Journal of Molecular Liquids 261 (2018) 513–519

Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

Molecular dynamics simulations of freezing-point depression of TIP4P/2005 water in solution with NaCl

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ARTICLE INFO

Article history:
Received 11 January 2018
Received in revised form 14 March 2018
Accepted 30 March 2018
Available online 6 April 2018

ABSTRACT

Molecular dynamics simulations have been performed on an aqueous solution of TIP4P/2005 water and NaCl using the direct coexistence technique to determine the equilibrium line ice/NaCl solution and the freezing point depression of water in presence of NaCl at different salt concentrations below the eutectic point. We used large samples in order to avoid finite size effects and to minimize the error on the determination of the freezing temperature. Our results are in excellent agreement with the experimental freezing point depression showing that the set of parameters used in this work for the water and NaCl is a very good choice to reproduce the thermodynamic properties of the water/NaCl system with molecular dynamics simulations.

1. Introduction

Water plays a crucial role in most physicochemical processes [1,2]. However, most of the water found in nature is not pure, it has a considerable content in salts. Around 96.5% of all the Earth's water is contained within the oceans as saltwater, while the remaining 3.5% is freshwater found in lakes and frozen water in glaciers and the polar ice caps. Among the possible salts dissolved that can be found in seawater, the NaCl is the main ionic component.

In presence of NaCl (or other salts), the freezing temperature of solution is lower than that of the pure water, and it gets lower and lower upon increasing salt concentration. Likewise, the content of ions (Na^+ and Cl^-) present in the solution is the key factor in the shift of the thermodynamic equilibrium line. Adding salt to the solution prevents the formation of ice and extends the region where water can be supercooled. Interesting modification of supercooled water phase diagram have been also found upon NaCl addition [3-5]. When water freezes from aqueous salty solutions, the salt ions are rejected from the solid phase and saturate the liquid phase giving rise to the appearance of the phenomenon known as brine rejection [6-8]. In addition to the brine phase, during the ice growth a small amount of ions can be accommodated in the solid lattice causing ice doping [8-14].

In Fig. 1, a schematic representation of the phase diagram for the system H_2O/NaCl is shown. As it can be seen, the freezing temperature of water decreases depending on the salt content up to a minimum value corresponding to the eutectic point (−21.1 °C and 23.3 wt% NaCl).

Thermodynamically, the freezing point depression can be explained as the decrease in the chemical potential of the solution compared to that of liquid water without presence of salt. This decrease in the chemical potential stabilizes the solution and reduces the tendency of the water to freeze resulting in a decrease of the water freezing temperature [15-20].

The formation of ice from salt aqueous solution is of central importance in a wide variety of processes [21-35]. As example, in chemical engineering, geochemistry, oceanography, in atmospheric and food science. Another application where the knowledge of the freezing conditions of water in presence of salt is crucial is the desalination of seawater [36-38], although at present commercial desalination is using high pressure reversed osmosis as technique for this purpose [39,40]. Also, water and ions control stability, dynamics, and folding in proteins [41-45].

Under ideal conditions, the freezing point depression, ΔT_F, depends linearly on the concentration of the salt and can be calculated as

$$\Delta T_F = i \cdot k \cdot m \tag{1}$$

where m is the molality of salt, k is a constant that does not depend on the solute but depends on the solvent (for water, $k = 1.853$ K·kg/mol) and i is the van't Hoff factor relative to the number of ion particles ($i = 2$ for NaCl). However, this universal expression fails outside the ideal regime. To describe the non-ideal behavior of salty solutions accurate models are needed to study processes

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https://doi.org/10.1016/j.molliq.2018.03.126

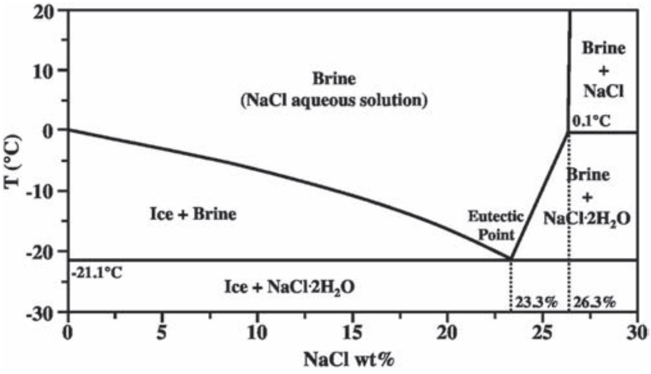

Fig. 1. Schematic representation of the phase diagram for the system H_2O/NaCl as a function of temperature and salt concentration.

related to the applications mentioned above. Several thermodynamic analytic models have been developed such as the Pitzer [46] and Bromley [47] models. These models are based on linear combinations of parameters from experimental data. Also, calculations based on thermodynamic modeling have been used to describe this non-ideal behavior for electrolyte solutions [48,49].

In the last decades, computer simulation has become a valuable tool not only to predict equilibrium conditions but also to understand many of the physicochemical processes at the microscopic level. In particular, the simulation in the field of water has provided excellent results thanks to the development of robust and reliable empirical potential models [50,51]. In view of the large number of applications focused on the study of water in presence of salt, a reliable prediction of phase behavior of water/salt system by computer simulation is required.

In the present simulation study we focus on the determination of the equilibrium line, and hence the freezing point depression, for the water/salt system using one of the most popular water potential models: TIP4P/2005 [52]. This water model proposed by Abascal and Vega in 2005 has become one of the most successful models in simulation of water due to the large number of water thermodynamic properties that it predicts in excellent agreement with the experiments [2,50,51,53,54].

The purpose of this paper is two-fold. First, we study whether the set of parameters chosen for the water and NaCl is able to predict the equilibrium line between NaCl aqueous solution and ice at different concentrations of NaCl. Second, we compare the freezing point depression obtained by molecular dynamics with the experimental values found in literature.

The paper is organized as follows: in the next section, the methodology used is described. In the third section, we analyze the results obtained for the equilibrium line of system NaCl/water, as well as a comparison of the freezing point depression obtained by molecular dynamics with experimental data. Finally, the main conclusions are discussed.

2. Methodology

To determine the equilibrium line of the water/NaCl system we use the technique of direct coexistence. This technique basically consists in studying the melting or growth of ice when a slab of ice I_h and a slab of liquid water (in our case a NaCl aqueous solution) are put in contact at a given pressure and temperature within the same simulation box. The slab of ice I_h acts as seed crystal in contact with a liquid phase. The direct coexistence is a robust and reliable technique that has been implemented in numerous studies to determine the phase equilibrium in different systems successfully [8,55-60]. This methodology allows us a direct and accurate evaluation of the freezing temperature (T_F) and thus to study the freezing point depression for the water/NaCl system.

In this work, we follow the protocol proposed in Ref. [8] to generate the initial configuration of ice I_h and NaCl aqueous solution. Although the ice I_h is hexagonal, it is possible to use an orthorhombic unit cell [22]. It was with this orthorhombic unit cell that we generated the initial slab of ice. We used the algorithm of Buch et al. [61] to obtain an initial configuration of ice I_h formed by 2000 water molecules with proton disorder and almost zero dipole moment satisfying the Bernal-Fowler rules [62]. The initial solid configuration was equilibrated about 50 ns at ambient pressure and temperature close to the melting point allowing the three different sides of the simulation box to fluctuate independently to avoid stress in the solid lattice obtaining the correct equilibrium density of ice.

Once the slab of ice I_h was equilibrated we built the configuration for the NaCl aqueous solution. The liquid phase was prepared from the previous ice configuration replicated four times. We performed a NVT simulation of about 10 ns at 400 K until the melting of the solid phase was completed, to obtain a configuration of 8000 liquid water molecules. The salt ions (Na^+ and Cl^-) were then added until reaching the desired concentration. These insertions were followed by a Np_xT simulation at ambient pressure and temperature close to the melting point about 50 ns to equilibrate the NaCl(aq) phase. During the equilibration the number of ions was adjusted to reach the concentration of the solution. To obtain a broad view of the equilibrium line we chose six different molar concentrations of the NaCl(aq) phase from 0.25 M to 3 M always below the eutectic point.

Finally, we generated the solid-liquid interface putting in contact the solid with the liquid phase. By convention, we chose the x axis perpendicular to the interface. Thus, the plane of ice I_h exposed at the interface was the secondary prismatic plane $(1\bar{2}10)$ since it has been shown that this plane exhibits the fastest dynamics [63,64]. As last step to complete the setting of the initial configuration, we equilibrated the system for a short time (20 ps) to equilibrate the interface.

Fig. 2 shows the snapshots of the initial configurations used in this study for the system ice/NaCl(aq) formed by a slab of ice I_h in contact with a water liquid phase containing Na^+ and Cl^- ions in solution at different concentration. In Table 1, the number of molecules of the liquid phase and the solid phase are shown. As it can be seen for all concentrations the system is formed by 2000 ice I_h molecules and 8000 liquid water molecules with a variable number of NaCl ion pairs depending on the concentration of the solution selected. The number of molecules in our systems is large enough to avoid the effects of finite size in the direct coexistence technique [65-67].

In our simulations, we used the popular TIP4P/2005 potential model [52] for the water molecules. This rigid and non-polarizable model has been designed to improve the description of ices and water, see for example Refs. [2, 50] and references therein. In TIP4P/2005, a LJ interaction site is located on the oxygen atom, positive charges are located on the positions of the H atoms, and the negative charge is located at a distance $d_{OH} = 0.1546$ Å from the oxygen along the H-O-H bisector. To describe the ion-ion interactions and the water-ion interactions we used a very recent new set of parameters proposed by Vega and co-workers [68], which predicts the solubility of NaCl in water at p, T normal conditions with a value of 5.8 m (moles of salt per kilogram of water, denoted as molality (m)) in good agreement with the experimental value (6.14 m [69]). This solubility value is one of the best predictions found in the literature for water/NaCl simulations. The potential parameters for both models as well as the cross interaction between the ions and the oxygen in water are given in Table 2.

We used the molecular dynamics package GROMACS (version 4.5.5) [70]. All simulations of our study of coexistence were performed in the Np_xT ensemble. The pressure is applied only in the

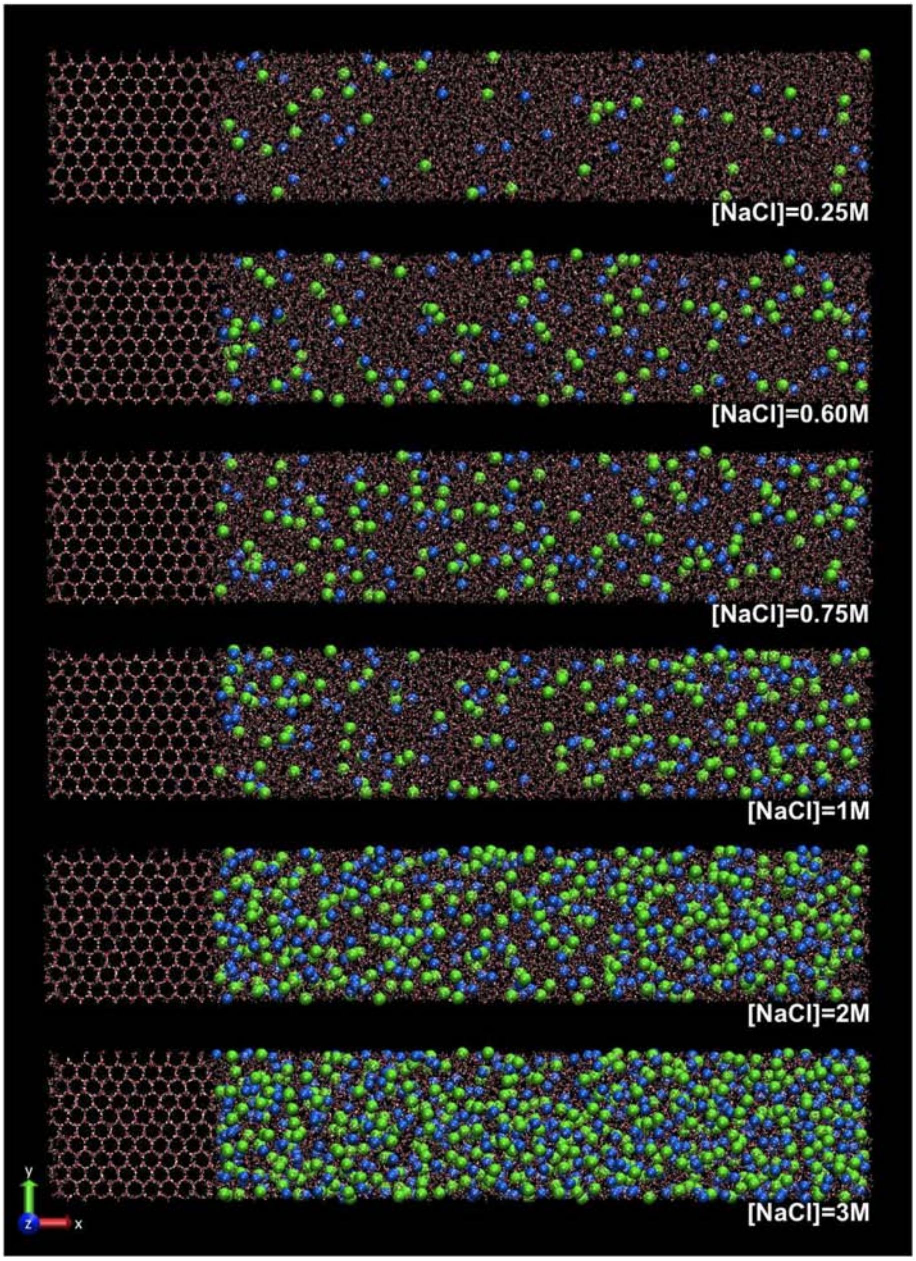

Fig. 2. Initial configurations for the ice/NaCl(aq) system at different molar concentrations. Water molecules are represented as sticks in red and white colors, Cl^- ions as green spheres and Na^+ ions are represented as blue spheres. The size of the ions is enlarged with respect to the water molecules for a clearer visualization. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

direction perpendicular to the interface (in our system the x-axis). Periodic boundary conditions were employed in the three directions of space. The geometry of the water molecules was enforced using constraints. The Lennard-Jones of the potential was truncated at 8.5 Å. Ewald sums were used to deal with electrostatics [71]. The Fourier part of the Ewald sums was evaluated by using the particle mesh Ewald (PME) method of Essmann et al. [71]. The width of

Table 1
Number of molecules for the phase of ice I_h and the NaCl aqueous solution for the different concentrations studied in this work.

M(mol/L)	NaCl wt%	n_{ice}	$n_{\text{water}}^{solution}$	$n_{\text{NaCl}}^{solution}$
0.25	1.5	2000	8000	36
0.60	3.5	2000	8000	87
0.75	4.4	2000	8000	110
1	5.8	2000	8000	146
2	11.7	2000	8000	300
3	17.5	2000	8000	456

Table 2
Potential parameters of TIP4P/2005 water model [52] and NaCl model [68] . The Lennard-Jones potential is defined as $U_{ij} = \frac{C_{ij}^{12}}{r_{ij}^{12}} - \frac{C_{ij}^{6}}{r_{ij}^{6}}$.

site	C_6(kJ•mol^{-1}•nm^6)	C_{12}(kJ•mol^{-1}•nm^{12})	q(e)
O	$0.30798 \cdot 10^{-2}$	$0.30601 \cdot 10^{-5}$	–
H	–	–	0.5564
M	–	–	−1.1128
Na^+	–	$0.83200 \cdot 10^{-7}$	+1
Cl^-	–	$0.52000 \cdot 10^{-4}$	−1
Na^+-O	$0.08000 \cdot 10^{-2}$	$2.09430 \cdot 10^{-7}$	–
Cl^--O	$0.15000 \cdot 10^{-2}$	$1.64480 \cdot 10^{-5}$	–

the mesh was 1 Å and we used a fourth-order polynomial. The real part of the Coulombic potential was truncated at 8.5 Å. The pressure was fixed using Parrinello-Rahman barostat [72] with a relaxation time of 2 ps. The temperature was fixed using Nosé-Hoover thermostat [73,74] with a relaxation time of 2 ps. The time-step used in the simulations was 2 fs.

One of the major disadvantages of the direct coexistence simulations is the stochastic nature of the technique [65-67]. In the vicinity of the equilibrium point it is possible to find for the same temperature a simulation where the ice melts and another where the ice grows. To avoid it and to have a greater precision in the determination of the equilibrium line we performed for each temperature selected five independent simulations using the same configuration but with different seed numbers in the initial velocities.

In phase equilibrium studies by direct coexistence for a single component, for example, water and ice without presence of ions, the simulation time to reach the equilibrium is relatively short around 20 ns in small systems [55,67]. However, this does not happen in multicomponent systems [6-8,57,75]. In our case, the dynamics of the ice/NaCl(aq) system is much more slow due to water-ion interaction and longer runs, in the order of microseconds, are needed to have a total growth of the ice. Our goal here is to determine the freezing temperature and it is not necessary for the system to melt or growth completely. Therefore, we limit the length of each simulation to 300 ns for each seed number. This time is sufficient to check if the system is above or below of the freezing temperature [8].

3. Results

The freezing point depression, ΔT_F, is the difference between the freezing temperature of the pure water, T_F (water), and the freezing temperature of the salt solution, T_F (solution), defined as

$$\Delta T_F = T_F(water) - T_F(solution). \tag{2}$$

To estimate ΔT_F it is necessary to know the freezing point of the water model. Vega and co-workers calculated the value of the melting/freezing point for the TIP4P/2005 model using different methodologies and they obtained a value of $T_F(\text{water}) = 250 \pm 2$ K [55,56,76]. Despite the robustness of their excellent results, the error bar of this measure does not allow to capture differences in the freezing temperature when the salt concentration is small since the freezing point depression at these low concentrations is smaller than the error bar itself. Recently, we have estimated the value of the freezing point for the TIP4P/2005 model with the greatest precision to date and the resulting value is $T_F(\text{water}) = 249.5 \pm 0.1$ K [67] with a reduction of the error bar of an order of magnitude with respect to the previous studies. This low error bar was obtained with a large sample and long simulations. Now using the same methodology the low error bar allows us to determine the freezing point depression in a wide range of concentrations with great precision.

In this work, we determine the equilibrium line for a solution of NaCl with different salt content. To calculate the freezing temperature of the NaCl solution, $T_F(\text{solution})$, we monitor the potential energy of the system in the direct coexistence simulations for each temperature selected. We perform for each temperature five independent simulations with different seed numbers in the initial velocities to avoid the effects of the stochastic nature of direct coexistence technique [65-67]. When the temperature is above the freezing point the ice phase melts until the system transforms completely into a liquid phase. This phase transition is associated with a marked increase in potential energy. On the contrary, at temperatures below the freezing point, the potential energy decreases continuously. This decrease in energy reveals the growth of the ice until the total freezing of the system is reached. In studies of direct coexistence where two phases are put into contact, the coexistence temperature is that where the energy of the system remains constant. However, in this type of simulations of coexistence it is not always easy to achieve a constant behavior of the potential energy since any small thermal fluctuation can initiate or accelerate the process of melting or growth of ice phase. Thus, when it is not possible to find simulations where the potential energy is constant, the freezing temperature is defined as the average between the lowest temperature for which the slab of ice melts and the highest temperature for which the slab of ice grows assuming that the behavior below and above the freezing point is symmetric since we have performed simulations at regular intervals of 0.5 K. The choice of potential energy as an indicator of the evolution of the system has been used in numerous works with excellent results [8, 55, 59, 67]. One might think that shorter times of simulation (around 10–20 ns) would be enough to determine the tendency of the system to freeze or melt. However, in our previous work [67] we showed how this trend in large systems like ours can change during the simulation being necessary longer simulations (around 100–300 ns) to be sure of the evolution of the potential energy.

Let us now present the results obtained from our simulations. In order to estimate the freezing temperature of the salt solution and the value of the freezing point depression for each salt concentration studied, we define ΔT as the difference between the freezing temperature of pure water, $T_F(water)$, and the trial freezing temperature of the ice/NaCl(aq) system, $T_T(solution)$. In Fig. 3, the evolution of the potential energy for the ice/NaCl(aq) system for a salt concentration of 0.25 M is shown. At $\Delta T = -0.5$ K the five independent simulations show an increase of the potential energy indicating that our system at this temperature is above the freezing temperature. At $\Delta T = -1.0$ K only one of the simulations shows the total melting of the system. The rest of the simulations analyzed reveal a slight increase of the potential energy without observing the complete melting of the system. At $\Delta T = -1.5$ K the behavior is opposite to that observed in the previous temperatures. The five trajectories analyzed show a decrease in the potential energy placing the system below the freezing temperature for this temperature. As it can be seen, the growth and melting rates from salt solutions are much lower than in pure water systems in agreement with previous studies of Vrbka and Jungwirth [6], Carignano et al. [75] and our previous work about spontaneous NaCl-doped ice [8].

The freezing temperature at this concentration for the ice/NaCl(aq) system is $T_F(\text{solution}) = 248.25 \pm 0.25$ K. This value is the average between the values of the lowest temperature where the system melts and the highest temperature where the slab of

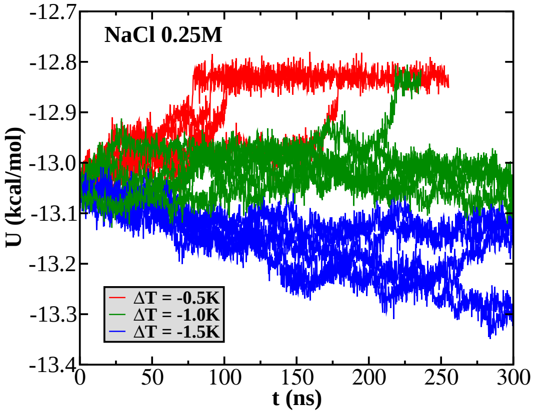

Fig. 3. Evolution of the potential energy as a function of time obtained at several temperatures for the ice/NaCl(aq) system with a salt concentration of 0.25 M. ΔT=$T_F(water)$ − $T_T(solution)$ where $T_F(water)$ is the freezing temperature for the TIP4P/2005 water model and $T_T(solution)$ is the trial freezing temperature of the ice/NaCl(aq) system.

Table 3
Freezing temperatures and freezing point depression for the ice/NaCl(aq) system studied for different salt contents. The concentration of NaCl is expressed in molarity (*M*) and mass percentage (wt%). T_F(*solution*) is the freezing temperature of the NaCl solution and ΔT_F is the freezing point depression of system. The units of the temperatures are given in Kelvin (K).

M (mol/L)	NaCl wt%	T_F (solution) (K)	ΔT_F (K)
0.0	0.0	249.5 ± 0.1	-
0.25	1.5	248.25 ± 0.25	-1.25 ± 0.35
0.60	3.5	247.0 ± 0.5	-2.5 ± 0.6
0.75	4.4	246.25 ± 0.25	-3.25 ± 0.35
1	5.8	245.0 ± 0.5	-4.5 ± 0.6
2	11.7	240.5 ± 0.5	-9.0 ± 0.6
3	17.5	234.0 ± 1.0	-15.5 ± 1.1

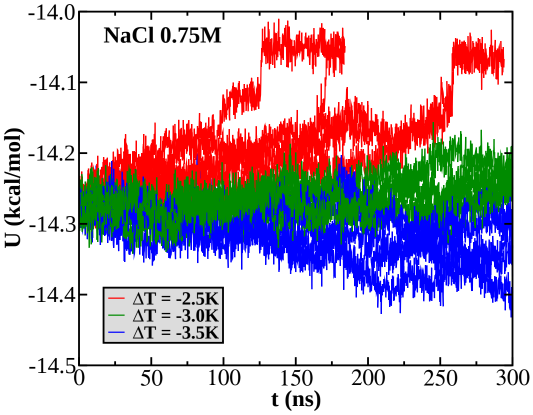

Fig. 5. Evolution of the potential energy as a function of time obtained at several temperatures for the ice/NaCl(aq) system with a salt concentration of 0.75 M. $\Delta T = T_F(water) - T_T(solution)$ where $T_F(water)$ is the freezing temperature for the TIP4P/2005 water model and $T_T(solution)$ is the trial freezing temperature of the ice/NaCl(aq) system.

ice grows. Thus, at 0.25 M the freezing point depression of the ice/NaCl(aq) system is situated at $\Delta T_F = -1.25 \pm 0.35$ K where ΔT_F is the difference between the freezing temperature of pure water and the freezing temperature of the 0.25 M solution. The error bar associated with the value of freezing point depression is given by the maximum error of the lowest temperature and the highest temperature plus the error associated with the value of freezing temperature of the pure water for the TIP4P/2005 model $T_F(\text{water}) = 249.5 \pm 0.1$ K. The value of the freezing temperature as well as the freezing point depression for this salt content and their error bar are give in Table 3.

In Fig. 4 and Table 3, the results for the salt concentration of 0.60 M are shown. At $\Delta T = -2.0$ K, three of the five trajectories analyzed show the complete melting of the system. The remaining two trajectories, although the melting of the system is not complete, show an increase in potential energy. At $\Delta T = -2.5$ K, the evolution of energy evidences the stochastic nature of the direct coexistence technique where the trajectories analyzed reveal both the melting of the system and the growth of the ice phase. This stochastic behavior indicates that we are at or very close to the freezing temperature of the system. At $\Delta T = -3.0$ K and $\Delta T = -3.5$ K, all the simulations studied reveal the growth of the slab of ice I_h. Thus, the value of freezing point depression for the salt concentration of 0.60 M is $\Delta T_F = -2.5 \pm 0.6$ K and the freezing temperature for this system is $T_F(\text{solution}) = 247.0 \pm 0.5$ K.

The results of the potential energy for the system with a concentration of 0.75 M are collected in Fig. 5 and in Table 3. At $\Delta T = -2.5$ K in all the simulations studied the system melt resulting in a clear increase in the potential energy. At $\Delta T = -3.0$ K for the five trajectories studied it can be seen how the system tends to slightly increase the potential energy. However, at $\Delta T = -3.5$ K the tendency is the opposite. The system at this level of subcooling decreases the potential energy and the slab of ice I_h begins to grow. The value of the freezing point depression as well as the freezing temperature for the salt content of 0.75 M is $\Delta T_F = -3.25 \pm 0.35$ K and $T_F(\text{solution}) = 246.25 \pm 0.25$ K, respectively.

The evolution of the potential energy for the system formed by a slab of ice I_h and a NaCl solution of 1 M is given by Fig. 6. All the simulations for $\Delta T = -3.5$ K reveal the melting of the system. Three of the five trajectories show the complete melting of system. In the other two trajectories, although the melting of the system is not complete, there is a clear increase in potential energy indicating that the system is clearly above freezing temperature. At $\Delta T = -4.0$ K, the trajectories studied show an increase in the potential energy. Only one of the simulations studied shows a decrease in the potential energy. At $\Delta T = -4.5$ K, we observe for all trajectories how the potential energy remains constant during the first 100 ns analyzed. After that time, we observe for the same ΔT how the system melts or grows depending on the initial seed number. At $\Delta T = -5.0$ K, in all the simulations studied the ice phase grows resulting in a decrease in the potential energy. Given the results obtained, the freezing point depression is $\Delta T_F = -4.5 \pm 0.6$ K and the freezing temperature for

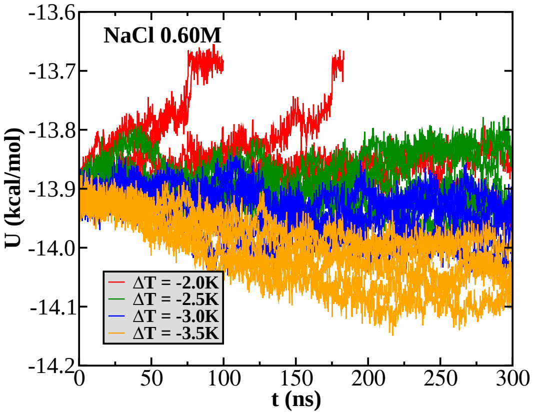

Fig. 4. Evolution of the potential energy as a function of time obtained at several temperatures for the ice/NaCl(aq) system with a salt concentration of 0.60 M. $\Delta T = T_F(water) - T_T(solution)$ where $T_F(water)$ is the freezing temperature for the TIP4P/2005 water model and $T_T(solution)$ is the trial freezing temperature of the ice/NaCl(aq) system.

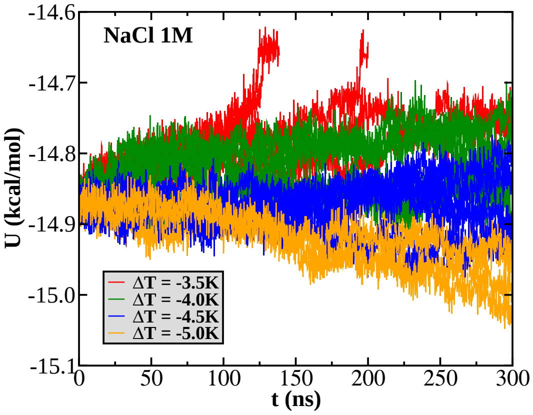

Fig. 6. Evolution of the potential energy as a function of time obtained at several temperatures for the ice/NaCl(aq) system with a salt concentration of 1 M. $\Delta T = T_F(water) - T_T(solution)$ where $T_F(water)$ is the freezing temperature for the TIP4P/2005 water model and $T_T(solution)$ is the trial freezing temperature of the ice/NaCl(aq) system.

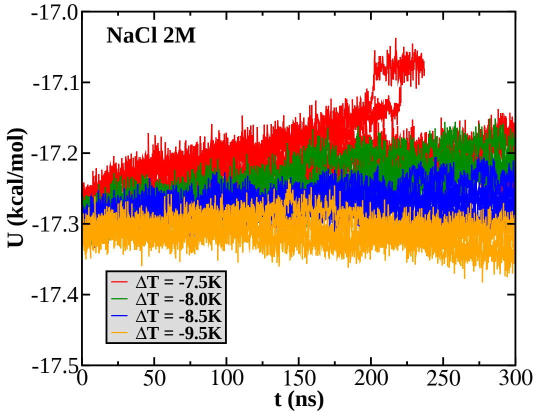

Fig. 7. Evolution of the potential energy as a function of time obtained at several temperatures for the ice/NaCl(aq) system with a salt concentration of 2 M. $\Delta T = T_F(water) - T_T(solution)$ where $T_F(water)$ is the freezing temperature for the TIP4P/2005 water model and $T_T(solution)$ is the trial freezing temperature of the ice/NaCl(aq) system.

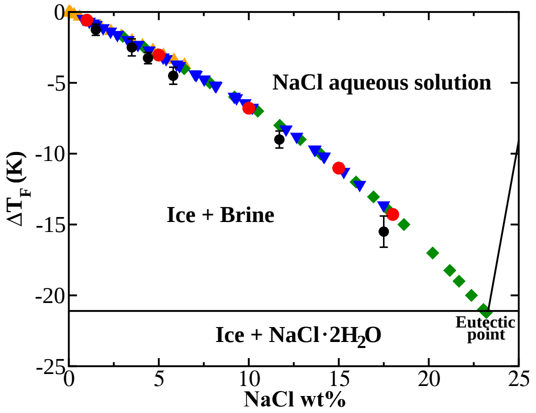

Fig. 9. Equilibrium line and freezing point depression for the system formed by a slab of ice I_h and a NaCl aqueous solution. Our results and their error bars obtained from simulation (black dots) are compared with a selection of experimental values found in the literature (orange triangles up [77], red circles [48], blue triangles down [78], green diamonds [79].(For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

this system is $T_F(\text{solution}) = 245.0 \pm 0.5$ K. These values are listed in the Table 3.

The results for the salt concentration of 2 M are shown in Fig. 7 and in Table 3. At $\Delta T = -7.5$ K, $\Delta T = -8.0$ K and $\Delta T = -8.5$ K the potential energy of system gradually increases. This increase in energy is more remarkable at temperatures far from equilibrium. Thus, at $\Delta T = -7.5$ K we observe the complete melting for two of the seed numbers studied. Conversely, at temperatures very close to the freezing temperature and despite the increase of potential energy high simulation times are necessary for a complete melting of the system. However, at $\Delta T = -9.5$ K the behavior of the system is practically constant until 200ns where the potential energy of the system begins to decrease slightly and the slab of ice I_h begins to grow. The value of freezing point depression for the salt concentration of 2 M is $\Delta T_F = -9.0 \pm 0.6$ K and the freezing temperature for this system is $T_F(\text{solution}) = 240.5 \pm 0.5$ K.

In order to have a broader view of the phase equilibrium line for the ice/NaCl(aq) system we extend our study to a concentration of 3 M. It is important that the salt concentration is below the eutectic composition in the equilibrium region of the phases of interest. As it can be seen in the Fig. 8 at $\Delta T = -13.0$ K, $\Delta T = -14.0$ K and $\Delta T = -14.5$ K the energy of the system tends to increase slightly for all seed numbers studied. At $\Delta T = -15.5$ K during the 300 ns of simulation time the potential energy remains approximately constant, apart from thermal fluctuations. Thus, $\Delta T_F = -15.5 \pm 1.6$ K corresponds to the freezing point depression for a salt concentration of 3 M and $T_F(\text{solution}) = 234.0 \pm 1.1$ K is the freezing temperature of system (see Table 3).

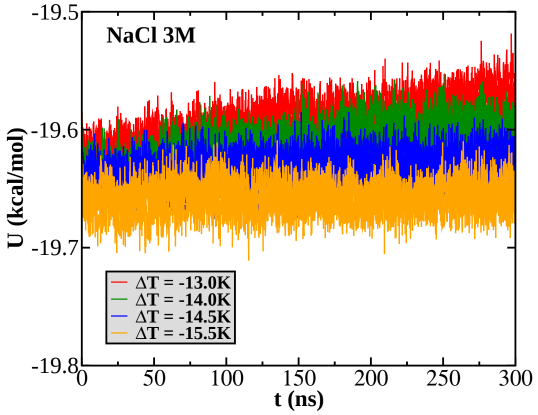

Fig. 8. Evolution of the potential energy as a function of time obtained at several temperatures for the ice/NaCl(aq) system with a salt concentration of 3 M. $\Delta T = T_F(water) - T_T(solution)$ where $T_F(water)$ is the freezing temperature for the TIP4P/2005 water model and $T_T(solution)$ is the trial freezing temperature of the ice/NaCl(aq) system.

Note that at higher concentrations of salt in solution the rate of melting and freezing is slower than at lower concentrations. This slow dynamics for higher concentrations is due to the increase of the water-ion interactions. The time required for a complete melting, and especially for a complete freezing of the system at high concentrations of salt is computationally very demanding. However, to determine the equilibrium line it is not necessary to complete the melting and freezing processes. It is enough to analyze the trend of the potential energy of the system and perform several simulations with different seed numbers for the same temperatures to avoid the stochastic nature of the technique. This tendency must however be sufficiently clear to be sure that the system will not change the trend of the potential energy [67].

Finally, we compare our results of the freezing point depression with a selection of experimental values found in the literature [48, 77-79]. As it can be seen in the Fig. 9, the results obtained by our simulations are in very good agreement with the experimental values within the statistical uncertainty, especially at low salt concentrations. Nevertheless, although within the statistical uncertainty, it can be seen a gradual underestimation of the value of freezing point at salt concentrations close to the eutectic point. The range of salt concentrations studied is broad enough to ensure that the potential used is an excellent choice to simulate the water-NaCl system and to reproduce the phase equilibrium lines successfully, especially at seawater conditions (NaCl 0.60 M). Since the purpose of our work was to reproduce the experimental line of freezing depression by simulation and test the ability of the potential models used, we considered that it was enough to study up to 3 M and not go beyond due to the high computational cost. The exploration of the eutectic point and its surroundings deserve a project to itself and we are working on it.

4. Conclusions

In summary, we performed molecular dynamic simulations using the direct coexistence technique to determine the equilibrium line of systems formed by a slab of ice I_h and aqueous solutions of NaCl. The freezing point depression of water in presence of NaCl at different salt concentrations is estimated. The water molecules were modeled using the popular TIP4P/2005 potential model [52] and a new set of parameters for the water-ion interaction [68].

We studied six different salt concentrations spanning from 0.25 to 3 M below the eutectic point. For each of the concentrations we determined the freezing temperature of the system simulating different temperatures. We performed for each temperature five independent simulations with different seed numbers in the initial velocities to prevent our results from the stochastic effects of the direct coexistence technique. The length of each simulation was 300 ns. The samples that we used are large (10,000 water molecules and a variable number of ions depending on the salt concentration studied) in order to avoid the finite size effect. The size that we chose for our simulations to prevent the effects of finite size was indicated by a previous study on the calculation of the melting point of bulk water [67].

We found that at high salt concentrations the rate of melting and freezing is slower with respect to low salt concentrations due to the water-ion interactions when the number of ions present in the system is increasing.

The results presented in this work for the equilibrium line and the freezing point depression of water at different salt contents obtained by simulation are in excellent agreement with the experimental freezing point depression data within the statistical uncertainty with a gradual underestimation at concentrations close to the eutectic point. Our results confirm that the set of parameters used in this work for the water and NaCl is a very good choice to reproduce the thermodynamic properties of the water/NaCl system by simulation and to reproduce quantitatively the freezing point depression of water, especially at seawater conditions. Our paper shows the direct coexistence as a very robust technique to estimate phase equilibria reliably.

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgments

We thank Carlos Vega and co-workers for having given us the NaCl-TIP4P/2005 interaction parameters prior to publication of their work.

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