Thermodynamic behavior and structural properties of an aqueous sodium chloride solution upon supercooling

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We present the results of a molecular dynamics simulation study of thermodynamic and structural properties upon supercooling of a low concentration sodium chloride solution in TIP4P water and the comparison with the corresponding bulk quantities. We study the isotherms and the isochores for both the aqueous solution and bulk water. The comparison of the phase diagrams shows that thermodynamic properties of the solution are not merely shifted with respect to the bulk. Moreover, from the analysis of the thermodynamic curves, both the spinodal line and the temperatures of maximum density curve can be calculated. The spinodal line appears not to be influenced by the presence of ions at the chosen concentration, while the temperatures of maximum density curve displays both a mild shift in temperature and a shape modification with respect to bulk. Signatures of the presence of a liquid-liquid critical point are found in the aqueous solution. By analyzing the water-ion radial distribution functions of the aqueous solution, we observe that upon changing density, structural modifications appear close to the spinodal. For low temperatures, additional modifications appear also for densities close to that corresponding to a low density configurational energy minimum. © 2008 American Institute of Physics. [DOI: 10.1063/1.2939118]

I. INTRODUCTION

The anomalous behavior of water has attracted the attention of scientists for a long time. Many fascinating features distinguish water from most other liquids. Among them, we point out the presence of a line of temperatures of maximum density (TMD) in the \( P-T \) plane and the power law divergences upon supercooling of the coefficient of thermal expansion, of the specific heat and of the isothermal compressibility.1-4

Molecular dynamics (MD) simulations of water modeled with ST2, SPC/E, TIP4P, and TIP5P potentials have shown the existence of a second critical point5-11 buried inside the supercooled region with a coexistence between a low density liquid (LDL) and a high density liquid (HDL). The deep supercooled region is not directly accessible to experiments, nonetheless signatures of the second critical point have been observed.12 In this picture, water anomalies are a direct consequence of the existence of the second critical point in the region of low temperatures and high pressures, the water spinodal line is non-entrant and correspondingly the TMD line bends to avoid crossing the spinodal line.

Because water is a rather unique solvent, the properties of aqueous solutions are also a topic of substantive interest. In particular, thermodynamic and structural properties of aqueous solutions of electrolytes are of importance because of the ubiquitous presence of these solutions in biological and geophysical systems. Besides the properties of aqueous solutions upon supercooling are significant for cryopreservation of biological tissues.13,14

As far as water itself is concerned, it is well known that the presence of solutes affects important properties such as melting point, boiling point, and viscosity. It is therefore important to understand to what extent thermodynamic properties of water are affected by the solutes upon supercooling. In fact while many studies in literature concentrate on ionic solutions at ambient temperature, very little has been done in the supercooled region. Differential scanning calorimeter measurements have shown15 that for low NaCl content, up to about 1 mol/kg, at ambient pressure, the TMD and the anomalous behavior of specific heat upon supercooling are still present, gradually tending to disappear upon increasing the salt content.

A large number of experiments and simulations focus on the hydration structure16-27 at ambient temperature of ionic solutions, that is to say on the arrangement of water molecules in proximity to the ions. At low concentrations, the presence of the ions perturbs the structure of water only locally, while it remains unaltered far away from the ions.24 Traditionally, ions have been divided in structure making (or cosmotrope) and structure breaking (or chaotrope) depending on the effect they have on water-water hydrogen bonds. The first appearance of these concept dates back to the Hofmeister’s series.28 More than thirty effects connected to the Hofmeister’s series28 can be found, nevertheless its greatest significance resides in the different degree of hydration of ionic compounds in aqueous solutions. Although some authors29 questioned the significance of the structure-making/breaking concept, mainly because of the difficulty in quantifying correlated properties, the majority of studies apply the usual definition.24 Structure-making ions break the hydrogen bonds of surrounding water molecules, thus allow-
ing a rearrangement of water molecules that results in an ordered hydration structure. Structure-breaking ions bend without breaking the hydrogen bonds of nearby water molecules, thus disordering the tetrahedrally coordinated network. So far it is not clear whether and how structure-making/breaking properties of ions are connected to modifications of thermodynamic properties of the solvent upon supercooling.

We present here a MD simulation study of an aqueous sodium chloride solution, in the following denoted as NaCl(aq), upon supercooling. The salt content in the aqueous solution amounts to c = 0.67 mol/kg. Its thermodynamic and structural properties are compared to a MD simulation of bulk water. The isotherms and the isochores are studied for both systems to investigate whether and to what extent the thermodynamic properties of water upon supercooling are modified in presence of a low concentration of ions. The analysis of the phase diagrams leads to the determination of the TMD line and the spinodal line.

The structural properties are also studied, calculating the partial radial distribution functions (RDFs) of water molecules around the ions. The RDFs’ features are analyzed also taking into account the structure-making properties of the Na\(^+\) and the structure-breaking properties of the Cl\(^-\) ions.

The paper is organized as follows. In Sec. II, we report the simulation details. The thermodynamic results are presented in Sec. III and discussed therein. In Sec. IV, we present the hydration RDFs and we discuss their trends as function of density. Conclusions are drawn in Sec. V.

### II. MODEL AND COMPUTER SIMULATION DETAILS

MD simulations are performed on two systems, bulk water and water with Na\(^+\) and Cl\(^-\) ions. The systems are simulated with the DL_POLY package\(^{31}\) using the TIP4P site model for water molecules.\(^{32}\)

The particles interact via short range Lennard-Jones (LJ) potentials and long-range coulombic potentials. Thus the interaction potential can be written as

\[
U_{ij}(r) = \frac{q_i q_j}{r} + 4\epsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r} \right)^{12} - \left( \frac{\sigma_{ij}}{r} \right)^6 \right],
\]

where ion-water and ion-ion parameters are taken from Koneshan and Rasiah calculation for LJ potential,\(^{46}\) based upon a reparametrization of Pettit and Rossky parameters\(^{33}\) for the Huggins–Mayer potential. The LJ parameter \(\epsilon_{ij}\) and \(\sigma_{ij}\) are obtained using the Lorentz–Berthelot mixing rules \(\epsilon_{ij} = \sqrt{\epsilon_i \epsilon_j}\) and \(\sigma_{ij} = (\sigma_i + \sigma_j)/2\). The LJ interaction parameters and the charges are shown in Table I along with masses and charges of the sites.

The cutoff radius is set to 9.0 Å and the long range coulombic interactions are treated by the Ewald summation method, with the convergence parameter \(\alpha\) (Ref. 34) set to 6.4/\(L\), where \(L\) is the edge length of the cubic simulation box in which the particles reside.

The MD simulations are carried out in the NVT ensemble. The temperature is fixed by the use of the Berendsen thermostat.\(^{35}\) The integration timestep employed is 1 fs.

In the case of bulk water, the system is simulated with 256 water molecules, while in the NaCl(aq) system we have 250 water molecules plus three sodium ions and three chloride ions. The corresponding concentration expressed as moles of solute per mass of solvent (molality) is \(c = 0.67\) mol/kg.

We span densities in the range \(0.80\ g/cm^3 \leq \rho \leq 1.1\ g/cm^3\) for the NaCl(aq) and \(0.80\ g/cm^3 \leq \rho \leq 1.05\ g/cm^3\) for bulk water. The analyzed densities and the corresponding boxlengths are reported in Table II for both systems.

<table>
<thead>
<tr>
<th>(\rho) (g/cm(^3))</th>
<th>NaCl(aq) (L_{\text{box}}) (Å)</th>
<th>Bulk (L_{\text{box}}) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>19.189</td>
<td>...</td>
</tr>
<tr>
<td>1.05</td>
<td>19.489</td>
<td>19.388</td>
</tr>
<tr>
<td>1.025</td>
<td>19.641</td>
<td>...</td>
</tr>
<tr>
<td>1.0</td>
<td>...</td>
<td>19.710</td>
</tr>
<tr>
<td>0.98</td>
<td>19.943</td>
<td>19.839</td>
</tr>
<tr>
<td>0.95</td>
<td>20.151</td>
<td>20.046</td>
</tr>
<tr>
<td>0.90</td>
<td>20.517</td>
<td>20.410</td>
</tr>
<tr>
<td>0.87</td>
<td>20.750</td>
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<tr>
<td>0.85</td>
<td>20.911</td>
<td>20.811</td>
</tr>
<tr>
<td>0.83</td>
<td>...</td>
<td>20.977</td>
</tr>
<tr>
<td>0.80</td>
<td>21.338</td>
<td>21.236</td>
</tr>
</tbody>
</table>

![Table II. Densities and boxlengths for NaCl(aq) and bulk water.](image-url)
III. THERMODYNAMIC RESULTS

We investigate how the thermodynamic behavior of water upon supercooling changes in the presence of a low concentration of Na\(^+\) and Cl\(^-\) ions with respect to the bulk by looking at isotherms and isochores obtained from simulated state points.

From the isotherms, the limit of mechanical stability can be determined in the framework of mean field theories from the divergence of the isothermal compressibility. The singularity points where

\[
\frac{dP}{d\rho} = 0
\]

define the spinodal line. They can be obtained searching for the minima of the \(P(T)\) curves.

In Fig. 1, we show the isotherms of the NaCl(aq) system obtained upon cooling for densities ranging from \(\rho = 0.80 \, \text{g/cm}^3\) to \(\rho = 1.1 \, \text{g/cm}^3\) and temperatures from \(T = 300 \, \text{K}\) to \(T = 210 \, \text{K}\). The spinodal line has been drawn joining the minima of the isotherms. The isotherms from \(T = 500 \, \text{K}\) to \(T = 350 \, \text{K}\) do not show a minimum and they have not been reported. The \(T = 300 \, \text{K}\) isotherm is the only one to have the minimum in correspondence of the density \(\rho = 0.85 \, \text{g/cm}^3\), all the other lower temperature isotherms show a minimum corresponding to the density \(\rho = 0.87 \, \text{g/cm}^3\).

We report in Fig. 2 the isotherms of bulk water in the \(P-\rho\) plane. We plot the bulk isotherms for densities ranging from \(\rho = 0.80 \, \text{g/cm}^3\) to \(\rho = 1.05 \, \text{g/cm}^3\) and temperatures ranging from \(T = 300 \, \text{K}\) to \(T = 210 \, \text{K}\). Analogous to what happens for the solution the highest temperatures isotherms, \(T = 500 \, \text{K}\), \(T = 400 \, \text{K}\), and \(T = 350 \, \text{K}\) do not exhibit minima (not shown). The spinodal line for bulk water, drawn joining the isotherms minima, shifts from \(\rho = 0.83 \, \text{g/cm}^3\), for \(T\) ranging from 300 to 260 K, to \(\rho = 0.85 \, \text{g/cm}^3\), for the lowest temperatures.

The comparison of the region of the \(P-\rho\) plane close to the spinodal line of the two systems is reported in Fig. 3. The density range is here \(0.80 \, \text{g/cm}^3 \leq \rho \leq 0.95 \, \text{g/cm}^3\). We observe that the NaCl(aq) isotherms minima are shifted to higher densities with respect to the bulk, moreover, the curves envelope is globally shifted to lower pressures. We note that the presence of the ions also changes the shape of the curves. The isotherms of the NaCl(aq) system appear in fact closer to each other than in the bulk phase.

In Fig. 4, we present a zoom of the region of the \(P-\rho\) phase diagram in the density range \(0.90 \, \text{g/cm}^3 \leq \rho \leq 1.05 \, \text{g/cm}^3\), in order to compare the isotherms of the two systems at high densities. In both systems, the \(T = 220 \, \text{K}\) and the \(T = 210 \, \text{K}\) curves cross the higher temperature isotherms and change the sign of their curvature. These effects are particularly evident for the bulk \(T = 220 \, \text{K}\) and \(T = 210 \, \text{K}\) isotherms and the NaCl(aq) \(T = 220 \, \text{K}\) isotherm. In bulk water, these changes of curvatures have been already observed\(^5\)\(^,\)\(^37\) and related to the existence of a second critical point. In fact, they are signatures of the approach of the system to the co-

FIG. 1. Spinodal line and isotherms of the NaCl(aq) solution in the \(P-\rho\) plane.

FIG. 2. Spinodal line and isotherms of bulk water in the \(P-\rho\) plane.

FIG. 3. Blow up and comparison of the NaCl(aq) and bulk spinodal line and isotherms in the \(P-\rho\) plane, in the density range \(0.80 \, \text{g/cm}^3 \leq \rho \leq 0.95 \, \text{g/cm}^3\). Symbols are as in Figs. 1 and 2.
existence between LDL and HDL phases. Therefore, we hypothesize also for the NaCl(aq) the existence of a second critical point. For the change of curvature, a shift toward higher densities can be noticed in the aqueous solution. This observation leads to infer that also the second critical point might consequently be shifted to a higher density with respect to the position in the bulk.

We now consider the isochores of the NaCl(aq) and the pure water systems reported in Figs. 5 and 6, respectively. The behavior of the TMD line can be extracted from the analysis of the isochores plane. In fact along the TMD line, the coefficient of thermal expansion

$$\gamma_v = \frac{\alpha_{\rho}}{K_T}$$

where $K_T$ is the isothermal compressibility. Therefore the TMD points lie on the line connecting the minima of the isochores. For both systems, the minima have been determined fitting the isochores with a fourth order polynomial function.

For the aqueous solution, the isochores in Fig. 5 are shown from $\rho=1.1$ g/cm$^3$ to $\rho=0.87$ g/cm$^3$ in the temperature range from $T=500$ K to $T=210$ K. The $\rho=0.87$ g/cm$^3$ isochore almost coincides with the spinodal line (see Fig. 1) also reported in Fig. 5. In Fig. 6, the isochores of the bulk water are reported from $\rho=1.05$ g/cm$^3$ to $\rho=0.85$ g/cm$^3$, in the same temperature range as above. Here the $\rho=0.85$ g/cm$^3$ isochore almost coincides with the water spinodal shown in the same figure. For both systems, the isochores with densities lower than that of the spinodal lines are not reported since they lie beyond the mechanical stability limit of the system.

For bulk water, we observe a spinodal extending to the region of negative pressures and non-re-entrant down to the lowest temperature investigated. This behavior has been already observed in literature for different potentials. $^6,8,37-42$ Also the aqueous solution displays a non-re-entrant spinodal line qualitatively similar to the bulk.

In the case of the aqueous solution, all the isochores above $\rho=0.87$ g/cm$^3$ exhibit a clear minimum. This result agrees with the experimental work by Archer and Carter $^{15}$ in which they find a TMD line for the solution at the concentration studied here. From the minima, via a fitting proce-
and HDL phases. It has been shown by Kumar that these energy extrema can be related to the existence of LDL in the bulk; the minimum is reached for negative pressures.

In the case of pure water (Fig. 6), only for the first four isochores, a minimum is found in the range of temperatures explored. The shape of the TMD line is in agreement with the results that can be found in literature.8,37

The comparison of the isochores planes of NaCl(aq) (Fig. 5) and bulk water (Fig. 6) reveals that in the P-T plane, the isochores of NaCl(aq) lie at lower pressures than the corresponding bulk curves. Besides, the concavity of the isochores in proximity to the minima is deeper in bulk water than in NaCl(aq). This is mirrored by the different pattern followed by the TMD line in the two systems.

The location of the second critical point for bulk TIP4P water is estimated to be at negative pressure by Tanaka,6 while it is found at positive pressures for ST2,8 TIP5P,9 and TIP4P-ew.11 From the behavior of our isochores, TMD and spinodal for both the bulk water and the aqueous solution, it is actually not easy to establish whether it falls at positive or negative pressures.

In Fig. 7, the TMD line of NaCl(aq) and bulk water are reported together with the spinodal lines of the two systems. Comparing the TMD lines we notice that apart from the mild temperature shift due to the colligative properties of the solutions, the TMD lines appear different in shape. In fact, spanning the same range of densities, the NaCl(aq) TMD extends in a region of pressures wider than that of the bulk. Therefore, the effect of the ions upon supercooling is not limited to give a rigid translation of the phase diagram.

While the presence of the ions seems to induce important changes in an anomalous thermodynamic property of water, the TMD, the limit of mechanical stability appears not affected by the ions. In fact from Fig. 7, we can see that the spinodal lines of the two systems are almost indistinguishable from each other.

In Fig. 8, we present the configurational energy per molecule, at T =220 K, as a function of the density. Two minima are present for TIP5P water confined between hydrophobic plates for ρ=0.88 g/cm³ and for ρ=1.39 g/cm³. The presence of this minimum in our system supports the existence of a liquid-liquid (LL) coexistence also in the aqueous solution.

IV. STRUCTURAL RESULTS

We discuss in this section the RDFs of the aqueous solution, g(r), computed averaging the equilibrated configurations. In the NaCl(aq) system at the salt content investigated, we do not observe significant changes in water-water RDFs with respect to the bulk system. Minor differences occur only in the secondary peaks, for low densities and in the deep supercooled region (not shown). It has been shown in a number of papers17–20 that the effect of the ions on water-water structure is similar to the one obtained applying an external pressure and that it becomes more evident upon increasing the salt content. The salt concentration in our system, ϵ =0.67 mol/kg, is probably too low to find clear evidence of this effect. Besides both sodium and chloride ions can be found in the central region of the Hofmeister series so that not very marked effect on water-water structure are expected.

We present in the following the analysis of the water-ion structure comparing RDFs along the isotherms T=300 K and T=220 K for densities from ρ=1.1 g/cm³ to ρ=0.80 g/cm³. We note that for the highest density at T =300 K the RDFs show different trends with respect to all other densities investigated. These trends likely anticipate a different behavior of the system at very high densities (not investigated in the present paper).

In Figs. 9 and 10, we show the sodium-oxygen and the sodium-hydrogen RDFs.

We observe that for both temperatures, the first and the second coordination shells of the gNa-O(r) are well defined showing the tendency of water to form stable hydration shells around the sodium ion, usually classified as structure making. For the gNa-H(r), the first shell is also well defined while the second shell is broader.

The position of the first peak of the gNa-H(r) is shifted to a higher distance with respect to the position of the first peak of the gNa-O(r). The difference between the two peaks is...
circa 0.6 Å indicating that the two hydrogens of the molecule lie symmetrically around the sodium ion. This result is confirmed by the coordination numbers of the first shell which we report in Fig. 11 together with the coordination numbers of the Cl–O and Cl–H.

We consider now more in detail the behavior of the $g_{\text{Na–O}}$ as function of the density. At $T=300$ K starting from $\rho=1.05$ g/cm$^3$ the peaks heights decrease significantly until they reach a minimum at the density of the spinodal line, $\rho=0.87$ g/cm$^3$. For densities lower than this value down to $\rho=0.80$ g/cm$^3$, the peaks heights slightly increase again. On going from high density down to the spinodal density along the isotherm, the Na$^+$ ions partially lose their structure-making ability due to the approach to the instability region, where the onset of large fluctuations and a tendency to demixing could appear.

At $T=220$ K the two peaks slightly sharpen as a consequence of decreasing temperature. Starting from $\rho=1.05$ g/cm$^3$, the height of the first peak of the $g_{\text{Na–O}}$ now shows a maximum in proximity of the energy minimum density, then it decreases showing a minimum on approaching the spinodal density. We observe close to the second peak the appearance of secondary shells especially for densities close to the spinodal and to the energy minimum density, e.g., a possible region of LL coexistence. This indicates that the second shell of hydration is less defined.

The $g_{\text{Na–H}}$, shown in Fig. 10, displays an analogous trend as a function of density both for $T=300$ K and $T=220$ K with respect to that observed in Fig. 9 for the sodium-oxygen pair. In particular we also observe here the appearance of secondary shells.

In Figs. 12 and 13 we show the $g_{\text{Cl–O}}$ and the $g_{\text{Cl–H}}$. For the $g_{\text{Cl–O}}$, we see a broad and structured first shell and a not well defined second shell. For the $g_{\text{Cl–H}}$, we observe a well defined first peak and a broad and structured second shell. At variance with the $g_{\text{Na–O}}$ and the $g_{\text{Na–H}}$, the first and the second shell are not always well defined for these RDFs because of the structure breaking property of the Cl$^-$ ion.
By comparing the positions of the first peaks of the $g_{\text{Cl-O}}(r)$ and the $g_{\text{Cl-H}}(r)$, we note an approximated charge ordering around the negative chloride ion. The partially positively charged hydrogens move closer to the ions and the first shell of the oxygen is placed around the first minimum of the $g_{\text{Cl-H}}(r)$.

We now analyze the behavior of the $\text{Cl}^-$ RDFs as a function of density for the two temperatures investigated. For the $g_{\text{Cl-O}}(r)$ at $T=300$ K, the first shell of oxygen is well defined only at $\rho=1.05$ g/cm$^3$. Below $\rho=1.05$ g/cm$^3$, a shoulder appears on the right side of the first peak. The peaks heights of the $g_{\text{Cl-O}}(r)$ show a trend similar to that of the $g_{\text{Na-O}}(r)$ while their shape is more strongly dependent on the density. On approaching the spinodal, the first peak merges with the shoulder resulting in a broad structure. The structure-breaking role of the $\text{Cl}^-$ ions seems to be reinforced close to the instability limit.

At $T=220$ K, the shoulder close to the first peak evolves in a second peak indicating a less stable configuration of the chloride hydration with respect to sodium. In fact, the first hydration shell is characterized by the existence of two possible equilibrium positions albeit close to each other for the chloride-oxygen pair. In this first shell, oxygens of two kinds are present, those tied to the hydrogens of the first shell of the $g_{\text{Cl-H}}$ and those tied to hydrogens belonging to the second shell of the $g_{\text{Cl-H}}$ that in fact also shows double peak structure (see Fig. 13). For this temperature, a structuring of the curves also appears for densities close to the energy minimum density and to the spinodal density.

For the $g_{\text{Cl-H}}(r)$, Fig. 13, the trend of the peaks intensities as a function of density are similar to those in Fig. 12 but the RDFs appear much more structured with a second and third shell evident at all densities. The second shell is modulated in a double peak structure for both temperatures. We also note that for both temperatures the first shell of hydrogens of the $g_{\text{Cl-H}}(r)$ is well defined at all densities, at variance with the second peak. It shows that hydrogens penetrate inside the shell of the oxygen for the attraction of the ions.

The broadening and the modulation of the oxygen first peaks and the hydrogen second peaks in the $g_{\text{Cl-O}}(r)$ and the $g_{\text{Cl-H}}(r)$, respectively, seem to be related to a competition between the formation of the hydrogen bonds and the repulsion/attraction of the chloride ion with respect to oxygen/hydrogen atoms.

We have seen that the $\text{Na}^+$ ions are able to form a sufficiently rigid shell of oxygen, see the first peaks in Fig. 9, breaking the hydrogen bonds when necessary while the $\text{Cl}^-$ ions can attract the hydrogens in a first shell and repel the oxygens, but they have little effect on the hydrogen bonding. Coordination numbers confirm this picture, see Fig. 11. They show in fact no correlation in trend between the first shell of oxygen and the second shell of oxygen around the chloride ion as a function of density.

For each of the four hydration RDFs, the peaks positions are compatible with what found in literature. The ion-ion RDFs (not shown) have a low statistic due to the low concentration. The positions of the peaks indicate the presence of clusters of positive and negative ions in agreement with what reported in several papers, both theoretical and experimental.
V. CONCLUSIONS

We performed MD simulations of a sodium chloride aqueous solution with concentration $c=0.67$ mol/kg and of bulk water upon supercooling at different densities. We used TIP4P water model both for the aqueous solution and for the bulk.

We studied how the thermodynamic behavior of bulk water is modified by the presence of ions and in particular the possible modification of the TMD and of the spinodal line. We found that while the presence of ions influences the shape and the position of the TMD, it leaves substantially unaltered the spinodal line with respect to the bulk. Besides the TMD curve appears broadened and it extends to much lower temperatures than bulk TMD. In a previous study of TIP4P water under hydrophobic confinement,\textsuperscript{36} it was found that both the spinodal line and the TMD are shifted toward higher pressures. In the case of the aqueous solution studied in the present work, the TMD line shifts also to lower temperatures and correspondingly its curvature broadens. In addition, the presence of the ions moves the isotherms and the isochores curves toward lower pressures and it slightly modifies their shape, especially in proximity to the minima of those curves. Therefore, although the limit of mechanical stability of the system remains unaltered in the solution, the effect of ions is not limited to a trivial pressure shift. The modification of the isotherms and the isochores curves and especially of the TMD shows that in the supercooled regime, the ions affect the thermodynamics of the system even at this low concentration.

In our aqueous solution, we observed at higher densities a crossing of the two lowest temperatures isotherms with the higher temperatures ones. It has been shown that the change of sign of the curvature of isotherms in this density region is connected to the existence of a second critical point in bulk water.\textsuperscript{7,37} We can consequently hypothesize the existence of a LL critical point also in the solution probably shifted to higher densities. The TMD shape is related to the position of the LL critical point hence our results indicate that the presence of ions stabilizes the HDL phase driving down in temperature the LL line. Interestingly, two recent experimental papers by Mishima\textsuperscript{45,46} on LiCl-water solutions seem to indicate a suppression of the transition to the low density amorphous like (LDA-like) water. This appears consistent with our TMD line shift. Besides, according to Holzmann et al.\textsuperscript{47} the shift to low temperatures of the TMD can be framed in a picture in which the free water, that is the water far from ions, becomes upon supercooling more mobile and pressurized.

The spinodal line, related to LDL properties, does not show any substantial modification with respect to the bulk at least when a small amount of ions is present. The shape of the curve describing the configurational energy as a function of the density (see Fig. 8) for the NaCl(aq) closely resembles what found by Kumar et al.\textsuperscript{43} for confined water in the low density region zone explored in this work. Importantly we observe the presence of a minimum analogous to the LL low density coexistence minimum observed in bulk water.

The structural analysis of the NaCl(aq), shown here for $T=300$ K and at $T=220$ K, revealed that the four hydration RDFs $g_{Na-O}(r)$, $g_{Na-H}(r)$, $g_{Cl-H}(r)$, and $g_{Cl-O}(r)$ display minima in peaks intensities in proximity to the density corresponding to the spinodal line at both high and low temperatures and the appearance of several secondary peaks for densities close to the spinodal line and to the configurational energy minimum, at low temperatures. Therefore we found that the spinodal line and the energy minimum, low density LL coexistence, affect significantly the hydration structure.

As regards structure-making/breaking effects, the traditional classification of Na$^+$ as structure making and Cl$^-$ as structure breaking\textsuperscript{23,24,48,49} appears confirmed in this work. Sodium ions in fact tend to break water hydrogen bonds favoring a rearrangement of the equilibrium positions of the molecules around the ion that results in the formation of definite hydration shells (especially the first one). On the other hand, the chloride having a greater ionic radius and thus a minor charge density is less effective in breaking the hydrogen bonds. Therefore its coordination shells are less defined and more disordered as also indicated by the presence of secondary peaks in the shell structures.

We have seen that all peaks intensities of our hydration RDFs follow a similar pattern as a function of the density. The presence of minima in the peaks heights is probably connected to the approach of the system to the spinodal line. On going from high density toward the spinodal density, Na$^+$ ions partially lose their structure-making ability while the structure breaking properties of the Cl$^-$ ions seems to be reinforced. Several extensions of this study can be proposed. In particular the analysis of higher densities and concentrations would be of the utmost interest in order to investigate how thermodynamic and structural properties change varying those variables. Indeed varying either the concentration or the chemical species of the solutes provides a tool to prepare a system with suitable properties, for example for cryopreservation.

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