

Structure of Ionic Liquid–Benzene Mixtures

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Neutron diffraction has been used to investigate the structure of liquid mixtures of 1,3-dimethylimidazolium hexafluorophosphate with benzene. Two concentrations of benzene were investigated, namely, 33 mol % and 67 mol %, and show similar structures in each case. The presence of benzene significantly alters the ionic liquid structure, in particular, in the cation–cation interactions, in agreement with the single-crystal structure described recently (Holbrey, J. D.; Reichert, W. M.; Nieuwenhuyzen, M.; Sheppard, O.; Hardacre, C.; Rogers, R. D. *Chem. Commun.* 2003, 476). In each case, the data was analyzed using an empirical potential structure refinement process.

1. Introduction

The drive toward cleaner industrial processes has led to the emergence of ionic liquids as an alternative solvent for reactions. Ionic liquids possess low vapor pressures; therefore, they release effectively no VOCs.¹ Ionic liquids have been extensively studied for applications in, for example, clean synthesis,² electrochemistry,³ and liquid crystals,⁴ and these have recently been reviewed at length.⁵ However, there have been relatively few studies concerning the structure of the ionic liquid itself. A number of simulations have been published concerning the structure of ionic liquids.⁶ Experimentally, both X-ray diffraction and neutron diffraction have been used.^{7–12} In addition, the dynamics of a range of ionic liquids has been studied, which also gives some indication regarding ion–ion interactions.¹³

Despite the large number of reactions performed in ionic liquids, little is known about the interaction of solutes with the solvent even though these contacts can strongly affect the reaction selectivity and kinetics. A number of studies have investigated the interactions of solvatochromic dyes with a range of ionic liquids.¹⁴ Using this methodology, the hydrogen bonding contributions can be isolated, and some degree of polarity of the ionic liquid has been estimated. Lynden-Bell and co-workers have reported simulations that examine the interaction of gases and small molecules with 1,3-dimethylimidazolium chloride and hexafluorophosphate salts, [dmim]Cl and [dmim][PF₆], respectively.^{15–18} Water has been examined in detail and is reported to form small clusters at low concentrations, whereas at high concentration, a more extensive water network is observed.^{15,17} The water is also observed to hydrogen bond strongly with the anion rather than the cation. This has also been shown experimentally using vibrational spectroscopy for a wide range of anions by Cammarata et al.¹⁹ For non-hydrogen-bonding solutes such as dimethyl ether and propane, the interaction is predominantly with the cation. The interactions of benzene with [dmim]Cl and [dmim][PF₆] have also been

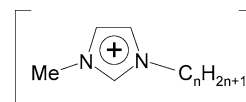


Figure 1. 1-Alkyl-3-methylimidazolium [dmim]⁺ structure, where $n = 1$ for the structure represents the [dmim]⁺ ion studied in this paper.

simulated. Comparing the interactions of charged and uncharged benzene showed the influence of the quadrupole moment.¹⁸ The interactions between the benzene and the ionic liquid were found to be much stronger when the simulation was performed with charges on the benzene atoms, illustrating the importance of electrostatics and therefore why aliphatic molecules are, in general, much less soluble in ionic liquids in comparison with aromatic molecules.

Herein, we describe neutron diffraction data obtained from benzene–[dmim][PF₆] mixtures. A schematic of the structure of the [dmim]⁺ cation is shown in Figure 1. It should be noted that [dmim]Cl could not be studied to compare with the simulations described above¹⁸ because of the very low solubility of benzene in the chloride ionic liquid. This study complements the NMR and single-crystal X-ray diffraction data recently reported for this system.²⁰ In this preliminary report, a range of ionic liquids were shown to dissolve benzene, toluene, and xylenes forming clathrate structures. In the case of [dmim][PF₆] and benzene, a crystal structure was obtained that showed the cage structure clearly. This paper provides further evidence of clathrate formation in the liquid state for two mixtures of benzene and [dmim][PF₆] at mole ratios of 2:1 and 1:2. Comparisons are made with the previously determined liquid structure of [dmim][PF₆]¹² and benzene.²¹

2. Experimental Section

Fully protiated and *d*₉-[dmim][PF₆] were prepared from the equivalent chloride salts²² by metathesis with NH₄PF₆ and ND₄PF₆, as described previously.¹² Each sample was a white crystalline solid and was analyzed by ¹H and ²H NMR, infrared and elemental analysis and showed >97% isotopic exchange. All samples were dried as liquids under high vacuum at 400 K, cooled, and stored in an N₂-filled drybox prior to

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TABLE 1: Lennard-Jones and Coulomb Parameters Used for the Reference Potential of the Simulation of Liquid Mixtures Containing Benzene and 1,3-Dimethylimidazolium Hexafluorophosphate^a

atom	$\sigma/\text{\AA}$	$\epsilon/\text{kJ mol}^{-1}$	q/e
H(2)	0.0	0.0	0.097
C(2)	3.9	0.79396	0.407
H(4,5)	0.0	0.0	0.094
C(4,5)	3.9	0.79396	0.105
N(1,3)	3.4	0.57341	-0.267
C(M)	3.9	0.79396	0.124
H(M)	0.0	0.0	0.064
P	2.2	7.177	0.740
F	2.66	0.59560	-0.290
C(benzene)	3.9	0.79396	-0.15
H(benzene)	0.0	0.0	0.15

^a The carbon and nitrogen atoms are defined as their position on the molecular skeleton with M referring to the methyl groups. The hydrogen atoms, H(*x*), are defined as being bonded to the *x* carbon atom. The Lennard-Jones parameters for interactions between unlike atoms were calculated by employing the usual Lorentz–Berthelot mixing rules.

being loaded into the sample cells. Protiated and *d*₆-benzene (Aldrich) were used as received.

The samples of benzene/[dmim][PF₆] were heated to 338 K in aluminum sample holders with 0.2-mm-thick vanadium windows sealed using a PTFE-coated Viton O-ring while in the diffraction vacuum chamber and were left for 10 min to equilibrate before measurements were taken. The temperature was maintained to $\pm 0.1^\circ$ using a Eurotherm PID temperature controller. The weight of the samples was taken before and after the measurements to ensure that no benzene had evaporated while in the vacuum chamber. After normalization with respect to the cell, spectrometer, and vanadium window, good reproducibility was found between the sample cells. The neutron diffraction data was taken using the SANDALS diffractometer at the ISIS pulsed-neutron source, Rutherford Appleton Laboratory, U.K. This instrument has a wavelength range of 0.05 to 4.5 \AA , and data is taken over the Q range of 0.05 to 50 \AA^{-1} . Throughout the text, 2:1 and 1:2 refer to the benzene/[dmim][PF₆] mole ratio. Samples containing combinations of protiated and perdeuterated [dmim][PF₆] and benzene were measured, and data analysis was performed using the ATLAS package.²³ The atomic density of the 1:2 sample was taken as 0.09 atom \AA^{-3} ²⁰ and 0.10 atom \AA^{-3} for a 2:1 sample.²⁴

The differential cross sections were fit using an empirical potential structure refinement process (EPSR) that generates configurations of molecules and ions that are consistent with the diffraction data. From these configurations, partial radial distribution functions and spatial ion density distribution are generated. The details of this method have recently been reported.²⁵ The full parameters of the reference potential used are given in Table 1.

3. Results and Discussion

Good agreement is found between the experimental and EPSR modeled differential cross sections as a function of Q for both the 2:1 and 1:2 benzene/[dmim][PF₆] liquid mixtures. The fit versus experimental data is illustrated for the 1:2 mixture in Figure 2. From the EPSR model, the partial radial distribution functions for the anion and benzene around a central imidazolium cation can be extracted, and these are shown in Figure 3 for the 2:1 mixture. It is noticeable that the radial distribution functions for both the anion and benzene are very similar. In each case, clearly defined shells of anions and benzene are formed around the cation at distances of approximately 5.0 and

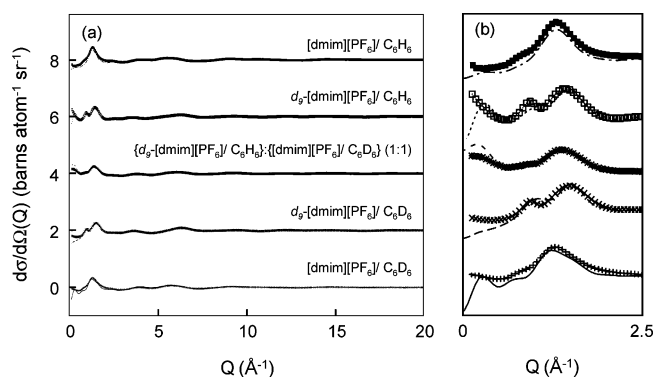


Figure 2. (a) Experimental (symbols) and EPSR fitted (line) differential cross sections as a function of Q for the 1:2 benzene/1,3-dimethylimidazolium hexafluorophosphate liquid mixture. (b) Magnified low- Q section from 0 to 2.5 \AA^{-1} .

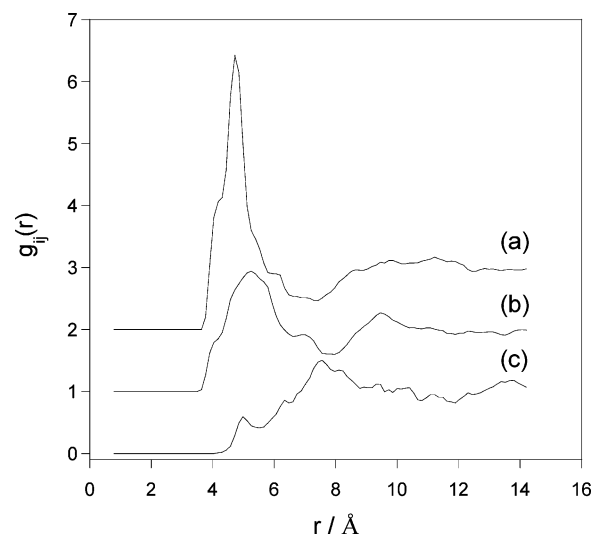


Figure 3. Comparison of the partial radial distribution functions for (a) the cation–anion distribution, (b) the cation–benzene distribution, and (c) the cation–cation distribution for the 2:1 mixture derived from the EPSR model. Each radial distribution function is calculated from the center of the imidazolium ring, from the center of the benzene molecule, and from the phosphorus atom.

9.6 \AA with the anions at a slightly shorter distance than the benzene. This is similar to that found for the [PF₆][−] radial distribution function in [dmim][PF₆] in the absence of benzene. In contrast, an expansion of the first shell is observed in the cation–cation radial distribution on the addition of benzene. In the pure ionic liquid, the cation–cation contact occurs at 6 \AA , which increases to 7.6 \AA for the 2:1 mixture. Strong ionic ordering is still observed even in the presence of benzene as found in both pure [dmim]Cl and [dmim][PF₆] ionic liquids reported previously (i.e. there is little overlap of the cation and anion features, even for the benzene-rich mixture). Similar data is observed for both the 1:2 and 2:1 mixtures.

Integrating the first-shell anion feature in the anion–cation partial radial distribution shows a decrease in the number of anions on the addition of benzene. Using a cutoff of 7.5 \AA (i.e. the minimum in the anion–cation partial radial distribution function), 6.8 anions are found without benzene present compared with 5.5 and 4.1 for the 1:2 and 2:1 mixtures, respectively. Each anion is displaced by approximately three benzenes. The number of benzenes found for the 1:2 and 2:1 mixtures using a cutoff of 8.0 \AA , corresponding to the minimum in the benzene cation partial radial distribution function, is 3.3 and 9.1, respectively. It should be noted that the anion

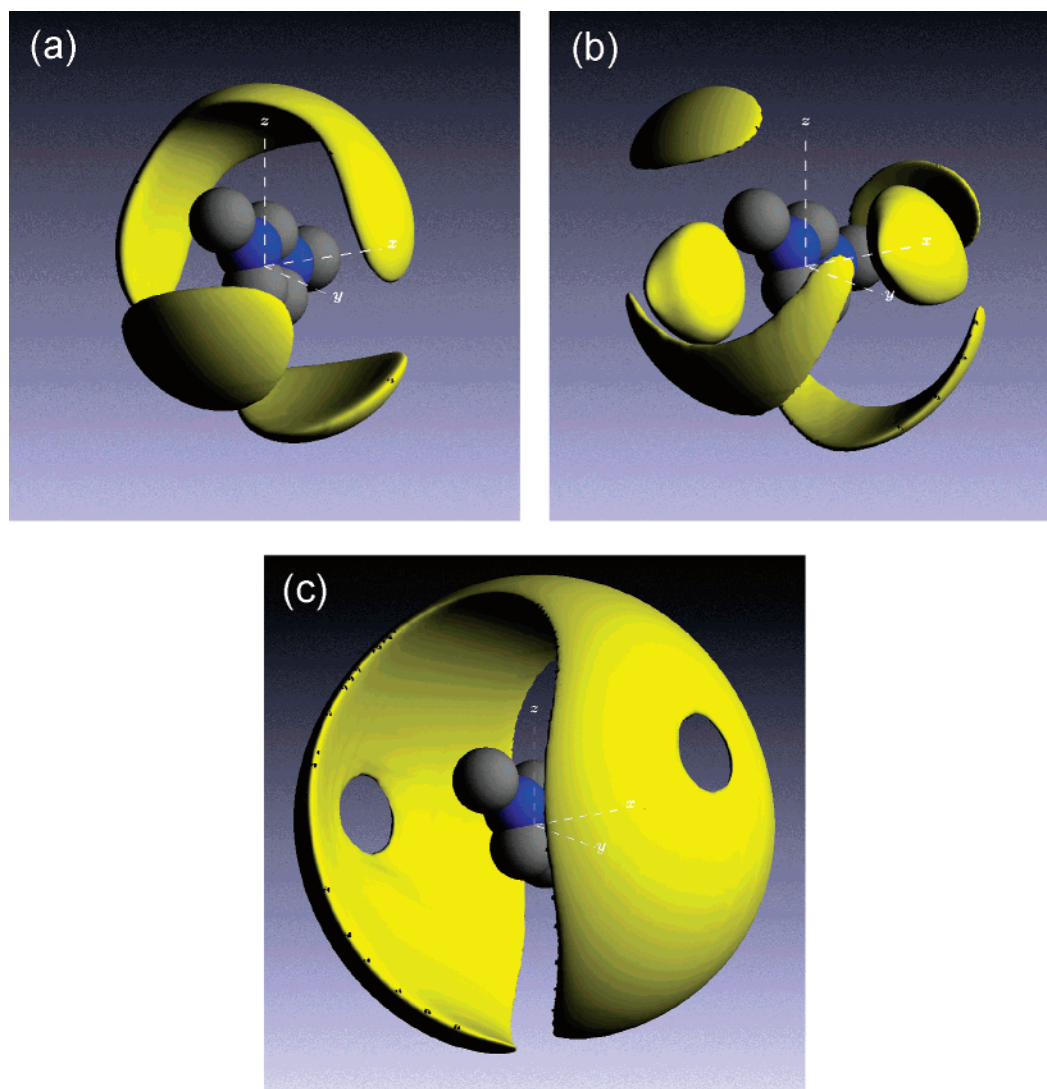


Figure 4. Probability distributions of (a) the hexafluorophosphate anion, (b) the benzene, and (c) the imidazolium cation around a central imidazolium cation in the 1:2 mixture derived from the EPSR model. In each case, the surface contours shown enclose regions where the probability density exceeds a specified value. The contour level was chosen so that the plotted surfaces enclose the top 25% of the molecules 0–8 Å from the central molecule for the anion and benzene and 0–10 Å for the cation.

coordination numbers using a cutoff of 8.0 Å are 6.4 and 4.8 for the 1:2 and 2:1 mixtures, respectively, which approximately correspond to the mole ratio of samples, as expected. This increase in the total number of molecules/ions in the first coordination shell indicates that the benzenes intercalate into the structure.

Figure 4 shows a comparison of the probability distributions for benzene, $[\text{PF}_6]^-$, and $[\text{dmim}]^+$ around the $[\text{dmim}]^+$ for the 1:2 solution; it should be noted that very similar distributions are also found for the 2:1 sample. As found for $[\text{dmim}][\text{PF}_6]$ in the absence of benzene, the anion forms a broad band around the middle of the cation ring interacting most strongly with the ring hydrogens and avoiding the methyl groups. In comparison, the benzene molecules interact with the methyl groups and the C(4,5) hydrogens, with little association with the C(2) hydrogen. Unlike the situation for the anion–cation interactions, where similar distributions were found with and without benzene, when the cation–cation probability distributions are compared, significant changes are observed. Without benzene, the cations occupy positions that are mutually exclusive to the anions; however, on addition of benzene, the cations form a similar distribution to that observed for the anion. Despite the change in the probability distribution, the cation hydrogen–cation

hydrogen contacts are similar for $[\text{dmim}][\text{PF}_6]$ and the 1:2/2:1 samples (i.e., H(M)–H(M) contacts dominate the cation interactions). Although the types of contact are similar, in the presence of benzene the contacts have shifted to longer distance, matching the increase in the cation–cation separation observed in Figure 3. In addition, the features become weaker, which is expected because the interactions will decrease at longer distances and will also be reduced by the dilution effect of benzene.

Figure 5a–d shows the probability distributions of the imidazolium cation and hexafluorophosphate anion around a central benzene molecule for the 2:1 mixture. It is clear that the cations interact strongly with the electron-rich π system and the anions reside around the ring, shown in Figure 5a and c, respectively. In the latter, the anions are found between the C–H bonds. At lower probabilities, the anions form a solid ring around the benzene, and if the second shell is examined, they then start to occupy positions above and below the plane of the benzene, shown in Figure 5d. Conversely, the second-shell cations form a ring around the benzene; however, the structure is much less well defined than for the anion distributions, with some probability density also being observed above and below the ring (Figure 5b). This structure is mimicked to some extent

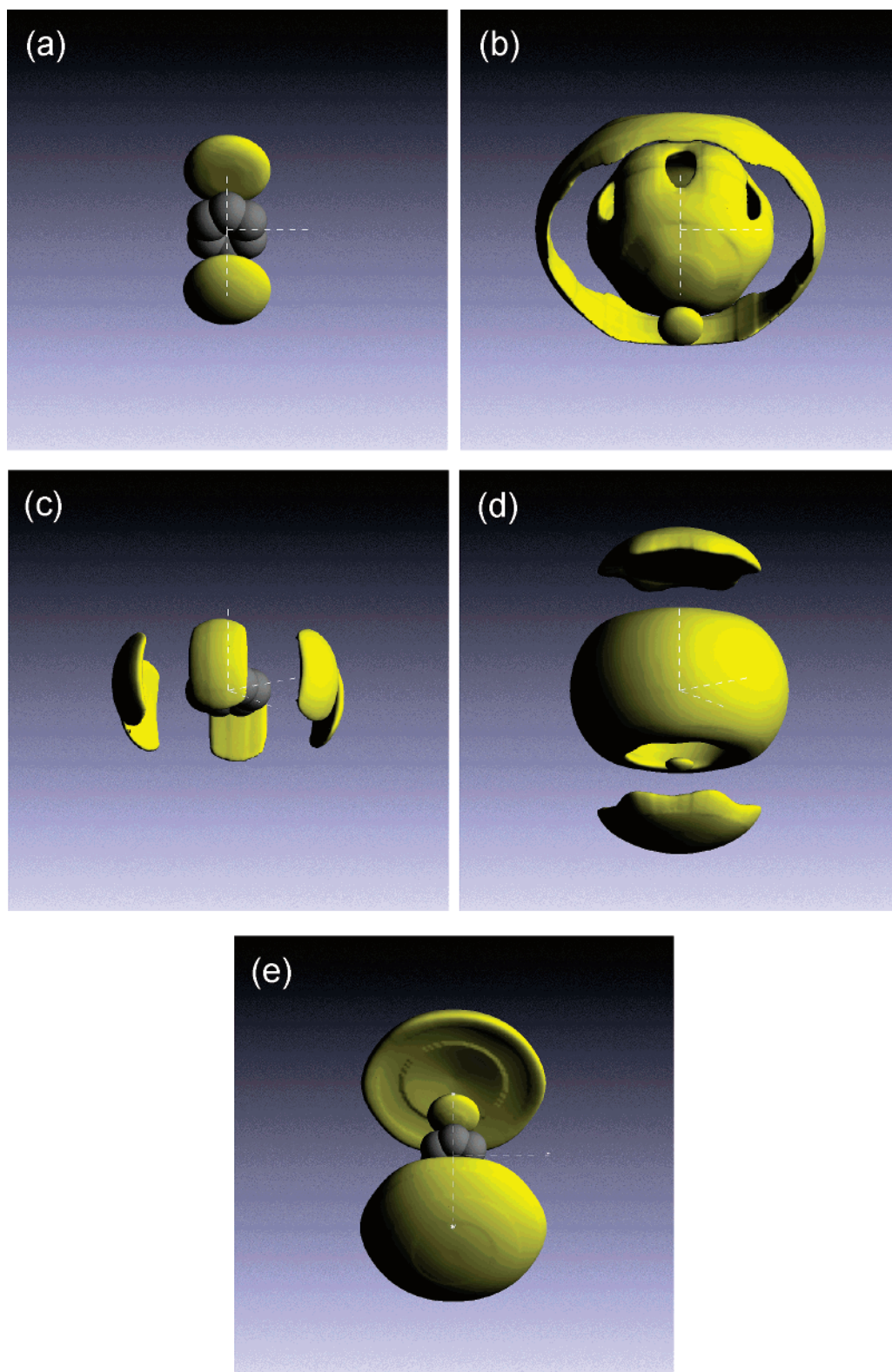


Figure 5. Probability distributions of (a and b) the imidazolium cation (2:1), (c and d) the hexafluorophosphate anion (2:1), and (e) the benzene (1:2) around a benzene molecule derived from the EPSR model. For distributions a and c, the contour level was chosen to enclose the top 5% of the molecules in the distance range of 0–8 Å, whereas for b, d, and e, the contours enclose the top 25% of molecules in the distance range of 0–12 Å.

for the 1:2 mixture, although the probability distributions are more isotropic around the central benzene molecule. This is expected because in the benzene-lean samples the structures are dominated by ion–ion interactions that reduce the effect of the ion–benzene interactions.

These distributions may be compared with the simulations performed by Lynden-Bell and co-workers.¹⁸ From the simulations, the cations were found to be closest above and below the benzene ring, whereas the anions occupied the equatorial positions, in agreement with the neutron data presented here.

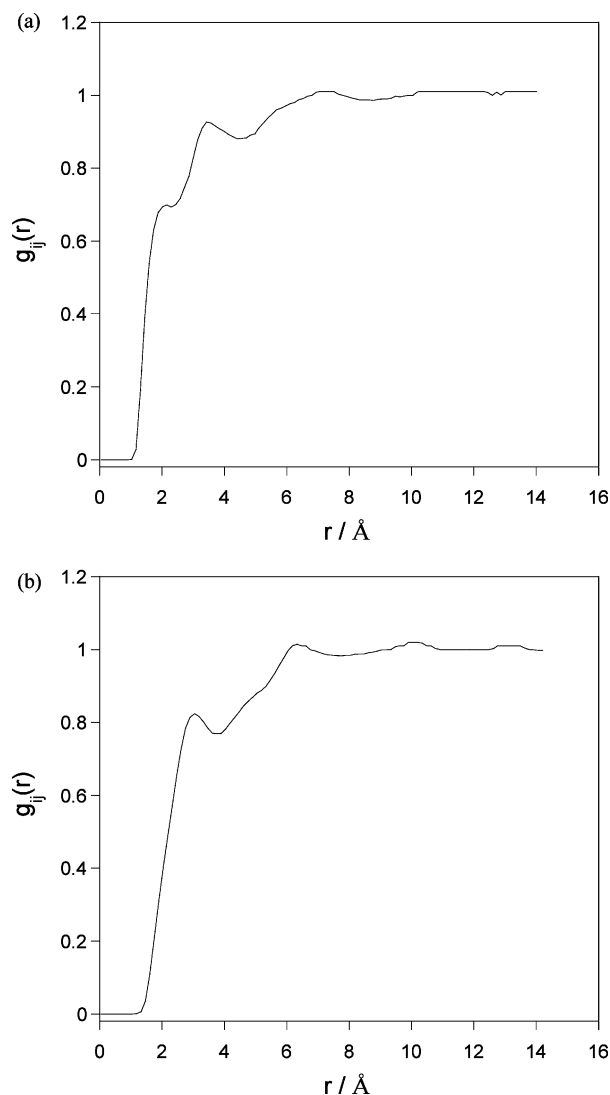


Figure 6. Partial radial distribution functions for (a) the cation methyl hydrogen–benzene hydrogen in the 1:2 mixture and (b) the benzene hydrogen–benzene hydrogen in the 2:1 mixture.

At longer distances, alternating cation–anion layers exist. Such an arrangement was consistent with the net positive charge for the ring hydrogens and net negative charge for the ring electrons. However, little change was observed for simulations containing one benzene, 33% benzene, and 67% benzene (i.e., the 2:1 and 1:2 mole ratio samples described in this paper). This is not in agreement with the neutron data, which showed only clearly defined distributions for the cations/anions where the ion–ion interactions were minimized.

The interactions between the ions and the benzene are dominated by the charge distribution around the benzene ring. However, on examination of the partial radial distribution functions for the H–H interactions between the cation and benzene, it is clear that short methyl hydrogen–benzene hydrogen interactions are present at 3.5 Å, as illustrated for the 1:2 mixture in Figure 6a. There is also some interaction with the hydrogens attached to the C(2) and C(4,5) positions on the cation, although these are much weaker.

The probability distribution for the benzene around a central benzene molecule for the 1:2 sample shows that the benzenes stack above and below the plane of the molecule. This structure is maintained even in the second benzene shell, shown in Figure 5e. However, with increasing benzene, the probability distribution of the benzene becomes more isotropically distributed

around the central molecule. In the benzene-rich samples, the benzene hydrogen–benzene hydrogen contacts become clearly observed, as shown in Figure 6b. This partial radial distribution function is similar to that found in liquid benzene reported by Cabaço et al.²¹ In liquid benzene, little orientational preference was observed for the benzene molecules, which agrees with the probability distribution observed for the benzene–benzene contacts for the 2:1 mixture. At this concentration, the mixture is a benzene solution of an ionic liquid, and the solution therefore starts to resemble liquid benzene.

For both the 1:2 and 2:1 samples, the cations show similar probability distributions around the $[\text{PF}_6]^-$ as found for the $[\text{dmim}][\text{PF}_6]$ without benzene (i.e., where the cations interact with the faces of the octahedron). The benzene distribution adopts a similar orientation to that of the cations. In each case, the ions/molecules orientate to maximize the interaction with the negatively charged fluorines and therefore increase the packing efficiency.

It is noticeable that similar probability distributions are observed for both the 2:1 and 1:2 mole ratios where the central point is an ion compared with the benzene molecule. The lack of difference for the two samples in the distributions around a central ion compared with the central benzene molecule simply reflects the strong ion–ion interactions that dominate the structure compared with the weaker quadrupolar interactions. However, these weaker interactions can result in significant changes in the structure, as shown by the major reorganization of the cation–cation probability distributions and the expansion of the liquid structure. Here these interactions compensate for the decrease in the packing efficiency of the cations, as shown by the increase in the cation–cation spacing.

Both the 2:1 and 1:2 mole ratio liquid mixtures show similarities to the crystal structure of $[\text{dmim}][\text{PF}_6] \cdot 0.5 \text{ C}_6\text{H}_6$. The crystal structure is based on channels formed by rings of alternating anions and cations, four ion pairs in total, approximately 8 Å in diameter. Within these channels, the benzene molecules are aligned parallel; however, this is due to an interaction with the cations and anions and is not due to benzene–benzene interactions because the intermolecular spacing is too long for significant interactions to be present (6.3 Å).²⁰ Despite the weak benzene–benzene interactions in the crystalline phase, it is noticeable that the benzene–benzene distribution in the solid phase, which shows interactions only above and below the ring, is still retained in the liquid phase for the benzene-lean mixture. The large change in cation distribution on adding benzene is evident with a comparison of the crystal structures of $[\text{dmim}][\text{PF}_6]$ and $[\text{dmim}][\text{PF}_6] \cdot 0.5 \text{ C}_6\text{H}_6$. As found in the liquid, short contacts are found for the cation hydrogens and the benzene hydrogens dominated by the methyl hydrogen contacts. In both the liquid and solid, these appear at approximately 3.5 Å. Methyl hydrogen– π contacts have been observed for other systems but are not often structure-defining.²⁶ These interactions are relatively weak compared with the packing energy and therefore possibly occur in the liquid only as a consequence of the increased degrees of freedom. It should be noted that, although some similarities exist between the liquid and solid state structures, the correlation is much weaker than that found previously between the crystal structure and the liquid structure for $[\text{dmim}][\text{PF}_6]$ and $[\text{dmim}]\text{Cl}$.^{11,12} This may simply reflect the increased complexity of the system.

The channels found in the crystal structure for $[\text{dmim}][\text{PF}_6] \cdot 0.5 \text{ C}_6\text{H}_6$ raise the possibility of forming a “liquid zeolite” using ionic liquids; however, with the exception that the benzene–benzene interactions show ring–ring packing for the 1:2

mixture, there is little evidence that the channels survive on melting. From a “snapshot” of the distribution of benzenes, anions, and cations in the EPSR model, a homogeneous distribution of benzenes throughout the ionic liquid is observed. This is in agreement with the benzene–benzene interactions that show only significant “liquid benzene”-like behavior in the benzene-rich samples, indicating little micelle formation. The homogeneous distribution observed shows the strength of the electrostatic interaction between the benzene and ions and explains why benzene is so soluble in this ionic liquid. This is in good agreement with the simulation results that also showed strongly negative interaction energies between the benzene and the ionic liquid.¹⁸ As postulated, presumably the reduced solubility of benzene in the chloride ionic liquid compared with the hexafluorophosphate reflects the much stronger hydrogen bonding of the anion and cation in the case of [dmim]Cl¹² that is not offset by the solvation enthalpy of the benzene.

Similar homogeneous mixtures have been proposed for water in ionic liquids where the hydrogen-bonding interaction with the ions breaks up the water–water interactions.¹⁶ This may be compared with mixtures of water in alcohols, for example, where the mixtures phase separate on a microscopic scale to form hydrophobic regions and hydrophilic regions.²⁷

Clearly, the extent of mixing of the distribution of solutes in solvents strongly depends on the relative interactions between the solute–solute and solute–solvent and can have significant consequences for chemical reactivity and stability. For example, in many ionic liquids, the hydrolytic stability of water-sensitive catalysts and chemical reactions are less sensitive to water²⁸ compared with many organic solvents because of the fact that the water is dispersed throughout the ionic liquid and cannot act like bulk water.

4. Conclusions

The addition of benzene to [dmim][PF₆] leads to an expansion of the cation–cation contacts. Around the benzene molecule, for the benzene-lean samples, alternating cation–anion layers are observed with the first-shell anions interacting with the ring hydrogens while the cations interact with the ring electrons. The incorporation of benzene is found to displace the anions with approximately three benzenes replacing each anion, suggesting benzene intercalation into the structure as found in the solid. Benzene is also found to be homogeneously distributed throughout the ionic liquid with no evidence of micellar formation.

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