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## Molecular Simulation

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# Ion Solubility in Ice: Calculation of Potentially Favorable Positions of $\text{Cl}^-$ and $\text{Na}^+$ Ions in the SPC/E Model of Ice 1 h\*

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**Favorable and unfavorable locations for positive and negative ions in the ice 1 h lattice are investigated by molecular dynamics methods. This is a first step in calculating the solubility of ions in ice as distinct from liquid water.**

**Keywords:** Ion solubility;  $\text{Cl}^-$  ions;  $\text{Na}^+$  ions; SPC/E model

## INTRODUCTION

Ions are much less soluble in ice than they are in water. This gives rise directly to the remarkable annual phenomenon of sea salt exclusion from the freezing water around polar regions, which results in essentially “fresh water” ice floating on top of the polar oceans. In this paper we begin a computer simulation study of the relatively solubility of ions in SPC/E ice 1 h [1], compared to water. This is also a necessary first step for computer simulation of the non-transitory part of the Workman-Reynolds effect [2].

The remainder of this paper is organized as follows. In the Second Section, we outline the methods employed to generate the potential energy surface plots. In the Third Section, the properties of the models used and simulation details are summarized. Results are presented in the Fourth Section and our conclusions are presented in the Fifth Section.

## METHODS

Calculation of the potential energy surface for an ion in any periodic form of water substance, e.g. ice 1 h,

is a straight-forward task. A locally developed molecular dynamics (MD) code was modified so that at each step, instead of performing actual molecular dynamics, only the potential energy of the ion at its current position within the ice lattice is calculated. The ion is then moved to another position and the potential energy calculated for the new position. The ion is moved in the XY plane of the simulation cell within a predetermined grid size and at constant Z. This effectively results in a potential energy surface “slice” through the system.

For this work a  $20 \times 20$  grid of size  $6 \times 6 \text{ \AA}$  was chosen starting at  $-3.5 \text{ \AA}$  and  $-6.5 \text{ \AA}$  for X and Y, respectively. Fifteen cross-sectional slices were taken from  $Z = -6.5 \text{ \AA}$  to  $0.5 \text{ \AA}$  at  $0.5 \text{ \AA}$  intervals which covers half of the stimulation cell in the Z direction. The basic structure of ice 1 h consists of a hexameric box and the unit cell is considered as a group of four water molecules. Each hexameric box in the ice structure contains two full and two half unit cells. The dimensions chosen for the contour plots in this work cover approximately one full hexameric box ensuring that every position an ion might occupy within the ice lattice is investigated.

## SIMULATION DETAILS

For this work, the SPC/E model of water [3] is used. The SPC [4] model has been reparameterized to SPC/E by inclusion of a polarization correction

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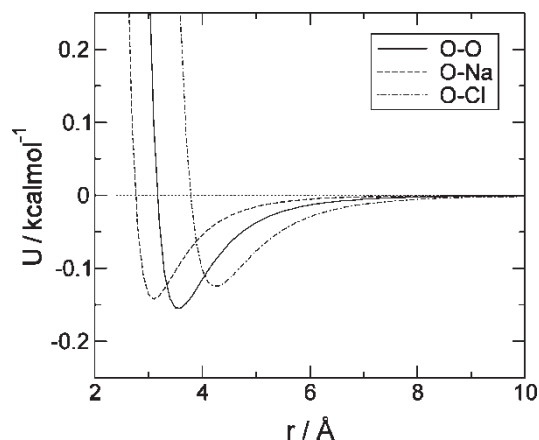


FIGURE 1 Lennard-Jones potentials for O,  $\text{Cl}^-$  and  $\text{Na}^+$  used in this work.

to the effective pair potential, improving the energy, density and pair correlation function values at 25°C. This model has proven to be one of the more robust but simple of the many interaction models for water [5] and is described below.

The SPC/E model of water is rigid and consists of three interaction sites. Centered on the "oxygen" site is a 12-6 Lennard-Jones (LJ) potential:

$$\phi(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6] \quad (1)$$

where  $\epsilon = 0.1554 \text{ kcal/mol}$  and  $\sigma = 3.16557 \text{ Å}$ . Point charges are fixed to the hydrogen and oxygen sites, with values of  $+0.4238e$  and  $-0.8476e$ , respectively. The O-H bond-length is constrained at  $1.00 \text{ Å}$ , and the H-O-H bond angle is fixed to be  $109.47^\circ$ .

Ion-water interactions are modeled by the sum of the Coulomb and LJ potentials such that

$$\phi(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6] - (q_i q_j)/r_{ij} \quad (2)$$

where  $q_i$  and  $q_j$  represent the charge on two interacting atoms  $i$  and  $j$  respectively, and  $r_{ij}$

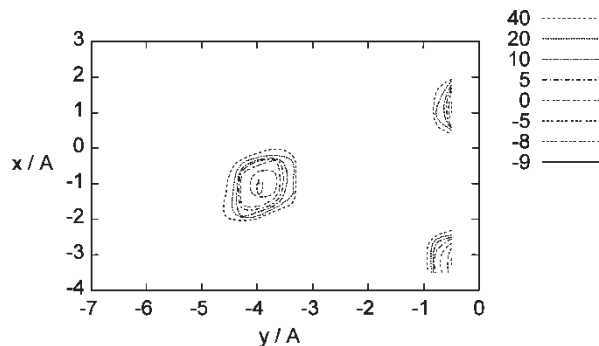


FIGURE 2 Potential energy in kcal/mol as a function of X and Y position of  $\text{Cl}^-$  ion in SPC/E ice 1h for  $Z = 0.0 \text{ Å}$ .

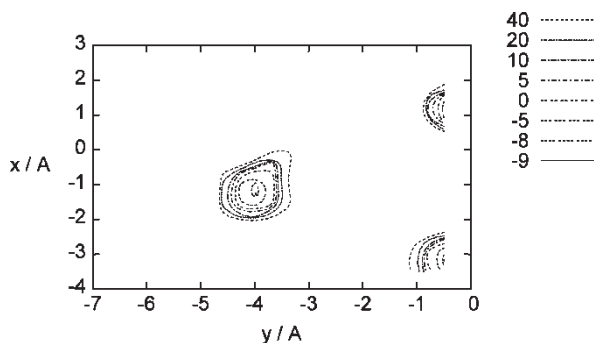


FIGURE 3 Potential energy in kcal/mol as a function of X and Y position of  $\text{Cl}^-$  ion in SPC/E ice 1h for  $Z = -1.5 \text{ Å}$ .

is the distance between them in angstroms. The ion-water LJ parameters are determined by combining the SPC/E oxygen-oxygen LJ parameters with sodium and chloride self-interaction parameters using the Lorentz-Berthelot combining rules.

For this work, the LJ parameters for chlorine and sodium ions from Smith and Dang [6] are employed. In defining the interaction parameters, they first fixed the ion polarizabilities to be approximately equal to experimentally derived values [7] and then the ion-water LJ parameters were determined by fitting to gas-phase binding enthalpy data for small chlorine [8] and sodium [9] ion-water clusters. Smith and Dang defined ion potentials for a polarizable model of water and for SPC/E water and found excellent agreement with the experiment. Their direct comparison of the properties of NaCl in the polarizable and SPC/E water showed that, although the polarization fluctuations do play a minor role in the system, the differences were smaller than the accuracy required in simulations. In concluding, they recommended the use of SPC/E water for studying aqueous systems in particular as the SPC/E model included the self-polarization correction. The potentials used in this work are shown in Fig. 1.

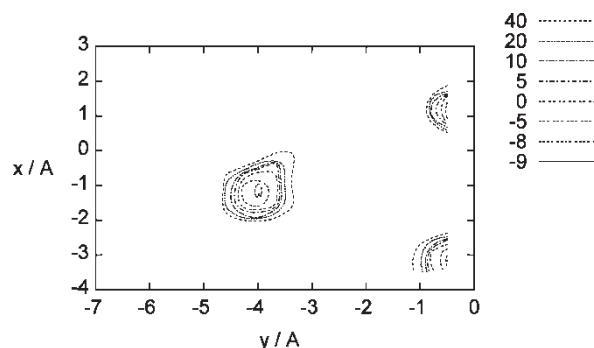


FIGURE 4 Potential energy in kcal/mol as a function of X and Y position of  $\text{Cl}^-$  ion in SPC/E ice 1h for  $Z = -2.0 \text{ Å}$ .

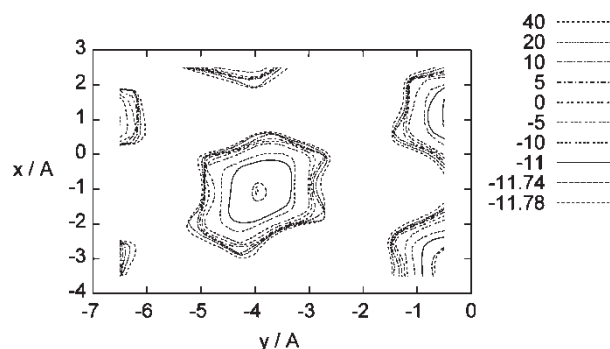


FIGURE 5 Potential energy in kcal/mol as a function of X and Y position of  $\text{Na}^+$  ion in SPC/E ice 1 h for  $Z = 0.0 \text{ \AA}$ .

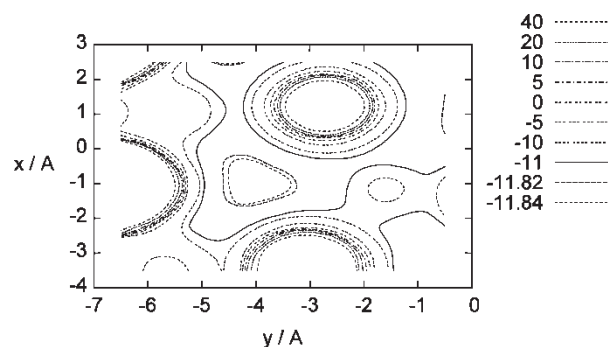


FIGURE 7 Potential energy kcal/mol as a function of X and Y position of  $\text{Na}^+$  ion in SPC/E ice 1 h for  $Z = -2.0 \text{ \AA}$ .

It is well known that in a MD model, the ice–water coexistence point at 1 atmosphere is not necessarily 273 K. In fact, for simple models it is considerably less [10–12]. To be safe, we investigate the stability of ions in SPC/E ice at 150 K, below the equilibrium melting point of the model.

All calculations were carried out using a modified version of the in-house MD package Solvent at 150 K. The system contains 96 water molecules and the cell dimensions are  $13.3 \times 15.5 \times 14.5 \text{ \AA}$ . Periodic boundary conditions are enforced and Ewald summation is used to account for long-range coulombic interactions.

## RESULTS AND DISCUSSION

This work was undertaken as a precursor to an investigation of solvation free energies of  $\text{Cl}^-$  and  $\text{Na}^+$  ions in bulk water and ice and the ice–water interface, to determine the most energetically favorable position for inserting either ion into the ice structure. Results conclusively showed that there is one favored position within the ice lattice for both  $\text{Cl}^-$  and  $\text{Na}^+$  ions.

Figures 1–3 show the potential energy contour plots for  $\text{Cl}^-$  ion at  $Z = -2.0$ ,  $-1.5$  and  $0.0 \text{ \AA}$ ,

respectively and Figs. 4–7 show the same for the  $\text{Na}^+$  ion. The most favorable ion position for both ions occurs has a potential energy of  $-12 \text{ kcal/mol}$  and occurs at  $Z = 0.0 \text{ \AA}$ , corresponding to approximately the middle of the cavity of the hexameric box. The results obtained for  $Z = -6.5 \text{ \AA}$  (not shown), being the equivalent position in the neighboring hexameric box, gives approximately the same potential values. Due to the larger size of the  $\text{Cl}^-$  ion, the potential surface is much more restrictive in comparison with the  $\text{Na}^+$  ion in the same position (Fig. 5).

The least favorable position (in terms of energy minima) occurs has potential energy of  $-11.78$  and  $-9 \text{ kcal/mol}$  for the  $\text{Na}^+$  and  $\text{Cl}^-$  ions, respectively and occurs at  $Z = -1.5 \text{ \AA}$ . This location has the same X and Y values as the most favorable position but

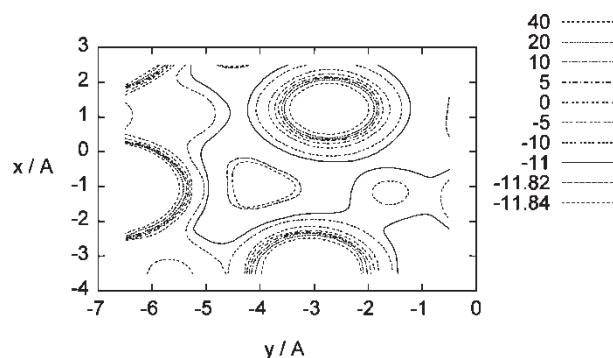


FIGURE 6 Potential energy in kcal/mol as a function of X and Y position in  $\text{\AA}$  of  $\text{Na}^+$  ion in SPC/E ice 1 h for  $Z = -1.5 \text{ \AA}$ .

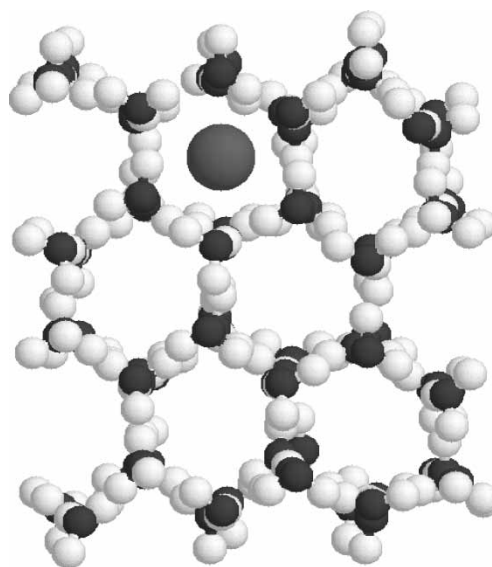


FIGURE 8 Molecular rendering of the ice lattice containing an ion in the most energetically favored position for either  $\text{Cl}^-$  or  $\text{Na}^+$  within the ice lattice. Oxygens are depicted as the smaller dark grey spheres, hydrogens are the white spheres and the ion is represented by the larger grey sphere.

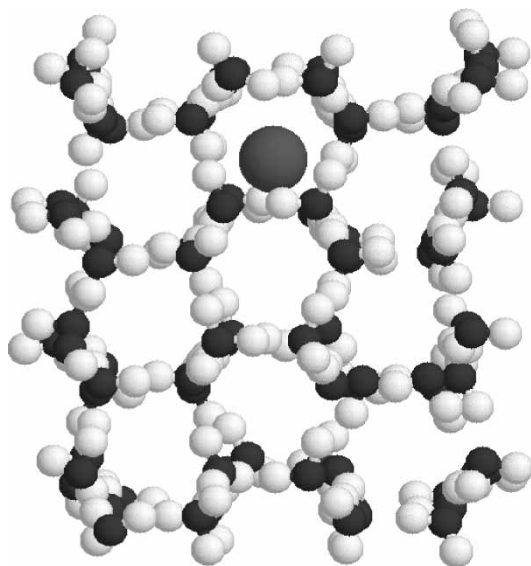


FIGURE 9 Molecular rendering of the ice lattice containing and ion in the most energetically favored position for either  $\text{Cl}^-$  or  $\text{Na}^+$  within the ice lattice as viewed from the side i.e. the system has been rotated  $90^\circ$  to the right from the representation shown in Fig. 8. Oxygens are depicted as the smaller dark grey spheres, hydrogens are the white spheres and the ion is represented by the larger grey sphere.

at  $Z = -1.5 \text{ \AA}$  the ion is now within the plane of ice separating two of the hexameric boxes. Figure 8 shows a molecular rendering of the ice lattice containing an ion in the most favorable position looking down the  $Z$  axis of the ice lattice (into the page), and Fig. 9 shows the same ion position viewed from the side i.e. with the lattice rotated to the right by  $90^\circ$  where the  $X$  axis of the system is now into the page.

The position is less favorable for the  $\text{Cl}^-$  ion than for the  $\text{Na}^+$  ion. In fact, the potential energy of the  $\text{Na}^+$  ion at this position is  $0.22 \text{ kcal/mol}$  more than the most favorable position, compared with a  $3 \text{ kcal/mol}$  difference for the  $\text{Cl}^-$  ion. At  $Z = -1.5 \text{ \AA}$  the contour plots for both ions display a definitive potential well, however at  $Z = -2.0 \text{ \AA}$  the  $\text{Na}^+$  is now on a much more shallow potential surface and the potential energy has slightly decreased, whereas the  $\text{Cl}^-$  surface still contains a well and the potential energy is unchanged.

The results obtained would indicate that a  $\text{Na}^+$  ion, once placed within the ice structure, is more likely to be move through the ice lattice, as opposed to a  $\text{Cl}^-$  ion which has higher potential barriers to overcome to pass through into neighboring cavities.

## CONCLUSION

In this study, we investigate the most and least favorable positions for a  $\text{Cl}^-$  and  $\text{Na}^+$  ion inserted within an SPC/E ice 1 h system at  $150 \text{ K}$ . The aim is to determine which positions would be ideal for each ion within the ice structure, as a preliminary step to an MD simulation of solvation free energies of  $\text{Cl}^-$  and  $\text{Na}^+$  ions in bulk ice and water and the ice–water interface. The most favorable positions for both ions was in the centre of the hexameric cavities, with both ions having a potential energy of  $-12 \text{ kcal/mol}$ .

## Acknowledgements

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