



Molecular dynamics simulations of alkali metal halides in supercritical water



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ABSTRACT

The solvation structure of water molecules around alkali metal halides in a supercritical condition (647 K and 217.55 atm pressure) has been investigated using classical molecular dynamics. Contact ion pairs are more stable than solvent assisted ion pairs. The hydration numbers of cations increase with the size of cations. For the anions, the hydration numbers decrease with increasing size of anions after Cl^- . Orientational distribution functions of solvent molecules are sharper for smaller ions. With an increase in the size of the anions, the water dipoles tilt more closely toward the ion oxygen vectors.

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1. Introduction

Electrolytes in aqueous medium have been a subject of extensive experimental and theoretical investigations [1–10]. These studies have been generally restricted to ambient temperatures. In recent years, supercritical fluids have drawn attention due to their technological and industrial applications when the Chemical Weapons Convention decided to eliminate chemical weapons and their production using environment friendly, safe, efficient and economical alternative technologies like supercritical water oxidation [11–15]. Supercritical water is water at temperatures above the critical temperature and at high pressures. In supercritical conditions, the physical properties of water are very different from those in ambient conditions. Water in supercritical conditions behaves almost as a non-aqueous fluid, providing a unique environment as a tunable reaction medium to study solute solvent interactions. The dielectric constant of water changes from 80 in ambient conditions, to 2 in supercritical conditions [16]. As a result, organic non-polar compounds like alkanes, aromatics, amino acids, nucleotides and molecular oxygen are completely miscible in water under supercritical conditions whereas, inorganic salts are sparingly soluble leading to far smaller values of ionic dissociation constants [17,18]. Experiments have shown that the association of ion pairs in supercritical water is very fast due to the very low solubility of salts in supercritical conditions. Whereas in water at ambient conditions either the contact ion pairs (CIPs) are absent else the stability of the CIP is much less than the stability of the CIP at

supercritical condition [19]. The precipitation of salts from reaction media is a major obstacle during the supercritical water oxidation [20,21]. The precipitation during reactions results in severe plugging of the reactor system within a few minutes of operations [22]. Moreover, supercritical water becomes highly corrosive if halogenated compounds like alkali metal halides are present in it.

Therefore, it is necessary to investigate a molecular level behavior of solvation and the nucleation of salts like alkali metal halides in supercritical water. A variety of approaches have been employed earlier to study ions and salts in supercritical water. Narayan and Antal [23] showed that in spite of very low dissociation constants, ions play an important role in catalyzing reactions in supercritical water. Wood et al. [24], Mesmer et al. [25] and Simonson et al. [26] showed that experimental findings support the presence of solvent molecules around ions at supercritical conditions. Cummings et al. [27] performed molecular dynamics simulations to study the solvation behavior of isolated sodium ion, chloride ion and neutral argon in water at two different states near critical conditions. Cochran et al. [28] extended this study and included molecular methanol as one of the solute molecules. On the basis of spectroscopic and computer simulation studies, they found that the number of hydrogen bonds per water molecule reduces to about one third as we move from ambient conditions to supercritical conditions. Rasiaiah et al. [29] have analyzed the structure of single ions at infinite dilution in supercritical water at 683 K and solvent density 0.35 g cm^{-3} . Cui and Harris [30], for the first time, discussed the issues regarding ion pairing and dissociation of Na^+Cl^- at supercritical conditions using molecular dynamics (MD). Gao et al. [31] calculated the potentials of mean force of Na^+Cl^- in supercritical water at two different pressures, 350 and 1000 atm. Chivalho et al. [32] performed the MD simulations of supercritical electrolyte solutions with three

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different ion–water models to study the cation–anion PMFs at infinitely dilute aqueous solutions of Na^+Cl^- . Therefore, simulations played a major role in obtaining a molecular level picture of the structure of the aqueous salt solutions above the critical point of water.

Very few studies have been carried out in supercritical water beyond the Na^+Cl^- ion pair as the solute [33–35,14]. To the best of our knowledge the association and analysis of solvent structure around all alkali metal halides in supercritical water have not been explored yet. The relevance of our present work lies here. Our interest is in comparing the stability of different ion pairs of different ion sizes at supercritical conditions with the help of MD simulations. We have also studied water structure around two ions when they approach each other. We have calculated the potentials of mean force for different cation–anion pairs (M^+X^-) and analyzed the solvent structure through radial distribution functions and coordination numbers of ions in their first solvation shells. The models and methods are described in Section 2. Results and discussions are given in Section 3, followed by conclusions in Section 4.

2. Models and methods

Classical molecular dynamics simulations are performed for the isothermal isobaric (NPT) ensemble using GROMACS 4.5.4 software package [36]. The systems studied consist of a single alkali metal halide ion pair surrounded by 689 water molecules in a cubical box with periodic boundary conditions. The side length of the simulation box is calculated from the experimental density of supercritical water and is adjusted to give the required density, 0.322 g cm^{-3} . Initial coordinates of the particles are chosen by using Packmol [37]. The temperature of the system is maintained at 647K using the velocity rescaling method [38]. Constant pressure of 217.55 atm is maintained using the Berendsen algorithm [39]. The internal geometries of the solvent molecules are held constant by using the SHAKE algorithm [40]. For the solutes, we have used the united atom optimized potential for liquid simulations (OPLS) force field [41]. The simple point charge (SPC) model has been used for water [42]. Cummings et al. showed that the use of the SPC water model for supercritical water yields properties including the dielectric constant in good agreement with the experimental values [28]. An additional reason for using the SPC water model is that the critical point of SPC water has been calculated computationally using the Gibbs ensemble simulation by de Pablo et al. [44]. Cui et al. showed that molecular dynamics study of ionic species in supercritical water gives an adequate description of the properties of the system [30]. The geometrical and potential parameters of solutes and solvents are given in the supplementary information (Tables S1 and S2).

The intermolecular potentials consist of site–site pairwise additive potentials, $U_{ij}(r)$ between ions and molecular sites. The short–ranged Lennard–Jones and the long ranged Coulombic terms contribute to $U_{ij}(r)$ as,

$$U_{ij}(r) = \frac{A_{ij}}{r^{12}} - \frac{C_{ij}}{r^6} + \frac{q_i q_j}{r} \quad (1)$$

The parameters, A_{ij} and C_{ij} , are obtained using the Lorentz–Berthelot combination rules, $\varepsilon_{ij} = (\varepsilon_i \varepsilon_j)^{1/2}$ and $\sigma_{ij} = (\sigma_i + \sigma_j)/2$. Here, $A_{ij} = 4\varepsilon_{ij}\sigma_{ij}^{12}$ and $C_{ij} = 4\varepsilon_{ij}\sigma_{ij}^6$. Particle mesh Ewald (PME) algorithm has been used to handle long–range electrostatics interactions, with a direct space cutoff of 1.0 nm and a grid spacing of 0.12 nm. For non–bonded van der Waals interactions, a 1.0 nm cut off is used.

The PMF between two ions i and j of electric charges q_i and q_j respectively, in the presence of a solvent of dielectric constant ε_r ,

is calculated by integrating mean force $F(r)$ between them which is the sum of the direct force $F_d(r)$ and the solvent contribution, $\Delta F(r)$.

$$F(r) = F_d(r) + \Delta F(r) \quad (2)$$

Here, $\Delta F(r) = \langle \Delta F(r,t) \rangle$, the angular brackets denote the ensemble average. The potential of mean force, $W(r)$, can be written as,

$$W(r) = W(r_0) - \int_{r_0}^r F(r') dr' + 2k_B T \ln \frac{r}{r_0} \quad (3)$$

$$W(r_0) = \frac{q_i q_j}{\varepsilon_r r_0} \quad (4)$$

The choice of $W(r_0)$ is done in such a way that, the calculated mean force potential matches the macroscopic Coulombic potential at large distances. It has been found that, the PMFs computed here are not very sensitive to the choice of the r_0 if r_0 is greater than 0.8 nm. In the present study, r_0 is taken to be 1 nm. A reference value of $W(r)$ is needed for integration from r_0 to r . A value of r_0 in the range of 0.8 nm to 1.5 nm has been used by several workers. The values of the solvent contribution to $F(r)$ are not significant for $r > r_0$ for $r_0 > 1.0 \text{ nm}$ [43].

The dielectric constants ε_r have been calculated from the fluctuations in the dipole moments. The distance between the ion pair is kept constant by applying the SHAKE algorithm. However, the individual Cartesian coordinates of the ion pairs are not fixed. The entropic force due to the increase in phase space with ion–ion separation is taken care of by adding the logarithmic term in Eq. (3) while calculating the PMFs. After 2 ns equilibration, 6 ns constrained molecular dynamics simulations were performed for the calculation of the PMFs. We have performed 81 simulations for the distances ranging from 0.2 nm to 1.0 nm with a constant distance interval of 0.01 nm for each mixture. The error bars in PMFs for all cases are found to be less than 0.5 kJ mol^{-1} .

We have done additional unconstrained molecular dynamics simulations for supporting the nature of the potentials of mean force. For this purpose, a number of trajectories are initiated in the range of the PMF that constitutes the ion association region. We have performed 500 ps NPT trajectories for each configuration in this region after releasing the constraint between the ion pairs. Although the integration time step for the calculation of PMF was 2 fs, the integration time step while calculating the ion–pair trajectories had been kept at 0.2 fs to get finer details regarding the stability of the ion pairs.

3. Results and discussion

3.1. Potentials of mean force and structural analysis

The PMFs of alkali metal chlorides are shown in Figure 1(a) and the PMFs of sodium halides are shown in Figure 1(b). The PMFs in ambient conditions can be generally classified into two regions, a contact ion pair (CIP) region and a solvent assisted ion pair (SAIP) region [45]. The first local minimum in the smaller ion pair distance segment is the CIP and the second local minimum at a larger ion pair distance segment is the SAIP. In supercritical conditions investigated here, at 647 K and 217.55 atm pressure and 0.322 gm cm^{-3} solvent density, we found that invariably the CIP is much more stable than the SAIP. In most of the cases, an SAIP is almost absent with the exception in a few cases where only a shoulder is observed in the SAIP region.

The positions and the depths of the CIPs are given in Table 1.

In the supercritical condition studied in the present Letter, among the alkali metal halides at the CIP configuration, Li^+F^- is the most stable ($\text{PMF} = -194.0 \text{ kJ mol}^{-1}$) and Li^+I^- is least stable ($\text{PMF} = -104.3 \text{ kJ mol}^{-1}$). When the cation is relatively small, like

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