Aqueous solutions of ionic liquids: microscopic assembly

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Aqueous solutions of ionic liquids are of special interest, due to the distinctive properties of ionic liquids, in particular, their amphiphilic character. A better understanding of the structure–property relationships of such systems is hence desirable. One of the crucial molecular-level interactions that influences the macroscopic behavior is hydrogen bonding. In this work, we conduct molecular dynamic simulations to investigate the effects of ionic liquids on the hydrogen-bond network of water in dilute aqueous solutions of ionic liquids with various combinations of cations and anions. Calculations are performed for imidazolium-based cations with alkyl chains of different lengths and for a variety of anions, namely, [Br]⁻, [NO₃]⁻, [SCN]⁻, [BF₄]⁻, [PF₆]⁻, and [Tf₂N]⁻. The structure of water and the water–ionic liquid interactions involved in the formation of a heterogeneous network are analyzed by using radial distribution functions and hydrogen-bond statistics. To this end, we employ the geometric criterion of the hydrogen-bond definition and it is shown that the structure of water is sensitive to the amount of ionic liquid and to the anion type. In particular, [SCN]⁻ and [Tf₂N]⁻ were found to be the most hydrophilic and hydrophobic anions, respectively. Conversely, the cation chain length did not influence the results.

1. Introduction

Room-temperature ionic liquids (RTILs) are molten salts composed of large organic cations and smaller organic or inorganic anions. Their inherent attractive physical and chemical properties make them potentially useful for a wide range of chemical and industrial applications.¹⁻² Amongst other properties, the melting point, viscosity, and density can be adjusted by varying the chemical structures of the component ions. This designer character is an advantage, as ILs can be tailored to suit the requirements of a particular process.³⁻⁶ Miscibility is another important property of ILs that changes with their structure. In addition to the interactions that exist in conventional organic solvents (hydrogen bonding, dipole–dipole, and van der Waals interactions), ILs have ionic interactions that make them very miscible with polar substances. Overall, the anion controls their water solubility, but the length of the alkyl chains of the cations is also important, owing to the hydrophobic nature of these chains. At the same time, the presence of alkyl chains determines the solubility in less polar fluids.

The behavior of ILs mixed with polar solvents is of great interest from both a fundamental and industrial viewpoint, due to their amphiphilic character. Especially intriguing are aqueous solutions of ILs, the thermodynamic properties and microscopic assembly of which have been studied considerably.⁵⁻²⁶

Despite these efforts, a deeper and more quantitative understanding of the molecular-level structure is still needed. Indeed, there is even controversy with similar simpler systems; it is generally assumed that ions dissolved in liquid water have a strong effect on the hydrogen-bond structure,²⁷⁻²⁸ however, Omta et al. reported that they had an negligible effect.²⁹ In this context, molecular simulation (MS) techniques represent a useful alternative to experiments, as MS allows the detailed exploration of molecular arrangements in fluids. Here, we present a comprehensive computational study of the influence of low concentrations of ILs on the H-bonding network of water, and of the water–IL interactions. In particular, we performed molecular dynamics (MD) simulations for dilute water/IL systems for a variety of anion types and imidazolium-based cations with a range of alkyl-chain lengths; the role of these factors was thus examined. The set of considered IL ion pairs is depicted in Figure 1. We used previously validated atomistic descriptions and intermolecular interactions. H-bond formation in water and the water–IL interactions were analyzed through radial distribution functions (RDFs; $g(r)$) and H-bond statistics.
which were determined by employing the geometric criterion of the H-bond definition.

2. Results and Discussion

The analysis of RDFs aids our understanding of the microscopic behavior of the water/ILs mixtures by providing information on the average intermolecular distances and the presence of H bonds. The atoms selected for the RDF calculations are specified in the Computational Details. Figures 2 and 3 display the RDFs corresponding to the anion–cation, anion–water, cation–water, and water–water pairs for different systems. These functions have been smoothed for clarity (see Figure S1 in the Supporting Information for the raw data). Figure 2 shows the effect of the anion type on the previously mentioned pairwise interactions for water/IL mixtures containing 16 IL ion pairs and 500 water molecules (approximately 1 M aqueous solution) with [C10MIM]^+ as the cation and a range of different anion types to investigate the effect of the anion type. The reference atoms for these RDFs are described in the Computational Details.

Figure 2. RDFs for a) cation–anion, b) anion–water, c) cation–water, and d) water–water pairs for mixtures of 16 IL ion pairs mixed with 500 water molecules (about 1 M) with [C10MIM]^+ as the cation and a range of different anion types to investigate the effect of the anion type. The reference atoms for these RDFs are described in the Computational Details.

Water interacts strongest with the H atom linked to the C atom located between the N atoms (H1), with the first RDF peak located below 2.6 Å. This finding is well-understood, as the proton on the C atom between the two N atoms is known to have more positive charge, and is in agreement with the literature. The interactions with the H atoms of the methyl group and the other H atoms of the imidazolium ring are rather weaker (first RDF peak is greater than 2.8 Å), but more significant than with those of the alkyl chain (hydrophobic nature), which are omitted. The characteristic extrema of water–water g_oo(r) (the subscripts denote the involved atoms) remain virtually unchanged in relation to those of bulk water, regardless of the anion type (Figure 2d). The same is observed for RDFs corresponding to the anion–cation, anion–water, cation–water, and water–water pairs for different systems. These functions have been smoothed for clarity (see Figure S1 in the Supporting Information for the raw data). Figure 2 shows the effect of the anion type on the previously mentioned pairwise interactions for water/IL mixtures containing 16 IL ion pairs and 500 water molecules (approximately 1 M aqueous solution) with [C10MIM]^+ as the cation and a range of different anion types to investigate the effect of the anion type. In general, it is present at about 5 Å, but the first peak for [SCN]^- is located at distances larger than 6 Å, thus indicating a weak cation–anion interaction. As apparent from Figure 2b, the influence of the anion type is even more prominent when it interacts with water. [SCN]^- is the most hydrophilic anion by far and the corresponding RDF exhibits a narrow peak at distances lower than 3 Å, suggesting strong ordering of water around this anion. This result is consistent with anion–cation interactions. These functions show noticeable first peaks followed by one or two more maxima of diminishing amplitude. According to the first hydration shells, we can predict the following order of increasing hydrophobicity of the selected anions: [SCN]^- < [NO_3]^-, [BF_4]^-, [PF_6]^-. We do not include [Br]^- in the sequence, as size can be a misleading factor; we will discuss this issue below. In addition, water ordering has also been observed around the imidazolium rings of the cations (Figure 2c), but to a lesser extent. The water–cation interaction is hardly influenced by the type of anion, as the position of the first peak is similar in all cases. To obtain a deeper understanding of water–cation interactions, Figure 4 shows the RDFs between the O atom of water and the H atoms of the cation head for [Br]^-. Water interacts strongest with the H atom linked to the C atom located between the N atoms (H1), with the first RDF peak located below 2.6 Å. This finding is well-understood, as the proton on the C atom between the two N atoms is known to have more positive charge, and is in agreement with the literature. The interactions with the H atoms of the methyl group and the other H atoms of the imidazolium ring are rather weaker (first RDF peak is greater than 2.8 Å), but more significant than with those of the alkyl chain (hydrophobic nature), which are omitted. The characteristic extrema of water–water g_oo(r) (the subscripts denote the involved atoms) remain virtually unchanged in relation to those of bulk water, regardless of the anion type (Figure 2d). The same is observed...
for $g_{\text{CO}}(r)$ (see Figure S2 in the Supporting Information). The positions of the first peaks and following minima are approximately 2.8 and 3.6 Å for $g_{\text{CO}}(r)$, and at 1.8 and 2.4 Å for $g_{\text{CO}}(r)$. This is a clear indication of stable H bonding. Finally, RDFSs corresponding to cation–cation pairs are included in the Supporting Information (Figure S3) and reveal weak interactions. The RDFSs in Figure 3 allow us to evaluate the effect on the pairwise interactions of the cation chain length (by comparing the center and the bottom plots) and of the amount of IL ion pairs (by comparing the top and the bottom plots) for a fixed anion type, in particular $[\text{TF}_2\text{N}]^-$. In a large cation the positive charge is more dispersed, and thus, the cation–anion and cation–water interactions are expected to be weaker. However, slight changes were observed when increasing the chain length from four to ten C atoms. The influence of the concentration is also almost negligible. Overall, at these IL concentrations water–water interactions unquestionably predominate.

As the RDFs corresponding to water–water interactions in the systems under study are almost identical to those of bulk water, regardless of the type of anion, IL concentration, and length of the alkyl chain of the cation, we employed the widely used distance–angle definition for H bonding in bulk water. A H bond is considered to exist between a pair of molecules if: 1) The respective O atoms are separated by less than 3.6 Å. 2) The O atom of the acceptor molecule and the H atom of the donor are separated by less than 2.4 Å. 3) The $\alpha$ angle is less than a threshold value, usually 30°, to account for linear H bonds. Following this criterion, the H-bond statistics of water in various solutions were computed. The calculations indicated that virtually all molecules are associated; only about one percent of molecules are monomers. The degree of association in terms of the average number of H bonds per molecule ($n_{\text{HB}}$) is characterized in Figure 5. Figure 5a shows the $n_{\text{HB}}$ values of water in bulk and in mixtures with ILS to evaluate the behavior of this variable as a function of the IL concentration (bottom x axis) and of the cation alkyl-chain length (top x axis). A slight weakening of the H-bonded network of water is observed in the dilute mixtures with ILS in relation to the bulk ($n_{\text{HB}} = 3.18$). The results are clearly more sensitive to the amount of IL than to the cation alkyl-chain length, which suggests that interactions with anions break more H bonds than the steric effects caused by the presence of long cation chains. The $n_{\text{HB}}$ value is almost the same as that of bulk water for the system with one IL ion pair and about 2.8 for that with 16 IL ion pairs. The average potential energy between the water molecules shows identical behavior (see Figure S4 in the Supporting Information), thus supporting these findings. The structure–energy relationship is also in agreement with these results, demonstrating the reliability of the procedure and the results. Figure 5b allows one to observe the effect of the anion type in the various mixtures. The lowest $n_{\text{HB}}$ values for water are obtained for solutions with $[\text{SCN}]^-$, and the highest values for those with $[\text{TF}_2\text{N}]^-$ and $[\text{PF}_6]^-$ This is in agreement with the previous comments on the degree of hydrophobicity. Notably, when there are 16 IL ion pairs in the system, the effect of increasing the chain length of the cations is likewise non-negligible. Finally, Figure S5 in the Supporting Information shows the $n_{\text{HB}}$ values as a function of the simulation time; the low fluctuations with respect to the mean values indicate that these are representative.

To gain an insight into the H-bond network of water, we computed the H-bond populations $l_i$ (percentages of water molecules involved in $i$ H bonds). The results for various sys-
tems containing $\text{Tf}_2\text{N}^-$ are displayed in Figure 6. Those for the remaining studied anions can be found in Table S1 in the Supporting Information. The highest percentages correspond to water molecules engaged in three H bonds, which represent about forty percent of the molecules, regardless of the considered mixture; this value is almost the same as that for the bulk. However, the fraction of molecules with four H bonds considerably decreases with respect to the bulk in favor of molecules with 1 and 2 H bonds ($f_1$ and mainly $f_2$). This variation is more prominent with increasing numbers of IL molecules, but is not sensitive to the length of the alkyl chain of the cation. Thus, even at low concentrations, the presence of ILs prevents the formation of the tetrahedral H-bond network of water. Likewise, we evaluated the distribution of the water-cluster size in the aqueous solutions of ILs (Figure 7). Small aggregates are the most probable, but the formation of extended H-bond networks composed of almost all water molecules is apparent from the figures. The complexity of this clustering is more affected by the amount of ILs than by the chain length or the anion type.

Next, we focused on water–anion interactions. We calculated the average minimum distances from the O atoms of the water molecules to the atoms of the anions that are more susceptible to interactions with the water molecules. The results are provided in Table 1 for mixtures with the highest studied IL concentrations and different ion combinations. These results again reveal that $\text{Tf}_2\text{N}^-$ and $\text{SCN}^-$ are the most hydrophobic and hydrophilic, respectively, of the studied anions. It is worth noting that the distances for the $\text{SCN}^-$ anion were particularly small, especially for the N atom, with values of approximately 2 Å; this suggests H-bond formation with water molecules. In contrast, distances from the water O atoms to the F atoms in $\text{BF}_4^-$ and $\text{PF}_6^-$ are short, as well as those to O atoms in $\text{NO}_3^-$. The longest distance is observed for Br\(^-\), which seems to conflict with the reported RDFs (Figure 2), this is consequence of considering the central atoms of the anions for the RDF calculations. The values in Table 1 correspond to the atoms of each anion that interact with the most with the water molecules. The reported minimum distances are hardly affected by the cation alkyl-chain length, however considerable changes are seen upon changing the type of anion.

Figure 8 displays the degree of anion hydration as a function of the distance between the water molecules and the anion, for mixtures with 16 IL ion pairs with cations with C\(_4\) or C\(_{10}\) chains and all the considered anions. More specifically, it shows the average number of neighboring water molecules for distances of less than 4, between 4 and 6.5 Å, and greater than 6.5 Å to the anion. The values for short distances represent the average water coordination of the anions. The lowest percentages in this range correspond to mixtures containing

**Table 1.** Average minimum anion–water distances for different aqueous solutions of ILs concerning anion type and cation chain length (IL concentration of about 1 m: 16 IL ion pairs).

<table>
<thead>
<tr>
<th>Anion</th>
<th>Atom</th>
<th>[C4MIM](^+)</th>
<th>[C10MIM](^+)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{BF}_4^-$</td>
<td>F</td>
<td>2.56</td>
<td>2.56</td>
</tr>
<tr>
<td>Br(^-)</td>
<td>Br</td>
<td>3.15</td>
<td>3.14</td>
</tr>
<tr>
<td>$\text{NO}_3^-$</td>
<td>O</td>
<td>2.57</td>
<td>2.57</td>
</tr>
<tr>
<td></td>
<td>N</td>
<td>3.02</td>
<td>3.01</td>
</tr>
<tr>
<td>$\text{PF}_6^-$</td>
<td>F</td>
<td>2.64</td>
<td>2.64</td>
</tr>
<tr>
<td>$\text{SCN}^-$</td>
<td>S</td>
<td>2.05</td>
<td>2.05</td>
</tr>
<tr>
<td></td>
<td>N</td>
<td>1.96</td>
<td>1.96</td>
</tr>
<tr>
<td>$\text{Tf}_2\text{N}^-$</td>
<td>F</td>
<td>2.71</td>
<td>2.73</td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>2.66</td>
<td>2.66</td>
</tr>
<tr>
<td></td>
<td>N</td>
<td>3.10</td>
<td>3.11</td>
</tr>
</tbody>
</table>
[Br]– as anion, and the highest to mixtures with either [SCN]– or [Tf₂N]–. These results show the importance of the interacting forces and also of the size of the anions for anion hydration. Most water molecules are located in the intermediate distance range for the different systems except for the most hydrophilic [SCN]– and hydrophobic [Tf₂N]– anions, for which the outstanding percentages of water molecules correspond to the shortest and furthest distances, respectively, from the anion.

Molecular graphics rendered using Materials Studio software are included to illustrate and further understand the above findings. Figure 9 shows representative snapshots from the simulations of the water/IL mixtures with 16 IL ion pairs with cations with C₁₀ alkyl chains and different anions. [Tf₂N]– anions move towards the cations, whereas [SCN]– is not only embedded in the aqueous solution, but also forms H bonds with water molecules, as previously mentioned. A snapshot of the formation of this cross molecule H bonding is depicted in Figure S6 in the Supporting Information. The opposite occurs in the mixture with [Tf₂N]– anion. Clear IL clustering and IL/water phase separation is observed, which supports the results of Figure 8. This is confirmed through calculations of the density profile (Figure S7 in the Supporting Information). This behavior is in agreement with previously reported works[18] and thus allows separation of mixtures involving water.[24] [Br]– anions are completely dissolved in water, despite not strongly interacting with water molecules (Table 1). This makes ILs containing this type of anion useful for colloidal applications.[25–26] The remaining considered ILs exhibit similar behaviors, which is consistent with the reported quantitative results.

3. Conclusions

A detailed study of the structure of water containing low concentrations of ILs, for ILs with a variety of anion types and with cations having a range of alkyl-chain lengths, by using molecular dynamics simulations with validated atomistic descriptions and intermolecular interactions was presented. Overall, water molecules remain highly H bonded, but a loss of the tetrahedral ordering that is typical in bulk water is observed. In particular, the fraction of molecules with four H bonds considerably decreases with respect to the bulk in favor of molecules with 1 and 2 H bonds. While the H-bond network of water weakens with increasing number of IL molecules, the influence of the cation alkyl-chain length is negligible. This suggests that anion–water interactions destroy H bonding in water more than the steric effects caused by the long alkyl chains of the cations. All or a portion of the anions are observed to be embedded in water, depending on their degree of hydrophobicity. Among the studied anions, [SCN]– and [Tf₂N]– were the most hydrophilic and hydrophobic, respectively. The former strongly interacts with water even leading to H-bond formation, whereas ion clustering and IL/water phase separation is observed for the solutions with [Tf₂N]– as the anion.
Computational Details

We considered 1–16 IL ion pairs mixed with 500 water molecules, with imidazolium-based cations with alkyl chains having from 2 to 10 C atoms and the following set of anions: bis(trifluoromethyl)sulfonylimide ([Tf2N]−), thiocyanate ([SCN]−), nitrate ([NO3]−), hexafluorophosphate ([PF6]−), tetrafluoroborate ([BF4]−), and bromide ([Br]−). For these systems, we conducted MD simulations using the RASPA code.[22] The initial configurations for the systems were generated by randomly placing the ILs and water molecules in a cubic box of 30 Å length. We used a time step of 1 fs. First, we performed NPT simulations for 1 ns to relax the system close to their equilibrium density. We fixed the temperature T and pressure p using a Nose–Hoover thermostat[13–16] and a Martyna–Tuckerman–Tobias–Klein barostat,[19] respectively. These simulations equilibrate over time; the total energy and cell volume fluctuate around a mean value. Then, we executed the production runs for 1 million steps (1 ns) in the NVT ensemble.

We evaluated the interactions using a classical force field including Lennard–Jones and coulombic terms for water and IL molecules. Water molecules were assumed to be rigid, whereas the intramolecular interactions of the ILs were described by harmonic bonds, bends, and dihedral angles according to Equation (1). The force-field parameters for the cations were taken from the reports of Canongia Lopes et al.[24] ([C4MIM]−), Kelkar and Maginn,[25] ([Tf2N]−), Yan et al.[26] ([NO3]−), Cadena et al.[27] ([PF6]−), Liu et al.[28] ([BF4]−), Chaumont and Wipff,[29] ([SCN]−), and Markovich et al.[30] ([Br]−). All the intermolecular force-field parameters are collated in Table S2 in the Supporting Information. Water was defined using the five-site TIPSP/Ew model.[31] Standard Lorentz–Berthelot combining rules were used to calculate the cross Lennard–Jones potential parameters. The Lennard–Jones cut-off radius was set to 12 Å. Periodic boundary conditions were employed in the three dimensions. Electrostatic interactions were computed using the Ewald summation technique,[31–33] whereas no tail corrections were applied for van der Waals interactions [Eq. (1)].

\[
\Phi_{\text{extra}} = \sum_{\text{bonds}} k_b (r - r_0)^2 + \sum_{\text{angles}} k_\alpha (\theta - \theta_0)^2 + \sum_{\text{dihedrals}} \left( \frac{1}{2} k_\phi [1 + \cos(n\phi)] \right)
\]  

(1)

For computation of the RDFS, we used the following criterion regarding the atom selection: We considered the O atom for water, the central atom of each anion, and the N atom of the imidazolium ring linked to the alkyl chain for the cation. The central atom coincides with the center of mass (and with the centroid of charge) due to symmetry for all the anions except for [SCN]−, the center of mass of which is slightly shifted towards the S atom. We assumed the central C atom for these calculations as a good approximation.

The definition of H-bond formation between water molecules involves the application of rigorous criteria. Here, the H-bond network of water in each system has been analyzed in terms of the relative configuration of two water molecules, that is, using the geometric criterion of H-bond formation. Specifically, the interaction between two water molecules is defined as a H bond for which the interatomic separations rOω and rOω are lower than certain cut-off values, which are given by the respective average distances of the first minimum location in the gOω(r) and gOω(θ) RDFS, and limitation of the angle ω between intermolecular O–O and covalent O–H vectors, where H forms the H bond, is fulfilled.

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