

A Simulation Study of Water–Dialkylimidazolium Ionic Liquid Mixtures

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Molecular dynamics simulations of mixtures of 1,3-dialkyl imidazolium ionic liquids and water have been performed in order to investigate the microscopic physical properties as a function of composition. The behavior of two ionic liquids has been compared, namely 1,3-dimethylimidazolium chloride and 1,3-dimethylimidazolium hexafluorophosphate. The hexafluorophosphate ionic liquids are known to be more hydrophobic as solvents than the corresponding chloride liquids. This is manifested in our simulations by differences in the signs of both the excess volumes and the enthalpies of mixing. However, there is surprisingly little difference in the microscopic properties. In both liquids, water molecules tend to be isolated from each other in mixtures with more ions than water molecules. When the molar proportion of water molecules reaches 75%, a percolating network of waters is found as well as some isolated molecules and small clusters. In all cases, molecular motion becomes faster as the proportion of water increases, although there are some differences in the details of the translational and rotational motion.

1. Introduction

Room temperature ionic liquids are solvents with many potential applications, as they have vanishingly low vapor pressures and can be recycled after use in organic reactions. Many types of chemical reaction can be carried out successfully in these solvents, and solvent recovery and the workup of products often depends on their relative solubility in different phases.^{1–4} Due to their ease of preparation, 1,3-dialkylimidazolium ionic liquids are popular as solvents. These are liquids containing substituted imidazolium cations and various anions. The imidazolium cation consists of a five-membered aromatic ring containing two nonadjacent nitrogen atoms; in different ionic liquids these carry alkyl groups of varying lengths. The properties of these liquids vary from being completely miscible with water (hydrophilic) to liquids which are immiscible with water (hydrophobic). In general, the hydrophobicity increases with the length of the alkyl side chain and is higher for larger anions such as $[\text{PF}_6]^-$ than for small ones such as Cl^- .⁵ The hydrophilic/hydrophobic behavior is important for the solvation properties of the liquids as it is necessary to dissolve reactants, but is also relevant to the recovery of products by solvent extraction. Extensive data are available on the miscibility of alkylimidazolium ionic liquids with water.^{6,7} This depends on the anion, the length of the alkyl chain, and the temperature. PF_6^- liquids dissolve less water than BF_4^- salts while chloride salts are miscible. The solubility of water increases with increasing temperature and with decreasing length of the alkyl side chain. It has also been found that ethanol enhances the solubility of water in alkylimidazolium ionic liquids, with a large range of total miscibility in the triangular phase diagrams.⁸ The solubility of water is an important factor for the industrial use of ionic liquids as green solvents. For example, one potential problem with ionic liquids is the possible pathway into the environment through wastewater.⁶ The water content of mixtures may also affect the rates and selectivity of reactions. For example, the products of the oxidation of toluene by dioxygen

in the presence of palladium change from benzaldehyde for low water contents to benzoic acid at high water contents (78 mol %) in $[\text{bmim}][\text{BF}_4]$.⁹ As water is a product of the reaction the ionic liquid must be dried every few cycles.

In this study we have simulated mixtures of water with two ionic liquids, 1,3-dimethylimidazolium chloride ($[\text{dmim}]\text{Cl}$) and 1,3-dimethylimidazolium hexafluorophosphate ($[\text{dmim}][\text{PF}_6]$). In general, chloride ionic liquids are miscible with water, while $[\text{PF}_6]^-$ ones are less hydrophilic. We find that the microscopic structural and dynamic properties of mixtures of these liquids with water are very similar, showing that the difference between hydrophilic and hydrophobic behavior is not reflected in very different behavior at the molecular level.

2. Technical Details

The models for the molecules of the ionic liquid were described in our earlier work,¹⁰ the $[\text{dmim}]^+$ cation being treated as a rigid, ten-site body with united methyl groups. The intermolecular potential consists of Buckingham-type interactions between atomic sites and coulomb interactions between the partial charges on these sites. Likewise, the Cl^- ion has a single site and a charge of $-e$ and the $[\text{PF}_6]^-$ anion is modeled as a rigid body with seven sites each containing partial charges and short-range Buckingham-potentials. For water, the well-known SPC/E-model developed by Berendsen¹¹ was used. The water–ionic liquid potential was the same as used in our earlier work on dilute solutions.^{12,13} Classical molecular dynamics simulations were performed with a modified version of the program DL_POLY¹⁴ in a NVT-ensemble at 400 K (127 °C) using the Berendsen thermostat and simple-cubic periodic boundary conditions. The long-range electrostatic interactions were computed by the Ewald summation. The time step used was 2 fs. The mixtures investigated had mole fractions of water $m = 0, 0.05\%, 25\%, 50\%, 75\%$, and 99.5%, and the numbers of molecules used in each simulation depended on the mixture and are given in Table 1. Note that the mole fraction m is computed treating the cation and anion as a single unit. The starting configurations for each mixture were obtained by

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TABLE 1: System Sizes for Different Runs

	mole % water (<i>m</i>)						
	0	0.5	25	50	75	99.5	100
molecule numbers							
[dmim] = [X]	192	192	192	192	192	1	
water		1	64	192	576	256	256
[dmim]Cl:							
system size/Å	33.1	33.1	33.7	34.8	37.9	20.46	20.3
density/kg dm ⁻³	1.18	1.18	1.17	1.15	1.10	0.92	0.91
[dmim][PF ₆]:							
system size/Å	37.25	37.25	37.78	38.75	41.4	20.51	20.3
density/kg dm ⁻³	1.49	1.49	1.47	1.42	1.33	0.93	0.91

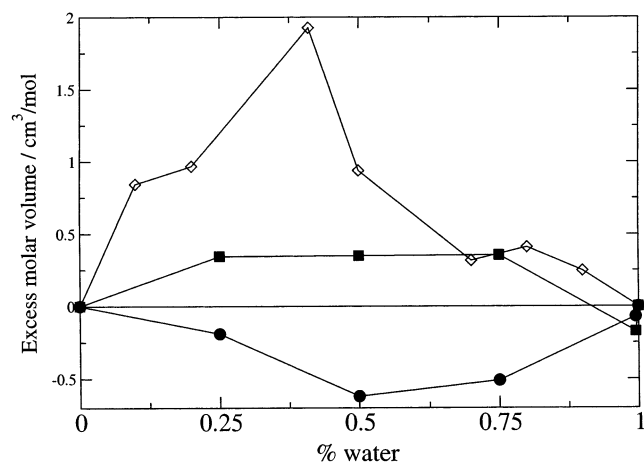


Figure 1. Excess molar volumes of the different mixtures. The square symbols are simulation results for [dmim][PF₆] and the circles for [dmim]Cl. Experimental data for a similar system, [bmim][BF₄] have been included for comparison (open diamonds).

expanding a configuration of the neat ionic liquid and inserting water molecules at random positions. Then extensive equilibration runs were performed, gradually adjusting the cell size to reduce the pressure to zero. Once the magnitude of the pressure was lower than 0.1 kbar, another equilibration run of 200 ps followed. After this procedure, several production runs with typical simulation times of 100 ps were carried out.

3. Static Properties

3.1. Excess Molar Quantities. The nonideality of the mixtures can be measured through the excess thermodynamic properties. We measured the excess volume of mixing and the excess energy of mixing of the mixtures. Figure 1 shows the excess molar volume V_m^{XS} as a function of the mole fraction of water. The first thing to note is the positive deviation for [dmim][PF₆] and the negative deviation for [dmim]Cl. Although there are no experimental data for these specific liquids, Torres¹⁵ has measured the excess volume of mixing for [bmim][BF₄] (1-butyl,3-methylimidazolium tetrafluoroborate) at $T \approx 360$ K, and her data are shown for comparison. The excess volumes of mixing are small compared to the molar volumes of the pure components, which are (in units of cm³ mol⁻¹ or 10⁻⁶ m³ mol⁻¹) 19.7 for water, 113.8 for [dmim]Cl, and 162.1 for [dmim][PF₆]. Although in principle the partial molar volumes of the components in any mixture could be found from the intercepts of the tangent to these curves with the axes, the accuracy is not sufficient to obtain reliable values.

In a liquid phase the enthalpy and energies of mixing are almost identical so that one can equate H_m^{XS} with U_m^{XS} . Figure 2 shows the excess molar energies of mixing, U_m^{XS} , of the different mixtures. The chloride liquid shows a negative excess while

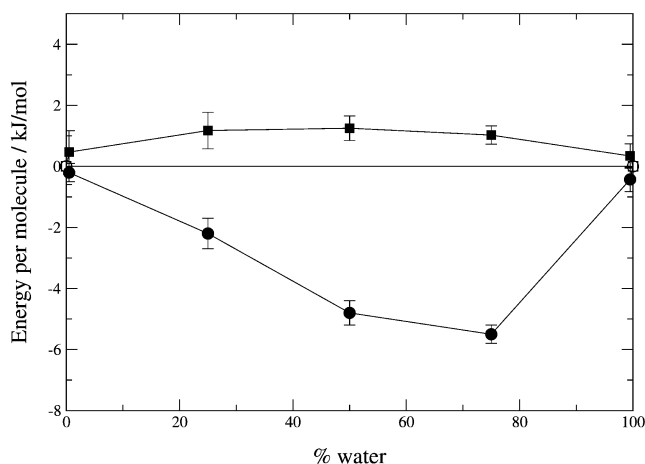


Figure 2. Excess energies of mixing for water with [dmim][PF₆] and [dmim]Cl. The square symbols are simulation results for [dmim][PF₆] and the circles for [dmim]Cl.

the [PF₆] liquid shows a positive excess (the same deviation as for the excess volumes). However, in both liquids the values of the excess quantities are less than 3% of the total value. The negative excess energy of mixing shows that the interactions are more attractive in water–chloride mixtures than in the pure components. Similarly, the interactions must be weaker in the water–PF₆⁻ mixtures than in the pure components. Whether or not the system will separate into two phases depends on the free energy of mixing. If the curvature of the molar free energy of mixing with respect to mole fraction changes sign, then phase separation would occur. It is not easy to obtain the entropy of mixing from simulations, and we have not done so. However, the entropic contribution can be divided into ideal and nonideal parts,

$$F_{\text{mix}} = U_m^{XS} + kT[f \ln f + (1 - f) \ln(1 - f)] - kTS_{\text{mix}}^{XS} \quad (1)$$

where the term in square brackets depending on the fraction f of water is the contribution from the ideal entropy of mixing and $-kTS_{\text{mix}}^{XS}$ is the nonideal entropic contribution. f differs from the mole fraction m . It is the ratio of the number of water molecules to the sum of the numbers of water molecules, cations, and anions, while m is the ratio of the number of water molecules to the sum of the numbers of water molecules and cations. As the contribution of the ideal entropy of mixing to the free energy is always negative, the total entropic contribution is unlikely to be positive, so that it is unlikely that any solution with a negative enthalpy (or energy) of mixing will show phase separation. Therefore our results suggest that our model of [dmim]Cl will always mix with water, but that [dmim][PF₆] may show phase separation at lower temperatures. This is in line with the experimental observations that chloride ionic liquids are more hydrophilic than [PF₆] ones,⁵ although our model of the [dmim][PF₆] may be miscible with water at lower temperatures than the real liquid.

3.2. Network Formation and Microscopic Structure. We studied network and cluster formation in the mixtures by monitoring the size of clusters of connected water molecules. For the purposes of this, we have defined two water molecules to be connected when the distance between the oxygen atoms is less than 3.5 Å, which is the position of the first minimum in the O–O radial distribution function of spc/e water. Molecules closer than this distance lie within the first shell and are normally hydrogen-bonded to each other. Hydrogen bonds can be defined by geometric or energetic criteria (or a mixture),¹⁶ but in any

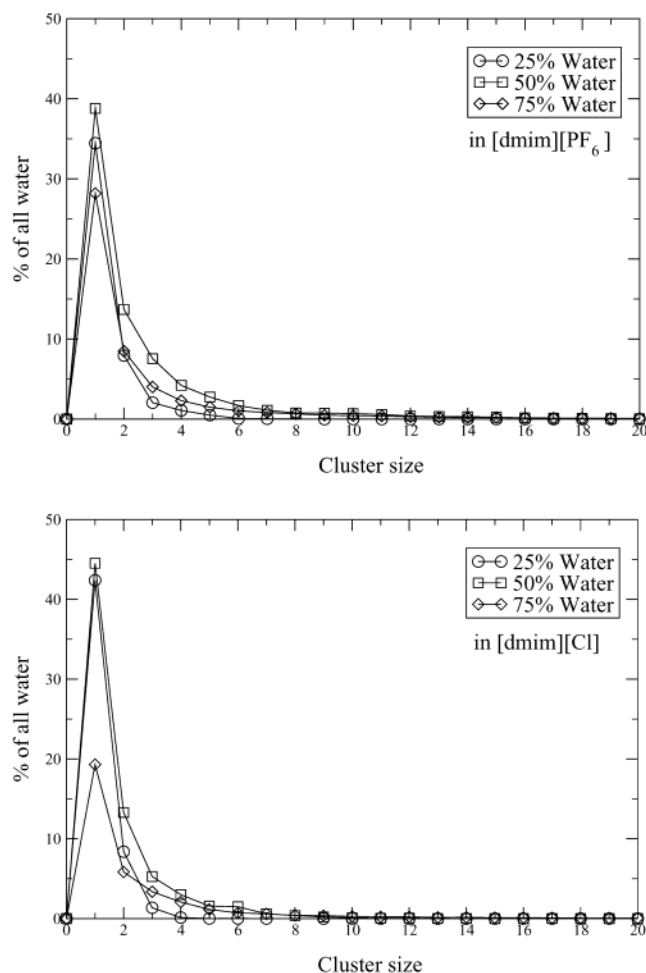


Figure 3. The size distribution of water clusters in mixtures of the two ionic liquids with water. The percentage of water molecules in clusters of different sizes is plotted against the cluster size. Above: [dmim][PF₆]-water mixture; below: [dmim]Cl-water mixtures. Although the two distributions are very similar, the PF₆-water mixtures tend to have slightly larger clusters at 50% water. In the 75% water case, more than 50% of all the water is part of an extended network, which is not displayed in diagrams above.

definition water molecules which are separated by more than 3.5 Å are not hydrogen-bonded to each other. A cluster is defined by molecules which are mutually connected, while a network is formed when a cluster is large enough to percolate from one cell to its image. Figure 3 shows the probabilities of finding small clusters of water molecules in the mixtures. In solutions with $m \leq 50\%$, there are no large clusters and 35–40% of the water molecules are completely isolated from each other. Even in the mixture with three water molecules per pair of ions ($m = 75\%$), between 20% and 30% of the water molecules are isolated from other water molecules. However, in this mixture there is also a network of water molecules which percolates throughout the sample (not shown in this figure). The percolating network fluctuates in size, with the most probable population in the [PF₆] ionic liquid containing approximately 75% of the water molecules, while in the chloride ionic liquid the most probable population is 80–85%. The finding that many water molecules are isolated from each other is in agreement with the conclusions of Welton and co-workers¹⁷ from infrared spectroscopy. It is a consequence of the strong interaction with the anions that we demonstrated in our earlier study of dilute solutions.¹² For example, in dilute solutions of water in [dmim]Cl, each water molecule is strongly hydrogen-bonded

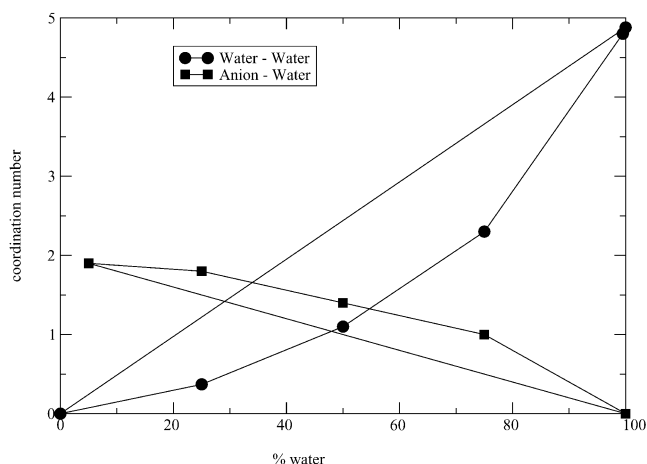


Figure 4. Coordination numbers of anions and water around water molecules in mixtures of [dmim]Cl and water. Note that there are more chlorides and fewer water molecules than in a random mixture (straight lines). The [dmim]PF₆ mixtures show the same tendency.

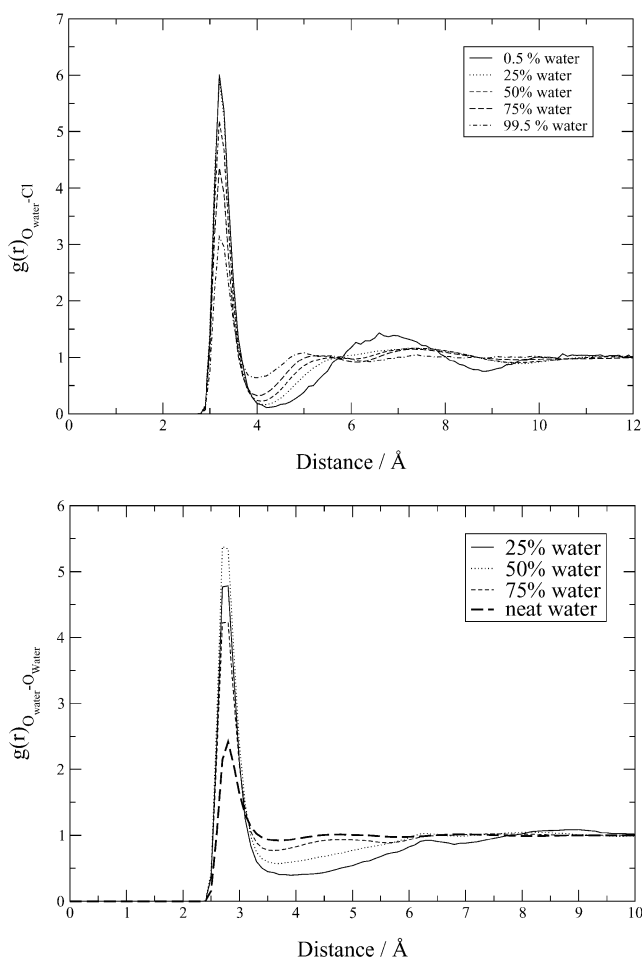


Figure 5. Radial distribution functions of chloride (above) and water (below) relative to a water molecule in [dmim]Cl-water mixtures. The water molecule site is on the oxygen atom. Note that the height of the first peak increases and the region just beyond the first peak decreases as the proportion of water decreases. This is consistent with the increase in proportion of small clusters shown in Figure 3.

to two chloride ions effectively forming the negatively charged species $[O(HCl)_2]^{2-}$.

Figure 4 illustrates this preference for water molecules to hydrogen-bond to the anions rather than to other water molecules. It shows the coordination numbers for water

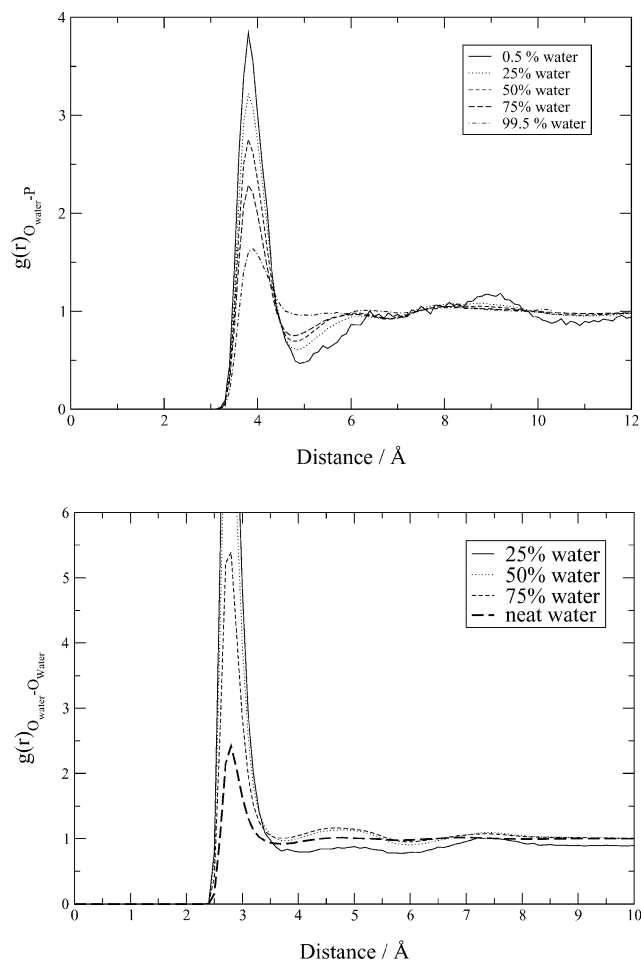


Figure 6. Radial distribution functions of anions (above) and water (below) relative to a water molecule in [dmim][PF₆]-water mixtures. The water molecule site is on the oxygen atom. The behavior of the water-anion distribution is similar to the [dmim]Cl-water mixtures.

molecules and anions around a water molecule as a function of composition. Clearly, there are fewer water molecules and more anions than would be expected from a simple linear correlation with composition. Although this graph has been plotted for data for [dmim]Cl, the data for [dmim][PF₆] mixtures are identical within the errors.

Figure 5 shows the radial distribution functions for water relative to both other water molecules and to anions in different mixtures of [dmim]Cl and water. The main changes with composition are (1) that the first peaks are sharper and higher in the mixtures with less water, and (2) that the region beyond the first peak gradually fills as the percentage of water increases. There is also a quantitative change in the position of the second peak in the anion-O radial distribution function in the most dilute solution. The changes in the more hydrophobic liquid mixtures ([dmim][PF₆]) are very similar and are shown in Figure 6. To interpret the changes in the anion-water radial distribution function, it is helpful to remember that the function represents both O relative to Cl (or P) and Cl (or P) relative to O. In mixtures that have a high proportion of water, it is easiest to think of the distribution relative to an anion. The growth of the second peak near 5 Å for Cl (or at 6 Å for the larger [PF₆] ion) is due to the establishment of a second shell of water molecules around the anion. In solutions with less water, this does not occur as most of the water molecules are isolated from each other. Thus there is a growing deficit of waters in this region as the mole fraction of water increases. Taking the other point

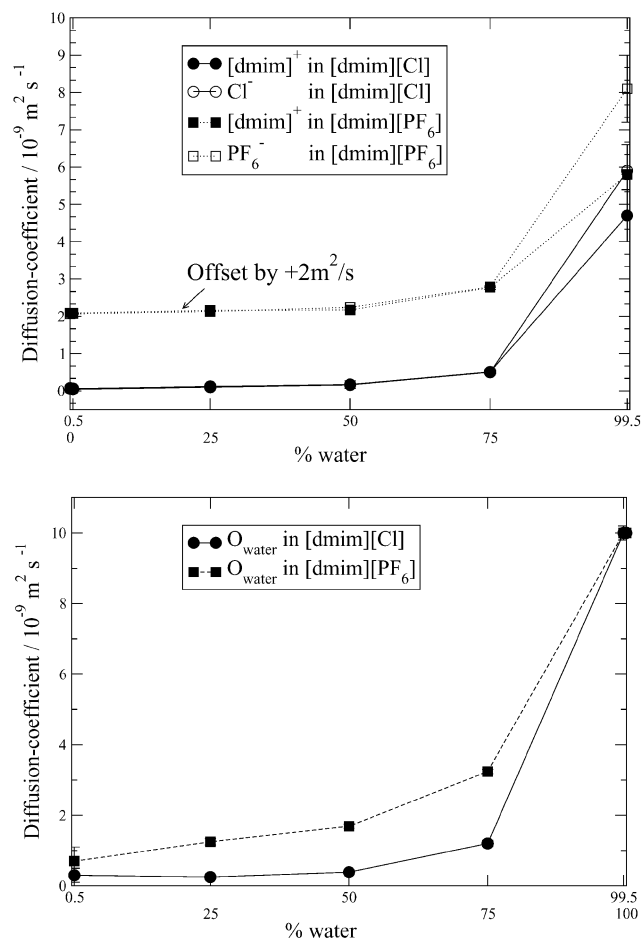


Figure 7. Self-diffusion coefficients of the different species as a function of composition. Above: ions; below: water molecules. Note that the diffusion of both cations and anions remains very low (upper diagram) until the water content is greater than 75%, while the water molecules diffuse faster in [dmim][PF₆]-water mixtures than in [dmim]Cl-water mixtures (lower diagram).

of view of the distribution of ions relative to a water molecule, one sees that the position of the second shell of anions relative to the water molecule is determined more by the water-anion-cation-anion and water-cation-anion interactions rather than the water-water-anion interaction as *m* decreases. However these functions contain no information about the relative orientation of molecules of different types. In the mixtures with few water molecules, the first peak represents anions which are hydrogen-bonded to a water, while other anions are found beyond 5 Å from the water molecule.

The distribution functions for water relative to water in the lower part of Figure 5 show the buildup of probability of water molecules in the region between 4 and 5 Å as the number of water clusters, and eventually the network, builds up as the mole fraction of water increases in [dmim]Cl mixtures. Thus mixtures with low fractions of water have a deficit of both chloride ions and water molecules in this region. The changes in the water-water distribution functions in the [dmim][PF₆] ionic liquids are less marked in this region.

4. Dynamics as a Function of Composition

Figure 7 shows the translational self-diffusion constants of both ions and water molecules as a function of composition. In general the diffusion constants increase as the proportion of water increases. This is expected as the energies of interaction

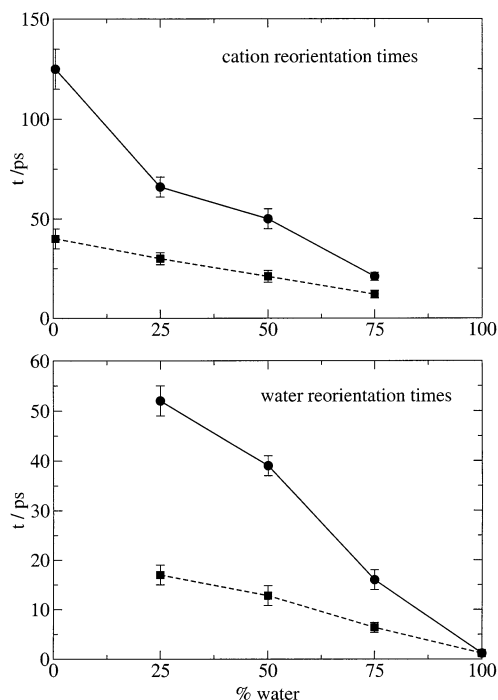


Figure 8. Reorientational times τ_1 of the dipole axes of [dmim]⁺ ions (above) and water molecules (below) as a function of composition. The square symbols are simulation results for [dmim][PF₆] and the circles for [dmim]Cl.

between water and the ions of the ionic liquids are smaller than those between the ions themselves. The ions (shown in the upper part of the figure) move very slowly even in mixtures with 75% water, and the diffusion constants are the same within the error bars for both anions and cations except in the very dilute solutions. The diffusion of the water molecules (shown in the lower part of figure) is more sensitive to both the composition of the mixture and the nature of the anion. Even at the lowest concentrations of water the diffusion constants of the water molecules are twice as large in the [PF₆][−] solutions as in the chloride solutions, and the increase with m is considerably more rapid in the [PF₆][−] solutions. This is due to the fact that the water molecules bind more strongly to the chloride ion than to the hexafluorophosphate. Experimentally there are few measurements of diffusion coefficients. Viscosity, however, is frequently measured and is found to be sensitive to the proportion of water in some ionic liquids.^{5,7} Our work suggests that the viscosity is likely to be more sensitive to the proportion of water in ionic liquids with anions which interact less strongly with water.

In addition to the translational diffusion, the reorientational motion is of interest, since this can be measured experimentally using NMR and infrared spectroscopy. The accessible quantities are the correlation times τ_c for the Legendre polynomials $P_\ell(\cos \alpha(t))$ which can be measured in the simulation from the asymptotic decay at long times:¹⁸

$$\langle P_\ell(\cos \alpha(t)) \rangle = A e^{-t/\tau_\ell} \quad (2)$$

where $\alpha(t)$ is the angle between a specified body fixed axis at time 0 and at time t . Figure 8 shows the reorientation times τ_1 for the dipole axes of [dmim]⁺ (above) and water (below) as a function of composition. The reorientation rates increase as the water content increases. In contrast to the translational diffusion rates, there is a marked difference between the chloride and [PF₆][−] liquids and a smoother change of correlation times with composition. Both anions and water molecules rotate more

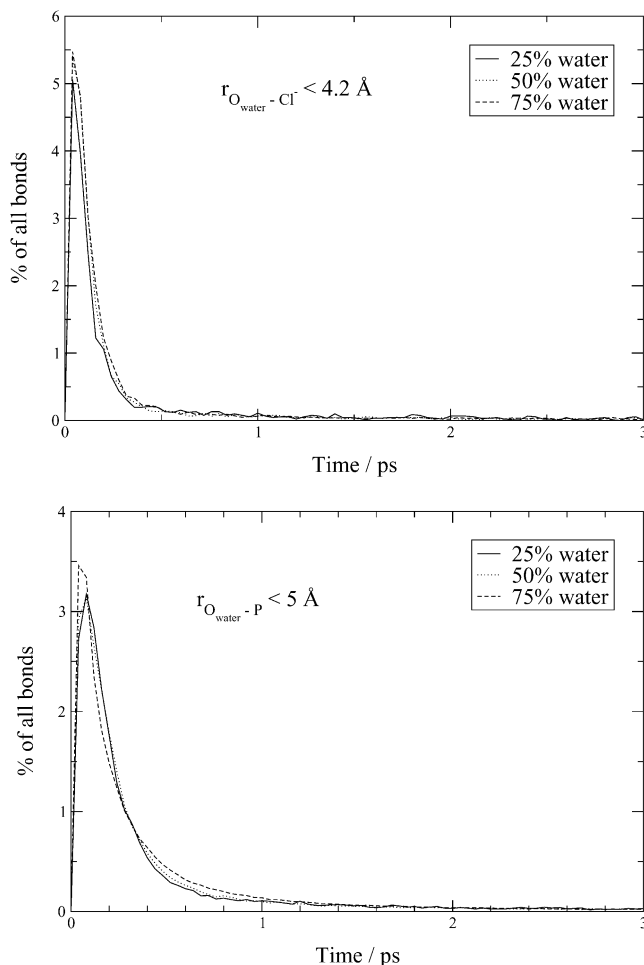


Figure 9. Lifetimes of hydrogen bonds between the anions and water molecules. Above: [dmim]Cl–water mixtures; below: [dmim][PF₆]–water mixtures.

slowly in the chloride liquid than in the [PF₆][−] liquid by factors of two or more.

The distribution of lifetimes of hydrogen bonds between water and the respective anion is shown in Figure 9 for the different mixtures. For this analysis, hydrogen bonds are defined solely by the distance between the oxygen and the Cl or P site on the anion of the ionic liquid being less than a critical value. The lifetime is defined as the time between the formation and breaking of a bond. If a bond is broken, and then reformed again, it is counted as a new bond. The distribution of lifetimes shown is found to be nonexponential, which is in agreement with previous studies of hydrogen bonds in neat water.¹⁹ Surprisingly the lifetimes of the bonds to the chloride ions are shorter than those to the [PF₆][−], but this may be partly due to the larger volume of the first shell of water in the latter case.

5. Conclusions

The analysis of both the local structure and the dynamics of the mixtures reveal that at low concentrations water molecules are isolated or exist in small independent clusters. At high water concentrations, a continuous water network appears which changes the mixture and its properties dramatically.

Some properties, such as the excess thermodynamic functions, the reorientational correlation times, and the water diffusion coefficients differ significantly between mixtures containing water and either the hydrophilic chloride or the hydrophobic [PF₆][−] ionic liquids, while others, such as the radial distribution

functions and the ion diffusion correlation times, are very similar in the two classes of ionic liquids and seem insensitive to the hydrophilicity of the ionic liquid. However it should be remembered that the excess thermodynamics quantities are direct measurements of the deviation from ideality and the magnitudes found are small, while changes in the radial distribution functions are more difficult to see.

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References and Notes

- (1) Seddon, K. R. *J. Chem. Technol. Biotechnol.* **1997**, 68, 351.
- (2) Wasserscheid, P.; Keim, W. *Angew. Chem.* **2000**, 39, 3772.
- (3) *Ionic Liquids in Synthesis*; Wasserscheid, P., Welton, T., Eds.; Wiley-VCH: New York, 2003.
- (4) Dupont, J.; de Souza, R. F.; Suarez, P. A. Z. *Chem. Rev.* **2002**, 102, 3667.
- (5) Seddon, K. R.; Stark, A.; Torres, M. J. *Pure Appl. Chem.* **2000**, 72, 2275.
- (6) Anthony, J. L.; Maginn, E.; Brennecke, J. F. *J. Phys. Chem. B* **2001**, 105, 10942.
- (7) Huddleston, J. G.; Visser, A. E.; Reichert, W. M.; Willauer, H. D.; Broker, G. A.; Rogers, R. D. *Green Chem.* **2001**, 3, 156.
- (8) Swatloski, R. P.; Visser, A. E.; Reichert, W. M.; Broker, G. A.; Farina, L. M.; Holbrey, J. D.; Rogers, R. D. *Green Chem.* **2002**, 4, 81.
- (9) Seddon, K. R.; Stark, A. *Green Chem.* **2002**, 4, 119.
- (10) Hanke, C. G.; Price, S. L.; Lynden-Bell, R. M. *Mol. Phys.* **2001**, 99, 801.
- (11) Berendsen, H. J. C.; Grigera, J. R.; Straatsma, T. P. *J. Phys. Chem.* **1987**, 91, 6269.
- (12) Hanke, C. G.; Atamas, N.; Lynden-Bell, R. M. *Green Chem.* **2002**, 4, 107.
- (13) Lynden-Bell, R. M.; Atamas, N. A.; Vasilyuk, A.; Hanke, C. G. *Mol. Phys.* **2002**, 100, 3225.
- (14) Forester T. R.; Smith W. 1995, http://www.dl.ac.uk/TCS/Software/DL_POLY/(Warrington: CCLRC, Daresbury Laboratory).
- (15) Torres, M. J. Ph.D. Thesis, QUB, 2001.
- (16) Bergman, D. L. *Chem. Phys.* **2000**, 253, 267.
- (17) Cammarata, L.; Kazarian, S. G.; Salter, P. A.; Welton, T. *Phys. Chem. Chem. Phys.* **2001**, 3, 5192.
- (18) Rothschild, W. G. *Dynamics of Molecular Liquids*; Wiley-Interscience: New York, 1984; Chapter 2.
- (19) Luzar, A.; Chandler, D. *Nature* **1996**, 379, 55.
- (20) de Andrade, J.; Boes, E. S.; Stassen, H. *J. Phys. Chem. B* **2002**, 106, 3546.