



# Solvation structures and dynamics of alkaline earth metal halides in supercritical water: A molecular dynamics study



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## ABSTRACT

Constrained molecular dynamics simulations of alkaline earth metal halides have been carried out to investigate their structural and dynamical properties in supercritical water. Potentials of mean force (PMFs) for all the alkaline earth metal halides in supercritical water have been computed. Contact ion pairs (CIPs) are found to be more stable than all other configurations of the ion pairs except for  $\text{MgI}_2$  where solvent shared ion pair (SSHIP) is more stable than the CIP. There is hardly any difference in the PMFs between the  $\text{M}^{2+}$  ( $\text{M} = \text{Mg}, \text{Ca}, \text{Sr}, \text{Ba}$ ) and the  $\text{X}^-$  ( $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$ ) ions whether the second  $\text{X}^-$  ion is present in the first coordination shell of the  $\text{M}^{2+}$  ion or not. The solvent molecules in the solvation shells diffuse at a much slower rate compared to the bulk. Orientational distribution functions of solvent molecules are sharper for smaller ions.

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## 1. Introduction

In the past few years, there has been a great interest in studies of the structure and dynamics of fluids at high temperatures and pressures. Supercritical fluids (SCFs) exist at temperatures above the liquid–vapor critical temperature and have densities between liquid and vapor states. The advantages of supercritical fluids as environmentally benign solvents arise from their non-toxicity, non-combustibility, availability and possibilities for modulating physical and chemical properties through minor changes of temperature or pressure. These fascinating features of SCFs lead to their important potentials as green alternatives to toxic organic solvents and there have been many industrial and technological applications of SCFs [1–7].

During the last decade, there has been considerable interest in using supercritical water (SCW) in pyrolysis [8], hydrolysis [9], oxidation [10], electrochemical reactions [11] and in material synthesis [12]. Physical properties of SCW are different from those of liquid water. While going from ambient to supercritical conditions, water tends to become a continuum like low dielectric solvent. The average number of hydrogen bonds in water is also reduced in supercritical conditions. The effect of an ion on nearby water dipoles changes with increasing temperature and pressure as a result of reduced dielectric screening. These resulting differences

have a direct consequence on the solvation properties of SCW. Ionic association occurs to a larger extent in SCW because of the lower solubility of ions in water under extreme conditions, which are characteristic of the supercritical fluids. Aqueous electrolyte solutions play an important role in many natural processes. Particularly, the thermodynamic properties of ions in supercritical water (SCW) have crucial roles in many geological processes [13]. Therefore, it is important to study and model the solvation structure and dynamics of aqueous electrolyte solutions in supercritical conditions at the microscopic level. The understanding of the chemical processes in these hydrothermal systems become critical due to their widespread applications as mentioned before. Ion hydration and ion–pair association in SCW have important consequences for hydrothermal technologies [14]. Aqueous fluids which occur ubiquitously in the earth's crust and upper mantle at higher temperatures and pressures are involved in magmatic processes, metamorphism, formation of ore deposits, etc. Thus, an understanding of how these processes occur at such elevated temperatures and pressures is directly related to the chemistry and physics of aqueous solutions in the earth's crust at high temperatures and pressures. Several studies have been reported on the structural properties of alkali metal ions at supercritical conditions [15–41]; yet little is known about ion association of alkaline earth metal halides at the extreme supercritical conditions [42–45]. Studies on the structural properties of alkaline earth metal aqueous solutions are relatively few in spite of their use in chemical engineering and environmental chemistry. From the point of view of fundamental chemical physics, there is an interest in

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understanding the differences and similarities between the solvation of monovalent versus that of divalent ions. Computer simulations prove to be an extremely potent tool in this respect. Structural properties of alkaline earth metal halides in ambient conditions have been studied by many authors [46–57]. Deublein et al. [58] developed new Lennard–Jones plus point charges for alkaline earth cations in aqueous solutions via molecular dynamics simulations. Naor et al. [59] performed Car–Parrinello molecular dynamics simulations of the calcium ion in liquid water to determine the structural and dynamical properties of  $\text{Ca}^{2+}$  ion. Potentials of mean force and solvation properties of  $\text{SrCl}_2$  in polarizable water have been studied using molecular dynamics simulations by Smith et al. [60]. Kohagen et al. [61] developed an accurate parameterization for the calcium ion based on the electronic continuum correction (ECC) approach. Todorova et al. [62] performed Car–Parrinello molecular dynamics (CPMD) simulations to investigate the structural properties of 1 and 2 molal (m)  $\text{CaCl}_2$  aqueous solutions. MD simulations of  $\text{CaCl}_2$  in liquid methanol have been performed by Kosztolányi et al. [63] and Owczarek et al. [64]. Molecular dynamics simulations of  $\text{CaCl}_2$  solutions in water and methanol–water mixtures, with methanol concentrations of 5, 10, 50, and 90 mol%, at room temperature, have been performed by Owczarek et al. [65]. The hydration and association of alkaline earth metal chloride aqueous solution under supercritical conditions have been studied by Zhu et al. [46]. They have studied the structural properties of alkaline earth metal chlorides in terms of radial distribution functions and running coordination numbers. Molecular dynamics simulations of the limiting conductance of  $\text{MgCl}_2$  and  $\text{CaCl}_2$  in supercritical water has been studied by Goo et al. [43]. A number of studies have been reported on the solvation structure and dynamics of alkaline earth metal halides in ambient conditions but to the best of our knowledge solvation structural study of alkaline earth metal halides in supercritical conditions has not been reported.

As a part of our computer simulation study on SCFs, classical MD simulations of alkaline earth metal halide ion pairs in supercritical water have been performed. In this study, our attention is focused on the solvation structure of the divalent alkaline earth metal cations and halide ions. In the next section, the methodology used in this work is outlined. This will be followed by results and discussions and finally conclusions.

## 2. Methodology and computational details

All the MD simulations have been performed in an isothermal–isobaric ensemble at  $T = 673$  K and  $P = 250$  bar using GROMACS package (version 4.5.4) [66]. In the present study, the SPC/E model has been used for water [67]. The initial configurations of the system were generated using Packmol [68]. The force fields and geometrical parameters for water and the ions are given in Tables S1 and S2 of Supplementary Content. The interatomic interactions between the ions and solvents are taken to be pairwise additive. The short-ranged interactions are described through Lennard–Jones potential and the long-ranged electrostatic interactions are modeled with a Coulombic potential. The pairwise interaction between  $i$  and  $j$  sites is given by the following expression,

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

where,  $q_i$  and  $q_j$  are the charges located at sites  $i$  and  $j$ , and  $r$  is the site–site separation. The terms  $A_{ij}$  and  $B_{ij}$  are determined from,

$$A_{ij} = 4 \times (\varepsilon_{ij}) \times (\sigma_{ij})^{12} \quad (2)$$

$$B_{ij} = 4 \times (\varepsilon_{ij}) \times (\sigma_{ij})^6 \quad (3)$$

whereas,  $\varepsilon_{ij}$  and  $\sigma_{ij}$  are calculated using the Lorentz–Berthelot mixing rules [69].

$$\varepsilon_{ij} = (\varepsilon_i \times \varepsilon_j)^{1/2} \quad (4)$$

$$\sigma_{ij} = \left( \frac{\sigma_i + \sigma_j}{2} \right) \quad (5)$$

The PMFs between the  $\text{M}^{2+}$  ( $\text{M} = \text{Mg}, \text{Ca}, \text{Sr}, \text{Ba}$ ) and  $\text{X}^-$  ( $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$ ) ion pair are calculated by integrating the mean forces acting on them. The mean force at a separation  $r$  is the sum of the solute–solute direct force and the ensemble average of the solute–solvent forces. That is,

$$F(r) = F_d(r) + \Delta F(r) \quad (6)$$

where,  $\Delta F(r) = \langle F(r, t) \rangle$ , the angular brackets denote the ensemble average.

Since the distance between the ion–pair is fixed, it reduces their rotational entropy which in turn is equivalent to an entropic force of magnitude  $-2k_B T/r$ . This is taken into account as [70–72],

$$\frac{-dW(r)}{dr} = F(r) - \frac{2k_B T}{r} \quad (7)$$

Integration of Eq. (7) yields the potential of mean force,  $W(r)$ ,

$$W(r) = W(r_0) - \int_{r_0}^r F(r) dr + 2k_B T \ln \left( \frac{r}{r_0} \right) \quad (8)$$

The choice of  $W(r_0)$  is required to be made in such a way that the calculated mean force potential matches the macroscopic Coulombic potential at long distances.

$$W(r_0) = \frac{q_i \times q_j}{\varepsilon_r r_0} \quad (9)$$

where,  $\varepsilon_r$  is the dielectric constant of the solvent. It has been found that the ion–ion PMFs studied here are not sensitive to the choice of  $r_0$  when  $r_0$  is larger than a few molecular diameters and so  $r_0$  is chosen to be 1.0 nm [73]. The error bars in PMFs for all cases are found to be around 0.2–0.5 kJ/mol. The simulated density of water in the cubic cell of 40 Å was 0.170 g/cc (at 673 K and 250 bar pressure) [74–76]. The alkaline earth metal ion ( $\text{M}^{2+}$ ) and two halide ions ( $\text{X}^-$ ) were added to the cubic cell with 642 water molecules.

The static dielectric permittivity ( $\varepsilon_r$ ) was computed in the NPT ensemble. For the calculation of dielectric constant, MD simulations for 100 ns have been performed in the NPT ensemble. The dielectric constant of water at 673 K and 250 bar pressure was found to be 3.775 by MD simulations which is close to the experimental value reported by Uematsu et al. [77]. All other technical details are given in the Supplementary Content.

## 3. Results and discussions

### 3.1. Potentials of mean force

The ion–ion PMFs are obtained by a direct integration of the total force according to Eq. (7). In a previous study of  $\text{Mg}^{2+}$ – $\text{Cl}^-$  ion–pair in water–ethanol binary mixtures in ambient conditions by Chatterjee et al. [78], it was observed that the solvation structure of the  $\text{Mg}^{2+}$ – $\text{Cl}^-$  ion pair depends on whether the second  $\text{Cl}^-$  is present in the solvation shell of  $\text{Mg}^{2+}$  or it is present in the bulk. In order to have a clear picture of the solvation structures in this present study, two sets of simulations have been done namely, (i) the second  $\text{Cl}^-$  is present in solvation shell of  $\text{Ca}^{2+}$  and (ii) the second  $\text{Cl}^-$  is present in the bulk. The PMFs for these two cases are shown in Fig. 1 for  $\text{CaCl}_2$ .

The differences in the PMFs are not large because the second chloride ion comes within the first solvation shell within 1 ns. The contribution from the configuration to the PMF (when the

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