



Solvation structure and dynamics of potassium chloride ion pair in dimethyl sulfoxide–water mixtures



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ABSTRACT

Structure and dynamics of potassium chloride ion pair in mixtures of dimethyl sulfoxide (DMSO) and water have been investigated using constrained molecular dynamics. We have obtained the potentials of mean force (PMFs) between the K^+ and Cl^- ions at 298 K over a wide concentration range of these mixtures. The results obtained are compared for relative stabilities of contact ion pair (CIP), solvent assisted ion pair (SAIP) and solvent separated ion pair (SSIP) in the mixtures with varying compositions. The stability of the CIPs decreases significantly as the mole fraction of water increases. The study of running coordination numbers at the first solvation shell suggests preferential solvation of ions by water in all the compositions and there is hardly any participation by DMSO molecules in the first solvation shell of the Cl^- ion. The extent of association of potassium chloride ion pair in water, DMSO and their mixtures is determined by calculating the association constants. We have calculated the diffusion constants of ions and solvent molecules in the first solvation shell around K^+ and Cl^- in all the compositions. The diffusion constants of the shell molecules are the smallest in the DMSO mole fraction ranging from 0.2 to 0.5.

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1. Introduction

The solvation of ions and ion pairs influences the nature of reactions in solution media [1,2]. The important role of ion pairs in several chemical and biochemical problems is well recognized [3–6]. Polar solvents like water, dimethyl sulfoxide (DMSO), methanol, dimethyl formamide, acetone, chloroform, dichloromethane and acetonitrile are involved in a large number of reactions. Many important chemical transformations occur in these solvents and therefore it is essential to have an understanding of solvation structure and dynamics of ion pairs in polar solvents and their binary mixtures.

DMSO is used in a variety of organic reactions. Its basic physicochemical properties play an important role in its broad applications [7,8]. DMSO is one of the most widely used polar aprotic nonaqueous solvent used in synthetic chemistry and biological/clinical processes [8]. It is highly polar and dissolves many aromatic and unsaturated hydrocarbons, organic nitrogen compounds, organo-sulfur compounds and many inorganic salts. A binary mixture of water–DMSO possesses unique physicochemical and biological properties and exhibit strong non ideal behavior [9–13]. The peculiar nature of DMSO and its binary mixtures with water invites an elaborate study on solvation structure and dynamics of solutes, not all of which have been reported so far.

KCl is an electrolyte of particular interest because of the wide range of its applications in chemistry and its biological significance [14–16]. The PMF derived through methods such as constrained MD simulations provides insight into solvation of ions and ion pairs that influences the nature of reactions in solution media [17–23]. Ion pairs play a significant role in a variety of chemical and biochemical processes. These include ionic reactions in various solvents, macromolecular catalysis, biochemical hydrolysis and stability of proteins. In any solvolysis reaction, or any reaction which involves the participation of the solvent, the complete ionization of stable solute molecule is preceded by the two ion pair states, namely, the contact ion pair (CIP) and the solvent separated ion pair (SSIP). The two ion pair states are characterized by the existence of well defined barriers in the ion–ion potential of mean force derived through the method such as constrained MD simulations.

The nature of interaction of ions with solvents/mixed solvents has been the subject matter of several studies [24–33]. The PMF calculations for the alkali halides such as NaCl in dimethyl sulfoxide [32,33] and LiI in dimethyl sulfoxide [34] have been reported earlier. Recently, potentials of mean force of NaCl ion pair in DMSO–methanol mixture has been reported to explain preferential solvation in the binary mixture [35]. Similarly, the PMF calculations for alkali halides/alkaline earth metal halides in water [36] and aqueous ethanol [37] have also been reported, but an elaborate work on PMF in a binary mixture of water and DMSO is yet to be reported. We have investigated the variation in solvent structure around the ions as a function of the ion pair separation in a system consisting of KCl ion pair in binary mixture of water and DMSO by performing PMF calculations. It is of interest to compare these solvation studies with studies in other solvent mixtures.

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The methodology and computational details are briefly described in Section 2. Results and discussion are given in Section 3 and our conclusions are summarized in Section 4.

2. The methodology and computational details

We have performed the MD simulations reported in the present work using GROMACS package (version 4.5.4) [38–41]. The united atom optimized potentials for liquid simulation (OPLS) force field has been used for DMSO [42,43] and water is modeled by SPC/E model [44]. The K^+ and Cl^- solutes are considered as charged Lennard-Jones particles. The values of the Lennard-Jones and electrostatic interaction potential parameters of solute particles (taken from the work of Dang and coworkers [45–50]) and atomic sites of water and DMSO are summarized in Table 1.

In order to simulate K^+ and Cl^- ions in mixtures of DMSO and water with varying compositions, the two ions were placed in a cubic simulation box of length 4.0 nm (Table 2). The initial configurations were obtained using Packmol software package [51]. The leapfrog algorithm with a time step of 2 fs was used to integrate the equations of motion [52]. 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 [40,41] were used for both the thermostat and barostat with coupling constants of 0.1 and 1.0 ps, respectively. We have also used Parrinello–Rahman algorithm for pressure coupling [53,54] for longer periods of simulations. Electrostatics were handled using the particle mesh Ewald (PME) method [39].

The details of the systems used in the simulations are given in Table 2.

The constrained MD methodology [55,56] has been used in the simulations in which intra solvent site–site distances are kept fixed by using SHAKE algorithm [57]. The interionic separation started from 0.2 nm and extended up to 1 nm with separation steps of 0.02–0.05 nm. The resulting PMF was fine-tuned by lowering the separation to as low as 0.002 nm around the first minimum. For each of the interionic separations of 0.2–1.0 nm, the system was equilibrated for 500 ps–1 ns and followed by a production period of 2–8 ns. After equilibrating for 500 ps using Brendsen pressure coupling, production runs each of 2–4 ns were carried out using Brendsen pressure coupling and Parrinello–Rahman pressure coupling for NPT ensembles. We have also carried out the production runs of 2–4 ns with NVT ensemble. The PMF curves obtained under different conditions were compared and found to be differing by less than 2 kJ/mol. These PMFs are given in the supporting information (Fig. S1).

The mean force between the ions was computed by using the pull method [42–45]. The potential of mean force (PMF) was obtained by integrating the mean force between the ion pair. The solvent–solvent, solute–solvent and solute–solute interactions are taken to be pair wise additive and comprise of Lennard-Jones and Coulombic terms. The site-site potential has been taken as

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

Table 1

Values of Lennard-Jones and electrostatic interaction potential parameters used in the simulations. The magnitude of electronic charge is denoted by e .

Atom/ion	σ /(nm)	ϵ /(kJ/mol)	Charge/ e
S_{DMSO}	0.356	1.65268	0.1390
O_{DMSO}	0.293	1.17152	–0.4590
CH_{3DMSO}	0.381	0.66900	0.1600
K^+	0.3250	0.521619	+1.0000
Cl^-	0.3785	0.521619	–1.0000
O_{water}	0.3166	0.65060	–0.8476
H_{water}	0.000	0.000	+0.4238

Table 2

Solvent 1 = DMSO; Solvent 2 = Water; x_i = mole fraction of solvent i ; n_i = number of molecules of solvent i in the cubic simulation cell of box length L ; ρ = density at 298 K; ϵ = dielectric constant. The box length (L) for each composition is about 4.00 nm (NPT ensemble).

Compositions	x_1	x_2	n_1	n_2	ρ (g/cm ³)	ϵ
1	0.00	1.00	00	2135	0.9970	78.54
2	0.10	0.90	167	1507	1.0425	77.50
3	0.21	0.79	284	1067	1.0725	74.85
4	0.35	0.65	378	702	1.0927	69.97
5	0.48	0.52	434	470	1.0983	65.01
6	0.91	0.09	528	59	1.0965	49.50
7	1.00	0.00	544	00	1.1004	46.70

where r is the site–site separation, α and β are the interaction sites on different molecules, q_{α} and q_{β} are the charges located at sites α and β respectively. The terms $A_{\alpha\beta}$ and $B_{\alpha\beta}$ are determined using following equations.

$$A_{\alpha\beta} = 4\epsilon_{\alpha\beta}(\sigma_{\alpha\beta})^{12} \quad (2)$$

$$B_{\alpha\beta} = 4\epsilon_{\alpha\beta}(\sigma_{\alpha\beta})^6 \quad (3)$$

The values of $\epsilon_{\alpha\beta}$ and $\sigma_{\alpha\beta}$ are calculated using the Lorentz–Berthelot rules.

$$\sigma_{\alpha\beta} = \frac{(\sigma_{\alpha\alpha} + \sigma_{\beta\beta})}{2} \quad (4)$$

$$\epsilon_{\alpha\beta} = (\epsilon_{\alpha\alpha}\epsilon_{\beta\beta})^{1/2} \quad (5)$$

For the system consisting of two ions (A, B) and N solvent molecules, the forces due to solute–solvent interactions along the inter-ionic axis are calculated as

$$\Delta F(r, t) = \mu \left[\frac{F_{AS}(r, t)}{m_A} - \frac{F_{BS}(r, t)}{m_B} \right] \hat{r} \quad (6)$$

where $F_{AS}(r, t)$ and $F_{BS}(r, t)$ are the total forces on the solute particles due to the 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 (bare) ion–ion force, $F_d(r)$ and the solvent contribution, $\Delta F(r, t)$. That is,

$$F(r) = F_d(r) + \Delta F(r) \quad (7)$$

where,

$$\Delta F(r) = \langle \Delta F(r, t) \rangle \quad (8)$$

Table 3

Association constants for K^+Cl^- ion pair in water–DMSO mixtures.

x_{DMSO}	Association constants K_a (M ^{–1})
0.00	0.13
0.10	0.50
0.21	1.13
0.35	6.98
0.48	3.38
0.91	4.48×10^2
1.00	2.78×10^5

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