Chemical Physics 447 (2015) 76–85

Contents lists available at ScienceDirect

Chemical Physics

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

Solvation structures of lithium halides in methanol–water mixtures

Atanu Sarkar [1], Mayank Kumar Dixit [1], B.L. Tembe *

Department of Chemistry, I. I. T. Bombay, Mumbai 400076, India

ARTICLE INFO

Article history:
Received 24 May 2014
In final form 26 November 2014
Available online 5 December 2014

Keywords:
Potentials of mean force
Ion pair distance residence times
Radial distribution functions
Running coordination numbers
Excess coordination numbers

ABSTRACT

The potentials of mean force (PMFs) for the ion pairs, Li^+—Cl^-, Li^+—Br^- and Li^+—I^- have been calculated in five methanol–water compositions. The results obtained are verified by trailing the trajectories and calculating the ion pair distance residence times. Local structures around the ions are studied using the radial distribution functions, density profiles, orientational correlation functions, running coordination numbers and excess coordination numbers. The major change in PMF is observed as the methanol mole fraction (x_{methanol}) is changed from 1.0 to 0.75. The stable contact ion pair occurring for $x_{\text{methanol}} = 1.0$ becomes unstable at and below $x_{\text{methanol}} = 0.75$. The preferential solvation data show that the halide ions are always preferentially solvated by water molecules. Although the lithium ion is preferentially solvated by methanol molecules, there is significant affinity towards water molecules as well.

1. Introduction

A study of the solvation properties of electrolytes is of great help in analyzing diverse areas such as aqueous–organic solvent mixtures, biomolecular systems and reaction media. The thermodynamic and transport properties of many water–alcohol mixtures have been well characterized [1–4]. The use of alcohols, specifically methanol and ethanol as the organic components in mixtures, becomes effective due to specific solvation properties like their ability to dissolve several compounds compared to other commonly used organic solvents [5].

Methanol–water mixtures exhibit anomalous behavior compared to the properties of corresponding pure solvents due to mutual association as well as the hydrophobicity of the methyl group. Both water and methanol are highly associated liquids, but there is a considerable difference in the nature of their hydrogen bond networks [6–11]. Water molecules form a three dimensional, tetrahedrally coordinated structure, via extension of the hydrogen bonded network and the cavities are filled with water monomers. Methanol, on the other hand, forms a zigzag polymer chain through hydrogen bonds. When the methanol–water mixture is taken into consideration, both solvents are connected by a common hydrogen-bonded network; the mixture is still heterogeneous at a molecular level, as the bulkier methyl group of methanol remains unable to replace the hydrogen from the tetrahedrally coordinated structure of liquid water. Water and methanol form separate, percolating structures due to the miscibility of both components.

Although neutron diffraction study [12,13] and X-ray spectroscopy [14] confirm the nature of the association of the solvents in the absence of ion-pairs, they cannot provide insights about the ion-coordination shell for lithium halides because the distance between the ions and the oxygens of either water or methanol are nearly the same [12,15–19]. Hence, molecular dynamics simulation becomes a very useful tool to provide structural information regarding the solvation around the ion pair.

In this endeavor, the role of computer simulations becomes significant [20–24]. Although several computer simulations of aqueous methanol solutions have been reported in literature, in most cases, the Monte-Carlo method has been employed [25–28]. Much attention has not been paid for the ion pairs in methanol–water mixtures, apart from calculations in dilute solutions [29–32]. Hawlicka et al. have been performed molecular dynamics simulations of sodium halides in methanol–water mixtures and they have studied the solvation structure, preferential solvation, residence times and diffusion of the ion pair and solvent shell molecules [33–40]. They observed that both sodium and chloride ions are preferentially solvated by methanol molecules in methanol–water mixtures with low mole fraction of methanol. When the methanol mole fraction is high, sodium is not preferentially solvated by methanol molecules, but chloride ion is preferentially solvated by methanol molecules. A study using radial and angular distribution functions show that the orientation and the number of water and methanol molecules in the coordination shell of sodium and chloride ions is independent of the compositions of the methanol–water mixtures [33]. Feakins and Watson have studied the

---

* Corresponding author. Tel.: +91 22 2576 4199.
E-mail address: bltembe@chem.iitb.ac.in (B.L. Tembe).

[1] Tel.: +91 22 2576 4199.

http://dx.doi.org/10.1016/j.chemphys.2014.11.019
0301-0104/© 2014 Elsevier B.V. All rights reserved.

preferential solvation of ions in non-aqueous solvents and their aqueous mixtures [41]. Wensink et al. performed molecular-dynamics simulations to study excess properties of mixing in methanol–water, ethanol/water, and 1-propanol/water mixtures [42]. Guevara-Carrion et al. calculated the dynamical properties in methanol–water mixtures including density, self-diffusion coefficient, and shear viscosity as well as excess volume and excess enthalpy of aqueous binary mixtures containing methanol and ethanol [43]. In order to investigate the effects of composition of the methanol–water mixtures on the diffusion of either an ionic or a neutral atomic solute, Chowdhuri et al. performed a series of molecular dynamics simulations [44]. The diffusion coefficients of ionic solutes are found to show positive deviations from ideality in the solvent mixtures. The neutral solute shows characteristics of hydrophobic solvation and its diffusion decreases monotonically with increase of methanol concentration. Paul et al. have performed molecular dynamics in liquid–vapor interfaces of water methanol mixtures of varying compositions at room temperature to study the equilibrium and dynamical properties like inhomogeneous density, anisotropic orientational profiles, surface tension, and the pattern of hydrogen bonding [45].

Thus, extensive computer simulation studies of the ion pairs in methanol–water mixtures can be devised to give reasonable structural predictions for these mixtures and can be extended to consider other hydrogen bonded liquids [32]. At the methanol mole fraction (x_{methanol}) of 0.25 in methanol–water mixtures, the thermodynamic properties exhibit maxima [46].

Our present work here is concerned with the solvation and structural aspects of lithium halides such as Li^+—Cl^-, Li^+—Br^- and Li^+—I^- in methanol–water mixtures. In our present paper, we have considered five compositions with $x_{\text{methanol}} = 0.00, 0.25, 0.50, 0.75$ and 1.00. 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

For the systems under study, one lithium halide ion pair and different numbers of water and methanol molecules have been used for different compositions. Initial coordinates of the particles are generally chosen by using Packmol [47]. The details of the systems under study are given in Table 1.

Table 1
Compositions and system characteristics of the simulation boxes of methanol–water mixtures.

System	x_{methanol}	x_{water}	n_{methanol}	n_{water}	Box-length, nm
1	1.00	0.00	2141	0	5.14
2	0.75	0.25	1200	400	4.71
3	0.50	0.50	800	800	4.38
4	0.25	0.75	400	1200	4.03
5	0.00	1.00	0	2141	4.04

The classical molecular dynamics simulations for the systems mentioned above were carried out using the GROMACS 4.5.4 software package [48]. For the solute and solvent molecules, we have employed the united atom Optimized Potential for Liquid Simulations (OPLS) force field [49]. The SPC model has been used for water [50]. The potential parameters used here are given in the Supplementary information (Tables S1 and S2). The internal geometries of the solvent molecules are fixed by using SHAKE algorithm [51]. 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,

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

The parameters, A_{ij} and C_{ij}, are obtained using the Lorentz–Berthelot combination rules, $\varepsilon_{ij} = (\varepsilon_i \varepsilon_j)^{1/2}$ and $\sigma_{ij} = \frac{\sigma_i+\sigma_j}{2}$ [52,53]. To handle the long-range electrostatics interactions, the particle mesh Ewald (PME) algorithm has been used [54], with a direct space cut-off 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. Classical MD simulations are carried out using NPT ensembles with periodic boundary conditions (PBC). The systems under study are maintained at a constant temperature of 300 K by using the velocity rescaling method [55] and at a pressure of 1.0 bar using the Berendsen algorithm [56].

Several methods such as umbrella sampling, constrained molecular dynamics and the RDF method are available to compute the PMF, $W(r)$. The umbrella sampling method has been used to calculate PMFs between ion pairs in water [57], dodecamers in water [58], asphaltenes in toluene and heptane [59], octanoate miceller aggregation [60] and fullerenes and its hydroxyl derivatives between lipid bilayer [61]. The constrained MD method has been used for the system like Na^+—Cl^- in water [62], DMSO [63], water–DMSO mixtures [64] and methanol–DMSO mixtures [65]. Hess et al. have performed constrained MD simulations of infinitely dilute NaCl in water [66] using GROMACS and computed the PMF between the Na^+—Cl^- ion pairs.

For small concentrations of solutes such as two solutes in the solvent, the umbrella sampling method and the constrained MD method are appropriate. The RDF method to obtain $W(r)$ through $-k_BT \ln g(r)$ is appropriate for large concentrations of solutes and has been used to calculate PMFs for many systems such as, Na^+Cl^- in water [67] and hydrophobic solutes in aqueous solutions of osmolytes [68,69]. A comparison of these methods has been provided by the work of van Gunsteren and coworkers [70]. If the free energy along the reaction coordinate (in our case, the ion-ion separation) varies more than several times k_BT (which is generally the case here), an unbiased or unconstrained simulation will not produce sufficient statistics for the ranges of distance values for which the $W(r)$ values are high.

In the constrained MD method used in the present work, the PMFs between two ions were determined by integrating the mean force acting along the internuclear axis of the ion pair. We have fixed the distance between ion pair by using SHAKE algorithm. The individual Cartesian coordinates of the ion pairs are not fixed. The mean force is the ensemble average of the sum of the ion–ion direct forces and the ion–solvent forces. After 2 ns equilibration, 6 ns simulations were performed for the calculation of the potentials of mean forces (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 around 0.5 kJ mol^{-1}.

The PMF between two ions i and j of electric charge q_i and q_j respectively, in presence of the solvent of dielectric constant ε, are calculated by integrating mean force $F(r)$ between them which is the sum of the direct force $F_d(r)$ and the solvent contribution, $\Delta F(r)$.

$$F(r) = F_d(r) + \Delta F(r) \tag{2}$$

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,

$$W(r) = W(r_0) - \int_{r_0}^{r} F(r')dr' + 2k_BT \ln \frac{r}{r_0} \tag{3}$$

$$W(r_0) = \frac{q_i q_j}{\varepsilon r_0} \tag{4}$$