Solvation structure of sodium chloride (Na+–Cl–) ion pair in acetonitrile (AN)–dimethyl formamide (DMF) mixtures

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ABSTRACT
Solvation structures of Na+–Cl– ion pair are investigated in acetonitrile (AN)–dimethylformamide (DMF) isodielectric mixtures. The potentials of mean force of Na+–Cl– in the five compositions of mixtures show minima corresponding to a contact ion pair (CIP) and a solvent-shared ion pair (SShIP). The solvent-separated ion pair minima are present in lower mole fractions of AN (x\textsubscript{AN} ≤ 0.50). CIPs are found to be more stable than the SShIPs. From a thermodynamic decomposition of the potentials of mean force, we find that the formation of the ion pair is entropically driven in these compositions. The most stable CIP is in pure AN. The local solvation structures around the ion pair are analysed through the running coordination numbers, excess coordination numbers, solvent orientational distributions and density profiles. We find that both Na+ and Cl– are preferentially solvated by DMF.

KEYWORDS
Potentials of mean force; solvent-shared ion pair; solvent-separated ion pair; excess coordination number; association constant

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1. Introduction
Nonaqueous solutions of electrolytes play an important role in chemistry and technology.[1] As many chemical and electrochemical reactions are carried out in mixed solvents, the physicochemical properties of binary mixtures need to be estimated and rationalised. Mixtures can have very different solvating abilities than the pure components.[2] N, N dimethyl formamide (DMF) and acetonitrile (AN) are aprotic dipolar organic solvents. They are widely used in chemistry due to their physicochemical properties such as the broad range of temperature over which they are in the liquid form, relatively high dielectric constants and good donor–acceptor properties. These properties enable them to be excellent solvents for a large number of compounds.[3] Amides are suitable model systems for the study of peptide and protein interactions in biological systems.[4] DMF is a universal solvent, widely used in peptide coupling in pharmaceuticals. It is also used in the development and production of pesticides, leathers, fibres, films, surface coatings and in electrochemical reactions.[5,6] DMF is used as a major solvent for the preparation of polycrylonitrile nanofibre.[7] AN 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.[8] AN contains a hydrophobic methyl group connected to a hydrophilic cyano group and thus can be thought of as an extremely small surfactant.[9] Salt solutions of monomeric amides have been used as models for binding salts to peptide groups in proteins and polypeptides.[10] AN and DMF are miscible in all mixture compositions and form non-azeotropic mixtures.[3] They have similar dielectric constants (ε, for DMF = 37.6 and ε, for AN = 36.0). These solvents have different Gutmann numbers,[11] which make them considerably different in their solvating capacities. Nasrabadi et al. performed an NMR study of the stoichiometry and stability of 30-crown-10 complexes with Ca\textsuperscript{2+}, Sr\textsuperscript{2+}, Ba\textsuperscript{2+} and Pb\textsuperscript{2+} cations in AN–DMF binary mixtures.[12] Gill et al. studied the solvation of Na\textsuperscript{+}, Cu\textsuperscript{+} and ClO\textsubscript{4}– in AN–DMF mixtures. They observed that the extent solvation depends on the composition.[13] Sajeevkumar and Singh studied the preferential solvation of lithium ions in AN–DMF mixtures through infrared spectroscopy. They observed that Li\textsuperscript{+} ions are preferentially solvated by DMF molecules.[10] Nain studied the interaction between AN and different amides through the Kirkwood–Buff theory of solutions.[14] Karkhaneei et al. performed \textsuperscript{23}Na NMR studies of stoichiometry and stability of sodium ion complexes with several crown ethers in AN–DMF binary mixtures.[15] AN–DMF binary mixtures are characterised by mutual destruction of dipolar structures and strong dipole–dipole interactions. DMF solvates cations preferably, AN solvates both cations and anions.[13,16] Therefore, it is interesting to study the solvation structure of Na+ Cl– ion pair in AN–DMF binary mixtures through classical molecular dynamic simulations. The details of simulation methods are given in Section 2, followed by results and discussion in Section 3. In Section 4, we present our conclusions.

2. Simulation methods
The united atom optimised potentials for liquid simulations (OPLS) force fields[17] are used for AN, DMF, Na+ and Cl–.[18–20] In the
and length, an (DMF), nan (nDMF) is the number of molecules of (DMF), l = simulation box
Details of systems used in simulations: x an (xDMF) is the mole fraction of AN, xDMF is the composition Table 3.
The geometrical parameters of AN and DMF.

Table 2. Geometrical parameters of AN and DMF.

| Sites  | Bond lengths/Å | Bond angles/(°)  |
|--------|----------------|------------------|
| AN     | C–N            | 1.170            |
|        | C–CH₃          | 1.460            |
|        | N–C–CH₃        | –                |
| DMF    | C–O            | 1.222            |
|        | C–N            | 1.335            |
|        | N–C–N          | 1.149            |
|        | O–C–C          | –                |
|        | C–N–CH₃        | –                |
|        | CH₃–N–CH₃      | –                |

All intermolecular interactions are taken to be the sum of site–site interactions, where site pair potentials that consist of Lennard Jones and Columbic terms, 

\[ U_{αβ} = \left( \frac{A_{αβ}}{r^{12}} - \frac{B_{αβ}}{r^6} \right) + \frac{q_α q_β}{r} \]  

(1)

where α and β represent interactions sites on different molecules, r is the site–site separation, q_α is the charge located at site α and q_β is the charge located at site β. The terms \( A_{αβ} \) and \( B_{αβ} \) are determined from:

\[ A_{αβ} = 4 \times (ε_{αβ}) \times (σ_{αβ})^{12} \]  

(2)

\[ B_{αβ} = 4 \times (ε_{αβ}) \times (σ_{αβ})^6 \]  

(3)

The terms \( ε_{αβ} \) and \( σ_{αβ} \) are calculated using the Lorentz–Berthelot mixing rules.[22]

\[ ε_{αβ} = (ε_α \times ε_β)^{1/2} \]  

(4)

\[ σ_{αβ} = (σ_α + σ_β)^{1/2} \]  

(5)

We have chosen OPLS model of DMF, the hydrogens of –CH₃ and –CH₃ are treated implicitly due to very high barriers for the rotation of the C–N bond.[19] All simulations are performed using the GROMACS 4.5.4 package.[21] The Lennard Jones parameters for the solvents and ions are given in Table 1. The geometrical parameters for AN and DMF are given in Table 2.

All intermolecular interactions are taken to be the sum of site–site pair potentials that consist of Lenard Jones and Columbic terms,

\[ U_{αβ} = \left( \frac{A_{αβ}}{r^{12}} - \frac{B_{αβ}}{r^6} \right) + \frac{q_α q_β}{r} \]  

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(5)

We have used particle mesh Ewald electrostatics [23] with a direct space cut-off of 1.5 nm Fornon-bonded van der Waals interactions, 1.5 nm cut-off is used. The geometries of DMF and AN molecules are constrained during the simulations using the LINCS algorithm.[24] The temperature of the system is maintained at 298 K by a velocity rescaling thermostat.[25] We have used the Berendsen barostat for equilibration and Parrinello–Rahman barostat for production runs.[26] The pressure of the system is fixed at 1 bar using the Berendsen barostat.[27] The system is equilibrated for 1 ns in a number, pressure and temperature (NPT) ensemble followed by 1 ns in an number, volume, temperature (NVT) ensemble. We have performed NPT trajectories for each distance (between the ions) from 2 to 10 Å for 10 ns using Parrinello–Rahman barostat.[28] The integration time step is 2 fs. The details of the simulation cells of the solvent mixtures are given in Table 3.

Density of solvent mixtures [29] is given in the Table S1 in supplementary information. The potentials of mean force (PMF), W(r) of the ions in the presence of the solvent can then be calculated as follows:

\[ W(r) = -\int F(r) dr = W(r_0) - \int F(r') dr' + 2kT \ln \left( \frac{r_{TS}}{r_0} \right) \]  

(6)

\[ W(r_0) = \frac{q_i q_j}{ε_i r_0} \]  

(7)

where F(r) is the mean force between the ion pair at distance r. The last term in Equation (6) takes into account the increase in entropy of the ion pair with increasing interionic distances. [30] 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. ε_i is the computed dielectric constant of the solvent mixture at 298 K. 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 on changing r_0, several aspects of ion association (positions of contact ion pair (CIP), solvent-shared ion pair (SShIP), transition state (TS), barrier heights) remain the same and are independent of the choice of r_0.[31]

3. Results and discussion

3.1. Potentials of mean force

The PMFs of the Na⁺–Cl⁻ ion pair in different compositions of AN (x_AN = 0.0, 0.25, 0.50, 0.75 and 1.0) obtained using Equation (6) are shown in Figure 1. In the derived PMFs, two types of structures are observed. In type I, CIPs, SShIPs and solvent-separated ion pairs (SSIPs) are seen, whereas in type II, only CIPs and SShIPs are seen.

PMFs of type I are observed in x_AN = 0.00, 0.25 and 0.50 and PMFs of type II are seen for x_AN = 0.75 and 1.00. CIPs are found to be more stable than SShIPs. The values of depths and positions of CIPs, TSs and SShIPs are given in the Table 4. From Table 4,
we note that the differences in the stabilities of CIPs are marginal for compositions $x_{AN} = 0.00, 0.25$ and 0.50. This is due to almost similar dielectric screening in these compositions. Similarly, we observe marginal differences in the running coordination numbers (Table 6) around Na$^+$ in these compositions, which support similar solvation shells in these compositions. The uncertainties in the PMFs range from 0.2 to 1.0 kJ/mol.

3.2. Ion pair distance residence times

The PMFs of the Na$^+$–Cl$^-$ ion pair can be confirmed by calculating the ion pair distance residence times (IPDRTs). IPDRT is an approximate measure of the length of time the ion pair resides at a particular distance. The IPDRT is defined as follows:

$$\text{IPDRT}(r) = \frac{\Delta t}{n_f} \sum_{i=1}^{N} \sum_{j=1}^{n_f} \delta_{r_i, r_i(\Delta t)}$$  \hspace{1cm} (8)

where $n_f$ 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 $\delta_{r_i, r_i(\Delta t)}$ is the Kronecker delta which is equal to 1 whenever $r = r_i(\Delta t)$ and 0 otherwise. The summation over $l$ corresponds to the initiation of trajectories at different initial values of the ion–ion separation $r = r_{\text{initial}}$. For $l = 1$, $r_{\text{initial}} = 0.23$ nm, for $l = 2$, $r_{\text{initial}} = 0.24$ nm and so on. The IPDRTs have been calculated by performing the dynamical trajectories of the ion pairs initiated at different ion–ion separations by releasing the constraint on the ion pair. Each trajectory is evolved for 1 ns. The IPDRTs for Na$^+$–Cl$^-$ ion pair in the five compositions of AN are shown in Figure 2.

From Figure 2, we see that intense peaks are observed around 0.27 nm which confirm the presence of the CIPs. The broad shallow peaks around 0.73 nm confirm the presence of SSIPs. For $x_{AN} = 0.00, 0.25$ and 0.50, small peaks are present around 0.91 nm. These indicate the presence of SSSIPs.

3.3. Thermodynamics of the ion pair association

The temperature-dependent PMFs are used to calculate the enthalpy and entropy contributions to the stability of the Na$^+$–Cl$^-$ ion pair in AN–DMF mixtures. The entropy and enthalpy contributions to the PMF are given as follows:

$$W(r) = \Delta H(r) - T\Delta S(r). \hspace{1cm} (9)$$

The entropy and enthalpy differences of the system at various distances can be derived from the following relationships.[32]

$$\Delta S(r) = -\left(\frac{\partial W(r)}{\partial T}\right) = -\left[\frac{W_T + \Delta T(r) - W_T(r)}{\Delta T}\right]$$  \hspace{1cm} (10)

$$\Delta H(r) = \left[\frac{\partial W(r)}{\partial \frac{1}{T}}\right] = W(r) + T\Delta S(r)$$  \hspace{1cm} (11)

We calculated $W(r)$ at three temperatures 278, 298 and 318 K. At higher temperatures, the CIPs are deeper, irrespective of mole fraction of AN. Increase in the depth of the CIP at higher temperatures is due to a decrease in dielectric screening. The effective interactions among the ions increase and greater association will occur at higher temperatures.[33] The PMFs of the ion pair for $x_{AN} = 0.50$ at different temperatures are given in Figure 3.

Using the PMFs at three different temperatures, the numerical derivatives with respect to temperature are calculated. These are shown in Figure 4 as a function of the mole fraction of AN.

The values $\Delta G$, $\Delta H$ and $-T\Delta S$ in kJ/mol at CIP and SSIP configuration in $x_{AN} = 0.00, 0.25, 0.50, 0.75$ and 1.00 are shown in Table 5.

From Figure 4 and from Table 5, we infer that in the five compositions of AN, both CIP and SSIP configurations are dominated by entropy. This is due to the ion pair formation that leads to randomness in the system by the release of the solvent molecules from their first solvation shells. As the mole fraction of AN increases beyond 0.5, the randomness of the system begins to increase significantly. This is due to the large molecules of DMF (in the solvation shells) displacing several AN molecules in the bulk on being released into the bulk when CIPs are formed. The
where \( n_{\alpha\beta} \) represents the number of atoms of type \( \beta \) surrounding species \( \alpha \) in a shell extending from 0 to \( R_{\text{min}} \) (the first minimum in the radial distribution function) and \( \rho_{\beta} \) is the number density of solvent. The running coordination numbers are actually the number of solvent molecules in the shells of the CIPs and SShIPs with one of the ions as the centre. The running coordination numbers of AN and DMF around Na\(^+\) and Cl\(^-\) are given in Table 6.

The running coordination number analysis shows that as the mole fraction of AN increases, the number of AN molecules around Na\(^+\) and Cl\(^-\) increases. The increase in the number of AN molecules around Na\(^+\) is not proportional to the mole fraction of AN. Also, the number DMF molecules around the Na\(^+\) decreases very slowly in comparison with the corresponding bulk mole fraction of DMF. From Table 6, we note that the solvation of Na\(^+\) is dominated by DMF molecules in the first solvation shell. For Cl\(^-\), both DMF and AN contribute to the solvation shells. We have also studied the local mole fractions of solvents in the solvation shells of ions.

**3.4. Running coordination numbers**

The effective composition of the solvation of the ion pair can be estimated using the running coordination numbers of solvents around the ions. The running coordination number is defined as follows:

\[
n_{\alpha\beta} = 4\pi \rho_{\beta} \int_0^{R_{\text{min}}} r^2 g_{\alpha\beta}(r) \, dr
\]  

where \( n_{\alpha\beta} \) represents the number of atoms of type \( \beta \) surrounding species \( \alpha \) in a shell extending from 0 to \( R_{\text{min}} \) (the first minimum in the radial distribution function) and \( \rho_{\beta} \) is the number density of solvent. The running coordination numbers are actually the number of solvent molecules in the shells of the CIPs and SShIPs with one of the ions as the centre. The running coordination numbers of AN and DMF around Na\(^+\) and Cl\(^-\) are given in Table 6.

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The local mole fraction of solvent molecules $\beta$ in the first solvation shell around the ions $\alpha$ is given by:

$$ x_{\alpha}^L(\alpha, R_{\text{min}}) = \frac{n_{\alpha}}{\sum_{\beta=1}^{n_{\text{components}}} \rho_{\beta} f_{\alpha \beta}(r) 4 \pi r^2 dr} $$

where $\beta$ is the number of components in the solvent mixtures. The local mole fractions ($x^L$) of solvent molecules in the first solvation shells around the ions as a function of the bulk mole fractions are given in Figure 5(a) and (b).

The local mole fraction of AN or DMF is calculated as $x_{\text{AN}}^L = \frac{n_{\text{AN}}}{n_{\text{AN}} + n_{\text{DMF}}}$. Here, $n_{\text{AN}}$ and $n_{\text{DMF}}$ are the number of AN and DMF molecules, respectively, in the first solvation shells of the ions. Figure 5(a) and (b) illustrates the strong dominance of DMF in the solvation shells of Na$^+$ and Cl$^-$ in the five compositions.

### 3.5. Excess coordination numbers

We have studied the preferential solvation through the excess coordination numbers (ECNs) around the Na$^+$ and Cl$^-$ ions in AN–DMF mixtures. The solutes can interact in different ways with the components of the solvent mixture, and this difference in the interactions is reflected in the compositions of the solvation shells.[2] The ECN is defined as:

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

Here, $4 \pi \rho_{\beta} r^2 g_{\alpha\beta}(r)$ is the average number of $\beta$-molecules around the $\alpha$-site in a spherical shell of width $dr$ and $4 \pi \rho_{\beta} r^2 dr$ is average number of $\beta$-molecules in the spherical shell with width $dr$ in the absence of the influence of $\alpha$. Therefore, $N_{\alpha\beta}$ represents the excess number of $\beta$-molecules around an $\alpha$-molecule.

The ECNs of AN and DMF molecules around Na$^+$ and Cl$^-$ ions in AN–DMF mixtures are shown in Figure 6(a)–(c).

### 3.6. Ion pair association constants

We have calculated the association constants of Na$^+$–Cl$^-$ ion pair in AN–DMF binary mixtures. The association constant is defined as follows:

$$ K_{\text{Na}^+\text{Cl}^-} = \frac{[\text{Na}^+][\text{Cl}^-]}{[\text{Na}^+\text{Cl}^-]} $$

where $[\text{Na}^+]$ and $[\text{Cl}^-]$ are the activities of Na$^+$ and Cl$^-$ ions, respectively, and $[\text{Na}^+\text{Cl}^-]$ is the activity of the Na$^+$–Cl$^-$ ion pair. The activities are calculated from the PMFs of the Na$^+$–Cl$^-$ ion pair in AN–DMF mixtures.
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 highest point of the TS barrier. The association constants for Na⁺–Cl⁻ have been given in Table 7.

The association constant of Na⁺–Cl⁻ ion pair is maximum in pure AN. $K_a$ values are consistent with the trends of the PMFs of Na⁺–Cl⁻ ion pair in the five compositions of AN.

### 3.7. Densities of solvent molecules around the 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 above the $x$–$y$ plane. The density profiles of AN and DMF around Na⁺–Cl⁻ in $x_{AN} = 0.5$ are shown in Figure 7. The density profiles for CIP are given in 7(a) and (b). For SShiP, they are given in 7(c) and (d), and for SSiP, they are given in 7(e) and (f), respectively.

#### Table 7. The association constants of Na⁺–Cl⁻ ion pair in AN–DMF binary mixtures.

| $x_{AN}$ | $K_a$ (L/mole) |
|----------|----------------|
| 0.00     | $9.59 \times 10^6$ |
| 0.25     | $5.87 \times 10^6$ |
| 0.50     | $6.47 \times 10^6$ |
| 0.75     | $1.30 \times 10^7$ |
| 1.00     | $2.20 \times 10^8$ |

Figure 6. (Colour online) ECNs around Na⁺ ion in AN–DMF mixtures with $x_{AN} = 0.25$, 0.50 and 0.75 (a), and ECNs around Cl⁻ ion in AN–DMF mixtures with $x_{AN} = 0.25$, 0.50 and 0.75 (b) and (c).

Figure 7. Density profiles of AN and DMF around Na⁺–Cl⁻ for $x_{AN} = 0.50$. The density profiles for CIP are given in 7(a) and (b). For SShiP, they are given in 7(c) and (d), and for SSiP, they are given in 7(e) and (f), respectively.
3.8. Orientations of solvent molecules in the solvation shells of ions in AN–DMF mixtures

In the CIP state, no solvent molecule is present in the region between Na\(^+\) and Cl\(^-\) ions [Figure 7(a) and (b)]. From Figure 7(c) and (d), we observe that solvation shells of AN and DMF are shared by the ions in the SShiP state. In the SSiP state, complete solvation shells of both DMF and AN are formed around Na\(^+\). Around Cl\(^-\), well-defined solvation shells of DMF and AN are not formed. The density profiles of AN and DMF around the Na\(^+\)--Cl\(^-\) for \(x_{\text{AN}} = 0.25\) and 0.75 are given in the supporting information [Figures S1 and S2]. The density profiles of DMF around Na\(^+\)--Cl\(^-\) in pure DMF at the SSiP state are given in Figure S3 in the supplementary information.

3.8. Orientations of solvent molecules in the solvation shells of ions in AN–DMF mixtures

The angular orientations of solvent molecules around the ions can be described by the angle \(\theta\) between (i) the vector connecting the ions and the nitrogen site of solvents and (ii) the dipole moment vector of solvent molecules. The angular distribution functions (ADF\(\text{s}\), \(P(\cos \theta)\), (averaged over 10 ns of simulations) as a function of \(\cos \theta\) are shown in Figure 8.

Form Figure 8(a), (c) and (e), we note that DMF molecules do not show a specific orientation around the Na\(^+\) and Cl\(^-\) ions in
their first solvation shells at the CIP, SShIP and SSIP states. The low values of the ADFs for $\theta = -180^\circ$ indicate that the antiparallel orientations of dipoles (with positive end of the dipole facing the positive ion) are not favoured. The ADFs of AN molecules in the first solvation shell of Na$^+$ show a broad peak for which $\cos \theta$ varies from 0.4 to 1.0 [Figure 8(b), (d) and (f)]. This suggests that the parallel dipolar orientations of AN molecules are preferred in the coordination shell of Na$^+$. In case of Cl$^-$, the ADFs show a broad peak for which $\cos \theta$ varies from $-0.40$ to $-1.0$. This suggests that the AN molecules tend towards an antiparallel dipolar orientation in the coordination shell of Cl$^-$. ADFs of DMF and AN molecules around Na$^+$ and Cl$^-$ in $x_{AN} = 0.25$ and 0.75 are given in the supplementary information [Figures S3 and S4]. As the mole fraction of AN increases, the peak heights of ADFs of AN around Na$^+$ and Cl$^-$ increase and the peak heights of ADFs of DMF around the Na$^+$ and Cl$^-$ decrease. As we go from CIP to SShIP state, the peak intensity of ADFs of AN increases.

Before we conclude, we briefly compare the behaviour of the Na$^+$ Cl$^-$ ion pair in AN–DMF and AN–DMSO mixtures. In both the mixtures, deeper minima in PMFs occur when the mole fractions of AN dominate. In AN–DMF mixtures, both Na$^+$ and Cl$^-$ are preferentially solvated by DMF molecules. In AN–DMSO mixtures, both the ions are solvated by DMSO molecules. This is in contrast with water–DMSO mixtures, wherein Na$^+$ is solvated by water and Cl$^-$ by DMSO molecules. The values of PMFs at the CIP minima are lower in AN–DMF mixtures (by about 8 kJ/mol) than in AN–DMSO mixtures. But the barrier heights from CIPs to TSs are nearly identical in both the mixtures for each composition. The values of PMF at SShIPs for both mixtures are very nearly the same (around $\sim 8$ kJ/mol), but the PMF values at the TSs are higher in AN–DMSO mixtures. Hence, the barrier heights from SShIPs to TSs are higher in AN–DMSO mixtures by about 7 kJ/mol in each composition. These differences are illustrated in Figure 9 for $x_{AN} = 0.5$.

In AN–DMF mixtures, the contributions of enthalpy increase (up to $x_{AN} = 0.50$) and then decrease with an increase in the mole fraction of AN. Contribution of entropy decreases up to $x_{AN} = 0.50$ and then increases with increase in the mole fraction of AN. The contribution of entropy in the formation of the ion pair is more in AN–DMSO mixtures than in AN–DMF mixtures.

4. Conclusions

We have performed constrained molecular dynamics simulations to study the potentials of mean force of the Na$^+$ Cl$^-$ ion pair in AN–DMF binary mixtures. In the lower mole fractions of AN ($x_{AN} \leq 0.50$), the PMFs show the presence of three minima corresponding to CIPs, SShIPs and SSIPs. The IPDRTs confirm the nature of PMFs. The differences in the stabilities of CIPs are marginal in $x_{AN} = 0.00, 0.25, 0.50$ and 0.75. At higher temperatures, the stability of a CIP is larger, irrespective of mole fraction of AN. The formation of this ion pair is entropically favourable in the five compositions of AN. The values of entropy and enthalpy approach each other in the formation of the CIP in pure AN. The preferential solvation analysis shows that Na$^+$ and Cl$^-$ are preferentially solvated by DMF. The orientational distribution functions show that DMF dipoles are not oriented strongly in the solvation shells, while the AN dipoles are oriented facing the cations and the anions, with the latter distributions being sharper.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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