Nonpolar, Polar, and Associating Solutes in Ionic Liquids

José N. Canongia Lopes,* Margarida F. Costa Gomes, and Agílio A. H. Pádua*

*Laboratoire de Thermodynamique des Solutions et des Polymères, Université Blaise Pascal Clermont-Ferrand/
CNRS, France, and Centro de Química Estrutural, Lisboa, Portugal/Instituto de Tecnologia Química e
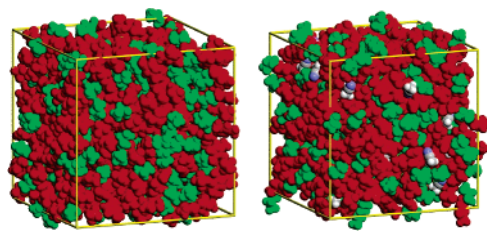Bioquímica, Oeiras, Portugal*

The existence of microphase segregation between polar and nonpolar domains in ionic liquids changes the way in which solvation can be understood in these media. Here, we perform a structural analysis on the solvation of nonpolar, polar, and associating solutes in imidazolium-based ionic liquids, where this novel way of understanding their nature as microsegregated solvents is correlated with their ability to interact with different species in diverse and complex ways.

Ionic liquids are important to chemists for two reasons: their vapor pressure is negligible at room temperature,[1] hence their status as green solvents, and depending on their ions, they can act as sophisticated solvation or reaction media (designer solvents).[2] Ionic liquids can dissolve a wide range of polar or nonpolar, organic or inorganic molecules, providing new paths to carry out chemical reactions or industrial separations.

It was recently reported in different molecular simulation studies[3–5] that ionic liquids exhibit medium-range ordering; that is, there are persistent microscopic domains in the liquid phase. Other simulation studies on the microscopic dynamics of ionic liquids have also pointed out their slow dynamics and the persistence of local environments, typical of the glassy state.[6] Several pieces of experimental evidence can also be related to these heterogeneities.[7] These include thermophysical properties such as viscosity, diffusion, and electrical conductivity[8] and spectroscopic data from fluorescence experiments.[9,10]

The segregation of polar and nonpolar domains in imidazolium-based ionic liquids with alkyl side chains of intermediate length[5] (Figure 1) changes the way in which solvation can be understood in these liquids. Here, we report a molecular simulation structural study on the solvation of nonpolar, polar, and associating solutes, where this novel way of understanding ionic liquids—their nature as microsegregated media—is correlated with their ability to interact with different species in diverse and complex ways.

Solutes and the ionic liquid were represented by explicit atom force fields.[11–14] Details of the simulations were similar to those adopted for pure ionic liquids.[5] Due to the slow dynamics of this type of system, special care was taken to ensure the attainment of equilibrium conditions, including the proper diffusion of the solutes in the ionic liquid media: (i) typical equilibration and production runs were implemented for more than 1 ns; (ii) multiple re-equilibrations through the use of temperature annealing and switching off and on of the Coulomb interactions[5] were performed; and (iii) for water, simulations

* To whom correspondence should be addressed. E-mail: jnlopes@ist.utl.pt (J.N.C.L.); agilio.padua@univ-bpclermont.fr (A.A.H.P.).

Figure 1. Snapshots of simulation boxes of $[C_4mim][PF_6]$, in which atoms belonging to the charged parts of the cation (imidazolium ring) and to the anion were colored in red and atoms belonging to the nonpolar part (alkyl side chain) were colored green: (left) pure ionic liquid; (right) acetonitrile solution.

were started from configurations of the three other solutions (see below) in which solute molecules were replaced by water. These systems were re-equilibrated for 1.5 ns, and all reached the same water–ionic liquid structures.

The solutes chosen were *n*-hexane (mole fraction $x = 0.1$), acetonitrile, methanol, and water (all with $x = 0.2$) in 1-butyl-3-methylimidazolium hexafluorophosphate, $[C_4mim][PF_6]$. At 330 K, these compositions correspond to one-phase systems.[15–17]
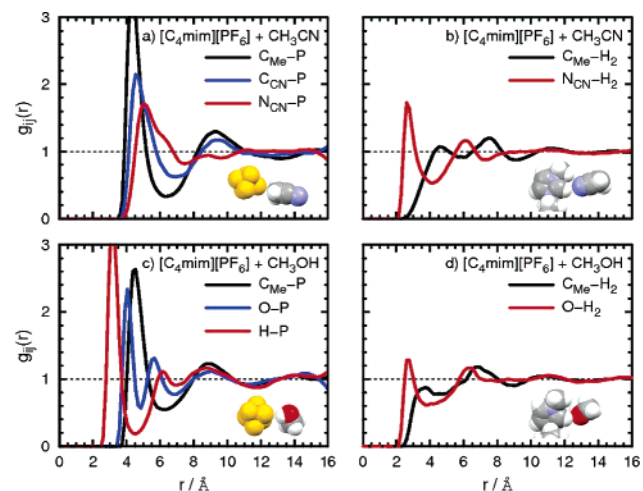
Solute–solvent radial distribution functions (rdf's) between a given solute atom and three sites on the ionic liquid are represented in Figure 2. The solvent sites are located on different regions of the ionic liquid: C_{4C}, the end carbon of the alkyl side chain, is found in the nonpolar region; H_2, connected to the imidazolium ring in the position between the nitrogen atoms, belongs to the charged part of the cation; and P is the central atom of the anion.

The relative positions of the solutes with respect to the different domains in the ionic liquid can be inferred from the comparison of the four solutions' rdf's. The two extreme situations are those of the hexane and water solutions where the solute is concentrated either in the nonpolar domain or in the charged domain (Figure 2a and d). Acetonitrile and methanol represent intermediate situations where interactions with both domains are present, although in different proportions. These facts can explain the relative solubility of the four solutes in $[C_4mim][PF_6]$ at 330 K: acetonitrile and methanol are soluble

Letters

*J. Phys. Chem. B, Vol. 110, No. 34, 2006* **16817**
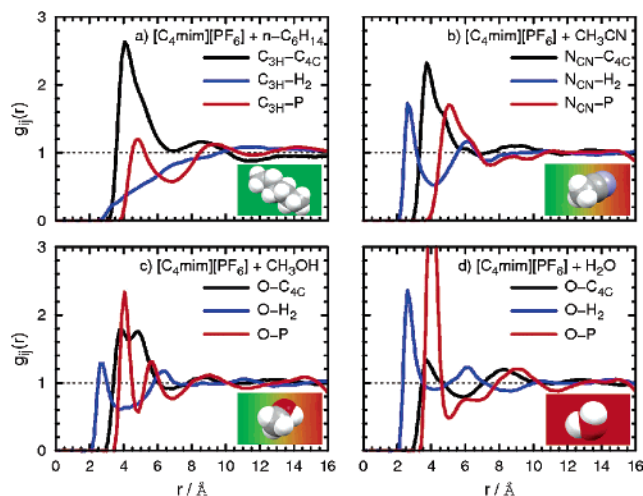
Figure 2. Solute−solvent radial distribution functions showing the position of the solutes relative to the different domains of the ionic liquid. The insets indicate schematically the preference of each solute for the nonpolar (green) or charged (red) domains (C_{3H} is a methyl carbon atom in *n*-hexane).

Figure 3. Solute−solvent radial distribution functions showing the orientation of methanol and acetonitrile relative to the anion (a and c) and the charged part of the cation (b and d) of the ionic liquid. The insets illustrate some of the most probable configurations.

in all compositions, whereas *n*-hexane and water have mole fraction solubilities of 0.11 and 0.29, respectively.[16,17]

The differences between the solutions of acetonitrile and methanol and the relative orientation of the solutes can be analyzed using the rdf's shown in Figure 3, where different sites in the solute molecule are correlated to a given site in the solvent. Figure 3a and c shows that both solutes interact strongly with the anion, with the interaction being less directional in the case of acetonitrile than in the case of methanol; compare the overlap of the rdf's in Figure 3a. In methanol, hydrogen bonding occurs between the hydroxy group and the anion's fluorine atoms, as can be seen by the sharp H−P peak at 3.2 Å followed by an O−P peak at 4.0 Å. The rdf's in Figure 3 also show that for acetonitrile the methyl group points preferentially toward the anion, whereas in methanol it points away from it. Conversely, the interactions of the hydrogen atoms of the imidazolium ring (H_2 is represented, but the situation is analogous for the other hydrogen atoms in the imidazolium ring, H_4 and H_5) are stronger with acetonitrile than with methanol (Figure 3b and d).
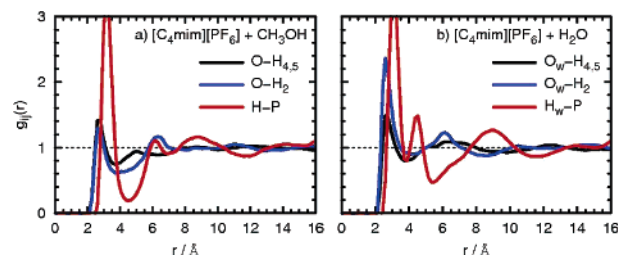
Figure 4. Solute−solvent radial distribution functions showing hydrogen bonding between methanol (a) and water (b) and the charged regions of the ionic liquid.

Methanol and water solutions are analyzed in the rdf's of Figure 4. The solute−anion interactions are very similar and are dominated by hydrogen bonding. In the case of water, the hydrogen bond signature is evidenced by the second H−P peak at 4.4 Å that corresponds to the other hydrogen atom of water, a feature that is obviously absent in methanol. Apart from the already mentioned interactions between methanol and the nonpolar regions of the ionic liquid shown in Figure 2c, the major difference between the two associating solutes is the stronger interaction between the acidic hydrogen atom H_2 of the cation and the oxygen atom of water, when compared to that of H_4 and H_5. Since water is smaller than methanol, its oxygen atom can interact more easily with the hindered H_2 atom of the cation.

The differences in relative position, orientation, and specific interactions between these four solutes (nonpolar, polar, and associating) and the different regions of the ionic liquid (nonpolar aliphatic chain, charged imidazolium ring, and anion) illustrate the complex microscopic structure of the ionic liquids.

These structural features can provide a sound molecular interpretation to a wealth of experimental results concerning the complex fluid-phase behavior of mixtures containing ionic liquids. Although data on gas solubility and liquid−liquid equilibria are available for a number of binary and a few ternary systems containing ionic liquids, the situation is still not satisfying with respect to a fundamental understanding of these properties.[18] The approach presented here can be useful in cases where competition/cooperation of the solutes for the identified domains of the ionic liquid can explain the reported effects of anti-[19] or cosolvency.[20] The same applies to the study of chemical reactivity in ionic liquids, for example, in phenomena related to the deactivation of water due to strong binding to the anion.[21]

Ionic liquids have also been used as stationary phases for gas chromatography, and separation of polar and nonpolar compounds was observed. Moreover, good resolutions are attained within each group.[22] This dual selectivity is compatible with the existence of the two types of domains predicted here. Polar and nonpolar species interact in their own way with the different parts of the ions, notably the cation. This confirms that the solvation of nonpolar, polar, or associating solutes in the ionic liquids can be very diverse, given the presence of the segregated domains.

References and Notes

(1) Earle, M. J.; Esperança J. M. S. S.; Gilea, M. A.; Canongia Lopes, J. N.; Rebelo, L. P. N.; Magee, J. W.; Seddon, K. R.; Widegren, J. A. *Nature* **2006**, *439*, 831.

(2) *Ionic Liquids in Synthesis*; Wasserscheid, P., Welton, T., Eds.; Wiley-VCH: Weinheim, Germany, 2003.

(3) Urahata, S. M.; Ribeiro, M. C. C. *J. Chem. Phys.* **2004**, *120*, 1855.

(4) Wang, Y.; Voth, G. A. *J. Am. Chem. Soc.* **2005**, *127*, 12192.

(5) Pádua, A. A. H.; Canongia Lopes, J. N. *J. Phys. Chem. B* **2006**, *110*, 3330.

(6) Hu, Z.; Margulis, C. J. *Proc. Natl. Acad. Sci.* **2006**, *103*, 831.

(7) Pádua, A. A. H.; Canongia Lopes, J. N. *ACS Symp. Ser.* **2006**, accepted.

(8) Tokuda, H.; Hayamizu, K.; Ishii, K.; Susan, M. A. B. H.; Watanabe, M. *J. Phys. Chem. B* **2005**, *109*, 6103.

(9) Mandal, P. K.; Sarkar, M.; Samanta, A. *J. Phys. Chem. A* **2004**, *108*, 9048.

(10) Paul, A.; Mandal, P. K.; Samanta, A. *J. Phys. Chem. B* **2005**, *109*, 9148.

(11) Jorgensen, W. L.; Maxwell, D. S.; Tirado-Rives, J. *J. Am. Chem. Soc.* **1996**, *118*, 11225.

(12) Price, M. L. P.; Ostrovsky, D.; Jorgensen, W. L. *J. Comput. Chem.* **2001**, *22*, 1340.

(13) Berendsen, H. J. C.; Grigera, J. R.; Straatsma, T. P. *J. Phys. Chem.* **1987**, *91*, 6269.

(14) Canongia Lopes, J. N.; Deschamps, J.; Pádua, A. A. H. *J. Phys. Chem. B* **2004**, *108*, 2038; **2004**, *108*, 11250.

(15) Zafarani-Moattar, M. T.; Shekaari, H. *J. Chem. Eng. Data* **2005**, *50*, 1694.

(16) Domanska, U.; Marciniak, A. *J. Chem. Eng. Data* **2003**, *48*, 451.

(17) Anthony, J. L.; Anderson, J. L.; Maginn, E. J.; Brennecke, J. F. *J. Phys. Chem. B* **2005**, *109*, 6366.

(18) Heintz, A. *J. Chem. Thermodyn.* **2005**, *37*, 525.

(19) Hong, G.; Jacquemin, J.; Husson, P.; Costa Gomes, M. F.; Deetlefs, M.; Nieuwenhuyzen, M.; Sheppard, O.; Hardacre, C. *Ind. Eng. Chem. Res.*, accepted, 2006.

(20) Blanchard, L. A.; Hancu, D.; Beckman, E. J.; Brennecke, J. F. *Nature* **1999**, *398*, 28.

(21) Amigues, E.; Hardacre, C.; Keane, G.; Migaud, M. E.; O'Neill, M. *Chem. Commun.* **2006**, 72.

(22) Anderson, J. L.; Armstrong, D. W. *Anal. Chem.* **2003**, *75*, 4851.