Chemical Physics Letters 662 (2016) 306–316

Contents lists available at ScienceDirect

Chemical Physics Letters

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

Research paper

Molecular dynamics simulations of Ca^{2+}—Cl^- ion pair in polar mixtures of acetone and water: Solvation and dynamical studies

Asrar A. Siddique, Mayank K. Dixit, Bhalachandra L. Tembe *

Department of Chemistry, Indian Institute of Technology Bombay, Powai, Mumbai 400076, India

A R T I C L E I N F O

Article history:
Received 21 January 2016
Revised 21 September 2016
In final form 22 September 2016
Available online 22 September 2016

Keywords:
Potentials of mean force (PMF)
Radial distribution function
Running coordination number
Preferential binding constant
Diffusion constant

A B S T R A C T

The potentials of mean force (PMFs) have been used to assess the relative stabilities of contact ion pairs (CIPs), solvent assisted ion pairs (SAIPs) and solvent separated ion pairs (SSIPs) in acetone-water mixtures containing a calcium chloride ion pair. In the case of Cl^-_{in} (the second Cl^- ion is placed within the solvation shell of Ca^{2+} ion), the CIPs are more stable than SAIPs for low mole fractions of acetone ($x_{acetone}$) whereas the SAIPs are more stable than the CIPs for large values of $x_{acetone}$. In the case of Cl^-_{out} (the second Cl^- ion is placed outside the solvation shell of Ca^{2+} ion), the SAIPs are marginally more stable than CIPs in neat water and for low $x_{acetone}$. However, CIPs become more stable than SAIPs with increase in $x_{acetone}$. The Ca^{2+}—Cl^- ion pair is preferentially solvated by water in all the mixtures.

1. Introduction

Various chemical and biochemical processes are significantly influenced by ion pairs. For several years, studies on solvation structure and dynamics of ion pairs in various solvents/mixture of solvents have been pursued by many researchers [1]. Binary mixtures of solvents such as dimethyl sulphoxide (DMSO)-water, acetone-water and DMSO-methanol show unusual properties in relation to the properties of respective pure components. These mixtures exhibit non ideal behaviour [2]. Acetone, for example, is a dipolar aprotic solvent and soluble in water in all proportions. Various physical properties of acetone-water mixtures such as density, viscosity and dielectric constants reflect their non-ideal behaviour. Aqueous solutions of acetone are good examples of mixed solvent systems/binary mixtures [3].

Alkali halides and alkaline earth halides have widespread applications in many chemical and biological processes. A detailed study of solvation properties of electrolytes such as NaCl and $CaCl_2$ in aqueous solutions and polar solvent mixtures is of considerable importance for a molecular level understanding of several chemical and biochemical transformations. Several theoretical studies have been undertaken to explain the molecular associations of ion pairs in aqueous and non-aqueous solutions but studies for ion pairs such as Ca^{2+}—Cl^- in non-aqueous solvents and mixtures are limited [4–7].

Megyes et al. [5] have used ab initio methods (cross-checked using DFT and MP2 methods) to show that the solvation number (coordination number) around Ca^{2+} ion is a function of solvent concentration and varies between 6 (for methanol) and 8 (for water) whereas for the counter ion, Cl^-, the number is 6 irrespective of the concentration of solvents. They attributed these observations to loose solvation around Ca^{2+} ion and stable solvation around Cl^-. They concluded that calcium ion solvation is sensitive to the nature of solvating molecules. Later, Megyes et al. [6,7] carried out molecular dynamics simulations and diffraction studies to investigate ion pairing in aqueous calcium chloride solutions. Besides solvation structural studies, their aim was to find the capabilities of each method to detect ion pair formation. Their results showed that MD simulations yield results in general accordance with experimental findings with a fair degree of accuracy.

Zavitsas [8] studied colligative properties of aqueous solutions of CaX_2 (X = Cl, Br, I) and $Ca(ClO_4)_2$ to determine hydration numbers around Ca^{2+} ion and showed that the number decreases with increase in temperature. Palka and Hawlicka [9] calculated the self-diffusion coefficient of Ca^{2+} and Cl^- at 298 K in aqueous solutions of alcohols. Further, they investigated the influence of alcohol concentration on the hydration shells of Ca^{2+} and Cl^-, and found that the alcohols destabilise the hydration shell of Cl^- whereas the hydration shell of Ca^{2+} depends on solvent structure. Plazanet and co-workers [10] measured vibrational modes of water in

---

* Corresponding author.
E-mail addresses: asrar@chem.iitb.ac.in (A.A. Siddique), dixit.mayank2@gmail.com (M.K. Dixit), bltembe@chem.iitb.ac.in (B.L. Tembe).

http://dx.doi.org/10.1016/j.cplett.2016.09.061

aqueous solutions containing $CaCl_2$ molecules to investigate the anharmonicity of the system and the dispersion of the excitation along the hydrogen bonds.

Fulton et al. [11] used the technique of X-ray absorption fine structure spectroscopy to study hydration and contact ion pairing of Ca^{2+} and Cl^{-} ions in supercritical aqueous solutions. Their study showed significant contact ion pairing at higher temperatures (>250 °C). According to them, the measurements provided a structural basis for understanding the solvation of Ca^{2+} in hydrothermal systems. Larentzos and Criscenti [12] studied the relative stability of alkaline earth metals ($M^{2+} = Mg^{2+}$, Ca^{2+}, Sr^{2+}, and Ba^{2+}) and their chloride complexes in aqueous solutions through molecular dynamics simulations using a flexible SPC water model with an internally consistent set of metal ion force field parameters. Their work highlighted the importance of appropriate force fields to produce thermodynamic properties with good accuracy.

Todorova et al. [13] employed Car–Parrinello molecular dynamics (CPMD) simulations to investigate the structural properties of 1 and 2 molal (m) $CaCl_2$ aqueous solutions, such as the radial distribution functions, coordination numbers, and dipole moments of water molecules in the first solvation shell. In these simulations, the first solvation shell of Ca^{2+} ion consists of six water molecules. Li et al. [14] performed systematic long time (5–20 ns) molecular dynamics (MD) simulations to study the structural and dynamical properties of $CaCl_2$ aqueous solutions over a wide range of concentrations ($\leqslant$9.26 m). These simulations reveal totally different structural characteristics than those obtained from short time runs.

Zhu et al. [15] used the MD method to simulate alkaline earth metal (magnesium, calcium, strontium and barium) chloride aqueous solutions under ambient and supercritical conditions. The results of simulations indicate that the solvent-separated ion pair is the main association pattern in dilute magnesium chloride solution and the microstructure of this alkaline earth metal aqueous solution is a synergistic action of hydration and association. Timko et al. [16] obtained the potential of mean force for the dissociation of a Ca^{2+}—Cl^{-} ion pair in water from *ab initio* molecular dynamics simulations. The *ab initio* results presented for the Ca^{2+}—Cl^{-} ion pair complement their earlier results for the Na^{+}—Cl^{-} ion pair. They have explicitly demonstrated the critical role played by water molecules in initiating the dissociation of an ion pair.

Computer simulations play an important role in molecular level understanding of ion transport. Due to the gap between molecular and observational timescales, a good understanding is difficult from experiments alone. Allen and co-workers [17] employed the MD technique and used PMF calculations as a tool for understanding ion permeation and selectivity in narrow channels. Their PMFs for potassium, calcium and chloride ions were used to explore the basis for the valence selectivity of narrow and uncharged ion channels.

Kosztolanyi and co-workers [18] have studied the structural properties of calcium chloride solutions on the basis of pair interaction energy distributions, radial distribution functions and the geometrical arrangement of methanol molecules in the solvation shell of the calcium ions. They have reported extensive contact ion-pair formation for higher concentrations of solutions.

The study of metal ions in solutions assumes significance because of manifestations of ionic effects in physicochemical and biochemical processes. Because of vital role of metal ions such as calcium ion in metabolism of living bodies, its study deserves attention. To the best of our knowledge, the numerous theoretical and experimental reports in literature are pertinent to aqueous solutions but limited attention has been given to aqueous mixtures of solvents such as DMSO, methanol and acetone. The solvation studies for alkali halide/alkaline earth metal halide ion pairs in water and these solvents such have been reported earlier, [4–7] but the work on PMFs and solvation studies of alkaline earth metal halide ion pairs in different compositions of acetone-water needs to be investigated in detail. In the present study, we have investigated the solvation structures and dynamics of Ca^{2+}—Cl^{-} ion pair in acetone-water mixtures with varying compositions. Methodology and computational details have been given in Section 2. Results and discussion are given in Section 3 and conclusions are presented in Section 4.

2. Methodology and computational details

We have performed MD simulations using GROMACS package, version 4.5.4 [19–22]. The united atom optimized potentials for liquid simulation (OPLS) force field have been used for acetone [23,24] whereas water is modelled by SPC/E model [25]. The Ca^{2+} and Cl^{-} ions are considered as charged Lennard-Jones particles [26]. The values of the Lennard-Jones and electrostatic interaction potential parameters of solute particles and different atomic sites of solvents are summarized in Table 1.

The Ca^{2+}—Cl^{-} ion pair is placed in a cubic simulation box of edge length 40 Å in the mixtures of acetone and water for different mole fractions of acetone. The simulations have been performed twice, firstly by fixing the position of the second Cl^{-} ion inside the solvation shell of Ca^{2+}, at a distance of 0.30 nm from the Ca^{2+} ion and then, secondly by fixing the second Cl^{-} ion outside the solvation shell, at a distance of 0.80 nm from Ca^{2+} ion. The initial configurations were obtained using the Packmol software package [27]. The leapfrog algorithm [28] with a time step of 2 fs was used to integrate the equations of motion. The isothermal-isobaric ensemble was used to maintain a temperature of 298 K and a pressure of 1 bar. The weak coupling algorithms of Berendsen and co-workers [21,22] were used for both the thermostat and barostat with coupling constants of 0.1 and 1.0 ps respectively for equilibration. We have also used Parrinello-Rahman algorithm for pressure coupling [29,30] for longer periods of simulations. Electrostatics was handled using the particle mesh Ewald (PME) method [20].

The details of the chosen solvent mixtures are given in Table 2.

We have computed densities of all the mixtures (Table 3) which are in good agreement with experimentally reported values [31].

The constrained MD methodology has been used in the simulations in which intra solvent atom - atom distances are kept constant by using the LINCS algorithm [32]. We have used two pull group constraints to fix the position of the second Cl^{-} ion, firstly within the solvation shell of Ca^{2+} ion at a distance of 0.30 nm, and secondly, outside the solvation shell of Ca^{2+} ion, at a distance of 0.80 nm from Ca^{2+}. The interionic separations vary from 0.20 nm and extend up to 1.0 nm with a separation step of 0.01 nm. For each interionic separation, the systems were equilibrated for 1 ns followed by production periods of 8 ns each using an NPT ensemble. We have observed in our earlier works [33–37] that PMFs obtained in simulations done for systems under NPT and NVT do not differ by more than 1 kJ, suggesting a good agreement between these two ensembles for the same system.

Table 1
Lennard-Jones and electrostatic interaction potential parameters. *e* represents the magnitude of the electronic charge.

Atom/ion	σ/(Å)	ε/(kJ mol^{-1})	Charge/e
Water- O	3.166	0.65060	−0.8476
Water – H	0.000	0.00000	+0.4238
Acetone – C	3.750	0.43932	+0.300
Acetone – CH_3	3.810	0.66944	+0.062
Acetone – O	2.930	0.87864	−0.424
Ca^{2+}	2.412	1.88136	+2.000
Cl^{-}	4.417	0.49283	−1.000