Energetic Arguments on the Microstructural Analysis in Ionic Liquids

Takeshi Kobayashi,* Jens Smiatek, and Maria Fyta

The interaction of ionic liquids (ILs) with additives or impurities is crucial for the performance of ILs in technological applications. In order to understand the interaction between these, an insight onto the microscopic arrangement of molecules is needed. As a representative case, 1-ethyl-3-methylimidazolium dicyanamide ([EMIM][DCA]) mixtures are studied with dimethyl sulfoxide (DMSO) and water in bulk phase using molecular dynamics (MD) simulations. Different molar fractions of DMSO and water are studied to elucidate the influence of the molecular solute concentration on the structuring of the ILs. The results indicate that DMSO-[EMIM][DCA] and water-[EMIM][DCA] mixtures are defined by quite distinct molecular interactions between the species. By increasing the DMSO or water concentration, in the former the solute molecules are repelled from the ions, while in the latter they accumulate closer to the ions. The differences arise from the weakening of the interactions between the ions imposed by the presence of the water molecules whereas DMSO promotes a strengthening of these interactions. Accordingly, this study provides a deep understanding of the IL behavior in combination with neutral solute molecules and allows for a proper selection of IL-solute combinations in view of specific technological applications.

1. Introduction

Room-temperature ionic liquids (ILs) are beneficial media for many technological applications. In contrast to other solvents, ILs combine a low volatility and high temperature stability with a low flammability in combination with a broad electrochemical stability window.[1–5] Due to these properties, ILs are often used as green solvents for various polar and apolar solutes,[1,3,13,15,19,25–38] as reaction media for purposes of chemical synthesis or as electrolytes for electrochemical devices.[10–17] In combination with water as the main solute, aqueous ILs were also proposed as stabilizing solutions for protein and DNA conformations.[18–24] On the other hand, the negative impact of water on the stability windows in electrochemical storage devices was also pointed out.[25] Despite the ambiguity for water-IL mixtures, various other protic and aprotic IL-solute mixtures with low concentrated neutral solvent molecules attracted a lot of interest over the last years.[1,13,15,19,25–38] In addition to the properties of IL-solute mixtures in a bulk solution, also the properties of the mixtures at interfaces are a strong focus of current research.[25,39] It has been found, for example, that certain factors such as the chemical properties, entropic effects, as well as the choice of anions and their combinations with solutes, strongly influence the spatial distribution of the different species.[17,25,40–43]

Different molecular sizes or shapes of both the ILs and the solute, as well as the polarity crucially affect the interactions of the ionic species at both in bulk solutions and at interfaces.[18,40–42,44–47] Furthermore, the hallmarks of solid or gaseous surfaces, for instance charged, uncharged, polar or apolar induce spurious differences in the expected mixture properties.[17,25,41,68–51] In view of designing new technological applications, what is often missing is a deep microstructural insight into IL solutions. Previous experimental and theoretical studies on IL-water and IL-DMSO mixtures in front of uncharged and purely repulsive surfaces revealed some interesting insights and have underlined the entropic effects on the molecular structuring.[29,52–54] However, due to strong electrostatic and dispersion interactions, it can be assumed that also enthalpic contributions play an important role.[55] Motivated by the above studies, here we propose a new qualitative measure of molecular interactions within IL bulk solutions. We assess and differentiate short range interactions of the IL with the solute molecules. Thereby, we introduce a novel theoretical approach for a straightforward interpretation of molecular interactions which yields insight into microstructural behavior that arises from the individual ions and solute species and their molecular compositions. This new measure, “effective interaction energies”, can be used for the further analysis, for instance, as the interaction energy terms in the calculation of the chemical potentials in a Lattice...
gas model. As representative IL solutions, we discuss IL-water and IL-DMSO solutions, which attracted some interest in the last years. In view of these, the paper is organized as follows: we begin with an outline of the methodology in Section 2, discuss the results of our MD simulations in Section 3 and provide a summary on the relevance of these outcomes in Section 4.

2. Theoretical Background

2.1. Effective Interaction Energies

In order to provide a detailed analysis of the enthalpic contributions to the interactions between the species, we describe the respective conservative long- and short range interactions between the different molecules in the solution. Thereby, we explicitly rely on force field methodology which already has shown its merits in the context of atomistic MD simulations for a broad range of systems. In the following, the indices \( i, j \) denote different species, namely cation, anion or solute. In standard classical atomistic force fields, the intermolecular potentials are typically represented by long-range (long) and short-range (short) interactions. It has to be noted that all forces are typically evaluated among atoms of molecules but here we neglect this point and assume short- and long range interactions as the sum of molecular interactions between the atoms of distinct species. The total interaction energy between molecules \( i \) and \( j \) per unit volume is expressed by

\[
E_{ij} = E_{ij}^{\text{short}} + E_{ij}^{\text{long}}
\]

\[
= (E_{ij}^{\text{short,LJ}} + E_{ij}^{\text{short,Coul}}) + E_{ij}^{\text{long}}
\]  

where both the short range interaction energy \( E_{ij}^{\text{short}} \) and longrange interaction energy \( E_{ij}^{\text{long}} \) are taken into consideration, respectively. Furthermore the short range interaction is divided into Lennard-Jones part \( E_{ij}^{\text{short,LJ}} \) and Coulomb part \( E_{ij}^{\text{short,Coul}} \). In order to provide a reliable estimate of interaction energies, we set 1 nm as a cut-off distance for the short-range interaction both for Lennard-Jones and Coulomb interactions after which we can observe a bulk behavior as shown in Section 3. In order to assess the interaction between each species in the solution, the effective interaction energy \( \gamma_{ij} \) between distinct molecular species \( i \) and \( j \) is defined through

\[
\gamma_{ij}^{\text{LJ/Coul}} = \frac{1}{2} \int_0^{r_{\text{cut}}} 4\pi r^2 E_{ij}^{\text{LJ/Coul}}(r)n_{ij}(r) dr, \quad i = j
\]

\[
\gamma_{ij}^{\text{LJ/Coul}} = \frac{1}{n_i n_j} \int_0^{r_{\text{cut}}} 4\pi r^2 E_{ij}^{\text{LJ/Coul}}(r)n_{ij}(r) dr, \quad i \neq j
\]

where \( E_{ij}^{\text{LJ/Coul}}(r) \) is the average interaction energy between one molecule of species \( i \) and one molecule of species \( j \) separated by a distance \( r \). The prefactor \( n_i \) is included as the species of type \( i \) are used as a reference. In order to take into account all molecules from species of type \( i \) and \( j \) within the volume slice, we multiply the corresponding value with the local number density \( n_{ij}(r) \) of species \( j \) around one molecule of species \( i \). Substituting Equation (4) into Equation (3) by taking also into account the definition of the radial distribution function \( g_{ij}(r) \) of species \( j \) around species \( i \), and also the cutoff radius \( r_{\text{cut}} = 1 \) nm for the short-range interaction yields

Equations (3) and (5) are different expressions for the same entity assuming homogeneous solutions. Notably, Equation (5) introduces a fixed reference position due to the introduction of the radial distribution function, whereas Equation (3) considers a bulk volume-like behavior. From the simulations, we can calculate directly \( E_{ij}^{\text{LJ/Coul}}(r) \) and \( \gamma_{ij}^{\text{LJ/Coul}} \) using Equation (3). \( r_{ij}^{\text{LJ/Coul}} \) can be also expressed in a different way by Equation (5) using the radial distribution functions \( g_{ij}(r) \). These values, \( \gamma_{ij}^{\text{LJ}} \) and \( \gamma_{ij}^{\text{Coul}} \), indicate by definition how the contributions of Lennard-Jones and Coulomb interactions in a local interaction between molecules \( i \) and \( j \) can be compared to the bulk for different solute concentrations.

2.2. Local/Bulk Partition Functions

In order to analyze the local accumulation of solutes around cations (index \( c \)) and anions (index \( a \)), we use the local/bulk partition functions\[^{19,57-60}\]

\[
K_i'(r) = \frac{\langle n'_i(r) \rangle}{\langle n'(r) \rangle} < n_i'(r) > \frac{1}{n_i/n}
\]

with \( i = c, a \) where \( < n_i'(r) > \) and \( < n'(r) > \) denote the average local number of solute molecules and all molecules within a distance \( r \) around the ions, respectively. \( n_i \) and \( n \) are the total number of species \( i \) and all species, respectively.
number of solute and all molecules in the simulation box. A value of $K_i^s > 1$ highlights a pronounced local accumulation of solute molecules near the cation or anion and $K_i^s < 1$ the opposite. The local/bulk partition functions together with the effective interaction energies will lead to important information on the preferential interaction between the species in the IL solutions.

2.3. Simulation Details

We study in detail the microstructuring and the properties of bulk IL mixtures. To this end, we perform atomistic molecular dynamics (MD) simulations for distinct IL solutions using as solutes, water or dimethyl sulfoxide (DMSO). The former is essential for biological applications and unwanted in energy applications. DMSO on the other hand is expected to be beneficial for technological applications. DMSO on the other hand is expected to be beneficial for technological applications. DMSO on the other hand is expected to be beneficial for technological applications. DMSO on the other hand is expected to be beneficial for technological applications. DMSO on the other hand is expected to be beneficial for technological applications. DMSO on the other hand is expected to be beneficial for technological applications. DMSO on the other hand is expected to be beneficial for technological applications. DMSO on the other hand is expected to be beneficial for technological applications.

For our atomistic MD simulations with the GROMACS 5.1.3 software package,[61–63] we have used the OPLS/AA force fields for the ions and DMSO.[64–66] with the SPC/E model for water.[67] Specifically the force field parameters are taken from ref. [65] for [EMIM]$^+$ and [DCA]$^−$, and from ref. [66] for DMSO. This combination has already been validated for bulk water-IL mixtures.[68] In all simulations, the temperature was kept at $T = 300$ K by an improved velocity-rescaling thermostat,[68] using a coupling time constant of 0.1 ps. Electrostatic interactions were treated through the particle mesh Ewald (PME) method,[69,70] where a real-space cutoff of 1.0 nm and a grid spacing of 0.16 nm with fourth-order interpolation scheme were used. The Lennard-Jones (LJ) interactions were truncated at 1.0 nm and shifted to zero. The equations of motion were integrated using the Leapfrog algorithm with an elementary time step of 2 fs. All bonds were constrained by the LINCS algorithm.[71] An energy minimization was first performed using a conjugate-gradient method, followed by an equilibration period of 10 ns under constant volume-constant temperature (NVT) conditions, and a subsequent equilibration run of 10 ns under constant temperature and constant pressure (NpT) conditions. The final NpT production runs had a length of 300 ns each. Positions and velocities of atoms were stored every 10 ps. For the initial configurations we have used computational boxes of dimensions 6.3 – 6.5 nm in the periodic $x$, $y$, $z$-directions in which all species were randomly inserted using the software package PACKMOL.[72] The corresponding numbers of molecules and ions for the respective mole fractions are shown in Table 1. The pressure was kept constant at $p = 1$ bar by an isotropic Parrinello–Rahman barostat[73] with a coupling time constant of 2 ps and a compressibility of $4.5 \times 10^{-5}$ bar$^{-1}$. Note, that the assignment of DMSO or water as solute or solvent depends on their concentration.[54] In order to simplify our discussion below, we use the term “solute” for either DMSO or water in this work.

3. Results

3.1. Effective Interaction Energies

We begin the analysis with the effective interaction energies between the species in the solutions as calculated through Equation (3). The results of the bulk solutions for all IL mixtures throughout the solute concentration range are summarized in Figure 2. Note that the error bars were less than 1%, thereby are not shown in the figure. As a first observation, in Figure 2a the DMSO has stronger LJ interaction with other species due to the larger size than water. The main difference is found in the cation-cation interaction. While the DMSO mixtures show decreasing trend, the water mixtures show the opposite. Note, that the cation-DMSO interaction almost coincides with the anion-DMSO interaction in the top right panel of this figure and is hidden behind the latter curve. For the Coulomb interaction, the interaction involving DMSO is decreasing while the water interaction is increasing with respect to the solute concentration. Furthermore the cation-cation interaction increases in the DMSO mixtures while in the water mixtures it decreases at $x_{sol} = 0.125$ and reaches a plateau. The cation-anion interaction shows the

![Figure 1](image-url)  
**Figure 1.** The atomic structures of a) [EMIM]$^+$, b) [DCA]$^−$, c) DMSO and d) water. The carbon (C), nitrogen (N), oxygen (O), and hydrogen (H) atoms are colored in cyan, blue, red, and white, respectively.
opposite trend between the DMSO and water mixtures, which decreases in the DMSO mixtures and increases in the water mixtures. Furthermore the strong anion-solute interaction in the water mixtures should be attributed to the hydrogen bonds between water and the anions as shown in the remainder of this work.

The comparison between the LJ and Coulomb interactions provide an insight on the strong contribution of LJ interaction to the difference between cation-solute interactions. The cation-solute Coulomb interaction shows a negligible difference, while the cation-DMSO has stronger LJ interaction than the cation-water. Water interacts mostly through Coulomb interactions with anions forming hydrogen bonds. With water due to its small size there is a negligible LJ interaction. The repulsive DMSO-DMSO interaction is significantly compensated by LJ interactions. According to these observations, the local ionic structure, which is based on the cation-anion interaction, is strengthened in the DMSO mixtures by adding DMSO and weakened in the water mixtures. In the DMSO mixtures, DMSO tend to strongly interact by Coulomb interaction with other molecules in a long range, and in the water mixtures this interaction is weaker. This is due to the fact that the dipole moment of 4.42D for DMSO is larger than the value of 2.35D for water, as calculated from our simulations. Note, that the respective experimental values are 3.960D for DMSO and 1.855D for water.[74] These trends in the dipole moments and the strong hydrogen bonds between water and anions are linked with our observation that the solute molecules in the second solvation shell around each species contribute more to the Coulomb interaction in the case of DMSO compared to water. DMSO interacts with other molecules equally within a distance of 1 nm. Water, though, interacts strongly in the close vicinity but weaker in larger distances. Therefore adding solutes does not require a rearrangement of the local ionic structure in the case of the DMSO mixtures, but requires a local rearrangement of ions in the water mixtures.

These trends can be confirmed by the radial distribution functions (rdfs) depicted in Figure 3. In panel (a) of this figure the rdfs for cations-anions are sketched, while in panel (b) the ion-ion rdfs are shown. For the latter, both the cations and anions are considered as ions. The cation-anion rdfs capture the interaction between direct cation-anion pairs. In contrast, the ion-ion rdfs provide more insights into the total ionic structure of the IL mixtures by including also cation-cation or anion-anion contributions. In the case of DMSO mixtures, the cation-anion rdfs have their first peaks at the same position for all concentrations. The first peaks increase with the concentration, showing that the ion pairing persists. This can be seen in a decreasing cation-anion effective interaction energies in the top panels of Figure 2. In the case of the water mixtures, increasing the concentration leads to
a shift of the first cation-anion peaks to shorter distances, while the peak height remains more or less constant, which indicates that the amount of associated cation-anion pairs decreases in the same manner as in the bulk solute concentration. The water molecules, which increase in number, are mixed with the ILs, so that they only change the favorable orientation between the cations and the anions. A further comparison of the cation-anion rdfs in panel (a) reveals an interesting trend in the first peaks. For water and DMSO the first peaks in the cation-anion rdfs are found at 0.4 nm and 0.6 nm, respectively. At first, this shows the more strongly bound ion-pair in water compared to the case in DMSO. Both peaks remain at their respective positions throughout the concentration range of water and DMSO. However, as the concentration increases, the peak heights increase in both mixtures, revealing more strongly bound ion-pairs in both mixtures. The change in effective cation-anion interaction confirmed through the results in Figure 2 is based on the persistent ion pairs in the DMSO mixtures and the orientational change in the water mixtures. Further analysis on the rdfs between center of mass of the cation and each atom in anion (atomic labels are shown in Figure 11) reveals additional details on the orientational change of anions around the cation in Figure 4.

Based on this figure, as the solute concentrations increase, the peaks of the rdfs between cation and the atoms in DMSO-mixtures increase in the same manner. On the other hand, in water mixtures, there is distinct difference in the rdf between cation and N4/N5 atom in the anion. The first and second peak around 0.2 nm and 0.35 nm decrease and the third peak at 0.4 nm increases. This implies that the N4/N5 atoms lose the capability to interact with the cations in the high water concentration of $\chi_{\text{sol}} = 0.875$. This relates to the fact that the over-accumulation of the water molecules around those atoms weaken the interaction between cation and the anions. This is explained more in detail in the following preferential position analysis. In the ion-ion rdfs for the water mixtures, the first peak shifts to shorter distances at high water concentrations, while the peak height converges to unity. This shift of the first peak and the decreasing peak value attribute to the change in the favorable orientation between cations and anions and the weakened ionic interactions including all cation-anion, cation-cation and anion-anion interactions.

On the other hand, in DMSO mixtures, no shift is observed in the peak position, while the height increases with an increased DMSO concentration. This trend implies that the cation-anion pair and the interactions between these pairs remain stable.

We next discuss the potentials of mean force (PMF) in Figure 5 as calculated from the radial distribution functions among ions using the following equation

$$A(r) = -k_B T \ln \frac{g(r)}{g(r=\infty)}$$

with the Boltzmann constant $k_B$. As observed in this figure, in DMSO mixtures, a steep minimum at $r = 0.6 \text{ nm}$ occurs throughout the whole solute concentration range. As discussed in ref. [75], this indicates that the ions are more associated at higher solute concentrations. A comparable behavior can be observed in IL-water mixtures up to $\chi_{\text{sol}} = 0.625$, where the ions show a pronounced negative PMF at the nearest minimum at $r = 0.6 \text{ nm}$. At $\chi_{\text{sol}} = 0.750$, the local minimum at $r = 0.6 \text{ nm}$ has a positive value and a new local minimum shows up at

Figure 4. The radial distribution functions between center of mass of the cation and the atoms in the anion. (Top panels) DMSO-[EMIM]$^+$[DCA]$^-$ mixtures and (bottom panels) water-[EMIM]$^+$[DCA]$^-$ mixtures. The results for the cation-N1 atoms (left), cation-N4/N5 atoms (center) and cation-C2/C3 atoms (right) for each mixture are depicted as a function of the solute concentrations defined in the legend.

Figure 5. The potential of mean force between a) cation and anion, and b) ion and ion in the DMSO-[EMIM]$^+$[DCA]$^-$ (top) and the water-[EMIM]$^+$[DCA]$^-$ (bottom) mixtures for the whole range of solute concentrations as described in the legend.
The local/bulk partition functions for solute molecules around cations (bottom) and anions (top) at different solute mole fractions. The solid lines correspond to the DMSO mixtures and the dashed lines to the water mixtures.

\[ r = 0.4 \text{ nm} \]. As a consequence, at this higher concentration, the local minimum at \( r = 0.6 \text{ nm} \) turns to be a local maximum and the local minimum at \( r = 0.4 \text{ nm} \) becomes more apparent. Accordingly, higher water concentrations induce a significant rearrangement of the local composition around the ions. These results are in a quite good agreement with experimental results.[76]

### 3.2. Local/Bulk Partition Functions and Preferential Molecular Positions

Based on Equation (6), the local/bulk partition functions for the mixtures are summarized in Figure 6. Both DMSO and water mixtures reveal a decreasing trend in the height of the peaks with respect to the solute molar concentration. This indicates a saturation of solute molecules close to the ions even for dilute mixtures (\( x_{\text{sol}} = 0.125 \)). With regard to the decreasing values, it can thus be concluded that the added solute molecules tend to be located in the bulk region instead in close distance to the individual reference molecules. Moreover, the polar molecules such as DMSO or water accumulate near the charged ions even if the solute is made of neutral species. However, there still exist distinct differences between DMSO mixtures and water mixtures. For example, due to the small size of the water molecules, these accumulate more than the DMSO molecules around the ions. In addition, while \( K_{\text{sol}} > 1 \) holds even at the highest water concentration indicating the preferential binding of water molecules to the ions, \( K_{\text{sol}} < 1 \) holds for the DMSO mixtures at the highest DMSO concentration \( x_{\text{sol}} = 0.875 \). The latter highlights the repelled behavior of DMSO molecules around the ions. These results support the conclusions obtained above for the effective interaction energies and their difference in the DMSO and water mixtures showing strengthened ion-ion interactions in the DMSO mixtures and the weakened ion-ion interactions in the water mixtures.

We further analyze these observations with respect to the orientation of the species around other species. Distinct characteristics are again observed in DMSO and water solutions as evident from Figure 7 for the solute molecules around the anions. In this, the preferential positions of the solute molecules around the anions are shown. Note, that in this and the following figures, the probability depicted is calculated by the number of occurrences at each rectangular grid point with 0.1 nm distances and divided by the total number of occurrences within 0.8 nm from the anions center of mass. It can at first be observed that solutes accumulate differently in DMSO mixtures and water mixtures. In DMSO mixtures, DMSO molecules accumulate near the negative side of the dipole moment direction in anions. The dipole moment is calculated by

\[
\bar{\mu} = \sum_i q_i (\bar{x}_i - \bar{x}_0)
\]

where \( q_i \) is the partial charge of atom \( i \) in a molecule and \( \bar{x}_i \) is the position of this atom. \( x_0 \) is the center of mass of the molecule. The partial charges and the direction of the dipole moments are shown in Figure 11. The calculated values of \( \mu \) for each species are 1.77D for [EMIM]+, 0.90D for [DCA]−, 4.42D for DMSO, and 2.35D for water.

In water mixtures, the water molecules accumulate near the highly negatively charged atoms. This difference arises from the different sizes of DMSO and water. The smaller water molecule is more flexible, can more easily reorient, and thus interacts strongly with charged atoms. For the larger DMSO molecule, the interactions to neighboring ions are more dispersion interaction orientated. More specifically, in DMSO, orientational preferences are absent. These findings differ in water solutions in which the water molecules are strongly accumulated close to the anion and its respective nitrogen atoms. This localization effect is stronger at low water concentrations, while it decays as more water is added into the solution. The accumulation close to the two nitrogen atoms can be understood based on the fact that the hydrogen atom in water has the largest positive charge, while these two nitrogen atoms (N4/N5 atoms in Figure 11) in [DCA]− define together the region of the highest negative charge. In combination with the small size of water, these atoms interact strongly and form hydrogen bonds. The average numbers of hydrogen bonds between the N4/N5 atom or N1 atom in [DCA]− and water molecule for different water concentrations are shown in Table 2.

At lower water concentrations, each water molecule forms nearly two hydrogen bonds with the N4 or N5 atom of [DCA]−. This means that most of the water molecules are trapped between interacting [DCA]− molecules. Apparently at lower solute concentration up to \( x_{\text{sol}} = 0.5 \) the water molecules accumulate about ten times nearer the N4/N5 atoms compared to the respective N1 atom. At high solute concentrations, the water accumulation near N4/N5 atom seems to be weakened, which corresponds to the ion-ion structural changes observed in the rdfs (Figure 3). This region has a total negative charge greater than \( -1 \) and interacts strongly with the cations. In fact, this charge is about \( -1.19e \) arising from the N1 atom in [DCA]−, the H1(H2), and O1 in water in Figure 11. In this way, water mediates the interaction between cation and anion due to the high electronegativity and chemical hardness leading to the strong affinity to the anion.[77–79] This leads to a weak cation-anion interaction in water mixtures. On the other hand, due to the smaller electronegativity, the preferential position of the species do not change in DMSO mixtures. Thus, the cation-anion interaction remain strong. In the case of solute molecules around the cations, the results in Figure 8 reveal
that the positions of the highly localized area are clearly different between the DMSO and water mixtures. For water mixtures it is more in plane of the imidazolium ring in the cation while the DMSO is localized at the top/bottom of the imidazolium ring. For the water molecules the localized area is near the anions localized in Figure 9 (anions around the cation) implying that these localization is mediated the accumulation of water around the anion. Moving to the anions around the cations in Figure 9, at $x_{\text{sol}} = 0.000$, the preferential position of the anion is close to that of the highest positively charged region. These preferences do not change qualitatively with the addition of DMSO. However, at $x_{\text{sol}} = 0.875$ the localization area of water is shifted to the top/bottom of the imidazolium ring. This shift is the manifestation of the peak shift of the cation-anion rdfs in Figure 3. On the other hand, the preferential positions of the cations are close to the negatively charged side of the anion in Figure 10. These preferential positions do not change with the addition of either DMSO or water even at high concentrations. Only for the water mixtures case, the preferential position is localized more on the top/bottom of the plane of the anion triangle, which relates back again to the peak shift of the cation-anion Rdfs in Figure 3.

In order to study the DMSO-solute interactions further, we have calculated the average number of weak hydrogen bonds as C3, C6 and C7 atoms in [EMIM]$^+$ as the donor and O2 atom in DMSO as the acceptor in Figure 11 (the donor-acceptor distance is < 0.32 nm and the angle is < 90° as stated in ref. [80]). It has been reported that the attachment of DMSO to these atoms via weak hydrogen bonds weakens the cation-anion interaction in the imidazolium-based ionic liquids.[81] In Table 3 the average number of weak hydrogen bonds between [EMIM]$^+$ (C6/C7/C3) and DMSO (O2) for different DMSO concentrations is summarized. Due to the systematic constraint, C6 and

![Figure 7](image_url)

**Figure 7.** The preferential positions of the solute molecules around the anion for both solutes at different concentrations as denoted by the legends on the left. The red colors and larger spheres denote a higher occurrence probability of the molecules.

| Mole fraction of solute $x_{\text{sol}}$ | 0.125 | 0.250 | 0.375 | 0.500 | 0.625 | 0.750 | 0.875 |
|--------------------------------------|-------|-------|-------|-------|-------|-------|-------|
| Number of hydrogen bonds per N4/N5 atom | 0.132 | 0.295 | 0.503 | 0.764 | 1.085 | 1.490 | 2.073 |
| Number of hydrogen bonds per N1 atom | 0.008 | 0.020 | 0.039 | 0.074 | 0.149 | 0.320 | 0.705 |
| Number of hydrogen bonds per water molecule | 1.900 | 1.833 | 1.741 | 1.603 | 1.391 | 1.100 | 0.693 |

**Table 2.** The average numbers of hydrogen bonds per N4/N5 atom or N1 atom in [DCA]$^+$ molecules and water molecules at different water concentrations. For the atom labeling refer to Figure 11.
Figure 8. The preferential positions of the solute molecules around the cation for both solutes at different concentrations as denoted by the legends on the left. The red colors and larger spheres denote a higher occurrence probability of the molecules.

Figure 9. The preferential positions of the cations around the anion for DMSO-[EMIM][DCA]− and water-[EMIM][DCA]− mixtures at different solute concentrations as denoted by the legends on the left. The red colors and larger spheres denote a higher occurrence probability of the molecules.
**Figure 10.** The preferential positions of the anions around the cation for DMSO-[EMIM]$^+$[DCA]$^-$ and water-[EMIM]$^+$[DCA]$^-$ mixtures at different solute concentrations as denoted by the legends on the left. The red colors and larger spheres denote a higher occurrence probability of the molecules.

**Figure 11.** The partial charge distribution in the molecules. The dipole moments are shown as arrows on each molecule.
C7 atoms in [EMIM]^+ are treated similarly, though there is a slight difference between those due to the asymmetric shape of [EMIM]^+. Our simulation results reveal the similar trend to the result from ref. [81]. Our results also reveal an increasing trend of average hydrogen bonds with respect to the DMSO concentration. However, as discussed already, the anion-cation interaction is strengthened by adding DMSO. Therefore, we conclude that the attachment of DMSO to the cations via hydrogen bonds does not weaken the anion-cation interaction. This can also be inferred from Figure 2, in which the Lennard-Jones contribution is much higher than the Coulomb contribution in the cation-DMSO interaction. This trend is based on the large size of the cation and DMSO. Finally, as can be inferred from Figures 7, 8, 10, and 9, the structural change around each molecule in DMSO-[EMIM]^+[DCA]− mixtures with respect to the solute concentration is negligible.

### 4. Conclusion and Summary

In this work, we have studied bulk DMSO-[EMIM]^+[DCA]− mixtures and water-[EMIM]^+[DCA]− mixtures using MD simulations. The influence of different DMSO/water concentrations on the structuring of the IL molecules has been investigated. The DMSO mixtures and water mixtures show distinct differences in the accumulation behavior of their molecules. In order to elucidate these differences, we have proposed the definition of effective interaction energies between the different species in the IL mixtures. These allowed us to provide important insight into the preferential energies related to different pairs of the species in the mixtures, as well as the preferential orientation and positioning of the species around other types of species. Our results reveal that in DMSO mixtures the cation-anion interactions increase with respect to the DMSO concentration, but decrease in water mixtures. This can be justified by the fact that the cation-anion pairs are weaker bonded in water mixtures at high water concentrations and stronger bonded in DMSO mixtures even at high DMSO concentrations. These differences can be explained by the higher electronegativity and chemical hardness of water than DMSO, which leads to the strong interaction of water with [DCA]− disturbing the cation-anion interaction. This cation-anion pair interaction rationalizes the accumulation behavior of the species in the solution mixtures. In DMSO mixtures, the interaction between cation-anion pairs is stronger than the DMSO-DMSO interaction.

Our results highlight the fact that the charge distributions of the molecules play an important role in the interaction between the species in IL-solute mixtures. In principle, the solute molecules, which have a high electronegativity like water, interact strongly with ions containing highly charged atoms (in our case [DCA]−). On the other hand, the solute molecules, which have a low electronegativity interact weakly with the charged particles leading to a weak influence on the ionic pair. Accordingly, in order to maintain an optimum interaction between ions, a proper choice is the combination of the solute molecules with low electronegativity such as DMSO. For practical applications requiring the persistence of ion pairs having a weak interaction with solute molecules, solutes with low electronegativity are appropriate. These results serve an optimum tuning of IL-solute mixtures for selected applications.

### Acknowledgements

The authors greatly acknowledge financial support from Deutsche Forschungsgemeinschaft DFG (grant number 35823783 – SFB 1333, subproject C6). T.K. also thanks the Physics Department of the University of Stuttgart for funding.

Open access funding enabled and organized by Projekt DEAL.

### Conflict of Interest

The authors declare no conflict of interest.

### Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

### Keywords

hydrogen bonds, interaction energy, ionic liquids, molecular dynamics simulations, solvent effects

Received: March 29, 2021
Published online: May 5, 2021

---

1. K. R. Seddon, A. Stark, M.-J. Torres, Pure Appl. Chem. 2000, 72, 2275.
2. R. D. Rogers, K. R. Seddon, Science 2003, 302, 792.
3. J. D. Holbrey, W. M. Reichert, S. K. Spear, R. P. Swatloski, M. B. Turner, A. E. Visser, Selection of Ionic Liquids for Green Chemical Applications, ACS Symposium Series, Vol. 836, ACS, Washington, DC 2003.
4. R. Hayes, G. G. Warr, R. Atkin, Chem. Rev. 2015, 115, 6357.
5. C. Reichardt, T. Welton, Solvents and Solvent Effects in Organic Chemistry, John Wiley & Sons, New York 2011.
6. P. Wasserscheid, E. T. Welton, Ionic Liquids in Synthesis, 2nd ed., Vol. 1, Wiley-VCH, Weinheim, Germany 2008.
7. H. Weingärtner, Angew. Chem. Int. Ed. 2008, 47, 654.
8. V. Lesch, A. Heuer, C. Holm, J. Smiatek, Phys. Chem. Chem. Phys. 2015, 17, 8480.
9. V. Lesch, A. Heuer, C. Holm, J. Smiatek, ChemPhysChem 2016, 17, 387.
