

The local order of supercooled water in solution with LiCl studied by NMR proton chemical shift

C. CORSARO^{(1)(2)(*)}, D. MALLAMACE⁽³⁾, S. VASI⁽²⁾, N. CICERO⁽³⁾⁽⁴⁾,
G. DUGO⁽³⁾⁽⁴⁾ and F. MALLAMACE⁽¹⁾⁽²⁾⁽⁵⁾

⁽¹⁾ *CNR-IPCF, Istituto per i Processi Chimico-Fisici
Viale F. Stagno D'Alcontres 37, 98158 Messina, Italy*

⁽²⁾ *Dipartimento MIFT, Sezione di Fisica, Università di Messina
Viale F. Stagno D'Alcontres 31, 98166 Messina, Italy*

⁽³⁾ *Dipartimento di Scienze biomediche, odontoiatriche e delle immagini morfologiche
e funzionali, Università di Messina - Viale F. Stagno d'Alcontres 31, 98166 Messina, Italy*

⁽⁴⁾ *Science4Life, spin-off Università di Messina
Viale F. Stagno D'Alcontres 31, 98166 Messina, Italy*

⁽⁵⁾ *NSE Department, Massachusetts Institute of Technology - Cambridge MA 02139, USA*

received 19 July 2016

Summary. — We study by means of Nuclear Magnetic Resonance (NMR) spectroscopy the local order of water molecules in solution with lithium chloride at eutectic concentration. In particular, by measuring the proton chemical shift as a function of the temperature in the interval $203\text{ K} < T < 320\text{ K}$, we observe a net change at about 235 K. We ascribe this result to the increase of the hydrogen bond interaction that on decreasing the temperature favors the formation of the network that characterizes the low density liquid phase of water. Furthermore, the Gaussian deconvolution of the NMR peak allows the investigation of the mutual difference between the chemical shift of water solvating lithium and chlorine individually. The thermal behavior of this quantity confirms previous results about the role of the temperature in the solvation mechanisms down to about 225 K. This temperature coincides with that of the so-called Widom line for water supporting the liquid-liquid transition hypothesis.

1. – Introduction

The Larmor frequency of the proton in a Nuclear Magnetic Resonance experiment depends on the values of the magnetic field that each proton feels. This corresponds to the vectorial sum of the static field B_0 and of the local field [1]. In turn, the local field

(*) Corresponding author. E-mail: ccorsaro@unime.it

depends on the local arrangement of atoms and molecules and provokes a shift from the proton Larmor frequency of an isolated proton. The presence of ions in the sample alters the shielding effect causing an additional shift of the resonance frequency. The entity of the shift depends on the type of ions and on their concentration [2].

The values of the chemical shift are usually referred to that of a standard that can be internal or external. By using an isolated water molecule in its gas phase as standard, one can gain information about the interaction of water molecules with their surroundings. In particular, the properties of the hydrogen bonding and thus of the water local order can be investigated by studying the proton chemical shift [3-7]. The variation of the chemical shift with the temperature accounts for changes in the local order of the studied molecule. This especially holds for systems that possess many orientational degrees of freedom, such as water and water systems, that are switched on or off by temperature changes. Note that also the rate of variation of the chemical shift, as well as the local arrangement of water molecules, is not influenced by the choice of the reference and depends on the type and concentration of ions. In particular, it was shown that the rate of variation of the proton chemical shift for pure bulk water is higher with respect to that of water in solution. This is probably due to the breakup of the hydrogen-bonded structure of bulk water on increasing temperature although water-anion H-bonds in basic anion solutions are much stronger than water-water H-bonds [2].

Aqueous solutions of salts have been studied since many years for their properties to lower the freezing point of water. The precise salt concentration for which the solution remains liquid up to the lowest temperature is called eutectic. The salt that possesses the lowest eutectic temperature, that is about 200 K [8,9], is lithium chloride (LiCl) and the eutectic concentration corresponds to a salt molar fraction of 20% (6.76 M). In this condition there are 7 water molecules per molecule of LiCl. Lithium chloride is the most soluble salt in water with the smallest cation and allows studying the polymorphism of water in the supercooled phase [10-12]. In fact, the use of aqueous solutions of lithium chloride allows to study water properties in a bulk-like condition in the supercooled regime well inside the so-called "No Man's Land" up to 200 K (eutectic temperature). In such a way, one can test the validity of the different physical scenarios hypothesized for water [13,14] that try to explain its many anomalies [15-21]. In particular, the existence of the Widom line [22] and of the associated liquid-liquid critical point [23] can be verified.

Even if the presence of ions in solution modifies the local structure adopted by water molecules, depending on the salt concentration, water/LiCl thermodynamical properties resemble those of bulk water [9,24-29]. The Li and Cl ions perturb in a different way the tetrahedral structure of water and in particular the Li cation is an enhancer of the water tetrahedral structure (structure maker) whereas the Cl anion tends to disrupt water structure (structure breaker) [30]. In fact, MD studies showed that for this system the Li-O radial distance is about 0.19 nm and the Cl-O radial distance is about 0.31 nm that must be compared with the O-O distance in pure water and in solution with LiCl which is about 0.27 nm [31]. In fig. 1 we report just the results of the cited MD study for LiCl aqueous solution at 14% of salt molar fraction with a corresponding picture of the water tetrahedron in the three different conditions. Note that from the top to the bottom the tetrahedral structure is more open and less rigid [31].

The presence of tetrahedral structures confirms that the water/LiCl solution allows the study of water properties in the supercooled regime in bulk-like conditions.

In this paper we extend our previous preliminary [32] and consolidated studies [33] by considering the proton chemical shift of the different local structures that water molecules adopt in the studied solution. We will shed more light on the open debate about the

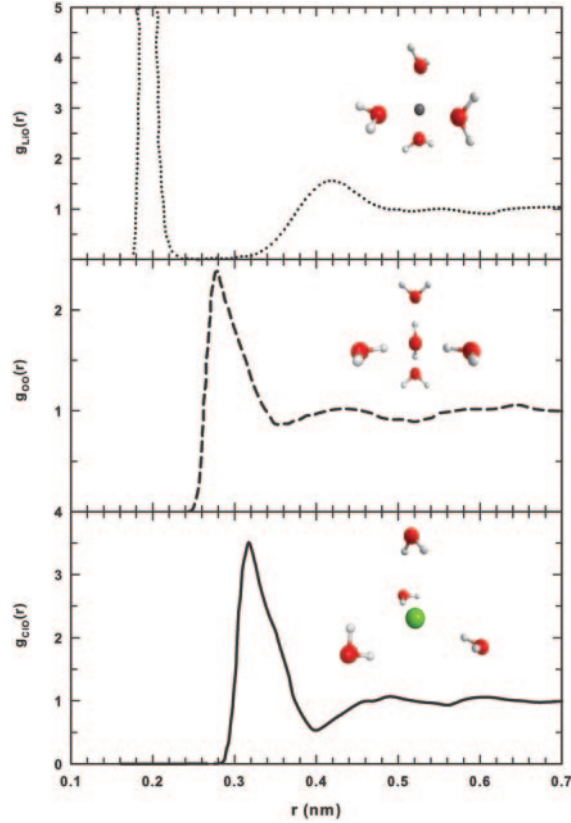


Fig. 1. – The pair correlation functions of the water oxygen atom in the three configurations obtained by MD simulations for 14% of salt molar fraction by Aragoñes *et al.* [31]. A snapshot of the tetrahedral symmetry that water molecules can adopt is depicted in each panel. From the top to the bottom the tetrahedral structure is more open and less rigid [31,33].

existence of a dynamical crossover in water solutions with LiCl [34,35]. The contrasting experimental observations are caused by the coexistence of different local structures and hence different relaxations that were probed by different techniques [36,37].

2. – Materials and methods

The methods describing the sample preparation and experimental procedures are reported elsewhere [33]. We must mention that we used as an external reference the tetramethylsilane signal calibrated at 0.00 ppm. In this study we acquired the NMR spectra by cooling down the solution from 320 K to 205 K in steps of 5 K, then we cool to 203 K and heat up to 318 K in steps of 5 K.

For water systems, the proton chemical shift δ provides information on the local hydrogen bond (HB) geometry being a function of the number of HBs and also of the intermolecular distances and angles [5]. Therefore the behavior of $\delta(T)$ gives details of the thermal evolution of the water local structure especially in the supercooled regime where hydrogen bond interactions are favored and generate clustering phenomena. Note that

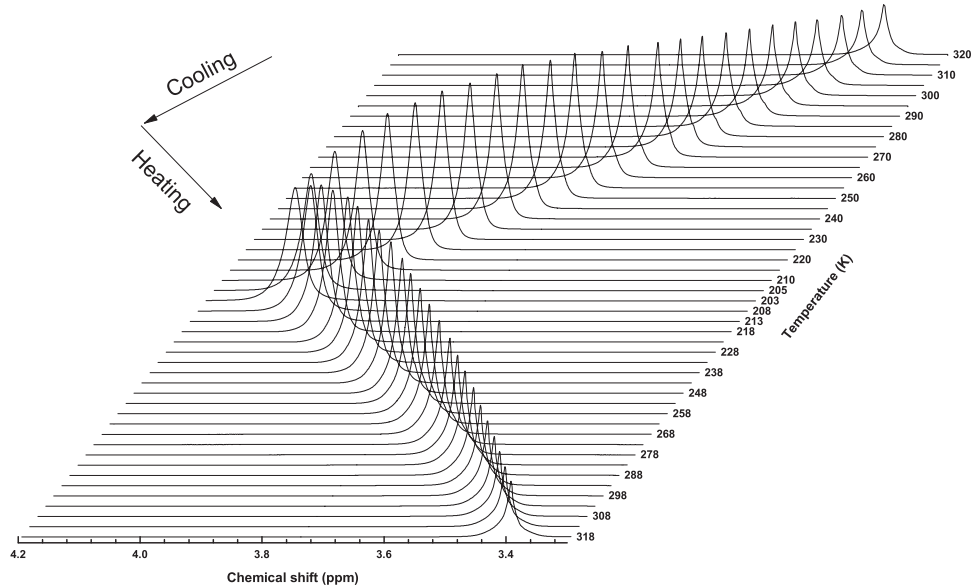


Fig. 2. – The proton NMR spectra of water/LiCl solution at eutectic point in a stack plot by varying the temperature. The arrows indicate the thermal path used for the experiments.

although the value depends on the chosen reference, its thermal behaviour does not [2, 4]. Furthermore, the enhancement of ions mobility in strong magnetic fields provokes the disruption of the hydrogen bonding [38] that is more evident at high salt concentration. This justifies the upfield shift of the proton resonance frequency and a smaller rate of changes with temperature.

The chemical shift, being a direct measure of the local order, corresponds essentially to the entropy [39] and its derivative with respect to the temperature is proportional to the configurational specific heat [7].

The recorded NMR spectra of aqueous solutions of LiCl at eutectic concentration are shown in fig. 2 in a stack plot at different temperatures. The arrows indicate the thermal path used for the experiments. Note that the process is completely reversible and that the magnetization shows a maximum at about 225 K [33]. The increase of the macroscopic magnetization on lowering the temperature (up to 225 K) in the considered thermal range is due to the corresponding increase of the polarization of water molecules on decreasing the thermal energy (or disorder).

As done before [32, 33], we have performed a Gaussian deconvolution with three components to best fit the spectra and extracted the obtained peaks position. In agreement with theoretical and simulations results [31, 40, 41], the three Gaussian components are described by three different widths that correspond to three slightly different dynamical regimes due to the individual rigidity of the local structure [33].

3. – Results and discussions

The measured peaks positions corresponding to the three Gaussian components are reported in fig. 3 as a function of the temperature.

As mentioned above, the presence of ions in solution provokes an upfield shift with

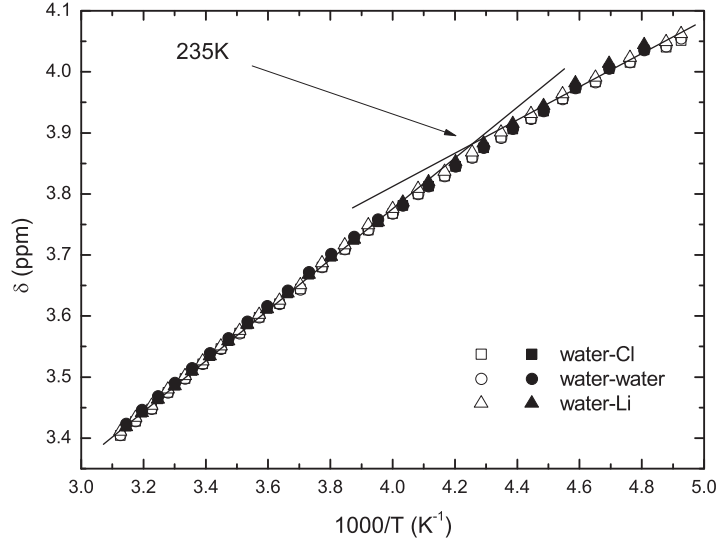


Fig. 3. – The thermal evolution of the chemical shift of the three studied contributions extracted by the NMR spectra for water/LiCl solution at eutectic concentration. The value refers to the signal of the tetramethylsilane at 0.00 ppm. Open and close symbols correspond to cooling and heating paths, respectively.

respect to the chemical shift of bulk water due to a deshielding effect provoked by their motion [2]. Note that the temperature behavior is the same for all the three components and that shows two different linear behaviors above and below $T \approx 235$ K. This indicates that the local order of water molecules and its temperature dependence changes when the water correlation length reaches its maximum value that is on approaching the temperature of the Widom line. This enhances the micro-segregation of the solution with the development of regions with higher solute concentration.

The increase in δ on lowering the temperature reflects the increase in the local order of the system due to the formation of high ordered structures and the development of the hydrogen bonded network of water. However, from these results no evidences on the different actions exerted by the presence of both Li cations and Cl anions can be inferred. This confirms that the water properties in solution with LiCl are not so altered by the presence of the salt at this concentration.

Although the temperature trend is the same for all the components, by looking at the mutual differences one can obtain more insight into the different actions exerted on water by the two ions and therefore into the dynamical evolution of the different local structures. In fact, in our previous work we observed that the ions exert on water a different influence by lowering the temperature [33]. Figure 4 reports the difference between the peak position of the Gaussian contributions of water around Li and Cl ions, that is the difference between the chemical shift value of the Gaussian function corresponding to water solvating lithium and that solvating chlorine.

The quantity reported in fig. 4 shows an interesting behavior as a function of the temperature. In particular, it decreases from 320 K to 280 K where it shows a minimum. Successively, on lowering the temperature it increases up to 240 K where it shows a maximum and then it decreases again until 225 K. Below this important temperature for

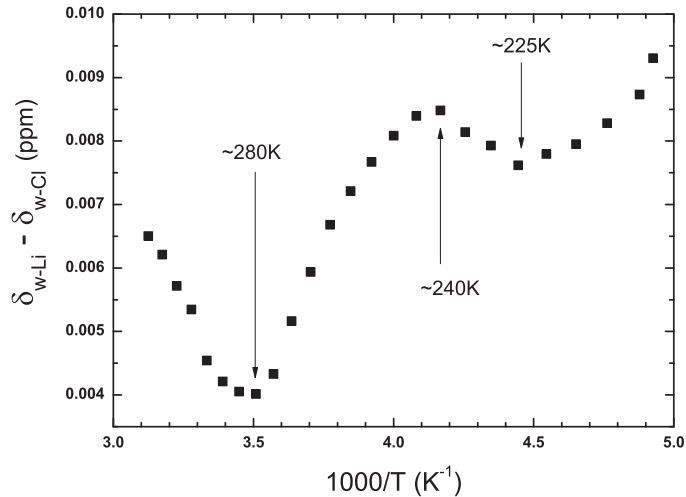


Fig. 4. – The difference between the chemical shift value of the Gaussian function corresponding to water solvating lithium and that solvating chlorine.

water, it increases again reaching values bigger than those at higher temperature. This result confirms that the local structure of water solvating the two ions changes with the temperature. Furthermore, these changes are different within different thermal regions. In particular, for $320\text{ K} > T > 280\text{ K}$ the difference between the chemical shift value of water solvating lithium and solvating chlorine decreases: the two Gaussian functions approach each other. In this thermal region water molecules belong to the coordination spheres of both lithium and chlorine with the same weight or probability [33]. For $T < 280\text{ K}$ the two Gaussian functions begin to move away reaching the maximum distance of about 0.0085 ppm at about 240 K meaning that the solvation of the ions occurs in a different way. This happens up to 225 K where the chemical shift difference shows a relative minimum. In fact, for $T < 225\text{ K}$ the chemical shift difference increases again and more rapidly, reflecting a net change in the ions solvation mechanism due to the development of an extended hydrogen bond network of water molecules. This is consistent with the crossing of the Widom line for water, below which Li and Cl ions constitute only local defects of the water hydrogen bond network [40, 42].

4. – Conclusions

In this work we have studied the proton chemical shift of water in solution with LiCl at eutectic concentration (20% alcohol molar fraction) as a function of the temperature by means of cooling and heating paths in the range $203\text{ K} < T < 320\text{ K}$. A Gaussian deconvolution with three components allowed us to study separately the thermal behavior of the different local structures that water adopts within the mixture. In fact, several simulations studies have shown the presence of different clusters dominated by water-lithium, water-chlorine or water-water interactions. Although the presence of ions in solution perturbs the local water structure, the thermodynamical properties of water/LiCl solutions (at the considered concentration) are very similar to those for water in a bulk-like environment. The starting temperature of our experiments (320 K) coincides with the temperature at which bulk water thermodynamic properties such as the isothermal com-

compressibility and the thermal expansion coefficient show peculiar behavior. In detail, at this temperature the former shows a minimum also by varying the pressure and the latter has the same value that is not dependent on pressure. Essentially, above 320 K water properties resemble those of a simple liquid because the strength and lifetime of hydrogen bonds are not enough to form the characteristic tetrahedral structure [43]. Our main result is the observation of a change in the local order of the system at about 235 K that is associated with the full development of the characteristic hydrogen bond network of water. Below this temperature the population of the so-called Low Density Liquid (LDL) phase of water dominates over that of the High Density Liquid (HDL) [44]. Furthermore, the chemical shift difference between the two Gaussian functions corresponding to water solvating the two ions reveals that the lithium and chlorine ions exert a different action on the water local structure for $T > 225$ K. In contrast, below this temperature the hydrogen bond interaction favors the water transformation into a four-coordinated low-density liquid enhancing the micro-segregation of the solution. This result is consistent with the existence of the so-called Widom line for water and for the associated liquid-liquid transition hypothesis.

REFERENCES

- [1] ABRAGAM A., *The Principles of Nuclear Magnetism* (Clarendon, Oxford) 1961.
- [2] SARE E. J., MOYNIHAN C. T. and ANGELL C. A., *J. Phys. Chem.*, **77** (1973) 1869.
- [3] MATUBAYASI M., WAKAI C. and NAKAHARA M., *Phys. Rev. Lett.*, **78** (1997) 2573.
- [4] HINDMAN J. C., *J. Chem. Phys.*, **44** (1966) 4582.
- [5] MODIG K., PFROMMER B. G. and HALLE B., *Phys. Rev. Lett.*, **90** (2003) 075502.
- [6] SEBASTIANI D. and PARRINELLO M., *ChemPhysChem*, **3** (2002) 675.
- [7] MALLAMACE F. *et al.*, *Proc. Natl. Acad. Sci. U.S.A.*, **105** (2008) 12725.
- [8] ELARBY-AOUIZERAT A. *et al.*, *J. Non-Cryst. Solids*, **104** (1988) 203.
- [9] MAURIN P. O. *et al.*, *Prog. Theor. Phys. Suppl.*, **126** (1997) 141.
- [10] MISHIMA O., *J. Chem. Phys.*, **126** (2007) 244507.
- [11] MALLAMACE F., *Proc. Natl. Acad. Sci. U.S.A.*, **106** (2009) 15097.
- [12] GALLO P., CORRADINI D. and ROVERE M., *J. Chem. Phys.*, **139** (2013) 204503.
- [13] DEBENEDETTI P. G., *J. Phys.: Condens. Matter*, **15** (2003) R1669.
- [14] ARCHER D. G. and CARTER R. W., *J. Phys. Chem. B*, **104** (2000) 8563.
- [15] MALLAMACE F., CORSARO C. and STANLEY H. E., *Proc. Natl. Acad. Sci. U.S.A.*, **110** (2013) 4899.
- [16] PALMER J. C. *et al.*, *Nature*, **510** (2014) 385.
- [17] MALLAMACE F. *et al.*, *J. Chem. Phys.*, **141** (2014) 18C504.
- [18] LIMMER D. T. and CHANDLER D., *J. Chem. Phys.*, **135** (2011) 134503.
- [19] MALLAMACE F., CORSARO C., MALLAMACE D., VASI C. and STANLEY H. E., *Faraday Discuss.*, **167** (2013) 95.
- [20] RUSSO J. and TANAKA H., *Nat. Commun.*, **5** (2014) 3556.
- [21] CUPANE A., FOMINA M., PIAZZA I., PETERS J. and SCHIRÓ G., *Phys. Rev. Lett.*, **113** (2014) 215701.
- [22] XU L. *et al.*, *Proc. Natl. Acad. Sci. U.S.A.*, **102** (2005) 16558.
- [23] POOLE P. H., SCIORTINO F., ESSMANN U. and STANLEY H. E., *Nature*, **360** (1992) 324.
- [24] GALLINA M. E. *et al.*, *J. Chem. Phys.*, **131** (2009) 124504.
- [25] BOVE L., DREYFUS C., TORRE R. and PICK R. M., *J. Chem. Phys.*, **139** (2013) 044501.
- [26] SANTUCCI S. C. *et al.*, *J. Chem. Phys.*, **131** (2009) 154507.
- [27] MAMONTOV E., FARAONE A., HAGAMAN E. W., HAN K. S. and FRATINI E., *J. Phys. Chem. B*, **114** (2010) 16737.
- [28] TURTON D. A., CORSARO C., MARTIN D. F., MALLAMACE F. and WYNNE K., *Phys. Chem. Chem. Phys.*, **14** (2012) 8067.

- [29] TURTON D. A. *et al.*, *Faraday Discuss.*, **150** (2011) 493.
- [30] COLLINS K. D., *Biophys. J.*, **72** (1997) 65.
- [31] ARAGONES J. L., ROVERE M., VEGA C. and GALLO P., *J. Phys. Chem. B*, **118** (2014) 7680.
- [32] CORSARO C. *et al.*, in *Recent Advances on Energy, Environment, Ecosystems, and Development, Proceedings of the International Conference on Energy, Environment, Ecosystems, and Development (EEED 2015)*, edited by MASTORAKIS N. E., RUDAS I., SHITIKOVA M. V. and SHMALIY Y. S. (INASE) 2015.
<http://www.inase.org/library/2015/barcelona/bypaper/EEED/EEED-08.pdf>
- [33] CORSARO C. *et al.*, *Physica A*, **442** (2016) 261.
- [34] NAKANISHI M., GRIFFIN P., MAMONTOV E. and SOKOLOV A. P., *J. Chem. Phys.*, **136** (2012) 124512.
- [35] MAMONTOV E., *J. Phys. Chem. B*, **113** (2009) 14073.
- [36] SUN Q., ZHOU C., YUE Y. and HU L., *J. Phys. Chem. Lett.*, **5** (2014) 1170.
- [37] ALIOTTA F. *et al.*, *Phys. Rev. B*, **86** (2012) 134301.
- [38] CHANG K.-T. and WENG C.-I., *Comput. Mat. Sci.*, **43** (2008) 1048.
- [39] ANGELL C. A., *Science*, **267** (1995) 1924.
- [40] LE L. and MOLINERO V., *J. Phys. Chem. A*, **115** (2011) 5900.
- [41] PETIT L., VUILLEUMIER R., MALDIVI P. and ADAMO C., *J. Chem. Theory Comput.*, **4** (2008) 1040.
- [42] KLOTZ S., BOVE L., STRAESSLE T., HANSEN T. C. and SAITTA A. M., *Nat. Mater.*, **8** (2009) 405.
- [43] MALLAMACE F., CORSARO C. and STANLEY H. E., *Sci. Rep.*, **2** (2012) 993.
- [44] MALLAMACE F., CORSARO C., STANLEY H. E., MALLAMACE D. and CHEN S.-H., *J. Chem. Phys.*, **139** (2013) 214502.