

Na⁺ Cl⁻ ion pair association in water-DMSO mixtures: Effect of ion pair model potentials

ATANU SARKAR, ANUPAM CHATTERJEE, S C TIWARI and B L TEMBE*

Department of Chemistry, IIT Bombay, Mumbai 400 076, India
e-mail: bltembe@chem.iitb.ac.in

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Abstract. Potentials of Mean Force (PMF) for the Na⁺ Cl⁻ ion pair in water–dimethyl sulfoxide (DMSO) mixtures for three DMSO mole fractions have been computed using constrained Molecular Dynamics (MD) simulations and confirmed by dynamical trajectories and residence times of the ion pair at various inter-ionic separations. The three ion-ion direct potentials used are 12-6-1, exp-6-1 and exp-8-6-1. The physical picture that emerges is that there is a strong contact ion pair (CIP) and strong to moderate solvent separated ion pair (SSIP) in these solutions. Analysis of local ion clusters shows that ions are dominantly solvated by water molecules. The 12-6-1 potential model predicts running coordination numbers closest to experimental data.

Keywords. Potential models; potentials of mean force; residence times; running coordination numbers.

1. Introduction

Sodium chloride, an important electrolyte in chemical, physical and biological sciences, has been a subject of detailed investigations for a long time, both experimentally and theoretically, in different solvents.^{1,2} According to the Arrhenius theory of electrolytic dissociation,³ NaCl, being a strong electrolyte, when placed in a polar solvent at ambient temperature, will completely ionize or dissociate into Na⁺ and Cl⁻ ions. But theoretical calculations for Na⁺–Cl⁻ in water, a polar protic solvent, by many workers have shown that the solvent-assisted ion-pair (SAIP) of NaCl is as stable as the contact ion-pair (CIP).^{4,5} Moreover, in a polar aprotic solvent Dimethyl Sulfoxide (DMSO), simulation studies show that the CIP is much more stable than the solvent separated ion pair (SSIP).⁶

As the DMSO–water hydrogen bond is much stronger than the water–water hydrogen bond, DMSO–water mixtures exhibit strong non-ideal behavior⁷ in various physical properties like density,⁸ viscosity,⁸ refractive index,⁸ dielectric constant,⁹ surface tension,¹⁰ freezing point,¹¹ heat of mixing,¹² etc. Mixtures of water and DMSO, because of their unique properties, have drawn special attention,^{13,14} specifically in the DMSO mole fraction (x_{DMSO}) range of 0.20 to 0.50, where the solvent mixtures show maximum deviations from ideal behavior.

Liu *et al.*, have shown that in the gas phase, *ab initio* calculations very accurately match the experimental value of interaction energy minimum between the Na⁺ and Cl⁻ ions.¹⁵ In both pure and mixed polar media, a description and structure of the potential of mean force (PMF)^{16–19} between the two ions at infinite dilution is now becoming available using computer simulations^{20–28} and integral equations.^{29,30} In the solution phase, many dynamical processes at the liquid–solid interface have been studied using molecular dynamics (MD) simulations based on several empirical model potentials.

In the present study, we use constrained classical molecular dynamics simulations. The same ion–solvent and solvent–solvent interaction models, but three different ion-ion direct potential models are used to calculate the PMFs for Na⁺–Cl⁻ in three DMSO–water solvent mixtures. Our interest here is to perform a detailed analysis of model dependent ion associations in water–DMSO mixtures. To our knowledge, the effect of such a change of ion-ion potentials on solvation structures has not been investigated in detail in solvent mixtures. The solvation structures can be further confirmed by studying dynamical trajectories which result when the constraint between Na⁺ and Cl⁻ is released at various interionic separations. These ion pair trajectories reflect the nature of the PMFs by causing the ion pair to settle in its stable configurations. Hence, their residence times in these relatively stable conformations are indications of the extent of solvent stabilization. Using the running co-ordination numbers, we have estimated the preferential solvation of the ions and the distributions

*For correspondence

of solvent molecules around the moving ion-pair during its transformation from one solvated configuration into another.

2. Computational: Models and methods

Details of the three systems studied at 298 K are given below.^{8,9,31}

- i. System I, $x_{\text{DMSO}} = 0.21$: 53 DMSO and 197 water molecules have been simulated in a cubical box of length 22.784 Å. Density of the solution is 1.0725 (g mL⁻¹) and dielectric constant is 74.85.
- ii. System II, $x_{\text{DMSO}} = 0.35$: 88 DMSO and 162 water molecules have been simulated in a cubical box of length 24.764 Å. Density of the solution is 1.0927 (g mL⁻¹) and dielectric constant is 69.97.
- iii. System III, $x_{\text{DMSO}} = 0.48$: 120 DMSO and 130 water molecules have been simulated in a cubical box of length 26.066 Å. Density of the solution is 1.0983 (g mL⁻¹) and dielectric constant is 65.01.

In all mixed solvent compositions, there is one Na⁺ and one Cl⁻ ion in every cubic box of slightly different box lengths. The ions are placed at the center of the box with equal distances from the center along the x-axis. Monte Carlo simulations are performed in order to eliminate any close site-site contacts. It takes about 200 ps of MD simulation to reach equilibrium.

Pair-wise interaction potentials are used in the present work. The short range part of the direct potential between Na⁺ and Cl⁻ is changed from the Lennard-Jones form³² (12-6) to the Huggins-Mayer form³³ (exp-6) and the Fumi-Tosi form³⁴ (exp-8-6). The constant terms of 12-6 function are functions of the energy parameter (ϵ_{ij}) and the distance parameter (σ_{ij}). The cross-interactions have been obtained by using the Lorentz–Berthelot rules.^{35,36} The constant of the repulsive interaction are related to the number of electrons and the electron density whereas the constant describing the attractive part is related to the strength of the van der Waals interaction. An extra r^{-8} term in the exp-6-1 potential model giving it the exp-8-6-1 form makes it a better starting point for describing interactions in alkali halides. The forms of the three inter-ionic potential models are given below.

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

$$U_{ij}(\text{exp}-6-1) = B_{ij} \exp\left(-\frac{r}{\rho_{ij}}\right) - \frac{C_{ij}}{r^6} + \frac{q_i q_j}{r} \quad (2)$$

$$U_{ij}(\text{exp}-8-6-1) = B_{ij} \exp\left(-\frac{r}{\rho_{ij}}\right) - \frac{D_{ij}}{r^8} - \frac{C_{ij}}{r^6} + \frac{q_i q_j}{r} \quad (3)$$

The potential parameters of the above three equations are given in the supplementary information (Tables S1-S3 in Supplementary Information).

Classical molecular dynamics simulations of the systems mentioned above were performed using our MD code. The simulation started with a 200 ps equilibration and then 1 ns NVT simulation was performed for the PMF calculations. The systems under study were maintained at a constant temperature of 298 K using velocity rescaling method with periodic boundary conditions (PBC). The ions are modeled using the OPLS all atom force field.²⁴ Water and DMSO were modeled by using SPC and P2 force fields respectively.³⁷⁻⁴² Chalaris and Samios⁴³ have recently carried out molecular dynamics simulations of the liquid mixture water-DMSO using different effective potential models. They found that the SPC/P2, TIPS2/P2 and TIP4P/P2 combined models yield the most reasonable descriptions of the mixture.⁴³ In an earlier study by our group we have checked the effect of ion pair force field, where we have used three different force field models, OPLS, Dang and JJ for Na⁺ and Cl⁻ ion pair.⁴⁴ We have found that the shape and position of the minima of the potentials of mean force does not change with the ion pair force field, only the depth of the minima is varied. The deepest CIP minima is observed for OPLS force field and hence it allows us to analyze the PMF better. To maintain the same ion-solvent and solvent-solvent interaction, these potentials are of the 12-6-1 model. The long range interactions were evaluated using the reaction field method. We have used both the simple reaction field and PME method to check the difference during the calculation of potentials of mean force. We have added the potentials of mean force for $x_{\text{DMSO}} = 0.21$, using 12-6-1 potential model obtained from both simple reaction field and PME method in the Supplementary Information (figure S1). We can see that the difference in the values of the PMFs is very small and the structure of the PMF is not altered.

To calculate PMFs, the method of constrained molecular dynamics is used wherein the intra-solvent site-site separations (using the Shake algorithm⁴⁵) and the ion-ion separations are held fixed. The equations of motion were solved numerically using the Verlet algorithm with an integration time step of 0.1 fs. Inter-ionic separations (r) from 2.0 to 8.0 Å with increments of 0.25 Å were considered for estimation of the PMFs. This constitutes a series of 25 MD simulations for each solvent composition in the case of each ion-ion direct potential model. For the system consisting of two ions (A, B) and N solvent molecules, the magnitude of the force between the ion pair (due to solute-solvent

interactions), acting along the inter-ionic axis is evaluated as,

$$\Delta F(r, t) = \mu \left[\frac{\vec{F}_{AS}(r, t)}{m_A} - \frac{\vec{F}_{BS}(r, t)}{m_B} \right] \cdot \frac{\vec{r}}{|r|} \quad (4)$$

Where $\vec{F}_{AS}(r, t)$ and $\vec{F}_{BS}(r, t)$ are total forces on solute particles A and B, respectively, due to solvent molecules; m_A and m_B are individual masses of the ions, μ is the reduced mass of the ion pair and $\left(\frac{\vec{r}}{|r|}\right)$ 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 summation of direct force between the two ions $F_d(r)$ and the force acting on the ions due to solvent contribution $\Delta F(r)$ gives the mean force. That is,

$$F(r) = F_d(r) + \Delta F(r) \quad (5)$$

where, $\Delta F(r) = \langle \Delta F(r, t) \rangle$, the angular brackets denoting an ensemble average. The potential of mean force $W(r)$, is then obtained by integrating the mean force. The PMF gives a quantitative measure of the effect of solvent structure.

$$W(r) = W(r_0) - \int_{r_0}^r F(r) dr \quad (6)$$

The choice of $W(r_0)$ is to be taken in such a way that the calculated mean force potential matches the macroscopic Coulombic potential in a medium of dielectric constant ϵ at long distances.

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

We have found that the ion-ion PMFs for solvent compositions studied herein are not sensitive to the choice of r_0 if r_0 is greater than 8.0 Å. We have used the experimental dielectric constants of the mixtures for calculating PMFs. The use of calculated ϵ in eq. (7) instead of experimental ϵ does not alter the calculated PMFs by more than 0.5 kJ mol⁻¹.

3. Results and Discussion

3.1 Direct Potentials

The positions and depths of the local energy minima of Na⁺-Cl⁻ depend on the ion-ion model potential used. The nature of the ion-ion potentials is shown in figure 1.

For the exp-6-1 and exp-8-6-1 potential model, if the inter-ionic distance becomes very small, there is a steep decrease in the potential of the whole system. This implies that within a critical distance, the ions will

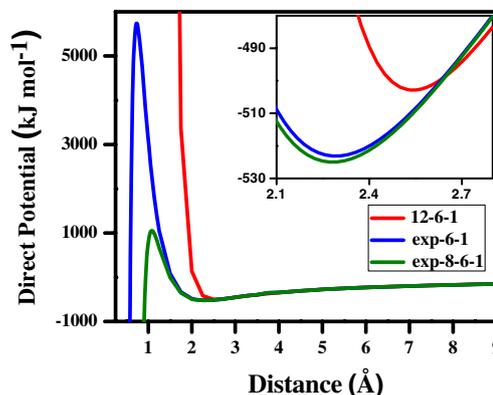


Figure 1. Direct potentials between Na⁺ and Cl⁻ ion using 12-6-1, exp-6-1 and exp-8-6-1 potential models (the positions and the depths of the CIP minima are shown in the inset).

come closer and coalesce which is unrealistic.⁴⁶ Hence a study of the ion-ion force and PMF for distances less than this critical distance is not relevant. The probability of such a collapse during simulations is rare. The short range potentials are shown to highlight the location of the turning point. In the gas phase, the differences in the minima of the three direct potentials are in the range of 20 kJ mol⁻¹. Table 1 shows the position and depth of the minima in gas phase potentials and the quantum mechanical calculations and JANAF experimental data.⁴⁷

We note from the table that the exp-6-1 and the exp-8-6-1 models may serve as a better starting point for studying the behavior of Na⁺ Cl⁻ ion pair in water-DMSO mixed solvent.

3.2 Potentials of Mean Force (PMFs)

Figure 2 shows a series of PMFs between Na⁺ and Cl⁻ with different ion-ion direct potentials in DMSO-water mixtures of different partial mole fractions.

Certain general trends can be noted from these figures. There is a contact ion pair (CIP) in all the cases

Table 1. Locations and depths of the CIP minima in the direct potentials between the Na⁺ and Cl⁻ ion pair using different potential models, QM/MM and experimental results.

Potential Model	Position of the minima (Å)	Depth of the minima (kJ mol ⁻¹)
12-6-1 (LJ+coulomb)	2.55	-502.80
Exp-6-1 (HM+Coulomb)	2.325	-522.79
Exp-8-6-1 (FT+Coulomb)	2.3	-524.95
G2-theory approximation ⁴⁷	2.4	-548.3
MP2 results	2.4	-554
Experimental JANAF results ⁴⁷	2.4	-556.6

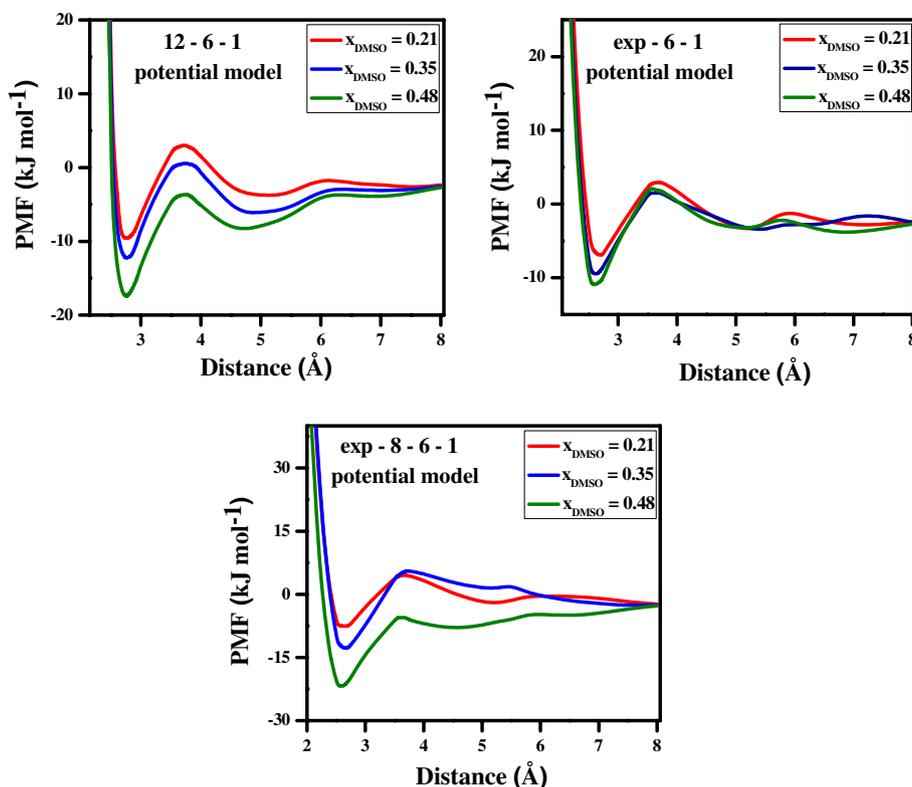


Figure 2. PMF for Na^+ and Cl^- as a function of ion-ion separation in different DMSO-water mixtures using the 12-6-1, exp-6-1 and exp-8-6-1 potential models.

along with solvent assisted ion pair (SAIP). In a contact ion pair (CIP), the cation and the anion are in physical contact. In a solvent assisted ion pair (SAIP), not a full but a part of a solvent molecule comes in between the ions. A representative picture of the CIP and SAIP is given below (figure 3).

With a gradual increase in the concentration of DMSO in the mixed solvent, the depth of CIP increases irrespective of the potential model used (table 2). The main cause for increase in the depth of the PMF is due to the change in the dielectric constant of the mixture. This is more due to the solvent rather than the solute-solute interactions.

In case of 12-6-1 potential model, the depths of the CIPs are -9.6 kJ mol^{-1} , $-12.2 \text{ kJ mol}^{-1}$ and $-17.4 \text{ kJ mol}^{-1}$ for $x_{\text{DMSO}} = 0.21, 0.35$ and 0.48 , respectively.

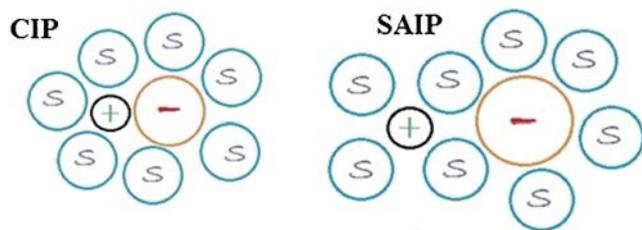


Figure 3. Representative picture of the contact ion pair (CIP) and solvent assisted ion pair (SAIP).

The corresponding changes in depths for the exp-6-1 model are less than that of the 12-6-1 model, whereas they are the largest for the exp-8-6-1 potential. At the CIP-SAIP transition state, for the 12-6-1 model, the PMF values are 3.0 kJ mol^{-1} , 0.57 kJ mol^{-1} and -3.7 kJ mol^{-1} for $x_{\text{DMSO}} = 0.21, 0.35$ and 0.48 , respectively. For the exp-6-1 model the corresponding differences at the transition state are much smaller. For the exp-8-6-1 model, the PMF values for $x_{\text{DMSO}} = 0.21$ and 0.35 are similar whereas the corresponding value for $x_{\text{DMSO}} = 0.48$ is lower by about 11 kJ mol^{-1} . The differences in the SAIP minima are much smaller for the 12-6-1 and exp-6-1 potentials, but the differences are larger for the exp-8-6-1 potential.

The differences between the $W(r_0)$ for different compositions are less than 0.5 kJ mol^{-1} . The positions of the CIP minima in the gas phase change from 2.5 to 2.325 to 2.3 \AA as the model potential changes from 12-6-1 to exp-6-1 to exp-8-6-1. However, the position of CIP minima in the PMF is 2.75 \AA for all potential models used. Because of the solvent forces, the difference at the CIP minima in the PMFs for different potential models is only around $2\text{-}3 \text{ kJ mol}^{-1}$ (we may recall that the differences in the gas phase minima were in the range of 20 kJ mol^{-1}). The solvent structures can be assessed by looking at the detailed solvent configurations. Additional evidence for the PMFs can be obtained by following

Table 2. Position and depth of the maximum and the minimum in the PMFs at different compositions using ion-ion direct potentials of 12-6-1, exp-6-1 and exp-8-6-1 nature.

x_{DMSO}	Min/max Potential model	1 st minimum (CIP)			1 st maximum			2 nd minimum (SAIP)		
		12-6-1	Exp-6-1	Exp-8-6-1	12-6-1	Exp-6-1	Exp-8-6-1	12-6-1	Exp-6-1	Exp-8-6-1
0.21	Position (Å)	2.75	2.75	2.75	3.75	3.75	3.75	5.25	5.25	5.25
	Depth (kJ mol ⁻¹)	-9.6	-7.1	-7.4	3.0	2.9	4.3	-3.8	-3.5	-2.1
0.35	Position (Å)	2.75	2.75	2.75	3.75	3.75	3.75	4.75	5.5	5.25
	Depth (kJ mol ⁻¹)	-12.2	-9.7	-12.2	0.57	0.5	5.5	-6.2	-3.5	1.4
0.48	Position (Å)	2.75	2.75	2.75	3.75	3.75	3.75	4.75	5.25	4.5
	Depth (kJ mol ⁻¹)	-17.4	-10.7	-21.1	-3.7	1.7	-6.1	-8.4	-5.3	-9.3

the trajectories when the distance constraint between the ions is removed and residence times are calculated for the ion pairs.

3.3 Residence Times of the Na⁺Cl⁻ Ion pair

As the ion pair moves from CIP to larger separations in the solvent, there is a minimum in the PMF corresponding to the partial insertion of a solvent molecule between the ion pair. This configuration may be referred to as solvent assisted ion pair (SAIP).⁴⁸ When a full solvent molecule (mostly water) comes in between the two ions, this configuration may be called a solvent separated ion pair (SSIP).

To obtain dynamical trajectories, the constraints between the ion pair are removed at the 1st transition states *viz.*, between the CIP and SAIP and the distances between Na⁺ and Cl⁻ are computed as a function of time. Over a 10 ps simulation, the trajectory data of $r(t)$ vs. t is converted into RT(r) (Residence Time) vs. r . The area under the residence time curve is proportional to the length of the time the ion pair spends at that distance. The changes in residence times with potential model for a fixed composition are shown in figure 4.

- i. For $x_{\text{DMSO}} = 0.21$, when the ion-ion direct potential is of 12-6-1 type, the trajectory shows that the ion pair settles at an inter-ionic CIP distance of 3.0 Å. For the direct potential model of exp-6-1

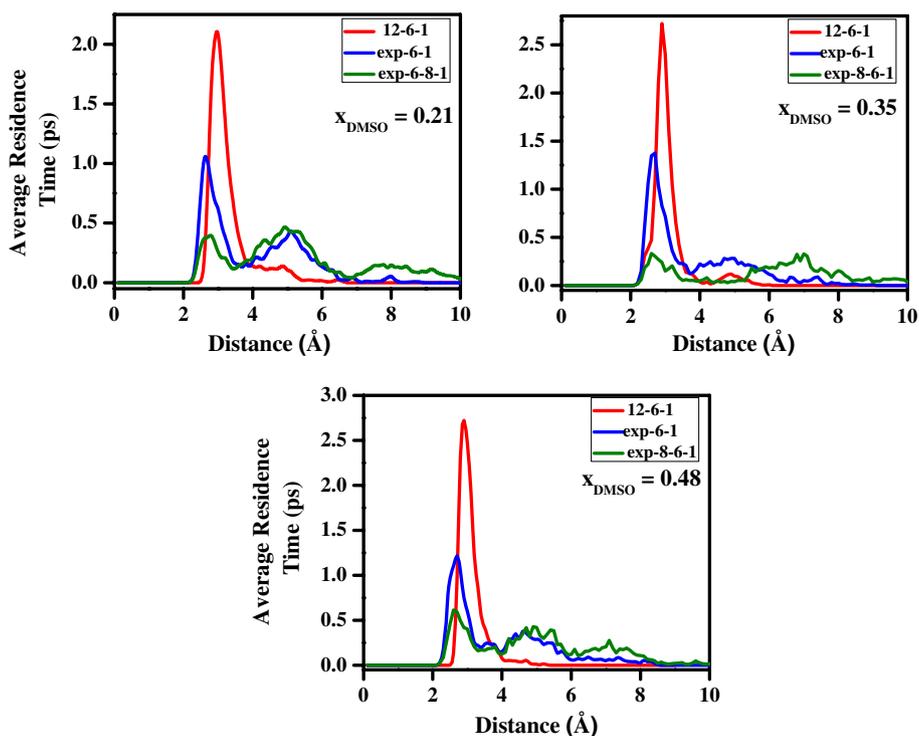


Figure 4. Trajectories and residence time graphs when the constraint between Na⁺ and Cl⁻ is released at the 1st transition state for DMSO–water mixture where $x_{\text{DMSO}} = 0.21, 0.35$ and 0.48 respectively for the 12-6-1, exp-6-1, exp-8-6-1 potential models.

nature, the ion pair is mainly located as a CIP and also significantly as an SAIP. For the exp-8-6-1 direct potential model, the trajectory and residence times show that the CIP is as stable as the SAIP with a significant amount of SSIP present.

- ii. For the DMSO-water mixture where $x_{\text{DMSO}} = 0.35$, in 12-6-1 ion-ion direct potential model, the ion pair mainly stays as the CIP but shows a small trace for the SAIP at 5 Å. The exp-6-1 trajectory and residence times show that, although the ion pair mostly remains as a CIP, a fair amount of SAIP is also found. For the exp-6-8-1 direct potential model, the results show the presence of a stable SAIP along with the CIP.
- iii. For DMSO – water mixture with $x_{\text{DMSO}} = 0.48$, the 12-6-1 the trajectory and residence times confirm that there is a strong CIP. For the exp-6-1 potential model, the CIP is more stable than the SAIP, but SAIP too is present to a significant extent. For exp-8-6-1 model, the trajectory and residence time results show the presence of a CIP and SAIP both of approximately similar extent.

Therefore, with a direct potential model of exp-6-1 nature, the behavior of ion pair in DMSO-water mixed solvent is similar to its behavior in pure DMSO,⁶ in spite of a major amount of water present in the mixture. For the exp-8-6-1 direct potential model, the ion pair behaves closer to NaCl in pure water⁵ even in presence of 48% DMSO in solvent mixture.

3.4 Clustering of Solvent Molecules around the Ion Pair

It is evident from solvent cluster analysis for different potential models that at CIP and SAIP the ions are surrounded by different numbers of DMSO and water molecules. However, the 1st solvation shell consists of a majority of water molecules. The local solvent clusters show that no solvent molecule is present between the ions in the CIP state (the 1st minima of the PMF graphs). In the ion-ion distance range of 3.75–5Å, no complete solvent molecule comes in between the ion pairs. A part of a solvent molecule (mostly water) comes between the ion pair. Therefore, it is more appropriate to call it a solvent *assisted* ion pair (SAIP) rather than a solvent separated ion pair (SSIP).

The preferential solvation of ions by the two solvents can be estimated by counting the average number of solvent molecules in spherical shells around the individual ions. In figure 5, we have given the running coordination numbers of Na⁺ and Cl⁻ ions for the 12-6-1 model for $x_{\text{DMSO}} = 0.48$. The running coordination numbers

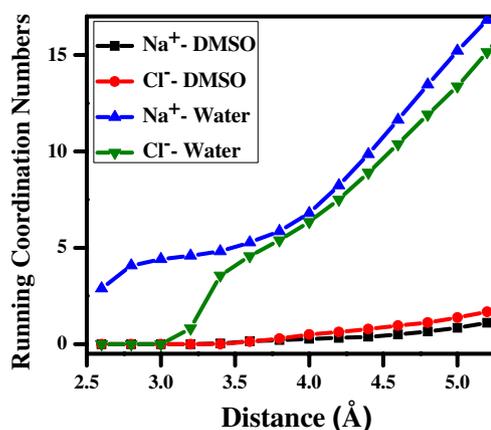


Figure 5. Running coordination number of solvent molecules around each ion at different ion-solvent distances. The composition for this system is $x_{\text{DMSO}} = 0.48$. The curve is obtained for the Na⁺Cl⁻ CIP configuration, when $r_{\text{NaCl}}^+ = 2.75$ Å.

for the three potential models and three compositions are given supplementary information (figure S2 to S10 in Supplementary Information).

It is evident from the running coordination numbers that the 1st solvation shells of both Na⁺ and Cl⁻ ions are made up of water molecules and no DMSO molecule comes in the 1st solvation shell until about a 5 Å radius around the ions. The DMSO shell is formed at a slightly closer distance for the Cl⁻ than the Na⁺. The solvent structures show that the solvation shell of Na⁺ is more compact than that of the Cl⁻. In the case of the 12-6-1 model, there are more water molecules in the 1st shell of the CIP than in the case of other two ion-ion potential models. The running coordination numbers for all compositions with all three potential models are given in the supplementary information. To confirm the preferential solvation of ion pairs by water molecules, two simulations have been performed. For the first simulation, the initial configuration had DMSO molecules packed inside a cube around the central ions, with water molecules on the periphery of the box. For the second simulation, a similar procedure was followed, but with water molecules inside and DMSO molecules outside in the initial configuration. It was found at the end of a 1 ns simulation in both cases, that the PMF between Na⁺ and Cl⁻ was similar, and both ions were preferentially solvated by water molecules. A representative picture of the CIP and SAIP is given in figure 6.

In our simulations, both the ions are preferentially solvated by water molecules but the PMFs have larger negative values as the composition of DMSO increases. DMSO molecules are larger in size and require a much larger volume to complete the first solvation shell around the ions. Feakins *et al.*, have experimentally

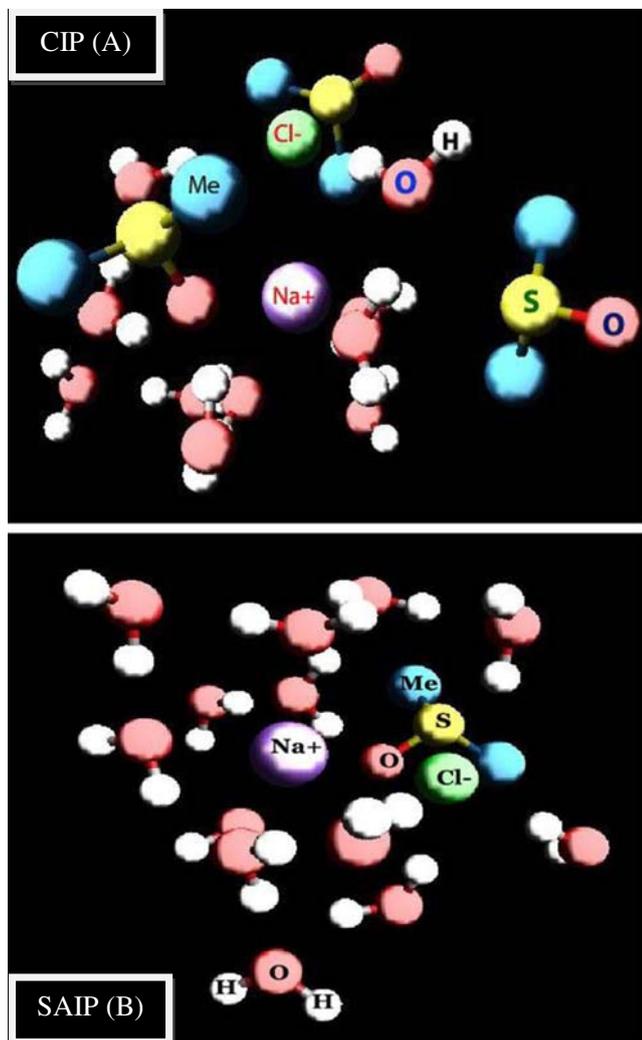


Figure 6. Local cluster of solvent molecules around the CIP (A) and SAIP (B) for DMSO-water mixture of composition $x_{\text{DMSO}} = 0.48$. At the CIP, there are 5 water molecules around Na^+ , but no DMSO molecule is present whereas for Cl^- there are 4 water molecules and no DMSO molecules in a spherical volume radius 3.5\AA . In a similar volume for SAIP, there are 5 water molecules around both Na^+ and Cl^- and no DMSO is present in either case. The purple spheres denote sodium ions, green spheres denote chloride ions, red spheres denote oxygen, white spheres denote hydrogen, yellow spheres denote sulphur and blue spheres denote the methyl group.

studied the preferential solvation of alkali metal halides in DMSO-water mixtures on the basis of Washburn numbers by using the emf method.⁴⁹ They have also found that the ions are preferentially solvated by water molecules than DMSO. In this present study, we note that the experimental solvation behavior is closer to simulation studies when the model potential is of 12-6-1 type. Weak preferential solvation of ions by DMSO molecules is consistent with the nuclear magnetic resonance evidence.⁵⁰

4. Conclusions

In this paper, we have considered the effect of different ion-ion potential models between Na^+ and Cl^- on the solvation structure of the NaCl ion pair. The three potential models used are the 12-6-1, exp-6-1 and exp-8-6-1. Constrained MD simulations have been performed on the Na^+Cl^- ion pair in three DMSO-water mixtures with different mole fractions of DMSO. The derived potentials of mean force for the ion pair using different potential models show the presence of a stable contact ion pair (CIP), a solvent assisted ion pair (SAIP), and a solvent separated ion pair (SSIP). The presence of a stable CIP for the exp-6-1 potential model in all three DMSO-water compositions is in contrast with the findings of a similar MD study done earlier for a much smaller time which did not show the existence of a stable contact ion pair in any of the mixtures.⁵¹ The derived PMFs have been tested by performing auxiliary MD simulations on the ion pair and generating dynamical ion pair trajectories. The residence times of the ion pair at different ion-ion distances have also been calculated by releasing the constraint on the ion pair at time $t = 0$, and trailing the ions for a considerably long time. The ion pair trajectories for all the compositions generally support the nature of the PMFs. The local solvent clusters show that the ion pair residing with an ion-ion separation of $3.75\text{--}5\text{\AA}$, is a solvent *assisted* ion pair. The running coordination numbers of the ions show that in all mixtures, the ions are preferentially solvated by water molecules. From the running coordination number data, it is seen that the solvation shells at CIPs for the exp-6-1 and exp-8-6-1 models contain fewer number of water molecules than the 12-6-1 model. In the study of solvent structure around the ion pair, we have found that for all potential models and compositions under study, the DMSO molecule is always out of the first solvation shell. However, DMSO compositions have a very important influence on the depth of the PMF at contact ion pairs.

In the case of Na^+Cl^- in the gas phase, the exp-6-1 and the exp-8-6-1 model seem to be closer to the QM-MM calculations.⁴⁷ The CIP minima of the direct potentials have differing locations in the gas phase. But in the solutions preferential solvation data shows that 12-6-1 still serves as a better potential model compared to the exp-6-1 and the exp-8-6-1 potential models. Experimental findings also support the results obtained from molecular dynamics simulations. Although, there is a significant scope for improving the direct ion-ion gas phase potential, in aqueous binary mixtures for future simulations, 12-6-1 potential model can be helpful in

predicting the properties of mixtures in a better way to be used as tunable media.

Supplementary Information (SI)

All the potential parameters of the ions, water and DMSO models are given in the supplementary information. The number of solvent molecules in a spherical volume with radius 3.5 Å around each ion of the ion pair at different interionic separations is provided. Numbers of solvent molecules within a spherical volume of radius 3.5 Å, 4.0 Å and 4.5 Å from the ions are also provided. The plots of running coordination numbers at CIPs and SAIPs for the three ion-ion potential models are provided for all compositions. Tables S1-S7 and figures S1 to S10 are provided in the Supplementary Information, which is available at www.ias.ac.in/chemsci.

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