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# Solvation structure of sodium chloride ( $\text{Na}^+ - \text{Cl}^-$ ) ion pair in dimethyl sulfoxide–acetonitrile mixtures

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## ABSTRACT

Constrained molecular dynamics method has been used to compute the potentials of mean force (PMFs) of  $\text{Na}^+ - \text{Cl}^-$  in dimethyl sulfoxide (DMSO)–acetonitrile (AN) binary mixtures. The PMFs are confirmed by calculating the residence times of the ion pair at various inter-ionic separations. Contact ion pairs (CIPs) are found to be more stable than the solvent shared ion pairs (SSHIPs). The stabilities of CIPs generally increase with increase in the mole fraction of AN. The running coordination number analysis shows that the coordination number of  $\text{Na}^+$  in pure acetonitrile is 4.6, close to the experimental value by FTIR and refractometric study. The preferential solvation study through the excess coordination numbers shows that both  $\text{Na}^+$  and  $\text{Cl}^-$  are preferentially solvated by DMSO, unlike the water–DMSO mixtures.

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## 1. Introduction

Polarity of solvents plays a significant role in reactions occurring in solution media [1,2]. Binary mixtures of dipolar solvents are good reaction media because one can easily change the polarity, solubility, etc., by altering the composition of a mixture. These solvents are important for selective dissolution and precipitation of reactants and products of a solution phase chemical reaction. The presence of ions changes the reactivity of solvents in many chemical reactions [3,4]. Addition of electrolytes not only increases the average polarity of the medium but also generally changes the reaction equilibrium by inducing salting in or salting out effects. Moreover, interaction between different solvent molecules and ions induces preferential solvation and hence modifies the average solvation structure around the ion pair [5]. Dimethyl sulfoxide (DMSO) and acetonitrile (AN) are widely used in chemistry, biochemistry and pharmacy [6–8]. The water–DMSO mixtures are used as cryoprotectants for biological tissues because they prevent water from freezing within cells. They are also used as coadjuvant drug carriers because of their high permeability across biomembranes [7]. Acetonitrile plays an important role in many biochemical processes. It is also used as a solvent in the preparation of oligonucleotides from monomers. AN is used in the manufacture of pharmaceuticals and photographic films [9]. Acetonitrile contains a hydrophobic methyl group connected to a hydrophilic cyano group and thus can be thought of as

an extremely small surfactant [10]. AN is unable to form a hydrogen bond in the classical way, either as a proton donor or as a proton acceptor [11,12].  $\text{CH}_3 - \text{CN}$  dimer forms a stable structure in an antiparallel dipolar arrangement with a N–H bond distance of 2.526 Å and a dimer stabilization energy of 4.56 kcal/mol. The linear arrangement of two  $\text{CH}_3\text{CN}$  molecules gives a dimerization energy of 2.5 kcal/mol, with a N–H bond length of 3.07 Å [13]. DMSO and AN possess very close values dipole moments, with values of 3.96 D (DMSO) and 3.92 D (AN). Also, they have similar dielectric constants with values of 46.70 (DMSO) and 36.71 (AN), indicating similar short range molecular interactions between them [11]. The solvation of ions in aprotic binary solvents does not show any specific interaction between solvent molecules which is largely determined by the ion–solvent interactions in the first solvation shell of ions [14]. In mixtures of aprotic solvents, the solvation of ions is mainly because of ion–dipole forces (electrostatic interactions) through the donation electron pairs by the strong donor solvent to the cation [15]. Kashyap et al. studied the Born free energy of solvation and partial solvent polarisation structure of ion pairs in DMSO–AN mixtures [5]. Troxler et al. studied the conformation and dynamics of 18-crown-6, cryptand 222 and their cation complexes in acetonitrile using molecular dynamics simulations [16]. Molecular dynamics simulations of DMSO–AN mixtures were performed by Bernardi et al. and they have observed that the non-ideal behaviour in DMSO–AN mixture is not affected by the choice of the potential model (three site or six site) of AN. They have noticed that DMSO is preferentially solvated by AN molecules [11]. Guárdia et al. has explained the solvation shell of  $\text{Na}^+ - \text{Cl}^-$  ion pair in pure acetonitrile [17]. Richardi et al. used the HNC approximation of molecular Ornstein–Zernike theory for the solvation of alkali halide ions in acetonitrile [18]. Das et al. observed that,  $\text{Na}^+$

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**Table 1**  
United atom force field parameters for AN [11], DMSO [23] and Na<sup>+</sup>–Cl<sup>–</sup> [24].

	Site	( $\epsilon/k_B$ )/(K)	$\sigma$ (Å)	$q/(e)$
AN	N	50.00	3.30	–0.398
AN	C	50.00	3.40	0.129
AN	CH3	191.00	3.60	0.269
DMSO	S	198.71	3.56	0.139
DMSO	O	140.86	2.93	–0.459
DMSO	CH3	80.49	3.81	0.160
	Na <sup>+</sup>	1.39	3.33	+1.000
	Cl <sup>–</sup>	59.22	4.41	–1.000

**Table 2**  
Geometrical parameters of DMSO [23] and AN [11].

Sites	Bond lengths/(Å)	Bond angles/(°)
S–O	1.496	–
S–CH3	1.800	–
O–S–CH3	–	107.2
C–N	1.170	–
C–CH3	1.460	–
N–C–CH3	–	180.0

**Table 3**  
 $x_{AN}$  and  $x_{DMSO}$  = mole fractions of AN and DMSO,  $N_{AN}$  and  $N_{DMSO}$  = number of molecules of AN and DMSO,  $L$  = simulation box length  $\rho$  = density at 298 K,  $\epsilon_r$  = calculated dielectric constant at 298 K.

Composition	$x_{AN}$	$x_{DMSO}$	$N_{AN}$	$N_{DMSO}$	$L$ (Å)	$\rho$ (gm/ml) <sup>a</sup>	$\epsilon_r$
1	0.0	1.0	0	540	40.07	1.0900	40.17
2	0.25	0.75	144	434	39.34	1.0338	41.68
3	0.50	0.50	311	311	38.42	0.9618	37.52
4	0.75	0.25	504	168	38.61	0.8777	32.94
5	0.0	1.0	730	0	39.34	0.7773	29.93

<sup>a</sup> Ref. [34].

ion is preferentially solvated by water molecules and Cl<sup>–</sup> ion is preferentially solvated by DMSO molecules in water–DMSO mixtures [19]. Marcus has reported that Na<sup>+</sup> ion is preferentially solvated by water molecules in water–AN binary mixtures [20]. We have performed MD simulations of sodium chloride in DMSO–AN binary mixtures. In Section 2, we describe the computational methodology used for this study. In Section 3, we present our results followed by conclusions in Section 4.

## 2. Computational details

We have performed MD stimulations using the GROMACS package (version 4.5.4) [21]. The united atom optimized potentials for

liquid simulation (OPLS) [22] force fields have been used for AN, DMSO and the Na<sup>+</sup>–Cl<sup>–</sup> ion pair. The force fields and geometrical parameters for AN, DMSO and the Na<sup>+</sup>–Cl<sup>–</sup> ion pair are given in Tables 1 and 2.

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

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

where,  $\alpha$  and  $\beta$  denote a pair of interaction sites on different molecules,  $q_{\alpha}$  = charge located at site  $\alpha$ , and  $q_{\beta}$  = charge located at site  $\beta$ ,  $r$  = site–site separation. The terms  $A_{\alpha\beta}$  and  $B_{\alpha\beta}$  are determined from,

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

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

whereas,  $\epsilon_{\alpha\beta}$  and  $\sigma_{\alpha\beta}$  are calculated using the Lorentz–Berthelot mixing rules [25].

$$\epsilon_{\alpha\beta} = (\epsilon_{\alpha} \times \epsilon_{\beta})^{1/2} \quad (4)$$

$$\sigma_{\alpha\beta} = \left( \frac{\sigma_{\alpha} + \sigma_{\beta}}{2} \right) \quad (5)$$

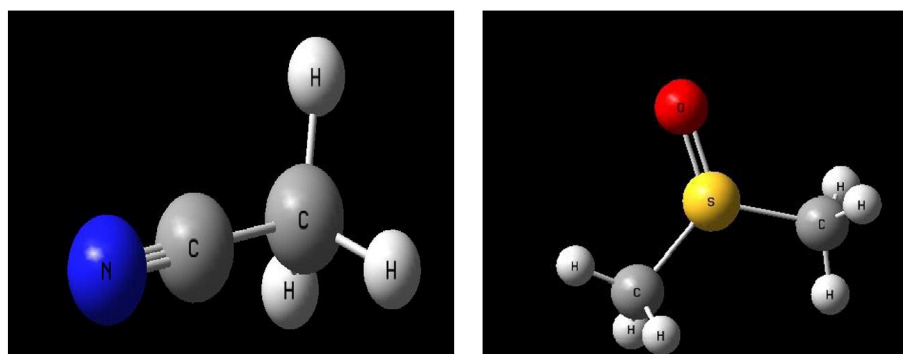
The potentials of mean force,  $W(r)$  of the ion pair in the presence of the solvent can then be calculated as,

$$W(r) = - \int F(r) dr = W(r_0) - \int_{r_0}^r F(r') dr' + 2kT \ln \left( \frac{r}{r_0} \right) \quad (6)$$

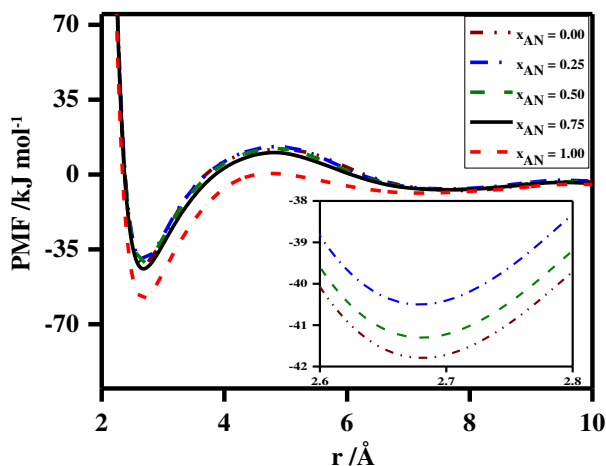
$$W(r_0) = \frac{q_i q_j}{\epsilon_r r_0} \quad (7)$$

where,  $F(r)$  is the mean force between ions (Na<sup>+</sup> and Cl<sup>–</sup>) at distance  $r$  and  $\epsilon_r$  is the dielectric constant of the solvent mixture at 298 K. The last term in Eq. (6) takes into account the increase of entropy of the ion pair with increasing interionic distances [26]. The distance  $r$  is varied from 2.0 to 10.0 Å with increments of 0.1 Å. The value of  $r_0$  is 10.0 Å for all compositions. The dependence of the results on the choice of  $r_0$  is very weak. Although the depths of PMF change by 1–3 kJ/mol, the ion association (positions of CIP, SShIP, TS, barrier heights) remains the same and is independent of the choice of  $r_0$  [27].

We have used Particle Mesh Ewald electrostatics [28] with a direct space cut-off of 1.5 nm and a grid spacing of 1.5 nm. For non-bonded van der Waals interactions, 1.5 nm cut-off is used. The geometries of



**Fig. 1.** Structure of acetonitrile (AN) and dimethyl sulfoxide (DMSO).



**Fig. 2.** PMFs of  $\text{Na}^+\text{--Cl}^-$  ion pair in all mixtures of DMSO–AN. The inset magnifies the locations of the CIP minima in the three compositions for  $x_{\text{AN}} = 0.0, 0.25$  and  $0.50$ .

DMSO and acetonitrile molecules are maintained during the simulations by using the SHAKE algorithm [29]. The temperature of the system is maintained at 298 K using velocity rescaling thermostat [30]. We have used Berendsen barostat for equilibration and Parrinello–Rahman barostat for production run [31]. The pressure of the system is fixed at 1 bar using Berendsen barostat [32]. The system is equilibrated for 1 ns in the NPT ensemble. We have performed NPT trajectories for each distance from 2 to 10 Å for 10 ns using Parrinello–Rahman barostat [33]. The integration time step is 2 fs. The details of solvent mixtures are given in Table 3.

The structure of acetonitrile (AN) and dimethyl sulfoxide (DMSO) are given in Fig. 1.

### 3. Results and discussion

#### 3.1. Potentials of mean force, $W(r)$

The potentials of mean force of the  $\text{Na}^+\text{--Cl}^-$  ion pair in different compositions of AN ( $x_{\text{AN}} = 0.0, 0.25, 0.50, 0.75, 1.0$ ) are obtained by using Eq. (6). The PMFs of the ion pair in different compositions of AN are shown in Fig. 2. Both the CIPs and the SSHIPs are present for all the compositions of AN with the CIP being more stable and dominant than the SSHIP whereas PMFs of  $\text{Na}^+\text{--Cl}^-$  ion pair in water–DMSO mixtures show the presence of mainly SSHIPs [18]. The computed PMFs show that CIPs occur at 2.7 Å and SSHIPs occur between 7 and 8 Å in all compositions of AN. In an SSHIP, a solvent molecule is present in the interionic region. The values of PMFs at contact ion pair (CIP), transition state (TS) and solvent shared ion pair (SSHIP) are given in the Table 4. The values of the minima in the PMF in the CIP state are  $-42.33, -41.02, -41.83, -44.60$  and  $-58.55$  kJ/mol for  $x_{\text{AN}} = 0.0, 0.25, 0.50, 0.75$  and  $1.00$  respectively. Deeper minima in the PMF

**Table 4**  
Values (kJ/mol) and positions (Å) of PMFs at contact ion pair (CIP), transition state (TS) and solvent shared ion pair (SSHIP) in  $x_{\text{AN}} = 0.00, 0.25, 0.50, 0.75, 1.00$ .

$x_{\text{AN}}$	Position of CIP	Value of PMF at CIP	Position of TS	Value of PMF at TS	Position of SSHIP	Value of PMF at SSHIP
0.00	2.7	−42.33	4.9	11.78	7.9	−7.45
0.25	2.7	−41.02	4.8	13.04	7.7	−6.73
0.50	2.7	−41.83	4.8	12.19	7.7	−7.07
0.75	2.7	−44.60	4.8	10.13	7.7	−7.09
1.00	2.7	−58.55	4.7	0.53	7.2	−8.66

**Table 5**

Running coordination numbers of  $\text{Na}^+$  and  $\text{Cl}^-$  ions in DMSO–AN mixtures.  $N_{\text{AN}}$  = number of AN molecules and  $N_{\text{DMSO}}$  = number of DMSO molecules,  $R_{\text{min}}$  refers to the location of the first minimum of the radial distribution functions (here, in Å).

$x_{\text{AN}}$	$x_{\text{DMSO}}$	$\text{Na}^+$			$\text{Cl}^-$			$N_{\text{AN}}$	$N_{\text{DMSO}}$
		$R_{\text{min}}$ for $N_{\text{AN}}$	$R_{\text{min}}$ for $N_{\text{DMSO}}$	$N_{\text{DMSO}}$	$R_{\text{min}}$ for $N_{\text{AN}}$	$R_{\text{min}}$ for $N_{\text{DMSO}}$	$N_{\text{DMSO}}$		
0.00	1.00	–	0.0	4.1	3.9	–	0.0	6.7	10.8
0.25	0.75	4.0	0.2	4.2	3.8	6.1	2.1	6.7	7.6
0.50	0.50	4.1	0.4	4.2	3.5	6.1	3.6	6.8	7.3
0.75	0.25	4.1	1.4	4.2	2.7	6.1	5.7	6.9	4.8
1.00	0.00	4.0	4.6	–	0.0	6.0	8.5	–	0.0

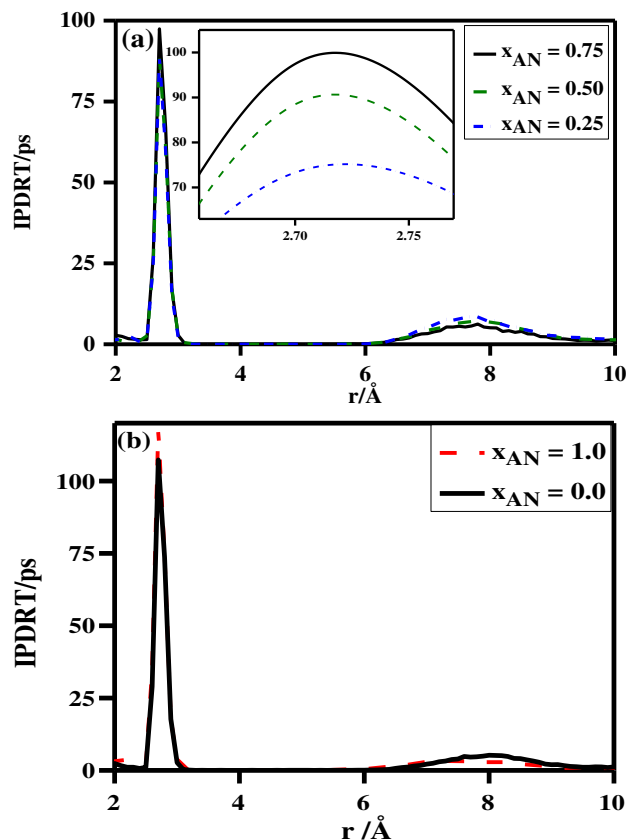
occur when the mole fraction of AN dominates. We have calculated the uncertainties in PMFs. These are in the range of 0.2 to 1.5 kJ/mol.

The mole fraction dependence of the relative heights of the transition state (TS) is very similar to that of the CIPs. The effect of composition in the location and the depth of the SSHIPs (located around 7.7 Å) is only marginal. The SSHIP minima values range from  $-8.66$  kJ mol $^{-1}$  to  $-6.73$  kJ mol $^{-1}$ .

The differences in the stabilities of CIPs for  $x_{\text{AN}}$  of 0.00, 0.25 and 0.50 are quite small. The marginal differences in the running coordination numbers around  $\text{Na}^+$  in these three compositions (which will be shown in Table 5 that follows) support the presence of similar solvation shells in these compositions. The values of contact ion pair (CIP), transition states (TS) and solvent shared ion pair (SSHIP) are given in Table 4.

#### 3.2. Ion pair distance residence times (IPDRTs)

The PMFs of the  $\text{Na}^+\text{--Cl}^-$  ion pair can be confirmed by calculating the ion pair distance residence times (IPDRTs). IPDRT is an approximate



**Fig. 3.** (a) IPDRTs  $\text{Na}^+\text{--Cl}^-$  ion pair in  $x_{\text{AN}} = 0.25, 0.50$  and  $0.75$ , (b) IPDRTs  $\text{Na}^+\text{--Cl}^-$  ion pair in pure AN and pure DMSO.

measure of the length of time the ion pair resides at a particular distance. The ion pair distance residence time is defined as

$$\text{IPDRT}(r) = \frac{\Delta t}{n_T} \sum_{l=1}^{n_T} \sum_{i=1}^N \delta_{r, r(i\Delta t)} \quad (8)$$

where  $n_T$  is the total number of initial configurations,  $\Delta t$  is the simulation time step,  $N$  is the number of steps in a given simulation and  $\delta_{r, r(i\Delta t)}$  is the Kroncker delta which is equal to 1 whenever  $r = r(i\Delta t)$  and zero otherwise. The summation over  $l$  corresponds to the initiation of the trajectories at different initial values of the ion–ion separation  $r = r_0$ . For  $l = 1$ ,  $r_0 = 2.0$  Å, for  $l = 2$ ,  $r_0 = 2.1$  Å and so on. The ion pair distance residence times (IPDRTs) have been calculated by performing the dynamical trajectories of the ion pairs initiated at different ion–ion separations. This is done by performing MD simulations on systems by releasing the constraint on the ion pair and then calculating the ion–ion separation vector at each time step. We have taken 69 interionic separations (in the range of 2.1 to 9.0 Å) as initial ion–ion distances and each trajectory is evolved for 500 ps using the Parrinello-Rahman barostat. IPDRTs for the ion pair are averaged over all the trajectories for each composition. We have calculated the IPDRTs for the  $\text{Na}^+ - \text{Cl}^-$  ion pair in three

DMSO–AN mixtures, pure AN and pure DMSO which are shown in Fig. 3(a) and (b).

From Fig. 3(a) and (b), we observe two peaks for all compositions of AN corresponding to CIPs and SSHIPs. An intense peak is observed around 2.7 Å which confirms the presence of CIP and a small shoulder is present around 7.7 Å which confirms the presence of SSHIP.

### 3.3. Radial distribution functions (RDFs)

In order to investigate the local solvation structure around  $\text{Na}^+$  and  $\text{Cl}^-$  ions in the DMSO–AN mixtures, we have calculated the ion solvent radial distribution functions. The ion solvent radial distribution function  $g(r)$  is the ratio of local density of solvent site at distance  $r$  from the ion and the bulk solvent density.

From Fig. 4(a) and (b), we observe that the lowest mole fraction of DMSO shows the maximum peak height in  $\text{Na}^+ - \text{O}$  (DMSO). This is because, the local density of DMSO in the  $\text{Na}^+$  shell is much larger than the bulk density for  $x_{\text{DMSO}} = 0.25$ . As the mole fraction of DMSO increases, the bulk density of DMSO increases but the increase in the local density is less than proportional to the mole fraction and hence the peak height decreases in RDFs (Fig. 4(a)). Similar trend is observed in the RDFs of  $\text{Cl}^- - \text{S}$  (DMSO) which is shown in Fig. 4(b). Fig. 4(c) and (d) represents the  $\text{Na}^+ - \text{N}$  (AN) and  $\text{Cl}^- - \text{C}$  (AN) RDFs. In the case of AN, the peak heights of  $\text{Na}^+ - \text{N}$  (AN) RDFs increase with an increase in

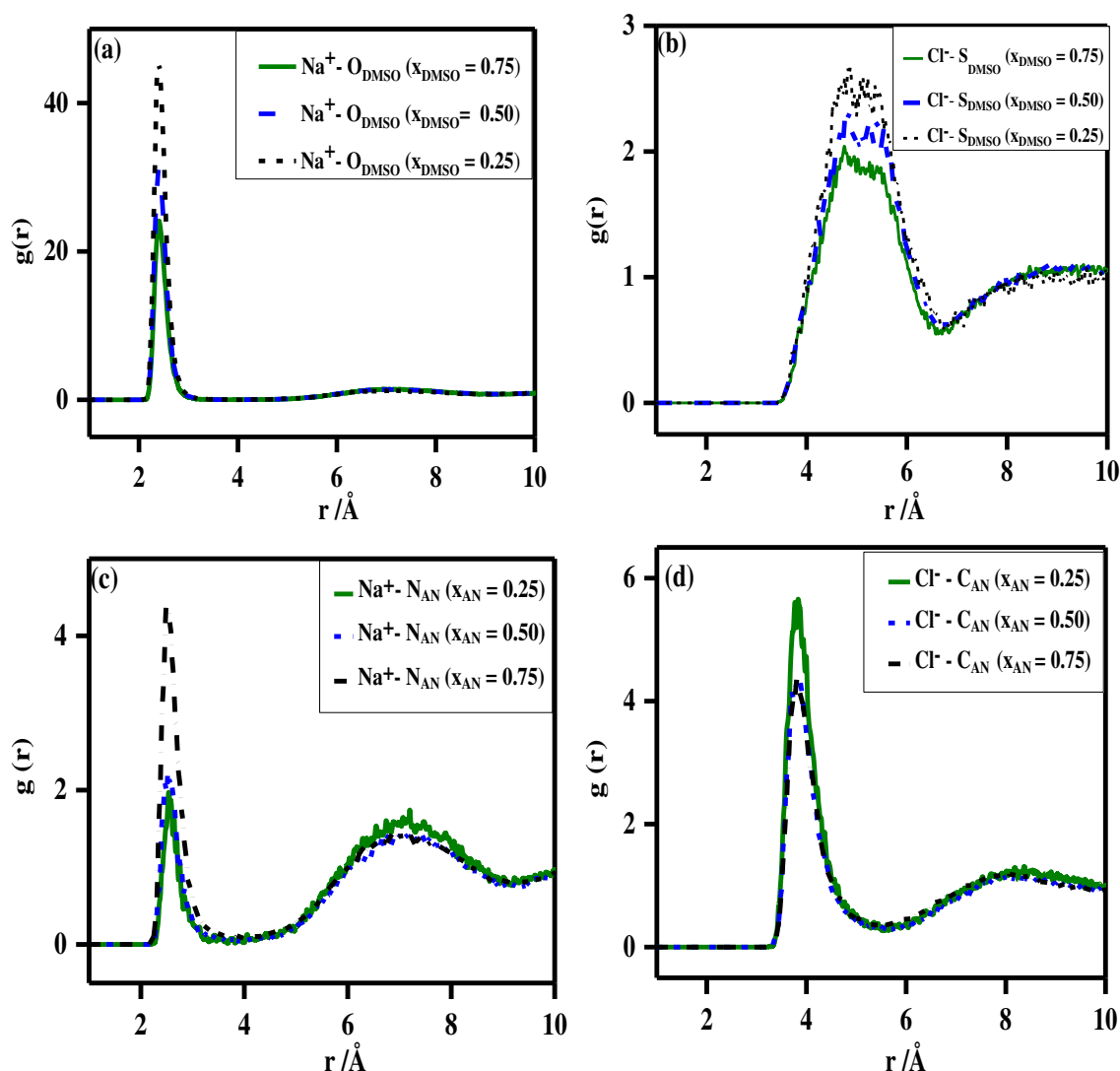


Fig. 4. (a), (b) Ion-solvent radial distribution functions for  $\text{Na}^+$  and  $\text{Cl}^-$  in DMSO; (c), (d) ion-solvent radial distribution function for  $\text{Na}^+$  and  $\text{Cl}^-$  AN, with  $x_{\text{AN}} = 0.25, 0.50, 0.75$ .

the mole fractions of AN as local densities increase with increasing bulk densities.  $\text{Na}^+ - \text{N}$  (AN) and  $\text{Na}^+ - \text{O}$  (DMSO) RDFs do not show any changes in the peak positions. The peak heights of  $\text{Na}^+ - \text{O}$  (DMSO) are ten times larger than the peak heights of  $\text{Na}^+ - \text{N}$  (AN) RDFs.

For  $\text{Cl}^- - \text{C}$  (AN), the peak height increases with decrease in mole fraction of AN. An explanation for this trend will be given after we consider the running coordination numbers.

### 3.4. Solvation shells around the ion pair

To study the effect of composition on the solvation structure around the ion pair, we have calculated the running coordination numbers around the ions. The running coordination number is defined as,

$$n_{\alpha\beta} = 4\pi\rho_{\beta} \int_0^{R_{\min}} r^2 g_{\alpha\beta}(r) dr \quad (10)$$

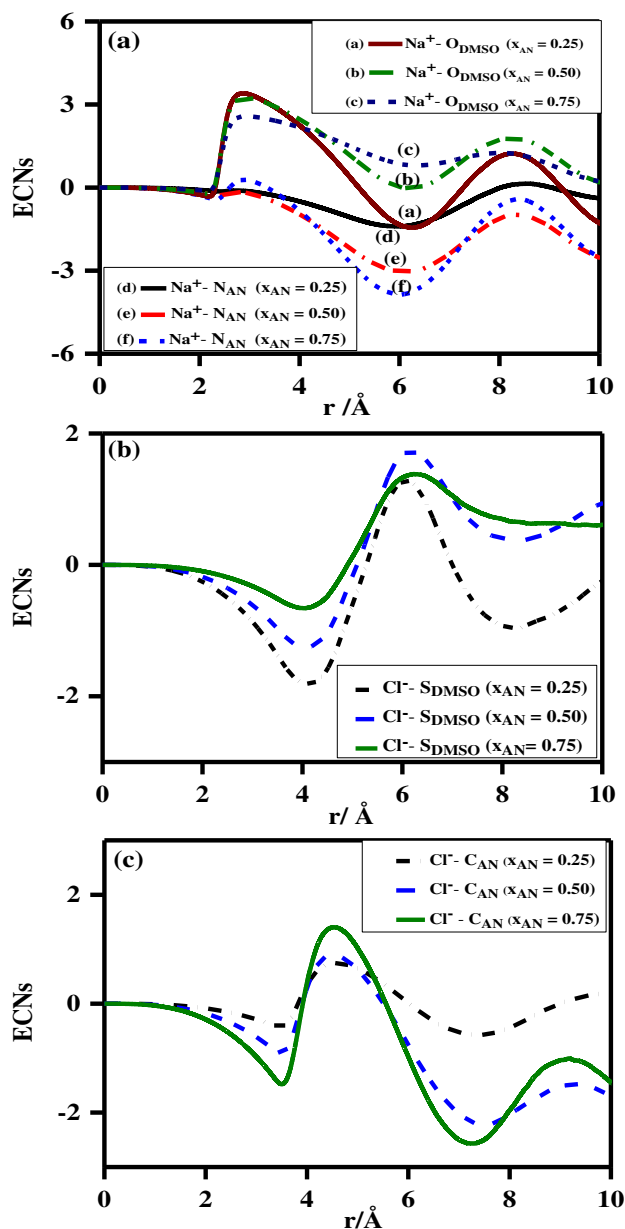


Fig. 5. (a) ECNs around  $\text{Na}^+$  ion in DMSO-AN mixture with  $x_{\text{AN}} = 0.25, 0.50, 0.75$ , (b) and (c), ECNs around  $\text{Cl}^-$  ion DMSO-AN mixture with  $x_{\text{AN}} = 0.25, 0.50, 0.75$ .

where  $n_{\alpha\beta}$  represents the number of atoms of type  $\beta$  surrounding species  $\alpha$  in a shell extending from zero to  $R_{\min}$  (the first minimum in the radial distribution function). The running coordination numbers are actually the number of solvent molecules in the shells of the CIP, SSHIPs, etc.

The running coordination numbers of DMSO and AN molecules around  $\text{Na}^+$  and  $\text{Cl}^-$  ions at the CIP are given in Table 5. It is observed from Table 5 that when mole fraction of AN increases from 0.0 to 1.0, the number of AN molecules increases around  $\text{Na}^+$  and  $\text{Cl}^-$  ions in CIP, but the increase is much less than the proportional increase in  $x_{\text{AN}}$ . Also, the number of DMSO molecules decreases very slowly (in comparison with the corresponding mole fractions of DMSO).

The uncertainties in the running coordination numbers after two set of simulations (5 ns each) are marginal (less than 0.05). The coordination number of  $\text{Na}^+$  ion in pure acetonitrile was found to be 4.6 by MD simulations which is close to the result obtained by Barthel and co-workers [35,36]. They reported a coordination number of 4 of  $\text{Na}^+$  in AN from FTIR spectroscopy. Camus et al. [37] estimated the coordination number of 5 for  $\text{Na}^+$  in AN by refractometric study. Guárdia et al. estimated a coordination number of 6.4 for  $\text{Na}^+$  in pure AN from an MD study [17].

The trends in the peak heights of  $\text{Cl}^- - \text{C}$  (AN) RDFs can now be understood in terms of RCNs. For  $x_{\text{AN}} = 0.25$ , the ratio of  $N_a/N_i$  at  $R_{\min} = 5.5$  Å is 2.1/2.125 and is nearly equal to 1. In this ratio,  $N_a$  is the actual coordination number at the mole fraction under consideration and  $N_i$  is the ideal mole fraction that would result if the local mole fraction would be the same as the RCN of pure AN multiplied by the bulk mole fraction of the mixture under consideration. Since RCN of pure AN is 8.5, the value of  $N_i$  in this case is  $8.5 \times 0.25 = 2.125$  as  $x_{\text{AN}} = 0.25$ . When  $x_{\text{AN}}$  increases to 0.50 and 0.75, the corresponding ratios are 3.6/4.25 ( $=0.84$ ) and 5.7/6.375 ( $=0.89$ ). As these ratios are less than 1 and are analogous to the ratios of local densities to bulk densities, the peak heights of  $\text{Cl}^- - \text{C}$  (AN) RDFs for  $x_{\text{AN}} = 0.50$  and  $0.75$  are smaller than the RDF peak height for  $x_{\text{AN}} = 0.25$ .

### 3.5. Excess coordination numbers (ECNs)

We have calculated the excess coordination numbers (ECNs) around the  $\text{Na}^+$  and  $\text{Cl}^-$  ion in DMSO-AN mixtures. The excess coordination number is defined as,

$$N_{\alpha\beta}(r) = 4\pi\rho_{\beta} \int_0^r r^2 [g_{\alpha\beta}(r) - 1] dr \quad (11)$$

Here  $4\pi\rho_{\alpha} r^2 g_{\alpha\beta}(r)$  is the average number of  $\alpha$  molecule in a spherical shell of width  $dr$  at radius  $r$  centred on  $\beta$  molecule and  $4\pi\rho_{\alpha} r^2 dr$  is average number of  $\alpha$  molecule in spherical shell. Therefore,  $N_{\alpha\beta}$  represents the excess number of  $\alpha$  molecule around a  $\beta$  molecule.

The excess coordination numbers of DMSO and AN molecules around  $\text{Na}^+$  and  $\text{Cl}^-$  ion in DMSO-AN mixtures are shown in Fig. 5(a), (b) and (c).

It is noticed from Fig. 5(a) that there is an excess of DMSO molecules (a deficit of AN) around  $\text{Na}^+$  ion in all compositions of AN. Therefore  $\text{Na}^+$  is preferentially solvated by DMSO in different mole fractions of AN. Fig. 5(b) and (c) shows that preferential solvation of  $\text{Cl}^-$  ion is

Table 6

The association constants for  $\text{Na}^+ - \text{Cl}^-$  in DMSO-AN mixtures.

Compositions ( $x_{\text{AN}}$ )	Association Constants of ion pair ( $\text{L mole}^{-1}$ )
0.00	$3.0 \times 10^5$
0.25	$1.9 \times 10^5$
0.50	$2.5 \times 10^5$
0.75	$7.8 \times 10^5$
1.00	$2.2 \times 10^8$



dominated by DMSO in comparison to AN. Hence both  $\text{Na}^+$  and  $\text{Cl}^-$  ions are preferentially solvated by DMSO molecules.

### 3.6. Ion–ion association constants

We have calculated the association constants of  $\text{Na}^+ - \text{Cl}^-$  ion pair in DMSO–AN mixtures. The association constant is defined as,

$$K_a = 4\pi \int_0^{r_a} r^2 e^{-W(r)/k_B T} dr \quad (12)$$

where,  $K_a$  is the association constant of the ion pair,  $W(r)$  is the PMF of the ion pair,  $k_B$  is the Boltzmann's constant,  $T$  is the temperature of the system and  $r_a$  is position of the height of the transition state barrier. The association constants for  $\text{Na}^+ - \text{Cl}^-$  are given in the Table 6.

The association constant of  $\text{Na}^+ - \text{Cl}^-$  ion pair is maximum in pure acetonitrile.  $K_a$  values are consistent with the trend of the PMFs of  $\text{Na}^+ - \text{Cl}^-$  ion pair in all mole fractions of AN, i.e., decrease initially for  $x_{\text{AN}} = 0.25$  and then monotonically increase up to  $x_{\text{AN}} = 1$ . The uncertainties in the association constants are around 10%.

### 3.7. Density profiles of solvent around ion-pair

The details of solvent distributions around the ion pair can be studied by looking at the density profiles of solvent molecules. The planes containing the interionic axis are considered for calculating the mean number densities of solvent sites. The densities of all planes containing the interionic axis are projected on the x–y plane. The density profiles of AN and DMSO around  $\text{Na}^+ - \text{Cl}^-$  in  $x_{\text{AN}} = 0.50$  at the contact ion pair (CIP) solvent shared ion pair (SShIP) are given in Fig. 6(a), (b), (c) and (d) respectively.

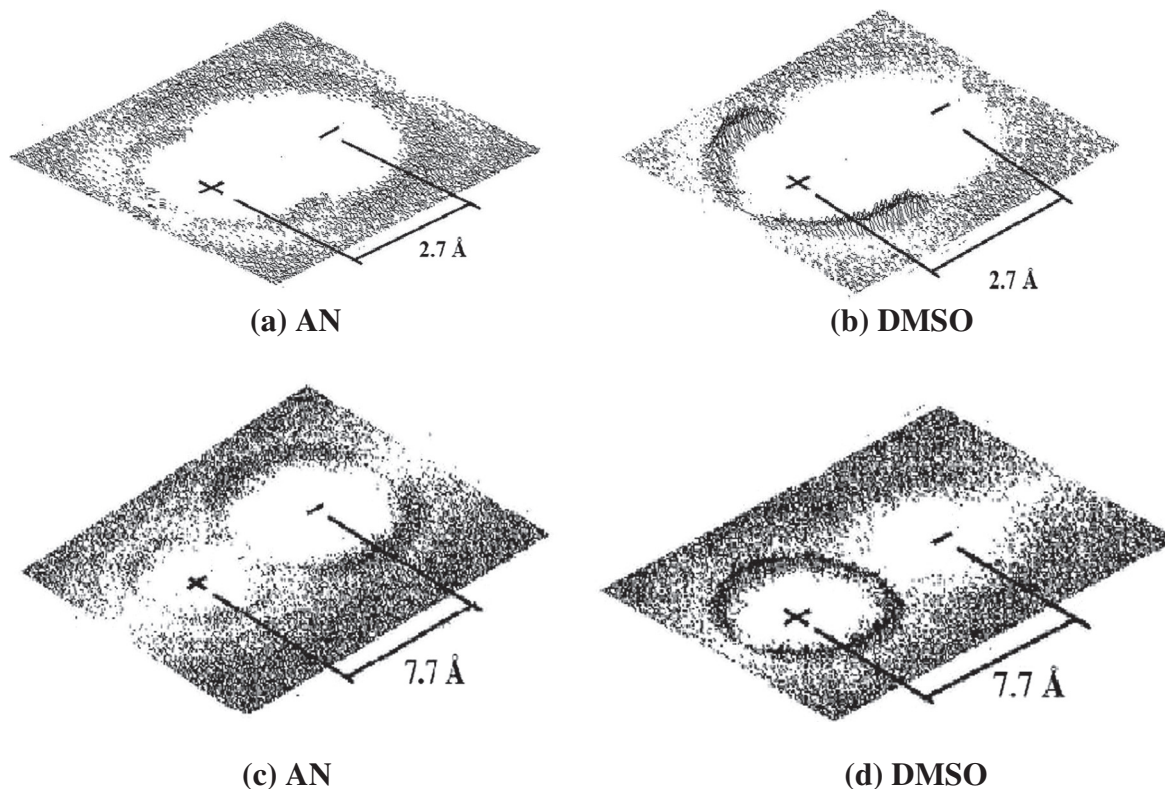
In the CIP states, no solvent molecule appears in the region between the ions. From Fig. 6(c), we observe that a nearly complete solvation shell of AN is formed around  $\text{Na}^+$  and  $\text{Cl}^-$  ions. From Fig. 6(d), we note that the solvation shells of DMSO is complete only around  $\text{Na}^+$ .

## 4. Conclusions

We have used the constrained molecular dynamics technique to simulate solutions of sodium chloride ion pair in DMSO–AN mixtures. The derived potentials of mean force show the presence of both a CIP and an SShIP in all compositions of AN whereas PMFs of  $\text{Na}^+ - \text{Cl}^-$  ion-pair in water–DMSO mixtures show the presence of a dominant SShIP. The stabilities of CIPs generally increase with increase in the mole fraction of AN. PMFs are confirmed by ion pair distance residence times. Barthel and co-workers reported a coordination number 4 of  $\text{Na}^+$  in pure AN from FTIR spectroscopy, Camus et al. estimated the coordination number 5 for the same which is in agreement with our values from MD simulations. The preferential solvation analysis shows that the first solvation shell of sodium ion is dominated by DMSO. For the chloride ion, the domination is not as much as in the case of sodium and both DMSO and AN contribute significantly to the first solvation shells. Unlike water–DMSO mixtures, wherein  $\text{Na}^+$  ion is preferentially solvated by water molecules and  $\text{Cl}^-$  ion by DMSO molecules, in DMSO–AN mixtures, both  $\text{Na}^+$  ion and  $\text{Cl}^-$  ion are preferentially solvated by DMSO molecules.

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**Fig. 6.** Density profiles of AN and DMSO around  $\text{Na}^+ - \text{Cl}^-$  in  $x_{\text{AN}} = 0.50$ . The density profiles for CIP for AN and DMSO are given in 6(a) and 6(b) respectively. For SShIP, they are given in 6(c) and 6(d) respectively.

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