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Molecular dynamics studies on the thermodynamics of supercooled sodium chloride aqueous solution at different concentrations

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Abstract

In this paper we compare recent results obtained by means of molecular dynamics computer simulations on the thermodynamics of TIP4P bulk water and on solutions of sodium chloride in TIP4P water. The concentrations studied are $c = 0.67, 1.36$ and 2.10 mol kg^{-1} . The results are checked against change of water–salt potential and size effects. The systems are studied in a wide range of temperatures, going from ambient temperature to the supercooled region. Analysis of simulated state points, performed on the isochores and on the isotherm plane, allowed the determination of the limit of mechanical stability and of the temperature of maximum density lines. While the presence of ions in the system does not affect the limit of mechanical stability with respect to the bulk, it causes the temperature of the maximum density line to shift to lower pressure and temperature upon increasing concentration. The occurrence of minima in the trend of potential energy as a function of density and the inflections in the low temperature isotherms suggest the presence of liquid–liquid coexistence for bulk water and for the sodium chloride solutions at all concentrations studied.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Although water is the long-standing subject of a vast amount of scientific literature, there is still lively interest in its anomalous properties. In fact, an understanding of the origin of the anomalous behaviour of water is a topic of great relevance for both liquid state physics and life sciences.

Water is the most abundant liquid on Earth [1]. In the ambient and in the biological world, water often behaves as the solvent in mixtures of several components. Thus the evaluation of the effect of the presence of solutes on the properties of liquid water is pivotal to understanding to what extent the anomalous properties of water in aqueous solutions are relevant in the natural and biological world.

The most known thermodynamic anomalies of water are the presence of a temperature of maximum density, $T = 277 \text{ K}$ at ambient pressure and the large increase of the thermodynamic response functions, such as the isothermal

compressibility K_T , the isobaric specific heat C_P and the coefficient of thermal expansion α_P (absolute value), upon supercooling [2–5].

Supercooled liquids are ubiquitous in nature, industry and technology [2]. If the lifetime of the metastable state is longer than the relaxation time of the system then a thermodynamic description of metastable liquids can be performed [2, 6].

For water, the experimental investigation of the reason for the appearance of the thermodynamic anomalies in the supercooled region is hampered by the nucleation temperature, $T_H = 235 \text{ K}$ at ambient pressure. However, experiments sustain the hypothesis that the experimentally observed amorphous phases can be connected to the normal liquid phase through a reversible thermodynamic path [7].

Thermodynamic anomalies of water can be encompassed in the *liquid–liquid critical point (LLCP) scenario*. In this framework, which was first proposed by Poole *et al* [8], the thermodynamic anomalies arise as a consequence of

the presence in the supercooled region of an LLCP, ending the coexistence line between a high density liquid (HDL) and a low density liquid (LDL). The coexistence line between the two liquids can be seen as the continuation of the coexistence line between the experimentally observed amorphous phases, the high density amorphous (HDA) ice and the low density amorphous (LDA) ice [9]. Theoretical works [10–14] and computer simulations with different water models [15–22] have confirmed the plausibility of the LLCP scenario. Although direct experimental observation has not been possible, indications of the presence of an LLCP have been found experimentally [9, 23]. Moreover, recently, two coexisting phases in deeply supercooled water have been observed by electron spin resonance [24]. The LLCP phenomenon is connected to metastability [8] in most systems but there is a class of cases in which it appears under thermodynamically stable conditions [25].

Alternatively, it has been shown that the thermodynamic anomalies of water can be framed in the *singularity free scenario* [26] in which the behaviour of the thermodynamic response function relates to local density fluctuations, or in the *critical point free scenario* [27] in which the HDL–LDL transition is pictured as an order–disorder transition.

It is well known that the thermodynamic properties of water are modified by the presence of solutes. Ionic solutions have been extensively studied in the past, focusing mostly on their hydration structure at ambient temperature [28–37] and also on the glass transition phenomenon [38]. Nonetheless very few studies focused on thermodynamic properties of ionic solutions in the supercooled region. For NaCl(aq) and NaNO₃(aq) it has been shown [39, 40] that the anomalous thermodynamic behaviour is preserved in solutions for concentrations from low to moderate and it gradually disappears upon increasing concentration. Hints of the presence of liquid–liquid coexistence have been also recently found in experiments on LiCl(aq) [41, 42].

In this paper we present the results of molecular dynamics (MD) computer simulation studies performed on bulk water and on NaCl(aq) at three different concentrations, namely $c = 0.67, 1.36$ and 2.10 mol kg^{-1} [43–45]. We discuss the choice of the interaction parameters between particles and we compare the results of the simulations performed with different system sizes. The behaviour of the potential energy as a function of density is presented for all systems. The simulated state points are reported both in the P – T isochore plane and in the P – ρ isotherms plane. Important thermodynamic loci such as the temperature of maximum density (TMD) line and the limit of mechanical stability line (LMS) can be extracted from the analysis of the P – T and P – ρ planes. These results are compared also with water confined in a hydrophobic environment made by soft spheres [46].

The paper is organized as follows. In section 2 we give the details of the simulations performed and we discuss the choice of the potential and the effects of the size of the system. In section 3 we show the results on the thermodynamics of the studied systems. Conclusions are given in section 4.

2. Methods

In this section we give the details of the simulation method that was employed to collect the data we present here. We also compare two different choices of interaction potential and finally study the effect of the size of the systems on thermodynamics.

MD simulations were performed on TIP4P [47] bulk water and on a solution of sodium chloride in TIP4P water [43–45]. The concentrations studied are $c = 0.67, 1.36$ and 2.10 mol kg^{-1} . Concentrations are given in moles of solute per mass of solvent (molality).

The range of densities spanned goes from $\rho = 0.80$ to 1.125 g cm^{-3} , while the range of temperatures goes from $T = 500$ down to 210 K . The temperature was controlled by the use of the Berendsen thermostat [48]. The integration timestep was 1 ps . The DL_POLY simulation package [49] was employed to perform the simulations.

Starting configurations were produced by putting the molecules on a face centred cubic lattice. The crystal was melted at $T = 500 \text{ K}$ and the temperature was step-wise reduced during equilibration runs. These were followed by production runs in which the thermodynamic averages were collected. Simulation times were progressively increased upon decreasing temperature in order to ensure the convergence of the computed thermodynamic quantities. Simulation times for equilibration and production runs span from 0.1 ns for the highest temperatures to 10 ns for the lowest ones. We found no differences in the equilibration and production times required up to the highest concentration we simulated.

Periodic boundary conditions were applied. The cutoff radius was set to 9 \AA . Usually the cutoff radius is set between 8 and 10 \AA [50]. Standard long range corrections to the Lennard–Jones (LJ) interaction were applied. Long range electrostatic interactions were dealt with using the Ewald summation method. The interaction potential between particles is given by the sum of the coulombic and LJ potentials

$$U_{ij}(r) = \frac{q_i q_j}{r} + 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r} \right)^{12} - \left(\frac{\sigma_{ij}}{r} \right)^6 \right] \quad (1)$$

where q is the electric charge and ϵ_{ij} and σ_{ij} are the LJ parameters. The ion–ion parameters were taken from the reparametrization performed by Koneshan and Rasaiah [30] for the LJ potential of Pettitt and Rossky (PR) parameters [51] originally calculated for the Huggins–Mayer potential. Ion–water LJ parameters were obtained by Lorentz–Berthelot mixing rules. This set of parameters was checked, for $\rho = 1.025 \text{ g cm}^{-3}$ isochore, against the Jensen and Jorgensen (JJ) ion–ion LJ parameters [52], with ion–water LJ parameters obtained by geometric mixing rules. The values of the ion–water and ion–ion LJ parameters of the two sets are reported in table 1.

Most simulations were carried out with the total number of molecules in the cubic simulation box, $N_{\text{tot}} = 256$. For the sake of the study of the finite size effect, the $\rho = 0.98 \text{ g cm}^{-3}$ isochore was simulated also with double and four-fold number of molecules. The number of particles was chosen in order to have a boxlength always larger than twice the cutoff radius.

Table 1. Ion–water and ion–ion LJ interaction parameters between atom pairs for the Pettitt–Rossky (PR) set [51] and for the Jensen–Jorgensen (JJ) set [52].

Atom pair	PR set		JJ set	
	ϵ (kJ mol ⁻¹)	σ (Å)	ϵ (kJ mol ⁻¹)	σ (Å)
Na–O	0.560 14	2.720	0.036 86	3.583
Na–H	0.560 14	1.310	—	—
Cl–O	1.505 75	3.550	1.389 57	3.561
Cl–H	1.505 75	2.140	—	—
Na–Na	0.119 13	2.443	0.002 09	4.070
Cl–Cl	0.979 06	3.487	2.970 64	4.020
Na–Cl	0.352 60	2.796	0.078 79	4.045

Table 2. Composition of the systems with different sizes.

Number of molecules	Bulk	c (mol kg ⁻¹)		
		0.67	1.36	2.10
$N_{\text{tot}} = 256$				
H ₂ O	256	250	244	238
Na ⁺ Cl ⁻	—	3	6	9
$N_{\text{tot}} = 512$				
H ₂ O	512	500	488	476
Na ⁺ Cl ⁻	—	6	12	18
$N_{\text{tot}} = 1024$				
H ₂ O	1024	1000	976	952
Na ⁺ Cl ⁻	—	12	24	36

The details on the number of molecules for each system, divided by chemical species are given in table 2.

Due to the lengthy simulation times required for equilibration and production runs in the supercooled states, the use of polarizable potentials could not be taken into account. On the other hand current state of the art simulations of ionic solutions employ a fixed point charge approximation even for high concentrations [28, 50, 53].

We now discuss the choice of the potential and we study what is the effect of increasing the size of the system on thermodynamics.

The TIP4P potential, employed to model water molecules in our simulations, has been proven to be a very reliable potential for the study of supercooled and solid bulk water [54]. Recently, different authors have pointed out how the choice of the ionic potential is crucial in determining the properties of aqueous ionic solutions [34, 50, 55, 56]. In order to estimate the effects of the ion–ion and ion–water LJ potential on thermodynamics, we simulated the $\rho = 1.025 \text{ g cm}^{-3}$ isochore using the two sets of LJ parameters reported in table 1. We stress that these sets of parameters are very different not only in the numerical values, but also in the way in which they were derived. In fact PR parameters were derived using an integral equation approach to produce an inter-ionic potential of mean force at infinite dilution for models reproducing alkali halides in water [51]. JJ parameters were obtained by Monte Carlo simulations, with the TIP4P water model, aiming to reproduce experimental free energies of hydration and experimental positions of the first peak of the ion–oxygen radial distribution functions. Moreover PR parameters, in order to balance electrostatic Cl–H interactions, include LJ

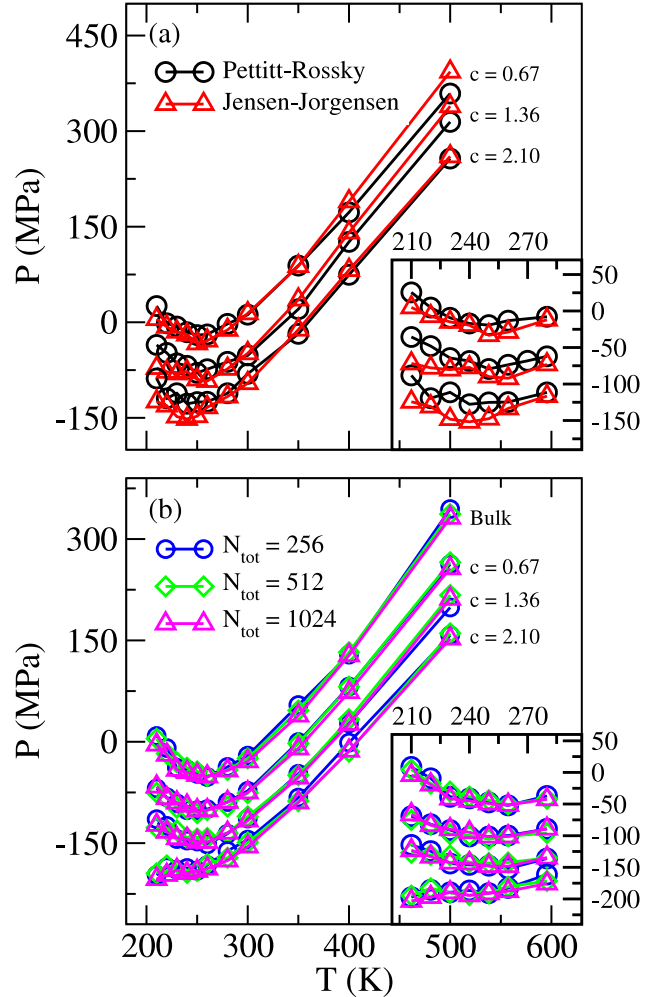


Figure 1. (a) Comparison of the $\rho = 1.025 \text{ g cm}^{-3}$ isochore for the $c = 0.67, 1.36$ and 2.10 mol kg^{-1} NaCl(aq) as obtained from simulations employing Pettitt–Rossky ion parameters [51] (circles) and Jensen–Jorgensen ion parameters [52] (triangles). (b) Comparison of the $\rho = 0.98 \text{ g cm}^{-3}$ isochore for bulk water and for $c = 0.67, 1.36$ and 2.10 mol kg^{-1} NaCl(aq) as obtained from simulations performed with the total number of molecules $N_{\text{tot}} = 256$ (circles), $N_{\text{tot}} = 512$ (diamonds) and $N_{\text{tot}} = 1024$ (triangles), employing the PR ion parameters. In the insets we show an enlargement of the low temperature region.

interactions between ions and hydrogen atoms in water, while in the JJ parameter set no LJ interaction between ions and hydrogen atoms occurs.

In figure 1(a) we report the $\rho = 1.025 \text{ g cm}^{-3}$ isochore for $c = 0.67, 1.36$ and 2.10 mol kg^{-1} NaCl(aq), simulated using PR and JJ LJ parameters sets. Pressure error bars, here and in the following, are within the width of the symbols. For the $c = 0.67 \text{ mol kg}^{-1}$ solution the two isochores look very similar for all temperatures. Upon increasing concentration only minor differences begin to appear. For $c = 1.36 \text{ mol kg}^{-1}$ the two points at the lowest temperatures $T = 210$ and 220 K are slightly different, with the points simulated with the JJ set falling at lower pressures. For $c = 2.10 \text{ mol kg}^{-1}$ the minimum of the curve simulated with the JJ set is deeper than that of the curve calculated with the PR set, causing low temperature points to fall at slightly lower pressure. We note

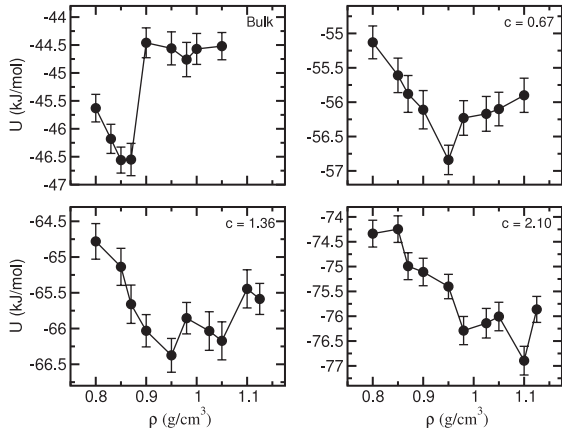


Figure 2. Potential energy per molecule as a function of density at $T = 220$ K for bulk water (top left panel), $c = 0.67$ (top right panel), $c = 1.36$ (bottom left panel) and $c = 2.10$ mol kg⁻¹ (bottom right panel) NaCl(aq). Error bars were derived considering root mean square deviations of potential energy.

that the overall shape and position of the curves simulated with the two sets are quite similar. We conclude that despite the fact that the LJ ionic potential details can have significant effects in determining the structural properties [34, 55, 56] of ionic aqueous solutions, they have a minor impact on thermodynamics, which seems to be mainly determined by longer range electrostatic interactions.

For computer simulations, the size of the system is often a source of discussion, since the calculated properties might depend on the size of the system. In figure 1(b) we report the $\rho = 0.98$ g cm⁻³ isochore simulated for bulk water and for $c = 0.67, 1.36, 2.10$ mol kg⁻¹ NaCl(aq) (PR LJ parameters), at three different system sizes, namely $N_{\text{tot}} = 256, 512$ and 1024. The detailed composition of the mixtures at the three sizes is given in table 2. We can note that no significant deviations in the curves appear, even for the biggest size systems and for the ones with the highest concentration. Thus we can affirm that, for our purposes, the increase in the size of the system does not affect the thermodynamic results and that the smallest simulation box, $N_{\text{tot}} = 256$, can be safely used to reliably reproduce the thermodynamic properties of the systems.

3. Thermodynamic results

In this section we present and discuss the thermodynamic results we obtained for our systems, with the use of the PR potential for ion–water and ion–ion interactions. We will first discuss the behaviour of the potential energy as a function of density and then we will present the P – ρ isotherms and the P – T isochore planes. Finally we will show together the results for the TMD and LMS lines of the studied systems.

In figure 2 we report the behaviour at $T = 220$ K of the potential energy as a function of density for bulk water and for NaCl(aq) at the three concentrations studied. Bulk water and the lowest concentration $c = 0.67$ mol kg⁻¹ NaCl(aq) show a minimum, in correspondence, respectively, with $\rho = 0.86$ g cm⁻³ and with $\rho = 0.95$ g cm⁻³. The two highest

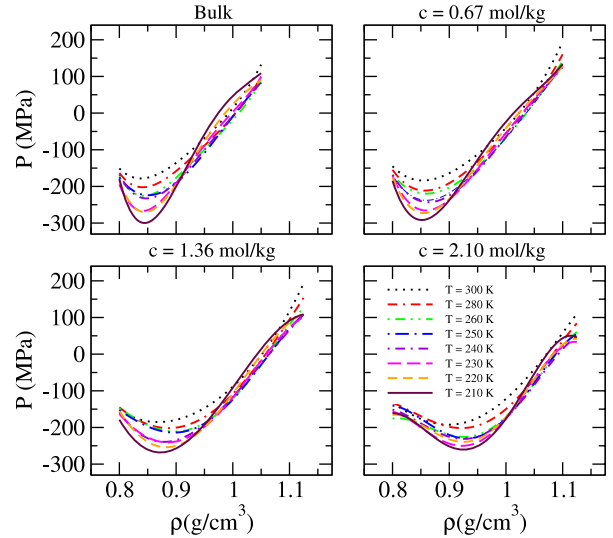


Figure 3. P – ρ isotherm plane for all the studied systems. The isotherms are reported for temperatures $T = 300, 280, 260, 250, 240, 230, 220, 210$ K and have been obtained by polynomial fitting of the simulated state points. The lowest density is $\rho = 0.80$ g cm⁻³ for all systems while the highest density is $\rho = 1.05$ g cm⁻³ for bulk water (top left panel), $\rho = 1.10$ g cm⁻³ for $c = 0.67$ mol kg⁻¹ NaCl(aq) (top right panel) and $\rho = 1.125$ g cm⁻³ for $c = 1.36$ and 2.10 mol kg⁻¹ NaCl(aq) (bottom left and bottom right panel respectively).

concentrations $c = 1.36$ and 2.10 mol kg⁻¹ both show two minima. They can be found at densities $\rho = 0.95$ and 1.05 g cm⁻³ for $c = 1.36$ mol kg⁻¹ and at densities $\rho = 0.98$ and 1.10 g cm⁻³ for $c = 2.10$ mol kg⁻¹. Kumar *et al* [57] reported the presence of two minima in the potential energy at $T = 220$ K, corresponding to the densities $\rho = 0.88$ and 1.39 g cm⁻³ for water confined between hydrophobic plates. The free energy is given by $F = K + U - TS$, with K thermal kinetic energy, U potential energy and S entropy. Although only the direct evaluation of the free energy F would give definitive evidence of two distinct phases, at low enough temperature the behaviour of U can be considered an estimate of the behaviour of F [16, 57, 58]. Thus in our case we can also infer that the presence of two minima for the highest concentrations can be seen as a signal of the presence of HDL–LDL coexistence. For bulk water and for $c = 0.67$ mol kg⁻¹ only one minimum can be seen in the spanned range of density, with the other one probably located at higher density (for water between hydrophobic plates the high density minimum is found at $\rho = 1.39$ g cm⁻³). Furthermore we note that upon increasing concentration the low density minimum shifts to higher densities and that the minima become closer to each other. This could be an indication that upon increasing concentration the liquid–liquid critical region narrows and the distinction between the two liquids tends to disappear.

In figure 3 we present the P – ρ isotherm planes for all the systems studied. Isotherms are reported for $T \leq 300$ K. For all systems evident minima can be observed. These minima in the isotherms correspond to the liquid–gas LMS. In fact as the

isothermal compressibility is given by

$$K_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T = \frac{1}{\rho} \left(\frac{\partial \rho}{\partial P} \right)_T \quad (2)$$

then the points where K_T goes to infinity mark the limit of mechanical stability. We can observe that, while at high densities the isotherms shift to lower pressures upon increasing concentrations, the minimum corresponding to the LMS becomes more shallow and the isotherms at low densities actually rise slightly in pressure.

For all systems the $T = 210$ K and the $T = 220$ K cross the higher temperature isotherms and inflect with a loop for the two highest concentrations. Inflections and crossing of low temperature isotherms are significant because it has been previously observed for bulk water that they are connected to the approach to liquid–liquid coexistence [8, 15]. Therefore, given this observation and the appearance of minima in the potential energy as a function of the density (see figure 2), we can hypothesize that all the systems we studied, up to the highest concentration, show the possible existence of an LLC.

We can also note that the density region where the inflections can be found becomes narrower upon increasing concentration. This is in agreement with the fact that minima in the potential energy become closer to each other and it seems to indicate that upon increasing concentration the liquid–liquid critical region narrows with a consequent weakening of the anomalous behaviour upon increasing concentration. A gradual weakening of anomalous properties such as the apparent divergence of the isobaric specific heat has been experimentally observed in an aqueous solution of salt [39].

In figure 4 we report the P – T isochore plane for all the systems analysed. The isochores are shown for temperatures $210 \text{ K} \leq T \leq 350 \text{ K}$. A state point at $T = 190 \text{ K}$ is also reported for $c = 2.10 \text{ mol kg}^{-1}$ and $\rho = 0.98 \text{ g cm}^{-3}$. Minima in the isochores can be found in all systems, for $\rho \geq 0.95 \text{ g cm}^{-3}$ in bulk water, $\rho \geq 0.90 \text{ g cm}^{-3}$ for $c = 0.67 \text{ mol kg}^{-1}$ NaCl(aq), for $\rho \geq 0.95 \text{ g cm}^{-3}$ for $c = 1.36 \text{ mol kg}^{-1}$ NaCl(aq) and for $\rho \geq 0.98 \text{ g cm}^{-3}$ for $c = 2.10 \text{ mol kg}^{-1}$ NaCl(aq). The minima in the isochores are points of the TMD line. In fact by definition the TMD line is the locus of the points for which the coefficient of thermal expansion α_P is zero. For α_P hold the relations

$$\begin{aligned} \alpha_P &= \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P = -\frac{1}{\rho} \left(\frac{\partial \rho}{\partial T} \right)_P \\ &= K_T \gamma_V = K_T \left(\frac{\partial P}{\partial T} \right)_\rho \end{aligned} \quad (3)$$

where γ_V is the thermal pressure coefficient.

Along with isochores and TMD points in figure 4 are also reported the points of the LMS line, calculated according to equation (2). For all systems the LMS line lies entirely in the negative pressure region and does not revert to positive pressure down to the lowest temperature investigated. Isochores lying below the LMS line are not reported in figure 4.

As we have already observed for isotherms (figure 3), the high density isochores also shift to lower pressure upon increasing concentration, while low density isochores lie to similar pressures. Looking at corresponding isochores, we

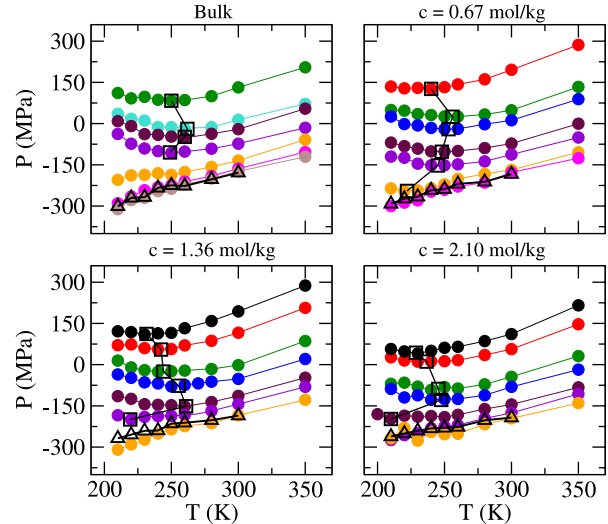


Figure 4. P – T isochore planes for the all the studied systems. Along with isochores, the TMD points (squares) and the LMS points (triangles) are reported. The range of temperatures is $210 \text{ K} \leq T \leq 350 \text{ K}$. From top to bottom isochores correspond to densities: bulk (top left panel) $\rho = 1.05, 1.00, 0.98, 0.95, 0.90, 0.87, 0.85 \text{ g cm}^{-3}$, $c = 0.67 \text{ mol kg}^{-1}$ NaCl(aq) (top right panel) $\rho = 1.10, 1.05, 1.025, 0.98, 0.95, 0.90, 0.87 \text{ g cm}^{-3}$, $c = 1.36$ and 2.10 mol kg^{-1} NaCl(aq) (bottom left and bottom right panel respectively) $\rho = 1.125, 1.10, 1.05, 1.025, 0.98, 0.95, 0.90 \text{ g cm}^{-3}$.

can observe that the range of pressures spanned decreases by roughly 50% on going from bulk water to the highest concentration solution. Thus the increase of the salt content has in the P – T plane an overall effect of progressively packing the isochores near the LMS line.

Several works performed at constant pressure pointed out that ions have an effect on the structure of water analogous to the application of an external pressure [36, 37, 59, 60]. Our findings are consistent with this picture, since we see that, at constant density, bulk water isochores coincide with isochores of the solution at higher densities.

In figure 5 we present a summary and a comparison of the TMD and LMS lines found for bulk water and for the NaCl(aq) at the three concentrations studied. For the sake of comparison we also report in the same figure data derived from TIP4P water confined in a hydrophobic environment of soft spheres [46]. The lines are a schematic representation of the data presented in figure 4. The range of temperatures reported in this figure is $210 \text{ K} \leq T \leq 300 \text{ K}$.

The effect of the addition of ions on the LMS line appears to be almost negligible. In fact the position and shape of the curve for the solutions remain similar to bulk water, with only a small rise in pressure for the two highest concentrations, at low temperatures.

In the case of hydrophobic confinement, the system can be thought of as behaving like a solution of small apolar solutes [46]. We observe for this system a noticeable shift of the LMS line to higher pressure, about 200 MPa. This shift could be due to large excluded volume effects determined by strong solute–solvent repulsion. Therefore we see that in the case of polar solutes, excluded volume effects are less relevant

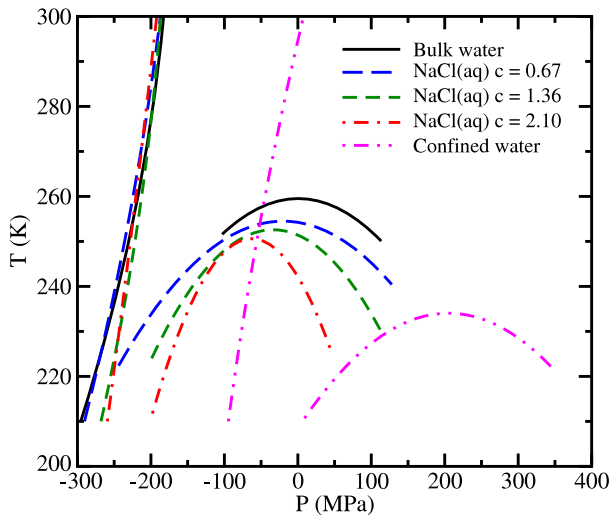


Figure 5. TMD and LMS lines for bulk water and for $c = 0.67, 1.36, 2.10 \text{ mol kg}^{-1}$ NaCl(aq) obtained from our simulations. In the figure are also reported the TMD and LMS lines obtained from simulations of water confined in a hydrophobic environment of soft spheres, as studied in [46].

and the LMS remains at similar pressures with respect to bulk water.

The influence of the ions on the TMD line is not as strong as for apolar solutes but is still quite pronounced. It is evident in fact that upon increasing concentration the TMD line moves to lower temperatures and pressures. We can notice that in the range of densities and temperatures spanned by our simulations, the TMDs of the solutions span a wider range of pressures with respect to bulk water. Nonetheless, upon increasing concentration the amplitude of the TMD line appears to narrow progressively. This is again an indication that in solution the increase of concentration leads to a restriction of the region of anomalous thermodynamic behaviour.

In the case of water in a hydrophobic environment, the TMD line also moves to lower temperatures, but to higher pressures. Thus we can hypothesize that the addition of solutes always causes the TMD line to shift to lower temperatures, with the direction of the shift in pressure determined by the polar or apolar nature of the solute.

4. Conclusions

In this paper we presented a study on the thermodynamic behaviour of NaCl(aq) solutions. In particular we presented a comparison of our recent data from MD simulations performed on bulk TIP4P water and on $c = 0.67, 1.36$ and 2.10 mol kg^{-1} NaCl(aq) solutions. The systems were studied in a wide range of densities and in a temperature range going from ambient temperature to the supercooled region.

It is of particular importance for these kinds of simulations to assess the dependence of the calculated quantities on the specific choice of ion and water interaction parameters and also to enquire about possible finite size effects. We discussed the choice of the parameters for the LJ part of the

interaction potential between particles, with particular regard to the inter-ionic potential. Our simulations were performed using Pettitt–Rosky [51] parameters and we checked the effect of changing parameters, simulating the $\rho = 1.025 \text{ g cm}^{-3}$ isochore also with Jensen–Jorgensen [52] parameters, for all the three concentrations of salt. We showed that the two sets of parameters for this part of the interaction potential lead to similar results for the thermodynamic behaviour of the systems.

In order to check for a possible dependence of thermodynamic properties on the size of the simulated systems, we conducted a study on the $\rho = 0.98 \text{ g cm}^{-3}$ isochore for bulk water and for $c = 0.67, 1.36, 2.10 \text{ mol kg}^{-1}$ NaCl(aq), simulating it at three different system sizes: $N_{\text{tot}} = 256, 512$ and 1024 . We demonstrated that no significant size effect took place for our systems. Since lengthy simulations are required for the supercooled region of the isochores, we used the $N_{\text{tot}} = 256$ system, this number being large enough to be reliable for the reproduction of thermodynamic properties.

The behaviour of the potential energy as a function of density was analysed and we showed that it presents one minimum for bulk water and for $c = 0.67 \text{ mol kg}^{-1}$ NaCl(aq), and two minima for $c = 1.36$ and 2.10 mol kg^{-1} NaCl(aq). We expect the second minimum for bulk water and for $c = 0.67 \text{ mol kg}^{-1}$ NaCl(aq) to be present at higher densities than those investigated in this work. Those minima have been related in the literature to the existence of two stable liquid phases [57], i.e. HDL–LDL coexistence. Upon increasing concentration it was shown that the low density minimum moves to higher density and that the low density and high density minima become closer to each other.

The simulated state points were reported in the P – ρ isochore planes and in the P – T isochore plane. The study of the P – ρ isochore plane revealed the presence for all systems of inflections of the low temperature isochore crossing higher temperature isotherms. These inflections are considered as a signal of the approach of the systems to liquid–liquid coexistence [15]. Upon increasing concentration the density region of the inflections narrows.

The calculated LMS and the TMD line, along with the isochores of the systems were reported on the P – T plane. We showed that upon increasing the salt content, the isochores progressively pack near the LMS line. The shift in pressure was also connected to the equivalence of the presence of ions to the application of an external pressure.

The comparison of the LMS lines for the studied system revealed that ions have little effect on the LMS line, with only a minor shift to higher pressures, for the $c = 1.36$ and 2.10 mol kg^{-1} , at low temperatures. In the case of water in the hydrophobic environment [46] the LMS is shifted to much higher pressures with respect to bulk water because of excluded volume effects. The TMD line was shown to be influenced by the presence of ions. In fact it shifts to lower pressures and temperatures upon increasing concentration. Moreover the amplitude of the TMD curve narrows. In the case of apolar solutes, the TMD line shifts to lower temperature and higher pressures. The negative/positive pressure shift of the TMD line can be connected to the polar/apolar nature of the solute.

We can summarize the results on the thermodynamic properties of the systems we studied stating that indications of the presence of liquid–liquid coexistence are present in bulk water and preserved in the NaCl(aq) up to the highest concentrations. Nonetheless we observe a weakening of these signatures upon increasing the salt content, with a restriction of the region of density anomaly. Extensive MD simulations aimed at determining the position of the LLC in bulk TIP4P water and in $c = 0.67 \text{ mol kg}^{-1}$ NaCl(aq) are currently in progress [61].

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