement with the literature, and indicates that the equivalent capacitance *C* of the circuit is basically related to the intrinsic characteristics of the cell, whereas the equivalent resistance *R* is the real and effective parameter representative of the analysed samples.[20]

Finally, the circuit modelling results were also used to further investigate the possibility of contamination



8 Absolute values of the differences between the equivalent resistances calculated for the LiCl *15c* solution and reference water, for all of the investigated lots



10 Absolute values of the differences between the equivalent resistances calculated for the reference water samples and LiCl solutions, ranging from *3c* to *15c* from lot M

of the liquid samples during the production process. The equivalent resistance R_{eq} was calculated for repeated measurements of each dynamisation of a given lot, from *3c* to *15c*. The results for both the LiCl solutions and the corresponding reference waters are presented in Fig. 9. The error bars were calculated by averaging the repeated measurements using different sample holders for each dynamisation. Once again, the non-monotonic behaviour of the LiCl solutions and the corresponding reference waters could be observed over several stages of successive dilutions and succussions, indicating that the possibility of contamination can be discarded. In Fig. 10, the modulus of the difference of the R_{eq} values of the LiCl and reference water solutions is plotted to show this non-monotonic behaviour.

Conclusions

In this work, comparative analyses were carried out by investigating the components of the impedance of LiCl solutions and distilled water samples prepared by three different pharmaceutical laboratories, in the frequency range 1 kHz$\leqslant f \leqslant$13 MHz.

Graphs constructed from the measured imaginary part of the impedance of the *15c* dynamisations of both the LiCl samples and the corresponding reference waters exhibited remarkable differences between the LiCl solution and reference water. The use of different sample holders and the execution of numerous repeated measurements yielded impedance curves with error bars that indicated that this difference could not be explained in terms of the intrinsic measurement uncertainties of the experiment. For every analysed sample of a given lot, the observed differences between the LiCl samples and the reference water samples were always verified, even though the absolute values of the measured quantities varied from lot to lot.

Making use of three different lots, measurements were carried out on the entire set of dynamisations of each lot (ranging from *3c* to *15c*), yielding curves that exhibited non-monotonic behaviour, which indicates that any contamination of the samples during the process of dynamisation can be ruled out.

The experimental data were used to model an equivalent RC circuit. For a given lot, the equivalent resistance R_{eq} was calculated for the *3c* to *15c* dynamisations of both the LiCl solutions and the corresponding reference water samples. Once again, the non-monotonic behaviour of the curves over the several stages of sample dynamisations indicates that any possible contamination can be discarded.

In conclusion, this experiment points towards the existence of real differences between the measured impedance of highly diluted LiCl solutions and the corresponding reference waters. Although the water from a given lot may suffer alterations during the process of dilution and succussion, due to oxygenation for example, the initial presence of LiCl somehow interferes with the impedance value of the samples, which is observed even at dilution levels in which the presence of the initially dissolved ions can no longer be identified.

One possible explanation for these results is that water clusters could be formed differently during each stage of the dynamisation process for each kind of liquid sample. The electric dipole of these clusters, which may have a permanent effect on all of the water molecules, could be responsible for the measured differences in the specimens' impedances.[23]

Hopefully the experimental data obtained and here discussed, clearly demonstrating a repeatable and measureable difference between pure water and ultra diluted solutions, will encourage other researchers with expertise in the impedance spectroscopy technique to replicate our experiment and even extend it to other substances besides the LiCl salt, so our knowledge about the physical laws that govern the high dilutions could be taken to a higher level.

Acknowledgements

The authors are very grateful to CNPq – Conselho Nacional de Desenvolvimento Científico e Tecnológico for the financial support received. The authors also acknowledge Professor M. Muramatsu and Professor T. Lamy for allowing the use of their laboratory facilities to carry out some of the experiments. The authors would also like to thank the staff of Sensitiva and Bento Mure laboratories, and special thanks to Mrs Cilene Camiloti and Mr Ademir V. Silva of laboratory Equilibrio for helping us to produce the majority of the samples used in this work.

References

1. P. Ball: 'Water – an enduring mystery', *Nature* 2008, **452**, 291–292.
2. R. M. Pashley, M. Rzechowicz, L. R. Pashley and M. J. Francis: 'De-gassed water is a better cleaning agent', *J. Phys. Chem. B*, 2005, **109B**, 1231–1238.
3. M. Francis, N. Gulati and R. M. Pashley: 'The dispersion of natural oils in de-gassed water', *J. Colloid Interface Sci.*, 2006, **299**, 673–677.
4. R. M. Pashley, M. J. Francis and M. Rzechowicz: 'The hydrophobicity of nonaqueous liquids and their dispersion in water under de-gassed conditions', *Curr. Opin. Colloid Interface Sci.*, 2008, **13**, 236–244.
5. M. Vedamuthu, S. Singh and G. W. Robinson: 'Properties of liquid water: origin of the density anomalies', *J. Phys. Chem.*, 1994, **98**, 2222–2230.
6. M. Choukroun and O. Grasset: 'Thermodynamic model for water and high pressure ices up to 2·2 GPa and down to the metastable domain', *J. Chem. Phys.*, 2007, **127**, 124506.
7. O. Mishima and H. E. Stanley: 'The relationship between liquid, supercooled and glassy water', *Nature*, 1998, **396**, 329–335.
8. T. Head-Gordon and S. W. Rick: 'Consequences of chain networks on thermodynamic, dielectric and structural properties of liquid water', *Phys. Chem. Chem. Phys.*, 2007, **9**, 83–91.
9. A. T. Hagler and H. A. Scheraga: 'Structure of liquid water. Statistical thermodynamic theory', *J. Phys. Chem.*, 1972, **76**, 3229–3243.
10. T. C. Barnes and T. L. Jahn: 'Properties of water of biological', *Q. Rev. Biol.*, 1934, **9**, 292–341.
11. J. K. Gregory, D. C. Clary, K. Liu, M. G. Brown and R. J. Saykally: 'The water dipole moment in water clusters', *Science*, 1997, **275**, 814–817.
12. L. Rey: 'Low temperature thermoluminescence', *Nature*, 1998, **391**, 418.
13. V. I. Lobyshev, R. E. Shikhlinskaya and B. D. Ryzhikov: 'Experimental evidence for intrinsic luminescence of water', *J. Mol. Liquids*, 1999, **82**, 73–81.
14. L. Montagnier, J. Aïssa, S. Ferris, J.-L. Montagnier and C. Lavallée: 'Electromagnetic signals are produced by aqueous nanostructures derived from bacterial DNA sequences', *Interdiscip. Sci. Comput. Life Sci.*, 2009, **1**, 81–90.
15. V. Elia,E. Napoli,M. Niccoli,N. Marchettini andE. Tiezzi: 'New physico-chemical properties of extremely diluted solutions. A

conductivity study at 25°C in relation to aging', *J. Solution Chem.*, 2008, **37**, 85–96.

16. M. Becchi, C. Avendano, A. Strigazzi and G. Barbero: 'Impedance spectroscopy of water solutions: the role of ions at the liquid-electrode interface', *J. Phys. Chem. B*, 2005, **109B**, 23444–23449.
17. G. Barbero, M.Becchi, A. Strigazzi,J. Le Digabel and A. M. Figueiredo Neto: 'Experimental evidence for the adsorption-desorption phenomenon on the spectroscopy impedance measurements of an electrolytic cell', *J. Appl. Phys.*, 2007, **101**, 044102.
18. V. Elia, L. Elia, M. Montanino, E. Napoli, M. Niccoli and L. Nonatelli: 'Conductometric studies of the serially diluted and agitated solutions of an anomalous effect that depends on the dilution process', *J. Mol. Liq.*, 2007, **135**, 158–165.
19. R. Roy, W. A. Tiller, I. Bell and M. R. Hoover: 'The structure of liquid water; novel insight from materials research; potential relevance to homeopathy', *Mater. Res. Innov.*, 2006, **9**, 98–103.
20. J. R. MacDonald (ed.): 'Impedance spectroscopy – emphasizing solid materials and systems'; 1987, New York, John Wiley & Sons.
21. F. Grasso, F. Musumeci and A. Triglia: 'Impedance spectroscopy of pure water in the 0·01 Hz to 100 kHz range', *Nuovo Cim. D*, 1990, **12D**, 1117–1130.
22. A. R. Miranda: 'Comparative studies of ultra-high dilutions of LiCl: impedance spectroscopy in the frequency range of 1 kHz to 13 MHz', PhD thesis, University of São Paulo, São Paulo, Brazil, 2008.
23. E. D. Giudice, G. Preparata and G. Vitiello: 'Water as a free electric dipole laser', *Phys. Rev. Lett.*, 1988, **61**, 1085–1088.