

Molecular Solutes in Ionic Liquids: A Structural Perspective

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ABSTRACT

Understanding physicochemical properties of ionic liquids is important for their rational use in extractions, reactions, and other applications. Ionic liquids are not simple fluids: their ions are generally asymmetric, flexible, with delocalized electrostatic charges, and available in a wide variety. It is difficult to capture their subtle properties with models that are too simplistic. Molecular simulation using atomistic force fields, which describe structures and interactions in detail, is an excellent tool to gain insights into their liquid-state organization, how they solvate different compounds, and what molecular factors determine their properties. The identification of certain ionic liquids as self-organized phases, with aggregated nonpolar and charged domains, provides a new way to interpret the solvation and structure of their mixtures. Many advances are the result of a successful interplay between experiment and modeling, possible in this field where none of the two methodologies had a previous advance.

Introduction

Applications of ionic liquids can be numerous,^{1,2} from catalysis,³ synthesis,⁴ separations, and electrochemistry⁵ to polymers⁶ and magnetic or nanostructured materials. Chemists very rapidly explored their potential to improve or create processes and materials. Physical chemistry is an underlying aspect of much research in ionic liquids, providing the insights into the molecular factors that determine their properties. The results range from quantitative physicochemical data that are essential for engineering processes to qualitative trends that guide when searching the best ionic liquids for a particular purpose.

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However, the most important contribution is to understand how ionic liquids actually work at the molecular level: chemistry shows us *what* can be done using ionic liquids; physical chemistry can tell us *why* ionic liquids work the way that they do.

From the molecular modeling and simulation standpoints, ionic liquids came about at just the right time. Today, the resources in computer hardware and in theoretical methods necessary to tackle systems with this kind of complexity are accessible to most research groups in the field. Ionic liquids are suited to be studied using quantum, molecular, or statistical mechanics, because (i) unlike macromolecules, they are constituted by smaller molecular units and their description does not require a broad range of time scales (glassy states excluded); (ii) unlike organometallic compounds, they are composed of organic residues that can fit into different families, and avoiding difficulties of quantum chemical methods to describe heavy atoms and transition metals.

However, ionic liquids are nontrivial. Composed of asymmetric, often flexible ions that are medium-sized molecular objects (10–100 atoms), they are more complex than the inorganic, high-temperature molten salts. A multitude of ionic liquids can be prepared through different combinations of cations and anions. In most applications, they are used in multicomponent mixtures, including molecular or other ionic compounds, and sometimes nanoparticles or surfaces. Only a minute sample of this universe can be studied experimentally to obtain physicochemical data and for some properties only. Understanding the key factors at the molecular level that determine the various properties and being able to predict them at least semiquantitatively are important research objectives. The sophisticated nature of the interactions present in ionic liquids (Coulombic and van der Waals forces, polarization and charge delocalization, flexibility, and conformational richness) makes their study using molecular dynamics a fascinating subject both from the theoretical and applied points of view.

This Account describes the strategy adopted in developing a model for molecular simulation of ionic liquids. It was initially used in free-energy calculations to predict

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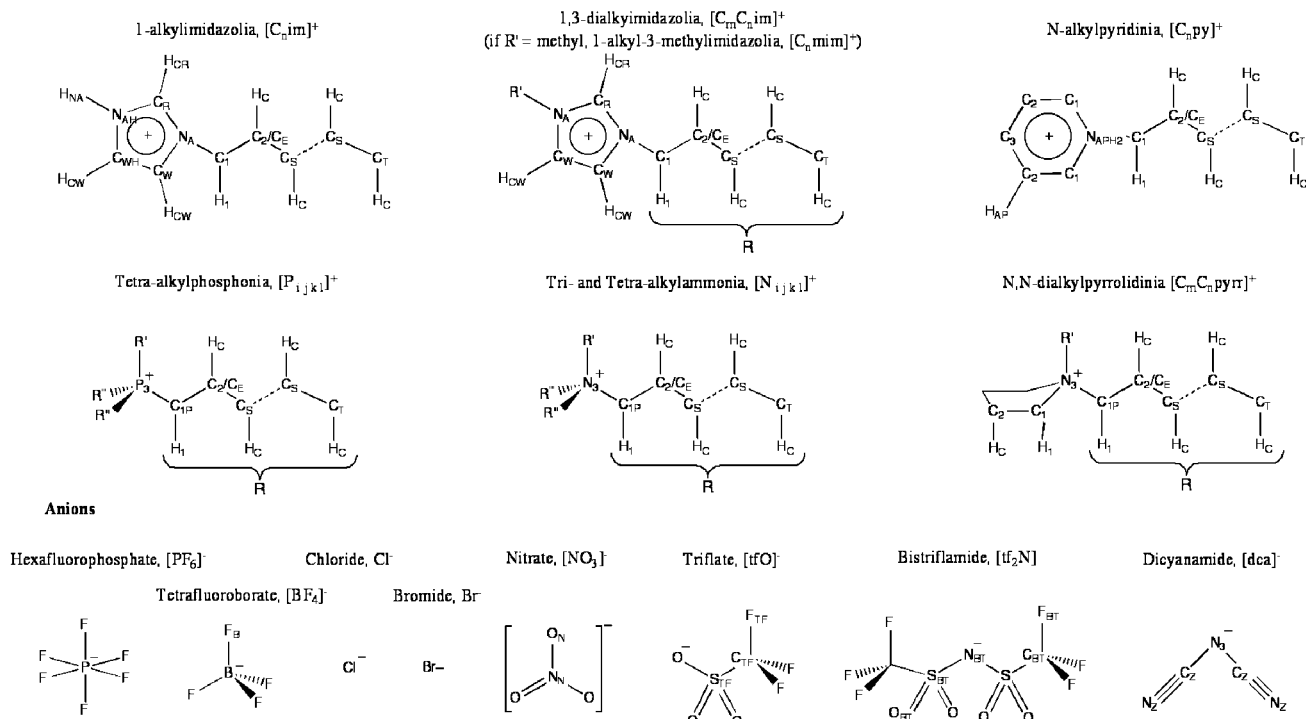


FIGURE 1. Ions parameterized in the all-atom force field for ionic liquids.

and explain the solubility of small molecules, mostly gases. Then, unexpected structural features of some common ionic liquids were observed using simulation, in the form of segregated charged and nonpolar domains. This provides a new view into ionic liquids as nanostructured solvents, capable of offering diverse environments to solutes, according to the polarity or associating character of the latter. At present, we investigate mixtures of ionic and molecular liquids from structural and thermodynamic perspectives.

Molecular Interaction Model

Some characteristics of ionic liquids, such as the interchangeability of cations and anions and the existence of families by the addition of homologous organic residues, were incorporated in the rationale behind our force field.^{7–9} The result is a systematic model that at this stage comprises six of the widely used cation families and eight different anions (Figure 1). Work is underway to include other ions.

The functional form and parameterization method chosen for the molecular force field were based on the optimized potential for liquid simulations all-atom (OPLS-AA)¹⁰ with specific terms, mainly those related with electrostatic charge distributions and torsion energy profiles, calculated individually for new cation or anion families (Figure 2). Our purpose is to calculate thermodynamic or transport properties of condensed phases in the bulk or at surfaces. The emphasis is on the parameters that affect geometry, conformations, and interactions. Stretching of covalent bonds and bending of valence angles are important for some properties but are not the central problem in developing a molecular simulation

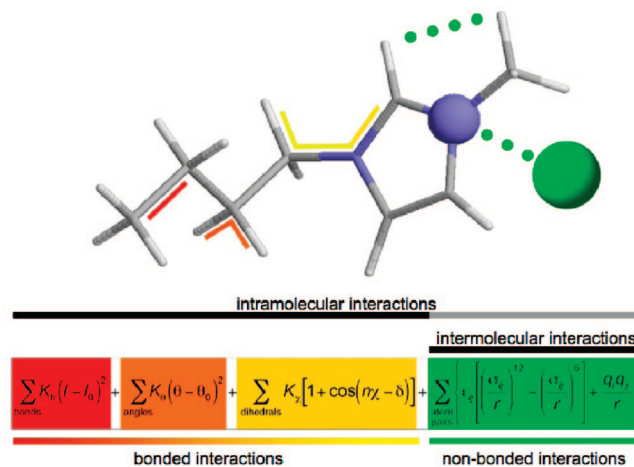


FIGURE 2. Functional form of the force field. Two atoms connected by a covalent bond interact through a harmonic stretching potential. Three atoms connected by two bonds interact through an harmonic bending term around the central atom. Four atoms connected by three bonds have a torsion energy term as a function of their dihedral angle. Atoms separated by four or more bonds interact through nonbonded terms (Lennard–Jones plus charges).

force field. Our efforts were concentrated on the high-level quantum calculation of three kinds of term: molecular geometries, electrostatic charge distributions (that affect intermolecular energies), and torsion energy profiles (that determine conformations). All are illustrated in Figure 3. The vibration force constants were taken, when available, from the assisted model building and energy refinement (AMBER) force field.¹¹ Repulsion–dispersion interactions of the Lennard–Jones type were taken from OPLS-AA¹⁰ that is specifically oriented toward liquid-state simulations. Concerning the Lennard–Jones parameters, in the ionic liquids described thus far by our model,^{7–9}

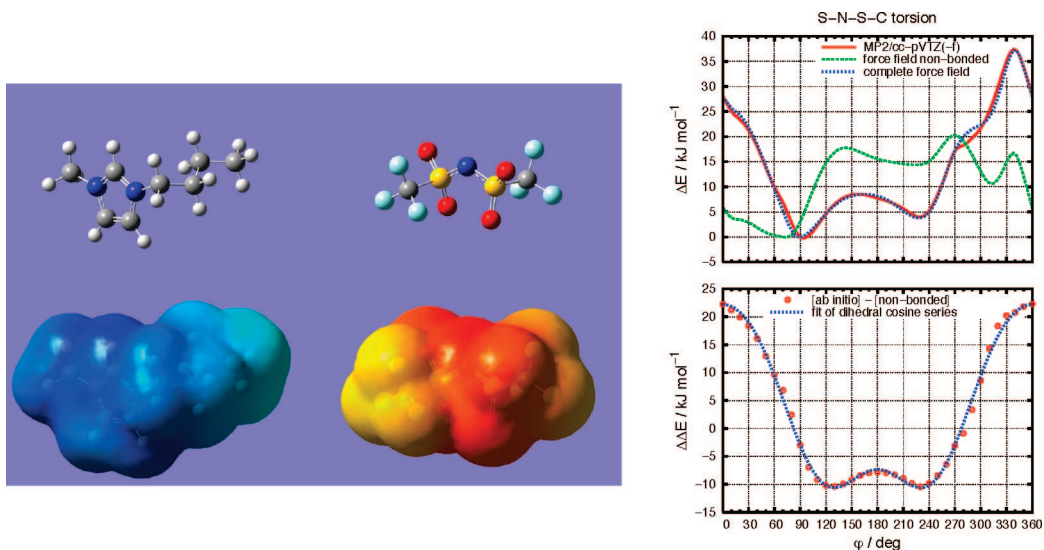


FIGURE 3. (Left) Electrostatic charge distributions on a 1-butyl-3-methylimidazolium cation, $C_4C_1im^+$, and on a bis(trifluoromethanesulfonyl)amide anion, tf_2N^- : blue corresponds to a positive charge, and red corresponds to a negative charge. The electron density on isolated ions was calculated ab initio at the level MP2/cc-pVTZ(-f), with geometries optimized at HF/6-31G(d). Partial charges were assigned to atomic sites by an electrostatic surface potential fit (ChelpG)¹² to reproduce the field around an ion. (Right) Torsion energy profile corresponding to the internal rotation of the dihedral angle S–N–S–C in tf_2N^- . Ab initio energies are plotted in red, and those obtained using the force field are plotted in blue, illustrating the agreement between the force field and the quantum calculations in this rather irregular torsion energy profile. The curve in green gives the contribution of intramolecular nonbonded interactions between Lennard–Jones sites and electrostatic charges.

no improvement upon OPLS-AA parameters was necessary to reproduce experimental properties: liquid densities, crystal structures, enthalpies of vaporization, and conformer distributions obtained by spectroscopy or neutron diffraction (Figure 4).

Internal consistency was maintained by always retrieving parameters from the same primary sources (OPLS-AA or AMBER) or, in the absence of such data, by always using the same estimation procedure involving quantum mechanics and molecular dynamics calculations. Results were checked against X-ray diffraction, IR and Raman spectroscopic, and thermodynamic data. Compatibility with the OPLS-AA was also built into our model by allowing a smooth transition between the parameterization of new parts of the ions (e.g., the imidazolium ring) and the organic residues already parameterized in OPLS-AA (e.g., alkyl chains). This is important to simulate systems containing ionic liquids and other species described by OPLS-AA, which includes many families of organic and biochemical compounds. Each ion was parametrized separately, by adding organic residues in a stepwise manner and by taking representative, average values for the electrostatic charges in ions of the same family, allowing for the transferability of the force field. These procedures entail some degree of approximation and heuristic choices, but we accepted the tradeoff of extreme accuracy in a few specific cases against a systematic, transferable, and more versatile force field.

Back in 2004 when our force field was first published,^{7,8} the only experimental data available to validate the force field in a systematic manner were density and volumetric-related data, both in the liquid and crystal. We concluded that the model could predict within 3% accuracy the density of a given ionic liquid both in the liquid and

crystalline phases and, in the latter case, the parameters of the unit cell were also correctly evaluated (Figure 4a). No systematic trends were devised in the 3% level of accuracy, and fine-tuning parameters for specific ions would certainly improve calculations for some cation–anion combinations but worsen the situation for others. This level of accuracy was accepted to guarantee the generality of the model.

A proviso was made at the time stating that energy-related data were necessary to fully validate the force field. These became available when the cohesive energy of ionic liquids was measured by calorimetry.¹³ This measurement was undertaken when the vaporization of ionic liquids had been observed below their decomposition temperature.¹⁴ The force field was able to predict the calorimetric results within 15% accuracy and also the trend of increasing values of vaporization enthalpy with an increasing alkyl side chain of the cation (Figure 4b).

Another, more subtle, validation of the force field had been obtained¹⁵ when different conformational analyses using Raman spectroscopical data and density functional theory (DFT) quantum-mechanical calculations^{16,17} were confronted with molecular dynamics simulations using our force field. The conformer distribution of different 1-alkyl-3-methylimidazolium cations included in different ionic liquids was similar irrespective if the result was obtained by simulation (MD), experiment (Raman), or theoretical calculation (DFT) (Figure 4c). Work is underway to validate the force field for other cation families, particularly pyrrolidinium,⁸ including the potential energy associated with the pseudorotation of the ring.¹⁸ A comparison with neutron diffraction results¹⁹ on conformer distributions also validated the force field for tf_2N^- (Figure 3).

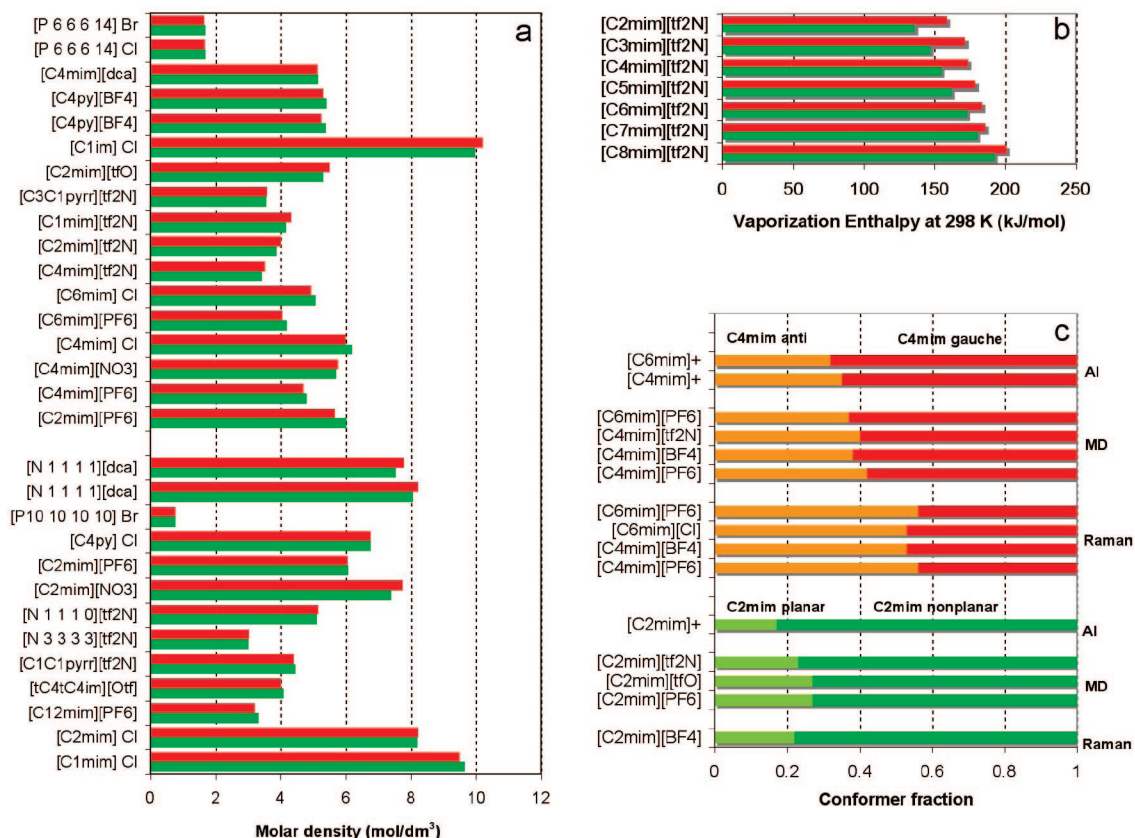


FIGURE 4. Validation of the force field using (a) density, (b) enthalpy of vaporization, and (c) conformer distribution data. In a and b, green and red correspond to experimental and simulation results, respectively. In c, planar/nonplanar refers to the position of the ethyl group of the 1-ethyl-1-methylimidazolium cation in relation to the imidazolium ring plane, whereas trans/gauche refers to conformations of the alkyl side chain in 1-butyl- and 1-hexyl-3-methylimidazolium around the two carbon atoms closest to the imidazolium ring.

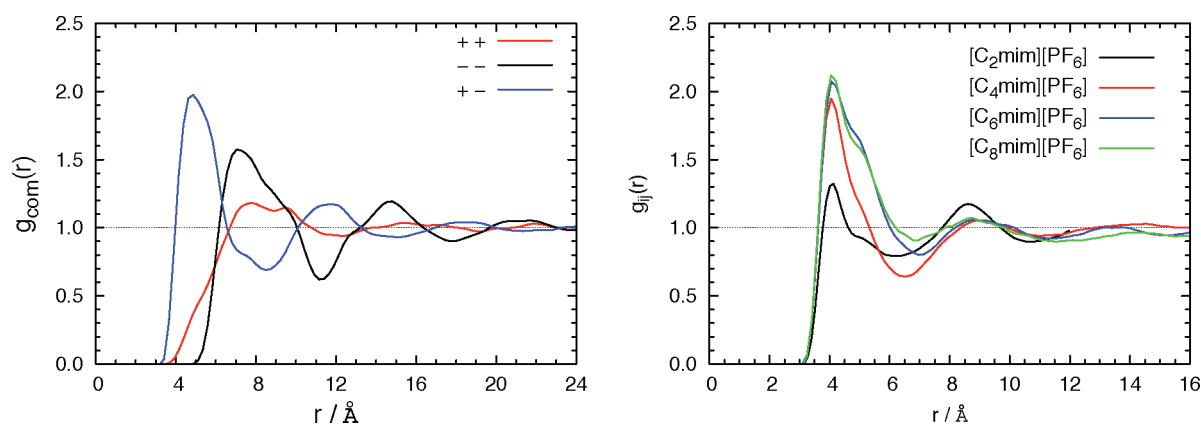


FIGURE 5. (Left) Ion-ion centers-of-mass radial distribution functions in liquid [C₆C₁im][PF₆], giving the probability of finding an ion pair at a certain distance compared to the average. (Right) Site-site RDFs between the end carbons of the alkyl side chains in [C_nC₁im][PF₆], showing aggregation of the side chains for $n \geq 4$.

Self-Organization and Liquid Structure

Molecular simulations of ionic liquids show that the main features of the liquid structure are defined by charge ordering, as in molten salts composed of small, rigid ions. This is the overall picture obtained from the distributions of centers-of-mass distances between ions (Figure 5): cation-cation and anion-anion radial distribution functions (RDFs) have a succession of peaks in phase, and cation-anion RDFs have peaks in opposition of phase with the previous ones.²⁰ In Figure 5, the cation-cation

RDF has peaks that are less marked than those of anion-anion pairs. This is because the cation is flexible and, according to the conformations adopted, the location of its center of mass is spread over a region of space. This does not happen to the rigid, octahedral PF₆⁻.

A more detailed analysis, using groups of atoms instead of centers of mass, provides a new structural insight:²¹ when the end carbons of the alkyl side chains are taken in [C_nC₁im][PF₆], it is observed that a strong first peak is present when the side chain is longer than butyl (Figure

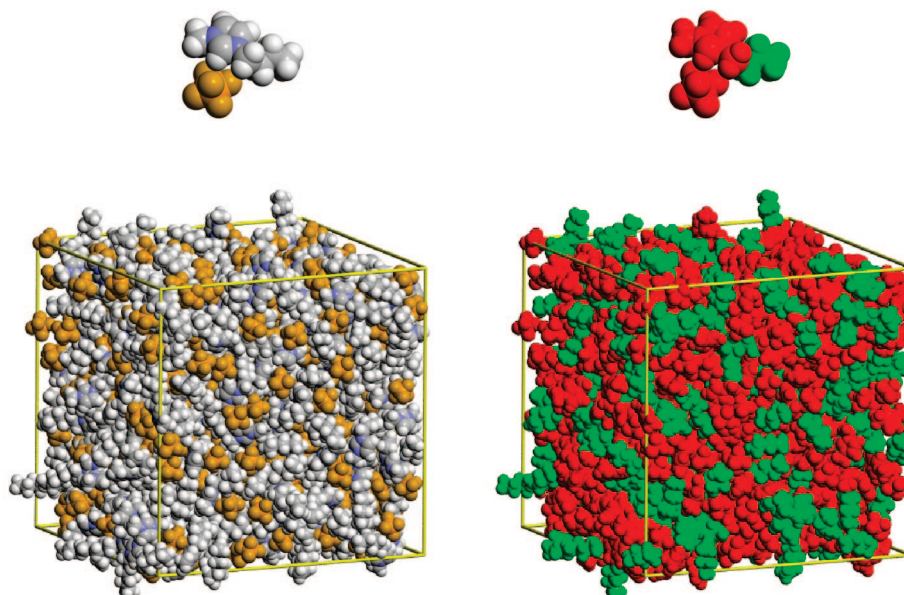


FIGURE 6. Color scheme to distinguish the “charged” zone, in red, corresponding in this case to the imidazolium ring of the cation (plus some atoms attached to it) and the entire PF_6^- anion, from the “nonpolar” side chain, in green. A segregation in domains is visible in liquid-phase simulations (250 ion pairs of $[\text{C}_6\text{C}_1\text{im}][\text{PF}_6]$ by molecular dynamics).

5). This is evidence of the aggregation of the side chains in nonpolar domains. The same kind of segregation in Figure 6 was observed using simulations with other anions, namely, the larger and flexible tf_2N^- . Adopting a color scheme to distinguish atoms belonging to the “nonpolar” parts of the ions from those belonging to the “charged” parts provides an excellent visual aid to perceive these structural heterogeneities²¹ (Figure 6).

Earlier molecular simulation studies had identified similar structural features, using models different from the present one: Urahata and Ribeiro²² reported prepeaks in static structure factors, interpreted as evidence of intermediate-range order, using an united-atom model (not every atom is explicitly represented). Wang and Voth²³ reported domain segregation using an even coarser model in which an imidazolium cation is represented by just four sites. Therefore, domain formation is not an artifact of the present force field. Authors studying dynamics in ionic liquids have systematically reported the slow, even glassy, dynamics of these systems and connected this to the persistence of local structures.²⁴

Many experimental observations may be related to the structural heterogeneities. Unfortunately, most neutron diffraction studies have been performed on ionic liquids with short side chains²⁵ that do not form domains. Before the simulation works that suggested the existence of such structures,^{21,23} experimentalists were not looking for them and the samples were neither chosen for that purpose nor isotopically labeled in the appropriate way. Nevertheless, less direct evidence exists.

Watanabe and collaborators studied dynamic properties of imidazolium ionic liquids as a function of the alkyl side-chain length.²⁶ As it becomes longer, the strong electrostatic interactions between charged groups are progressively diluted and replaced by weaker van der Waals forces. Viscosity should decrease, and conductivity

and diffusion should increase. This is indeed observed for the shortest side chains, but from $[\text{C}_4\text{C}_1\text{im}][\text{PF}_6]$ onward, the trends are reversed. The formation of microdomains that, according to simulation happens exactly at this point, is a plausible explanation for a decreased ionic mobility.

When using ionic liquids as stationary phases for gas chromatography,²⁷ it was observed, as expected, that the ionic liquids can separate polar molecules. However, surprisingly, it was shown that they have an excellent resolving power for the homologous series of *n*-alkanes. This dual nature as stationary phases can be related to the simultaneous polar and nonpolar character of the ionic liquids.

Fluorescence of probe molecules²⁸ shows a red shift that is a sign of a glassy state or the presence of organized assemblies, such as micelles. The fluorescence of the ionic liquids themselves²⁹ leads to the same conclusions. Direct spectroscopic evidence of the existence of specific local structures whose size depends upon the length of the alkyl side chains has been recently obtained.³⁰

Recent calorimetric information further supports the simulation results. The enthalpy of vaporization of ionic liquids¹³ shows that the increment per $-\text{CH}_2-$ group in the side chain along a series of alkylimidazolium salts coincides with the trend observed for solid *n*-alkanes. Another study³¹ showed very similar progressions in heat capacity and entropy between the series of liquid $[\text{C}_n\text{C}_1\text{im}][\text{tf}_2\text{N}]$ and the liquid *n*-alkanes. These results imply that, in the ionic liquid, the side chains reside in alkane-like environments.

Also, the pronounced self-organization of the ionic liquids (“supramolecular” solvents)³² has been suggested as the cause for the quality of nanostructured materials and nanoparticles synthesized therein. This self-organization has often been explained by a network of hydrogen bonds (notably in the presence of water).³³ We have seen

hydrogen bonds between appropriate cations and anions and also in the presence of water or alcohols. However, our picture of the structured nature of ionic liquids is less restrictive. These media appear as dominated by the cohesive force between the ionic charges, forming a network of associated ions. When one (or both) of the ions contains a nonpolar group, this group tends to be excluded from the charged network by energetic reasons. If the side chains are small, the ionic liquids will have a fluid structure quite similar to that of a molten salt. However, if the nonpolar groups constitute an important and accessible part of the ions, these groups will eventually aggregate in nonpolar domains,²¹ paying an entropic price in exchange for an energetic reward. If the nonpolar side chains become too long, then liquid-crystalline phases appear.³⁴ It is the intermediate situation that seems most interesting from our point of view, because the corresponding ionic liquids have been mostly considered as being associated but homogeneous phases.

An interesting extension of the nonpolar tail aggregation discussed above to provide a solvation environment is the use of ionic liquids with fluorinated side chains³⁵ acting as surfactants to establish a dispersion of a fluorinated phase³⁶ in a conventional ionic liquid. In this case, the aggregation behavior of fluorinated side chains is evident.

Solvation of Different Compounds

The notion that, in some ionic liquids, two kinds of spatial domains exist completely modifies the way that solvation can be understood in these media. Different solutes, according to their polarity or tendency to form associative interactions, will not only interact preferably with certain parts of the individual ions but may also be solvated in distinct local environments.³⁷ Examples are shown in Figure 7.

Nonpolar molecules will be solvated and tend to reside in the nonpolar domains. In the same manner as the nonpolar side chains of the ions, these solutes will be excluded from the ionic network because of the cohesive energy of the charged groups. In Figure 8, a strong peak appears in the RDF between the methyl groups of *n*-hexane and the end carbon of the alkyl side chain of the cation, whereas only very weak correlation exists between the alkane and both the cation head group and the anion. Dipolar solutes, for example, acetonitrile, will interact closely with the charged head groups but also with the nonpolar domains. This balanced behavior is evident from the comparable heights of the first peaks of three RDFs of acetonitrile, in Figure 8. This makes acetonitrile an excellent solvent for many ionic liquids. Associating solutes, such as alcohols or water, will form powerful hydrogen bonds with the charged parts of the ions and will be solvated in the ionic domain. In the examples shown by the red curves in Figure 8, the stronger hydrogen bond will be between the H of the hydroxy group or water and the anion.^{37–39} Weaker hydrogen bonds exist between the H connected to the C₂ carbon of the imidazolium ring and the oxygen in the alcohol or water.³⁷ Besides different

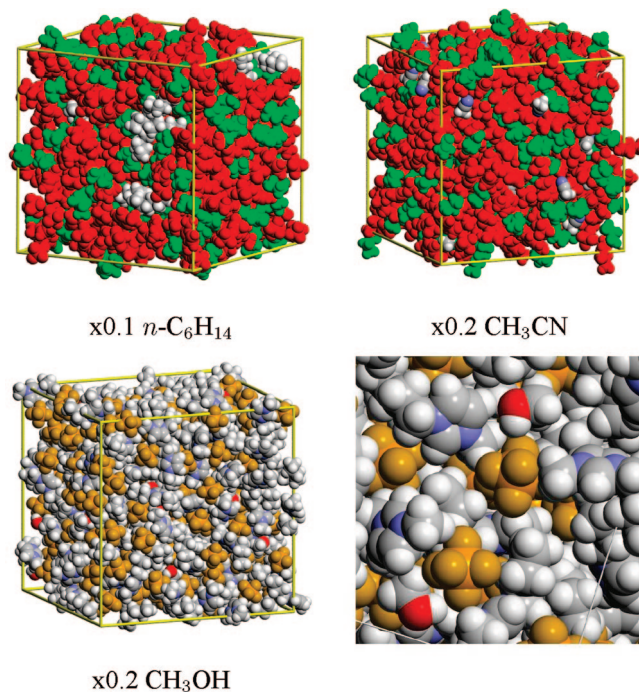


FIGURE 7. Interaction of *n*-hexane, acetonitrile, and methanol with the nonpolar and charged domains of the ionic liquid [C₄C₁im][PF₆]. The alkane is located in the nonpolar domains. Acetonitrile, a dipolar molecule, has balanced affinities for both kinds of domain. Methanol establishes strong hydrogen bonds with the anion and weak hydrogen bonds with the hydrogen in C₂ of the imidazolium cation. The ionic liquid in the box containing methanol was not color-coded to highlight the red color of the oxygen atoms of the alcohol and emphasize the interaction between the hydroxy group and the PF₆⁻.

positioning with respect to the ions, the polarity of the molecular compounds also induces marked orientational effects, as illustrated in Figure 8.

The solvation of gaseous alkanes in the ionic liquids can also be understood in terms of the spatial domains. The solubility of methane and ethane was studied in ionic liquids based on C₄C₁im⁺.^{40,41} Solubility increases with the size of the alkane, something that cannot be explained by free volume or electrostatic solute–solvent interactions.^{42,43} One possible explanation is that the solubility of these solutes is determined by the size of the microdomains in the ionic liquid. It is expected that the solubility of an alkane, such as butane, should increase with the size of the nonpolar domains in the ionic liquid and even exhibit a discontinuity when the nonpolar domain in the solvent becomes large enough to accommodate the solute.

Mixtures of Ionic and Molecular Liquids

When the entire composition range of a mixture between an ionic and a molecular liquid is spanned, several different regimes will be found. Starting from the neat ionic liquid, a medium composed entirely of ions, initially, the molecular compound will be a diluted solute, interacting with the domains of the ionic liquid as described above. As the concentration in the molecular compound increases, it will tend to aggregate on the domain toward which it has a greater affinity. At a point, the presence of

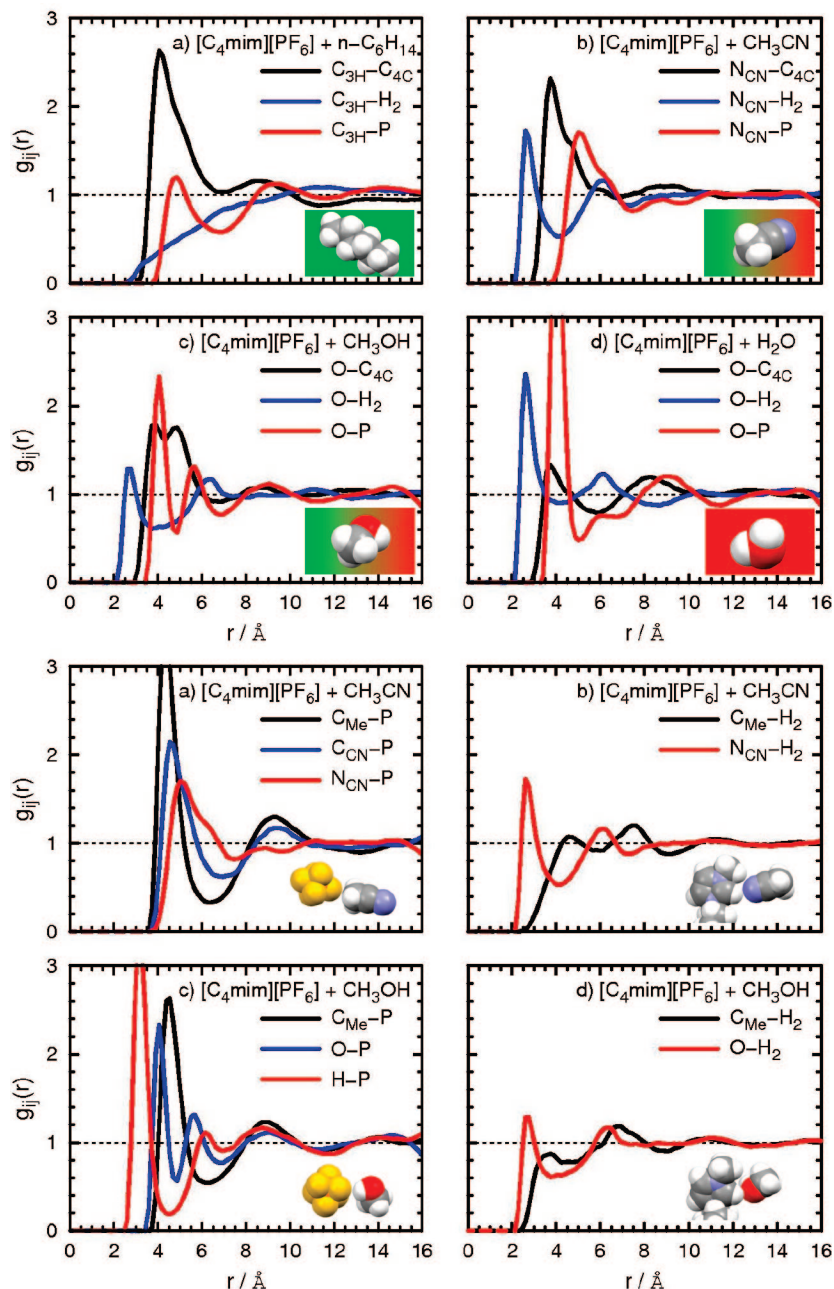


FIGURE 8. RDFs illustrating the placement of the solutes, *n*-hexane, acetonitrile, methanol, and water, in terms of the domains of the ionic liquids (four plots on top). RDFs in black denote the location of given atoms of the solute with respect to the end carbon of the nonpolar tail; blue lines are RDFs between solute atoms and hydrogen bonded to the C₂ carbon of the imidazolium ring (a site of positive charge); and RDFs in red are between solute atoms and the anion. The solute orientations with respect to the ions are also shown (four lower plots), by providing site–site RDFs between different atoms of the solutes and a given site on the ionic liquid. The sequence of the first peaks of the RDFs indicates the orientation of the solutes.

the molecular compound will cause a disruption of the ionic network. From then on, the ionic liquid becomes the minority component and its ions will form different sorts of aggregates (micelles or ion clusters) in the molecular liquid, depending upon the solvent properties of the latter. Finally, once low concentrations in the ionic liquid are reached, it will behave as an electrolyte in solution.⁴⁴ Snapshots of simulation boxes with mixtures of ionic and molecular liquids that are miscible in all proportions at room temperature are shown in Figure 9, at a series of compositions.

These different regimes have consequences for the properties of the mixtures, an understanding of which can provide valuable guidelines for the use of ionic liquids in many applications. Pitzer and collaborators had already studied the entire composition range of a mixture between an ionic and a molecular liquid,⁴⁴ illustrating for example the nonmonotonic behavior of the conductivity of the mixture as a function of composition: in the diluted electrolyte regime, conductivity initially falls from the infinite-dilution value because of ion pairing. It then goes up as the number of ion pairs increases. Further on, it

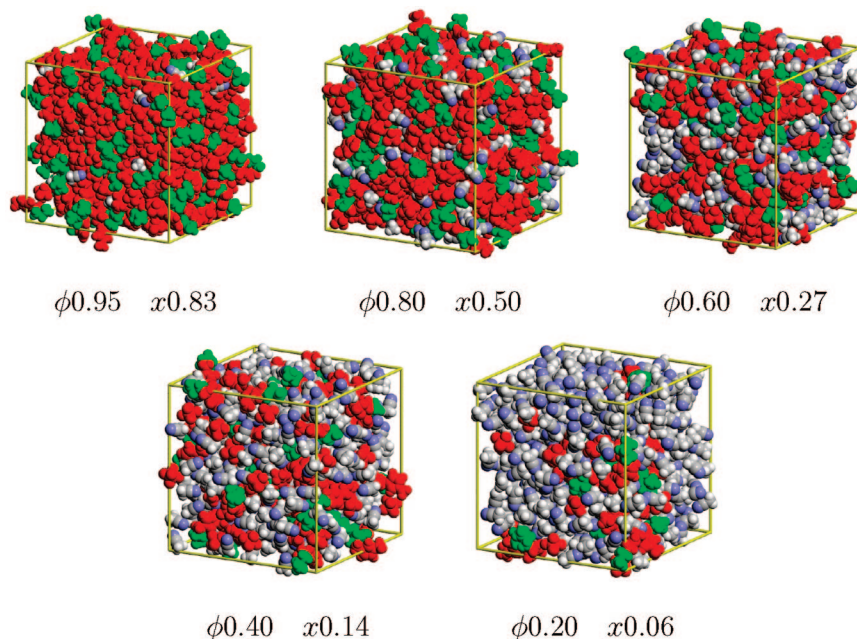


FIGURE 9. Mixture of $[\text{C}_4\text{C}_1\text{im}][\text{PF}_6]$ with acetonitrile at different compositions, identified by the volume fraction, ϕ , and the mole fraction, x , of ionic liquid. Because the ionic liquid and the molecular compound have very different molecular sizes and weights, the volume fraction is for many purposes a convenient quantity to express composition.

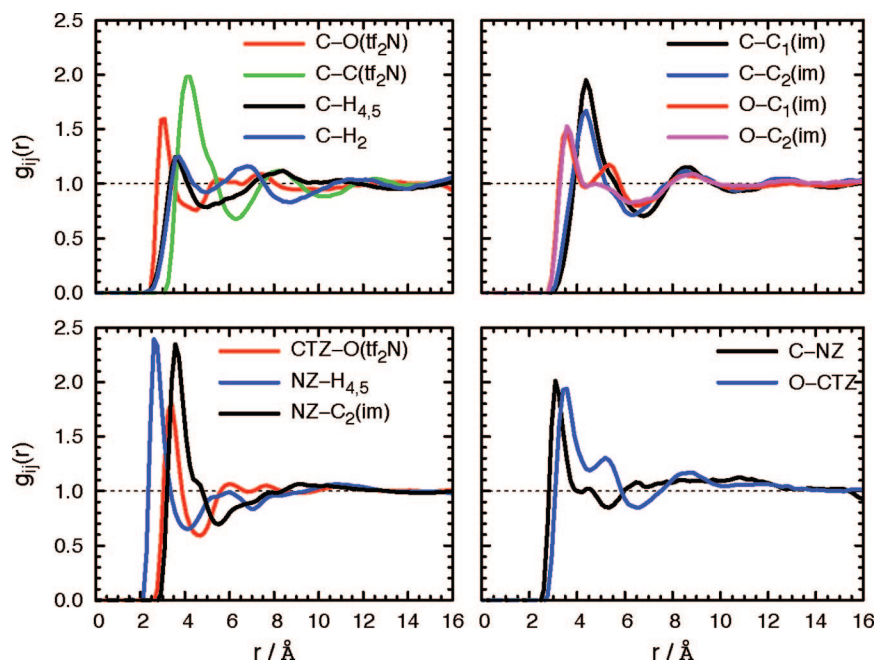


FIGURE 10. RDFs illustrating the solvation of carbon dioxide in the mixture of $[\text{C}_2\text{C}_1\text{im}][\text{tf}_2\text{N}]$ and acetonitrile. The curves in the upper plots denote the location of carbon dioxide (upper left) and acetonitrile (upper right) with respect to the solvation sites in the ionic liquid. The lower plots illustrate the competition of carbon dioxide for the acetonitrile solvation sites in the ionic liquid (lower left) and the location of carbon dioxide with respect to acetonitrile.

will decrease again once the high viscosity of a concentrated salt mixture becomes the dominant factor.

The addition of a molecular compound to the ionic liquid also changes its solvation properties of the liquid. For example, the solubility of different gases can be enhanced by the presence of dissolved carbon dioxide.⁴⁵ Water⁴⁶ or acetonitrile,⁴⁷ on the contrary, cause a decrease on the solubility of CO_2 . No evidence for disruption of the ionic liquid structure could be found,⁴⁷ and the

decrease in CO_2 solubility can be explained by the competition of the two molecular species for the solvation sites of the ionic liquid (Figure 10). Concurrently, interactions between acetonitrile and CO_2 are also significant and important to explain the solvation of the gas in the mixture.

Aggregation of ionic liquids in water has been extensively studied.^{33,48} For example, in $[\text{C}_4\text{C}_1\text{im}][\text{BF}_4]$ with water, a totally miscible system, the presence of an

aggregation transition has been reported⁴⁹ at a mole fraction of ionic liquids around 0.01. Although micelle formation is to be expected for longer chain ionic liquids, it seemed unusual for short to intermediate chain cations.

Conclusion and Outlook

Ionic liquids have many remarkable properties. Independent of their eventual success in technological applications, they provide a challenging terrain of study for physical chemists. The level of complexity of their molecular structures and interactions makes them truly adapted to the present tools of physical chemistry, experimental or theoretical.

One important goal of research into the physicochemical properties of ionic liquids is the interpretation of the effect of the molecular structure on their properties (thermal, solubility, miscibility, viscosity, diffusion, and electrical conductivity) and those of their mixtures with molecular liquids. These mixtures are generally highly asymmetric, with components having large differences in molecular size, shape, and kinds of dominant interaction. As such, their theoretical treatment is complicated, and reductions to models that are too simplified may fail to capture the most unique aspects.

No large base of experimental information exists for these systems; therefore, measurements and theoretical interpretation advance at equivalent paces, in a very interesting interplay: sometimes, molecular models are used to interpret some experimental observation, and other times, some kind of behavior is found using simulation that prompts experimentalists to devise methods to validate the results of the model. The nanoscale domain formation in ionic liquids is an example of the latter.

Within the specific topic of this Account, studies progress toward relating the structured nature of ionic liquids and their mixtures with other species to their applications in catalysis,^{50,51} in synthesis, and also in the formation of nanostructures.^{32,52}

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