Journal of Molecular Liquids 178 (2013) 78–83

Contents lists available at SciVerse ScienceDirect

Journal of Molecular Liquids

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

Potentials of mean force of sodium chloride ion pair in dimethyl sulfoxide–methanol mixtures

Mayank Kumar Dixit, B. L. Tembe *

ARTICLE INFO

Article history:
Received 29 July 2012
Accepted 14 September 2012
Available online 3 December 2012

Keywords:
Potential of mean force
Contact ion pair
Solvent assisted ion pair
Solvent separated ion pair
Solvation structure of ion pair

ABSTRACT

The constrained molecular dynamics technique has been used to simulate solutions of sodium chloride ion pair in pure methanol (MeOH), pure dimethyl sulfoxide (DMSO) and DMSO–MeOH mixtures with MeOH mole fractions (x_{MeOH}) of 0.25, 0.50 and 0.75. The potentials of mean force (PMFs) of the sodium chloride ion pair have been computed for all the above compositions. The PMFs for the pure solvents indicate that contact ion pairs (CIPs) are more stable than the solvent separated ion pairs (SSIPs). In the mixtures, contact ion pairs (CIPs) dominate the PMF and solvent assisted ion pairs (SAIPs) persist in all the compositions. As the mole fraction of DMSO increases, the stability of CIP increases. In all three solvent mixtures, the Na^+-Cl^- ion pair is preferentially solvated by MeOH molecules. These results have been confirmed by dynamical ion pair trajectories for long times. A study of the running coordination numbers in the CIP and SAIP/SSIP configurations shows that the number of DMSO and methanol molecules around the ion pair does not change significantly with composition beyond $x_{MeOH}=0.50$.

1. Introduction

Many important chemical transformations occur in ionic and polar media and therefore it is essential to have an understanding of the nature of ion pairs in polar solvents. Most of the organic reactions are studied in solvents like water, dimethyl sulfoxide (DMSO), methanol (MeOH), dimethyl formamide, acetone, chloroform, dichloromethane, and acetonitrile. Many of these solvents are important in chemical and biological processes. DMSO is a highly polar solvent that dissolves many aromatic and unsaturated hydrocarbons, organic nitrogen compounds, organo-sulfur compounds and many inorganic salts. It is also miscible with most of the common organic solvents such as alcohols, esters, ketones, lower ethers, chlorinated solvents and aromatics. Methanol is the precursor of formaldehyde and it is used as a fuel [1]. The liquid-phase properties of methanol are strongly affected by hydrogen bonding. A deep knowledge of hydrogen bonding in methanol has important applications in various areas including liquid state theories, solvent effects in organic reactions and the structure and reactivity of biomolecules. The mixtures of DMSO–MeOH have importance as tunable reaction media [2]. The dielectric constant, relaxation, viscosity and other transport properties of mixtures depend upon the compositions of the mixtures. The solution of Na^+-Cl^- ion pair has widespread importance in chemistry and biochemistry [3–5]. The potentials of mean force (PMF) of the ion pairs show multiple minima [6–17]. The multiple minima represent CIP, SAIP and SSIP. The aqueous alkali chloride or bromide solutions have been compared with the aqueous dimethyl phosphate and acetate solutions [18]. The contact ion pair mechanism occurs in the aqueous alkali chloride or bromide solutions and a solvent-mediated ion pair mechanism dominates in the aqueous dimethyl phosphate and acetate solutions [18]. With the help of the PMFs, we can determine the equilibrium distribution between CIP and SAIP/SSIP. The potentials of mean force have been used in the studies of reaction rate constants of chemical reactions [19,20] and PMFs are used to determine free energy, entropy and enthalpy changes for ligand-cavity binding [21]. We have performed MD simulations of Na^+-Cl^- in pure MeOH, pure DMSO and in mixtures of DMSO-MeOH. In Section 2, we describe the model and the method used in the present study. In Section 3, we present our results followed by conclusions in Section 4.

2. The models and the method

The mean forces between the ion pairs in our work are calculated using the technique of constrained molecular dynamics [22,23], wherein the ion pairs are kept at fixed distance by imposing constraints on the ion pairs [24,25]. We used the shake algorithm [25,26] to retain the geometry of molecules during the simulations. We used periodic boundary conditions [27,28], and the Verlet algorithm [29] to integrate the equations of motion of the particles. The PMFs are obtained by integration of the mean force between ion pairs (Eq. (7)).

The $Na+-Cl-$ ion–ion PMFs have been calculated in the presence of the pure solvents and three selected solvent compositions of the DMSO-methanol mixtures. We have performed several MD

---

* Corresponding author at: Department of Chemistry, Indian Institute of Technology, Bombay, Powai, Mumbai, 400076, India. Tel.: +91 22 2576 4199; fax: +91 22 2576 7152.
E-mail address: bltembe@chem.iitb.ac.in (B.L. Tembe).

0167-7322/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.molliq.2012.09.026

Table 1
Solvent 1 = MeOH; Solvent 2 ≡ DMSO; x_i = mole fraction of solvent i; n_i = number of molecules of solvent i in the cubic simulation cell of edge length L; ρ = density at 298 K; ε = dielectric constant.

Composition	x_1	x_2	n_1	n_2	L(Å)	$\rho^a/(\mathrm{g\ ml}^{-1})$	ε^a
1	0.25	0.75	125	375	37.47	1.0510	46.40
2	0.50	0.50	250	250	35.84	0.9930	45.00
3	0.75	0.75	375	125	34.12	0.9109	40.25

[a] Reference: [34].

simulations of the Na^+-Cl^- ion pair in pure solvents and DMSO–methanol mixtures. For MeOH, we have taken 124 MeOH molecules and Na^+-Cl^- ion pair in a cubic box of edge length 20.27 Å. This corresponds to an experimental density of 0.7918 g ml^{-1} for MeOH at 298 K. For DMSO, we have taken 229 DMSO molecules and Na^+-Cl^- ion pair in a cubic box of edge length 30.0 Å. This system corresponds to an experimental density of 1.1 g ml^{-1} for DMSO at 298 K. The details of the chosen solvent mixtures are given in Table 1. For most of the computations (except in case of pure DMSO, which we did for comparison), we have used our own MD program. For the pure DMSO, we have also performed MD simulations using GROMACS package (version4.5.) [30–33].

2.1. The interaction potentials

The united atom optimized potentials for liquid simulation (OPLS) force field is used for methanol, DMSO and the Na^+-Cl^- ion pair. The parameters [34–36] are given in Tables 2 and 3.

2.2. Computation of intermolecular interactions

The solvent–solvent, solvent–solute, and solute–solute interactions are taken to be pair wise additive and comprise of the Lenard–Jones and Columbic terms

$$U_{\alpha\beta} = \left(\frac{A_{\alpha\beta}}{r^{12}} - \frac{B_{\alpha\beta}}{r^6}\right) + \frac{q_\alpha q_\beta}{r} \tag{1}$$

where α and β denotes a pair of interactions sites on different molecules, r is the site–site separation, q_α is charge located at site α, q_β is the charge located at site β. The terms $A_{\alpha\beta}$ and $B_{\alpha\beta}$ are determined from

$$A_{\alpha\beta} = 4\,\varepsilon_{\alpha\beta}\left(\sigma_{\alpha\beta}\right)^{12} \tag{2}$$

$$B_{\alpha\beta} = 4\,\varepsilon_{\alpha\beta}\left(\sigma_{\alpha\beta}\right)^{6} \tag{3}$$

whereas $\varepsilon_{\alpha\beta}$, $\sigma_{\alpha\beta}$ are calculated using Lorentz–Berthelot rules.

$$\varepsilon_{\alpha\beta} = \left(\varepsilon_{\alpha\alpha} * \varepsilon_{\beta\beta}\right)^{1/2} \tag{4}$$

Table 2
The geometrical parameters for MeOH and DMSO [35].

Sites	Bond length, (Å)	Bond angle/(°)
S–O	1.496	–
S–CH_3	1.8	–
O–S–CH_3	–	107.2
CH_3–S–CH_3	–	99.2
O–H	0.945	–
C–O	1.43	–
C–-O–H	–	108.5

Table 3
United atom OPLS force field parameter for MeOH, DMSO [35] and sodium chloride [36].

Sites	σ/(Å)	$(\varepsilon/k_B)/(K)$	q/(e)
C^{DMSO}	3.81000	80.49000	0.16000
S^{DMSO}	3.56000	198.71000	0.13900
O^{DMSO}	2.93000	140.86000	−0.45900
C^{MeOH}	3.78000	104.23000	0.26500
O^{MeOH}	3.07000	85.60000	−0.70000
H^{MeOH}	0.00000	0.00000	0.43500
Na^+	3.33045	1.1586	+1.00000
Cl^-	4.41724	49.236	−1.00000

$$\sigma_{\alpha\beta} = \left(\sigma_{\alpha\alpha} + \sigma_{\beta\beta}\right)/2 \tag{5}$$

2.3. Details of the simulations

We have performed MD simulations on the NVE ensemble with one Na^+-Cl^- ion pair and 500 solvent molecules. The system is placed in cubical boxes with periodic boundary conditions. The temperature of the system is kept constant (room temperature) using velocity rescaling. Half of the box length is used as the cut off for Lennard–Jones forces. Reaction field method [37,38] is used for estimating the long range effects of electrostatic forces. The modified Coulombic interaction is calculated by

$$U^{coul}_{\alpha\beta}(r) = \frac{q_\alpha q_\beta}{r} + q_\alpha q_\beta\left(\frac{\varepsilon_{RF}-1}{2\varepsilon_{RF}+1}\right)\frac{r^2}{R_c^3} \tag{6}$$

where, εRF is the dielectric constant of the continuum surrounding the sphere of radius Rc.

The total simulation time is 2 ns in our MD simulation. For the system consisting of two ions (A, B) and N solvent molecules, the force due to solute-solvent interaction, acting along the interionic axis is calculated as

$$\Delta F(r,t) = \mu\left[\frac{F_{BS}(r,t)}{m_B} - \frac{F_{AS}(r,t)}{m_A}\right]\hat{r} \tag{7}$$

where, $F_{BS}(r,t)$ and $F_{AS}(r,t)$ are the total forces on the solute particles B and A due to solvent molecules; m_A and m_B are the individual masses of ions; μ is the reduced mass of the ion pair and $\hat{r}$ is the unit vector along the AB direction. The $\Delta F(r,t)$ values are calculated at each time step and then averaged over the whole simulation. The total mean force between the ions is the sum of the direct ion-ion force, $F_d(r)$ and the solvent contribution. $\Delta F(r,t)$. i. e.

$$F(r) = F_d(r) + \Delta F(r) \tag{8}$$

where

$$\Delta F(r) \equiv <\Delta F(r,t)> \tag{9}$$

The angular bracket denotes an ensemble average. The potential of mean force, $W(r)$ of the ion pair in the presence of the solvent can then be calculated as

$$W(r) = -\int F(r)dr = W(r_0) - \int_{r_0}^{r} F(r)dr \tag{10}$$

$$W(r_0) = \frac{q_i q_j}{\varepsilon r_0} \tag{11}$$

distance r is ranging from 2.2 to 9.0 Å with increments of 0.2 Å.