

# Accounting for the Unique, Doubly Dual Nature of Ionic Liquids from a Molecular Thermodynamic and Modeling Standpoint

LUÍS PAULO N. REBELO,\*  
 JOSÉ N. CANONGIA LOPES,  
 JOSÉ M. S. S. ESPERANÇA,  
 HENRIQUE J. R. GUEDES, JOANNA ŁACHWA,  
 VESNA NAJDANOVIC-VISAK, AND  
 ZORAN P. VISAK

*Instituto de Tecnologia Química e Biológica, Universidade Nova de Lisboa, Av. República, Apartado 127, 2780-901 Oeiras, Portugal*

Received March 6, 2007

## ABSTRACT

The fascinating, complex behavior of ionic liquids is analyzed using a molecular perspective that emphasizes the doubly dual nature of ionic liquids underlying the existence of cations and anions forming high- and low-charge-density regions. Our work bridges the liquid, gas, and solid phases spanning 5 years of research on themes as diverse as the vaporization, liquid–liquid demixing, solidification, and thermophysical behavior of ionic liquids and their mixtures and solutions.

## Introduction

Ionic liquids are in. It all (re-)started some 10 years ago and has gained momentum since 2001, when it was realized that room-temperature molten salts could be used to replace traditional volatile organic solvents.<sup>1</sup> This potential substitution was publicized both as “green” and “designer” because of four claimed characteristics of ionic liquids as a class: their almost null volatility,<sup>2,3</sup> generally

Luís Paulo Rebelo was born in 1960 in Lisbon, Portugal. In 1989, he received his Ph.D. degree in physical chemistry from the Universidade Nova de Lisboa (UNL). He has been a Visiting Scientist at Cornell University (1985), University of Tennessee (1990–1991 and 1996), and Princeton University (1997). He joined the Instituto de Tecnologia Química e Biológica (ITQB) in 2000, where he is currently an Associate Professor and Head of the Technology Division. He was Member of the Board of Directors of the Portuguese Chemical Society (1987–1989), Editor of the Bulletin of the Portuguese Chemical Society (1995–1996), and Member of the Board of Directors of the Instituto de Biologia Experimental e Tecnológica (2005–present). Rebelo's research interests are centered on molecular thermodynamics of liquids and liquid solutions, in particular, isotope effects, ionic liquids, polymer solutions, and metastable liquids.

José Canongia Lopes was born in 1965 in Lisbon, Portugal. He obtained his Ph.D. degree in chemical thermodynamics from the Instituto Superior Técnico (IST), Lisbon, in 1993. He has been a Visiting Scientist at the Imperial College, London, U.K. (1996) and at the Université Blaise-Pascal, Clermont-Ferrand, France (2006). He is currently an Assistant Professor at IST and also (since 2005) at ITQB, where he holds a post of Invited Assistant Professor. His main research interests lie in the areas of molecular modeling of complex fluids and materials.

José Esperança received his Ph.D. degree (2004) from the New University of Lisbon. He is currently a postdoctoral fellow in Rebelo's group at ITQB, with expertise in high-pressure speed-of-sound and density measurements.

null flammability,<sup>4</sup> thermal stability,<sup>5</sup> and the interchangeability between thousands of possible cations and anions that can be used to program these salts in a tunable fashion.<sup>6</sup> During those early days, it was soon realized that the thermophysical properties of ionic liquids, ionic liquid mixtures, and ionic liquid solutions had to be quantitatively investigated to take full advantage of their use as new media in chemical processes. Nowadays, it is obvious that these studies also impact a wealth of other fields ranging from physics, materials, environment, to life sciences.<sup>7</sup> Currently, it is also obvious how the burgeoning number of distinct ionic liquids that have been examined has revealed how much they vary and that simplistic generalizations and behavior extrapolation should be avoided.<sup>8</sup>

In this Account, we review our laboratory's most exciting findings on the thermophysical behavior of ionic liquid-containing systems and how they have advanced our understanding of their unique characteristics.

**Early Days.** Our first investigations focused on their mixtures with common molecular fluids<sup>9–11</sup> and their thermophysical behavior in broad ranges of temperatures and pressures.<sup>12–14</sup> Surprising discoveries include, for instance, (a) the quasi-ideality of binary mixtures of ionic liquids, although low-temperature liquid–liquid phase splitting is sometimes found,<sup>15,16</sup> (b) demixing phenomena of ionic liquid solutions upon a temperature increase,<sup>17–19</sup> (c) the formation of liquid clathrates and inclusion crystals in their mixtures with aromatic compounds,<sup>20,21</sup> and (d) the existence of a plethora of phase changes, which are triggered by the interplay between the water/alcohol cosolvent effect<sup>9,11,12,22</sup> and the CO<sub>2</sub> antisolvent outcome.<sup>10,23,24</sup>

From the point of view of their structure, recent simulation studies<sup>25</sup> supported by indirect experimental data<sup>26,27</sup> indicate that ionic liquids are nanostructured, i.e., composed of microsegregated polar and nonpolar domains. Furthermore, with regard to their interactions, neutral molecules interact preferentially with either the anion or the cation (or parts of the latter) or even with both at the same time but in spatially distinct ways. This doubly dual nature of ionic liquids can help explain at a

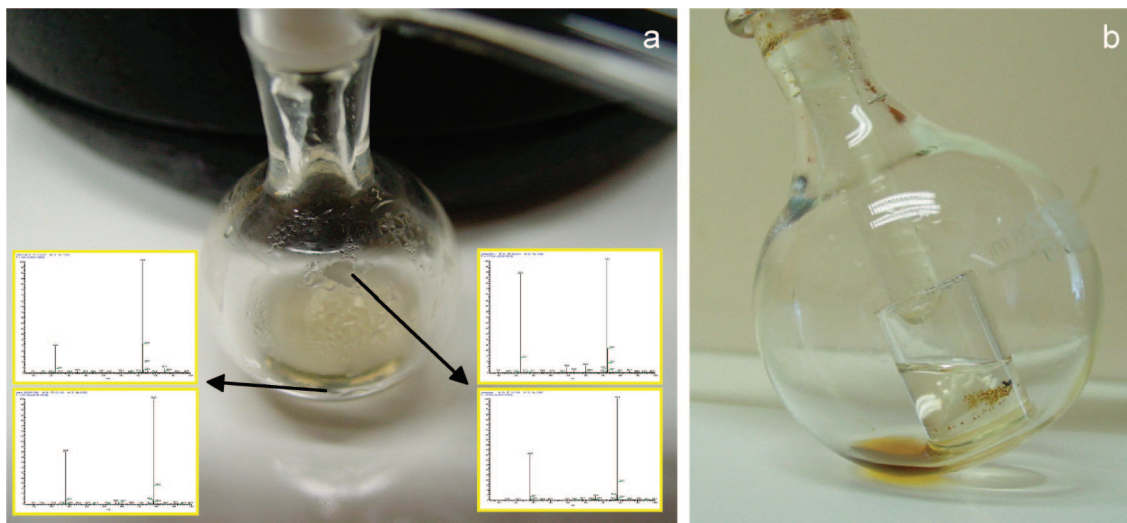
\* To whom correspondence should be addressed. Telephone: +351-21-4469-441. Fax: +351-21-4411-277. E-mail: luis.rebelo@itqb.unl.pt.

Henrique Guedes is an Assistant Professor at the New University of Lisbon and has spent several periods of sabbatical leave at the ITQB. His main research interests focus on experimental thermodynamics.

Joanna Łachwa received her Ph.D. degree (2003) from the Warsaw University of Technology. She was a postdoctoral fellow at ITQB, with expertise in solid–liquid and liquid–liquid equilibria.

Vesna Najdanovic-Visak obtained her Ph.D. degree (2004) from ITQB (Rebelo and Nunes da Ponte's groups), with expertise in fluid-phase diagrams involving supercritical CO<sub>2</sub>.

Zoran Visak received his Ph.D. degree (2004) from ITQB. He is a postdoctoral fellow in Rebelo's group at ITQB, with expertise in fluid-phase equilibria and liquid metastability.



**FIGURE 1.** (a) First successful thermal vaporization and recondensation of a pure aprotic ionic liquid,  $[C_{10}mim][NTf_2]$ , *in vacuo*. Insets show the similar ESI-MS spectra of the recondensed liquid and residue, which denotes the absence of decomposition. (b) Snapshot showing a distillation of  $[C_4mim][NTf_2]$ . Note the color-free distillate.

fundamental level many of the extraordinary properties of these liquid salts, a class of “distinctively complex” solvents. Ironically, the doubly dual nature of the ionic liquids was confirmed in our laboratories by two independent lines of research: one concerned with ionic liquids in the gas phase and the other concerned with ionic liquid crystals.

### Ionic Liquids in the Gas Phase

Although many of the molecular dynamics (MD) studies were useful for predicting structural properties of ionic liquids,<sup>28</sup> they lacked validation when it came to energy-related properties. Vapor pressure (and its temperature dependence) and, concomitantly, the enthalpy of sublimation or vaporization of a condensed phase are among those fundamental properties needed to contribute to the development and testing of accurate molecular models. In the case of ionic liquids, the preformed opinion that they were involatile impaired any development in this area. Critical parameters are also obviously essential for the implementation of  $p$ - $V$ - $T$  equations of state. This state of affairs led to the development of a new line of inquiry into the properties of ionic liquids that eventually led to their distillation,<sup>3</sup> the measurement of their enthalpy of vaporization,<sup>26</sup> and the characterization of their vapor-phase structure.<sup>29</sup>

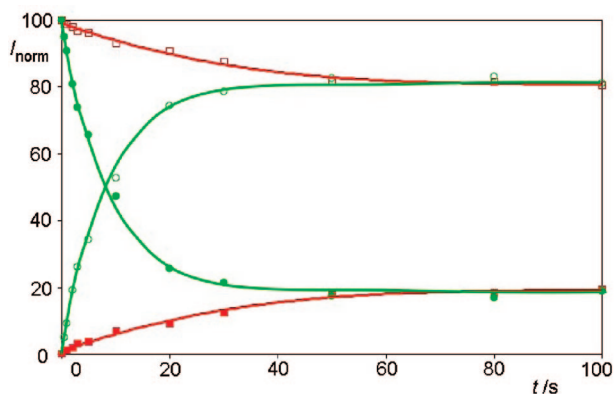
**A Window of Opportunity.** The prediction of the critical temperature of a pure substance based on the temperature dependence of its surface tension and liquid density can be accomplished through the use of empirical equations based on the corresponding states principle and dimensional analysis arguments.<sup>2</sup> The normal boiling temperature is ca. 60–70% of the critical temperature; therefore, hypothetical normal boiling point temperatures were estimated. Although the results must be seen as crude estimations, they allowed us to identify the 1-alkyl-3-methylimidazolium bistriflamide family as the most promising candidate for a successful distillation, i.e., ionic

liquids that combined relatively low estimated normal boiling point temperatures with relatively high temperatures marking the onset of degradation.

**Distilling the Undistillable.** Preliminary distillation tests<sup>2</sup> confirmed the possibility of distilling 1-decyl- and 1-dodecyl-3-methylimidazolium bistriflamide at a reduced pressure of about 1 Pa and temperatures around 450 K (see Figure 1). These observations encouraged us to embark on a systematic study of the distillation of different families of ionic liquids in collaboration with two other laboratories [Queen’s University Ionic Liquid Laboratories (QUILL), Belfast, U.K., and National Institute of Standards and Technology (NIST), Boulder, CO].<sup>3</sup>

The study corroborated our preliminary predictions and showed that distillations are possible for a rather large number of commonly used ionic liquids. These observations laid to rest a paralyzing and invalid assumption that had dominated and restricted the field of ionic liquids since its origins and opened up new ways of taking advantage of their properties. It was even possible to perform fractional distillation in mixtures of two ionic liquids with different combinations of anions and cations. These studies allowed us to establish the most probable mechanism of transfer to the vapor phase at reduced pressure and moderate temperature: most aprotic ionic liquids pass into the vapor phase with their constituent anions and cations, keeping their integrity (no proton- or alkyl-transfer reactions). This has been very recently corroborated by several spectroscopic investigations of the gas phase of neat ionic liquids<sup>29,30</sup> aiming at establishing the nature of this rarefied phase. The other point to be addressed concerned the direct measurement of the enthalpy of vaporization of an ionic liquid.<sup>26</sup>

**It Takes Two To Tango.** From an experimental standpoint, the main challenge when trying to determine the nature of the gas phase of an ionic liquid undergoing a process of thermal distillation is the low-vapor pressure.<sup>31</sup> The problem was solved in a collaborative project with



**FIGURE 2.** Positive-mode ion–molecule reaction (from FTICR mass spectra) showing the kinetics of the reaction between the cations  $A^+$  produced by electronic impact with the naturally occurring neutral ion pairs (NIPs, AX) present in the vapor phase of an ionic liquid (AX =  $[C_4\text{mpyr}][\text{NTf}_2]$ ). The reaction  $A^+ + AX \rightleftharpoons A_2X^+$  is shown both in the direct (green) and reverse (red) directions: filled symbols,  $A^+$  cations; empty symbols,  $A_2X^+$  aggregates.

the University of Lisbon and ITN, Portugal, by using Fourier transform ion cyclotron resonance mass spectrometry (FTICR–MS).<sup>29</sup> The high-resolution apparatus used in this work has the possibility of thermally distilling the sample from a container adjacent to the trap inside the vacuum chamber and is particularly advantageous for the study of vapors evolving from low-vapor-pressure materials.

These results demonstrated that, for a wide range of ionic liquids under conditions similar to those encountered in their reduced-pressure distillations, the gas phase above an aprotic ionic liquid,  $A^+X^-$ , consists of tight neutral ion pairs, [AX], with no free ions or higher aggregates (either charged or neutral). Figure 2 shows the profile obtained from the reaction between the naturally occurring (by thermal vaporization) neutral ion pairs and the cations produced by electron impact. Conversely, the gas phase above a protic ionic liquid,  $[\text{BH}]^+X^-$ , consists of isolated neutral molecules, B and HX.

Therefore, these two classes of ionic liquids are conceptually and empirically distinct (see Figure 3).

**Heat of the Moment.** The underlying belief that it would be impossible to vaporize an aprotic ionic liquid avoiding its decomposition impaired the study of enthalpies of vaporization for a long time. Very recently, several samples of 1-alkyl-3-methylimidazolium bistriflamide,  $[C_n\text{mim}][\text{NTf}_2]$ , in which “mim” stands for methylimidazolium and “ $C_n$ ” refers to the alkyl side chain with “ $n$ ” carbons, with alkyl side chains ranging from ethyl to octyl, were subjected to high-precision, vacuum-vaporization drop microcalorimetry,<sup>26</sup> a study emerging from a collaboration with the Universities of Oporto and Aveiro, Portugal.

The enthalpy of vaporization results, ranging from 136 to 192 kJ/mol (ethyl to octyl) at 298 K, were compared with MD simulations assuming that the ionic liquids in the gas phase are present as neutral ion pairs (see Figure 4). The predictive power of the model is very good because no data related to the energetics of these particular

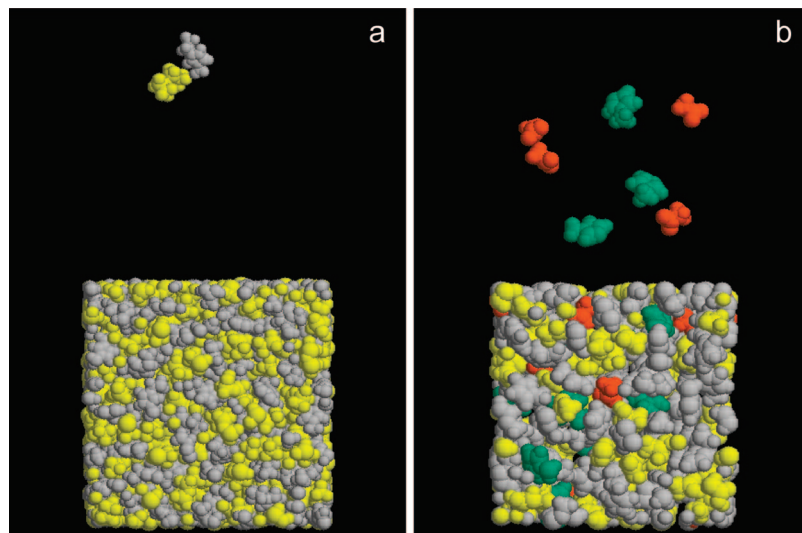
systems were introduced during the force-field parameterization. The force field is indeed validated by the experimental data, thus closing a rather long cycle that led us to an extremely important breakthrough in the field of ionic liquids: the recognition that they can be effectively distilled.

Unexpectedly, the first facet of the dual nature of ionic liquids (the existence of polar and nonpolar microdomains) is also corroborated by the gas-phase data described above. As stated, the enthalpies of vaporization increase with an increasing side-chain length. It should be noted that, if the charged parts of the cation and anion had come further apart because of the presence of longer alkyl side chains, the electrostatic forces would have decreased their intensity and the experimental trend would not have been observed. However, if ionic liquids are seen as three-dimensional polar networks permeated by nonpolar territories, the trend exhibited by the enthalpy of vaporization data perfectly fits the following reasoning: as the alkyl side chains become longer, the nonpolar domains increase in size but the ionic network (because it is segregated from the nonpolar regions) remains intact; a swelling process occurs. Thus, while the van der Waals interactions are enhanced, the intensity of the Coulomb forces is kept invariable, a fact that is confirmed by calculating the two contributions to the total vaporization enthalpy estimated by MD simulation.<sup>26</sup>

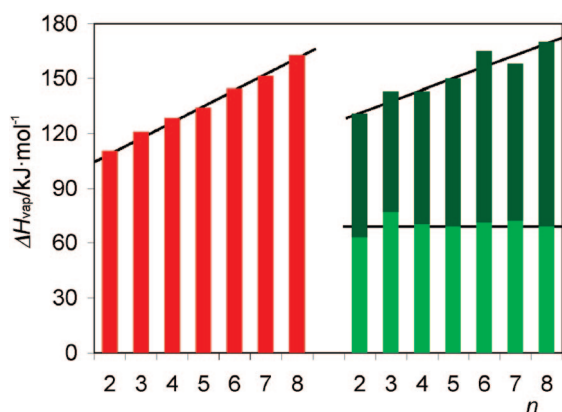
## Ionic Liquids and Inclusion Crystals

The second aspect of the dual nature of ionic liquids, different interactions between molecular solutes and the cationic and anionic components of the salt, is already implicit in the fact that there are segregated polar and nonpolar domains: if the latter are composed of the alkyl side chains of the cations (such as in the case of imidazolia and pyrrolidinia) and/or anions (viz. in the case of alkylsulfates and alkylsulfonates) and the polar region constitutes the remainder of the anion and the remainder of the cation, it seems intuitive that a nonpolar solute (e.g., *n*-hexane) will interact preferentially with the noncharged region of the cation and/or anion; the converse will be true for dipolar or associative solutes (e.g., water) (see Figure 5).

In the other extreme of dilution regimes, for instance, an ionic liquid that is initially infinitely diluted in water, one can easily find surfactant-like behavior provided that the low-charge density domains are sufficiently massive and that macroscopic phase separation does not preclude micelle formation. This is not surprising because one of the most popular surfactants, sodium dodecyl sulfate (SDS), is an ionic salt composed of a compact (cat)ion,  $\text{Na}^+$ , and a long-alkyl-chain-containing anion,  $[\text{C}_{12}\text{SO}_4]^-$ , whose melting point is close to 200 °C. A possible corresponding family of ionic liquids, one with a compact (an)ion,  $\text{Cl}^-$ , is that of the 1-alkyl-3-methylimidazolium cations,  $[C_n\text{mim}]^+$ . Unequivocally, for  $n$  greater than or equal to 8, critical micelle concentrations (cmc’s) are easily determined using a variety of techniques.<sup>32</sup>



**FIGURE 3.** Thermal vaporization of two distinct classes of ionic liquids. Cations, gray; anions, yellow. (a) Aprotic (1-methyl-3-ethylimidazolium bistriflamide,  $[C_2mim][NTf_2]$ ) versus (b) protic (methylimidazolium acetate,  $[Hmim][CH_3COO]$ ). In b, the ionic species in the liquid phase are in equilibrium with the neutral molecules of methylimidazole (green) and acetic acid (orange).



**FIGURE 4.** Experimental (red) versus simulation (green) values for the enthalpy of vaporization of  $[C_nmim][NTf_2]$ . The simulation bars show the increasing contribution of the van der Waals interactions (dark green) in comparison with an invariant Coulomb contribution (light green).

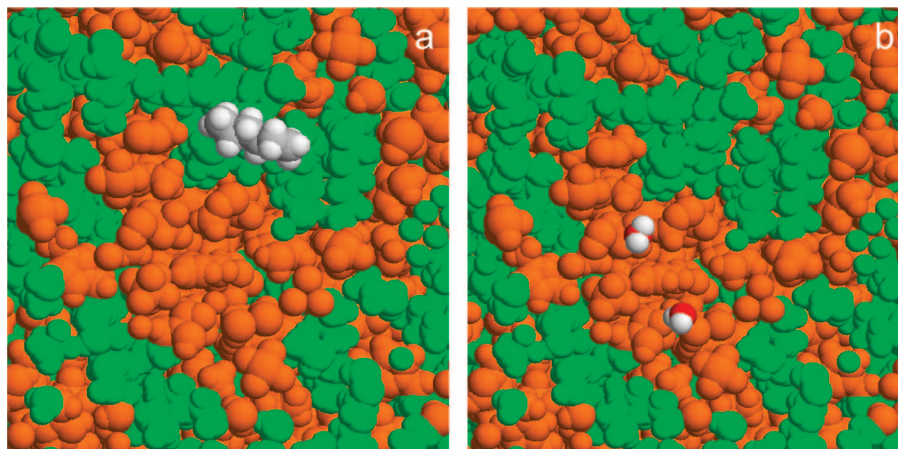
However, even in the case where segregation into two different domains does not occur and the polar network is ubiquitous (for instance, in dimethylimidazolium- or 1-ethyl-3-methylimidazolium-based ionic liquids, the alkyl side chains are so short that the nonpolar region is absent), there are solutes that exhibit different ways of interacting with the cations and anions. Benzene and other (small) aromatic molecules provide us with good examples of such behavior.

**Liquid Cages.** The issue of the formation of cage-like (liquid clathrate) structures in mixtures of ionic liquids with aromatic compounds was already addressed.<sup>21</sup> In those studies, a range of ionic liquids was shown to interact with benzene, toluene, and xylenes forming clathrate-type structures in the liquid phase. In the specific case of mixtures containing benzene and the ionic liquid dimethylimidazolium hexafluorophosphate,  $[dmim][PF_6]$ , the structures in the crystalline and liquid phases were inferred from X-ray and neutron diffraction results, respectively.

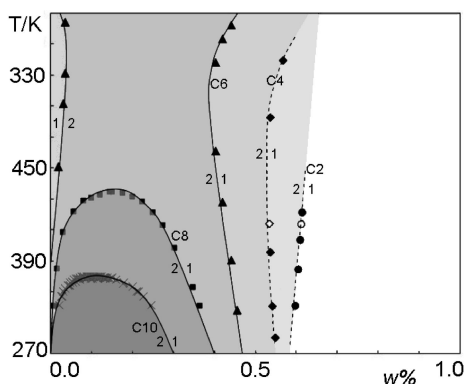
In our first work in this area,<sup>18</sup> we showed that benzene and other arenes are quite soluble in but not completely miscible with  $[C_nmim][NTf_2]$  for alkyl chain lengths,  $n$ , lower than 10 but become completely soluble at room temperature for  $n > 10$ . In the cases of short alkyl chains in the imidazolium ring ( $n < 6$ ), the resulting immiscibility limits correspond to certain quasi-temperature-independent composition ratios of ionic liquid/arene (see Figure 6). From the existence of these almost fixed composition ratios, one was able to infer the existence of liquid clathrates in the mixtures: one could add aromatic compounds to an ionic liquid solution until the former surrounded the ions of the latter in cage-like structures. However, at that point, further addition of the aromatic compound compromised the integrity of the polar network and liquid–liquid demixing occurred: i.e., one phase was composed of the pure aromatic compound, and the other phase was composed of the “saturated” ionic liquid.

**Congruent Melting.** Solid–liquid equilibrium measurements were added to the fluid-phase diagrams described above. In this new line of research, the melting temperatures of solutions of benzene in  $[C_2mim][NTf_2]$  were measured as a function of composition.<sup>20</sup> The most conspicuous and original feature of the corresponding phase diagram, apart from the liquid–liquid immiscibility window ending at the previously reported<sup>18</sup> mole ratio of 3:1 (benzene/ionic liquid), is the existence of a congruently melting compound at the equimolar composition,  $[C_2mim][NTf_2] \cdot C_6H_6$ , whose melting temperature of +15 °C is well above those of both benzene (+5.5 °C) and  $[C_2mim][NTf_2]$  (−15 °C). This type of behavior had never been reported for ionic-liquid-containing mixtures. The compound is an inclusion crystal with a 1:1 molar ratio of benzene/ionic liquid, whose structure was then determined by X-ray diffraction (Figure 7).

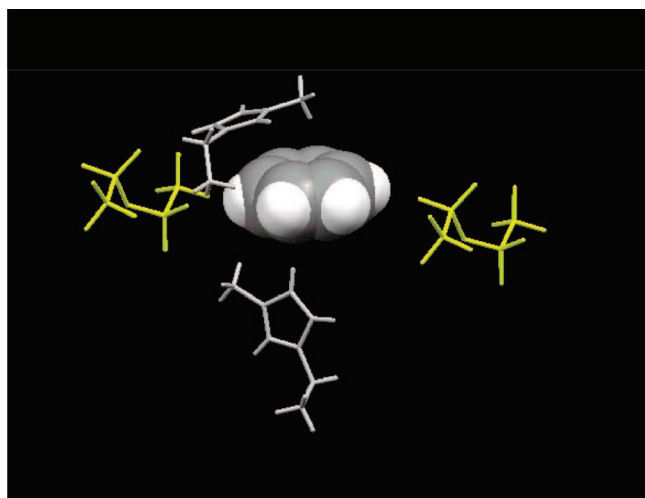
Several interesting conclusions can be drawn from the analysis of the X-ray structure<sup>20</sup> and its comparison with the previously published structure<sup>21</sup> of the  $([C_1mim]-$



**FIGURE 5.** Low-charge (green) and high-charge (orange) density domains in  $[\text{C}_8\text{mim}][\text{NTf}_2]$ , showing schematically its preferential spatial interactions with (a) an apolar solute (*n*-hexane) and (b) a dipolar and/or associative solute (water).



**FIGURE 6.** Fluid *T*-composition phase diagram of  $[\text{C}_n\text{mim}][\text{NTf}_2]$  plus benzene. The progressively darker shaded areas (from  $n = 2$  to 10, labeled as C2, C4, . . . , C10) identify immiscibility, two-phase regions. Symbols represent experimental data, and borderlines [between one-phase (1) and two-phase (2) regions] are guides to the eye.



**FIGURE 7.** Interactions between one benzene molecule and  $[\text{C}_2\text{mim}][\text{NTf}_2]$ . The image shows equatorial interactions of the aromatic plane with the anions and axial interactions with the cations.

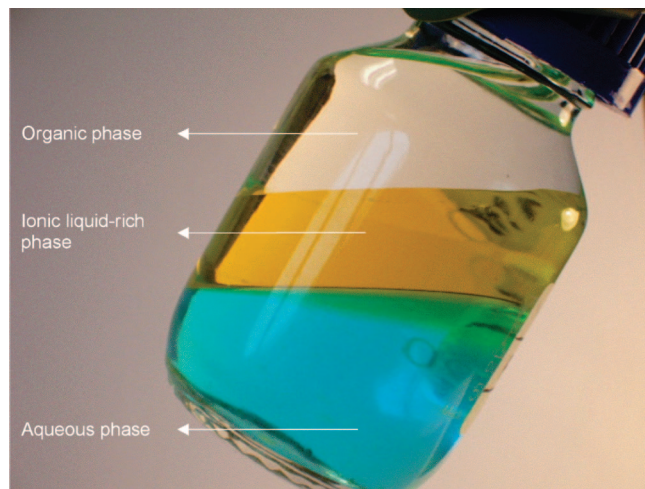
$[\text{PF}_6]_2 \cdot \text{C}_6\text{H}_6$  inclusion compound: (i) The interactions between the  $[\text{NTf}_2]^-$  anion and the benzene molecule occur mainly between the hydrogen atoms of the latter and the oxygen atoms of the sulfonate groups of the

former. The anions cluster around the benzene molecule mainly in the plane of the aromatic ring, and the interactions occur in that same plane. (ii) The interactions between the imidazolium cations and benzene are mainly between aromatic rings or interactions between the acidic hydrogens in the cation and the  $\pi$  electrons of benzene; i.e., the cations occupy positions above and below the plane of the benzene aromatic ring. (iii) Although the general pattern of interactions is similar in the 1:2 benzene/ $[\text{C}_1\text{mim}][\text{PF}_6]$  and 1:1 benzene/ $[\text{C}_2\text{mim}][\text{NTf}_2]$  crystals, the overall structure is quite distinct and reflects the difference in the molar ratios of benzene/ionic liquid. In the  $([\text{C}_1\text{mim}][\text{PF}_6])_2 \cdot \text{C}_6\text{H}_6$  crystal, the benzene molecules occupy channels within the structure of the ionic liquid. In  $[\text{C}_2\text{mim}][\text{NTf}_2] \cdot \text{C}_6\text{H}_6$ , the structure has to allow for a higher proportion of benzene molecules, forming a tube-like structure with a rectangular cross-section around the ionic liquid cations. As one moves from the 1:2 to the 1:1 type of inclusion compound, the observed trend suggests how cage-like structures of liquid clathrates can assemble at higher proportions of benzene (e.g., 1.5:1 or 2:1 of benzene/ionic liquid). In other words, from the perspective of the structure of the benzene molecules, the ionic liquid plus aromatic system evolves from one-dimensional stacks, to tube-like orientations, and finally, to cage-like arrangements.

The dual nature of the benzene interactions (equatorial with the anions and polar with the cations) allows for the benzene molecules to permeate the ionic structure without disrupting it and justifies the increased stability of the inclusion crystal. These facts illustrate the second facet of the dual behavior of ionic liquids in their relation with neutral solute molecules: the latter can (and do) interact differently with the cation and anions.

## From a Doubly Dual Nature to a Complex Fluid-Phase Behavior

The two aspects of the dual character of ionic liquids can be combined to shed some light on how the behavior of these novel fluids can be understood: a polar network that, because of the high asymmetry and charge delocalization

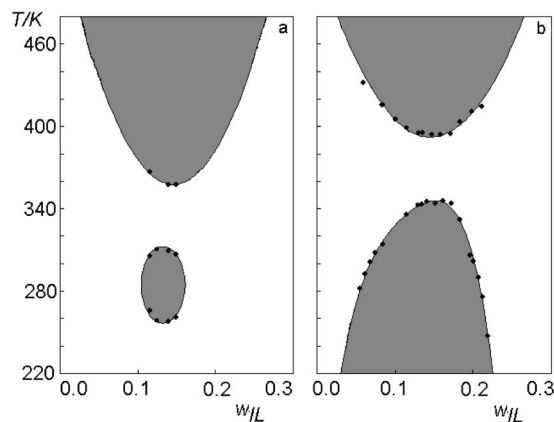


**FIGURE 8.** Photograph of three liquid phases produced by mixing phosphonium chloride,  $[P_{6,6,6,14}Cl]$ , with *n*-hexane and water, using  $CuSO_4$  as a dye. The intermediate-density ionic-liquid-rich phase contains significant amounts of *n*-hexane and water (and  $CuSO_4$ , with its distinctive yellow color in  $[P_{6,6,6,14}Cl]$ ), whereas the upper phase is almost pure *n*-hexane and the bottom phase contains water and copper sulfate.

of its constituent ions, is flexible enough to be permeated by nonpolar domains (generally attached to its cationic component) or molecules of quadrupolar, dipolar, or even associative nature. Whenever present, the nonpolar domains will also be able to dissolve nonpolar solutes. The richness of the solvation properties exhibited by ionic liquids (see Figure 8 and its caption) is a reflection of their doubly dual nature, and the intricacy of some of the phase diagrams studied by our group mirrors the preference or competition of different solutes for those dual characteristics.

**Mapping Islands.** One striking example of a complex phase diagram depicting what is usually termed as closed-loop immiscibility was obtained using mixtures containing ionic liquids of the 1-alkyl-3-methylimidazolium bistriflamide family and tri- or tetra-chloromethane.<sup>17,19</sup> In fact, not only closed-loop behavior (an immiscibility island) was detected but also demixing at even higher temperatures (i.e., an immiscibility dome) was found (see Figure 9). This kind of very rich fluid-phase behavior can be classified as type VII according to the extension of the Scott and van Konynenburg classification<sup>33</sup> (S&vK) and has hardly ever been observed for real systems.

When the size of the alkyl side chains of the ionic liquid are allowed to vary in quasi-binary mixtures of  $[(C_4mim)[NTf_2]]$  plus  $[(C_5mim)[NTf_2]]$  plus  $CHCl_3$ , changing and fine-tuning the relative sizes of the nonpolar region and polar network, the subtle balance between the entropic and enthalpic contributions to the Gibbs energy of the mixture is tipped over in one direction or the other, thus creating a series of mixing and demixing phenomena. This richness underlies several changes in the sign of the enthalpy of mixing upon the temperature change as well as distinct temperature dependences of the entropy of mixing.<sup>17</sup>



**FIGURE 9.** Fluid *T*-composition phase diagrams of quasi-binary mixtures of (a)  $[(C_4mim)[NTf_2]]$  plus  $[(C_5mim)[NTf_2]]$  plus  $CHCl_3$  and (b)  $[(C_5mim)[NTf_2]]$  plus  $(CHCl_3$  plus  $CCl_4)$ , in which the two-phase regions correspond to the shaded areas. The two pseudocomponents have a composition ratio corresponding to  $[C_{4.33}mim][NTf_2]$  in a and  $CH_{0.94}Cl_{3.06}$  in b.

In quasi-binary mixtures of  $[(C_5mim)[NTf_2]]$  plus  $(CHCl_3$  plus  $CCl_4)$  the closed-loop immiscibility behavior is replaced by a miscibility gap (S&vK, type IV). In  $(CHCl_3$  plus  $CCl_4)$  mixtures, different proportions of the two chloroalkanes permit us to manipulate the number of available hydrogens available for specific interactions with both the cation ( $\pi$  electrons of the ring) and the anion (oxygen). In this case, the two solutes,  $CHCl_3$  and  $CCl_4$ , show different affinities for the ionic liquid, with the latter probably showing a preference for the nonpolar domains and the former exhibiting a differentiated proclivity for the anion or the cation.

**Cooperation and Defection.** The previous example illustrates how the complex nature of an ionic liquid can be used to produce very intricate fluid-phase behavior, at a scale quite uncommon for the majority of molecular liquid mixtures. It can also be used to produce changes in the relations (interactions) between two molecular components of a mixture. Here, we are not just talking about subtle, well-balanced effects (that produce the intricate behavior) but also about quite dramatic ones that fall generally into the categories of co- or antisolvency effects.

Our first studies demonstrated that, although some ionic liquids present immiscible domains with both water<sup>34</sup> and alcohols,<sup>35</sup> surprisingly, the addition of water to mixtures of ionic liquids with alcohols markedly increases mutual solubility (cosolvent effect).<sup>9,11,12,22</sup> The ratio of water to alcohol content can be profitably used as a tool for fine-tuning desired situations of total miscibility, partial miscibility, or almost complete phase separation. In contrast, pressurized carbon dioxide ( $CO_2$ ) acts as an antisolvent<sup>10,23,24</sup> for ternary ionic liquid-ethanol-water mixtures. Thus, several switches in the number of phases are possible, allowing for reactions to be carried out in a single phase, leading to increased rates as well as catalyst immobilization, and, at a later stage, easy product separation produced by biphasic conditions. Generally, pressurized  $CO_2$  can be used as a strategy to trigger the precipitation of many solutes.<sup>36</sup>

**Table 1. Effective Size of Several Anions,  $V_a^*$ , and Cations,  $V_c^*$ , at 298.15 K and 1 bar<sup>14,40</sup>**

$V_a^*$ (cm <sup>3</sup> mol <sup>-1</sup> )									
[Cl] <sup>-</sup>	[Br] <sup>-</sup>	[NO <sub>3</sub> ] <sup>-</sup>	[CH <sub>3</sub> CO <sub>2</sub> ] <sup>-</sup>	[BF <sub>4</sub> ] <sup>-</sup>	[PF <sub>6</sub> ] <sup>-</sup>	[NTf <sub>2</sub> ] <sup>-</sup>	[CH <sub>3</sub> CH <sub>2</sub> SO <sub>4</sub> ] <sup>-</sup>		
25.9	27.8	39.1	53.0	53.4	73.7	158.7	91.4 <sup>a</sup>		
$V_c^*$ (cm <sup>3</sup> mol <sup>-1</sup> )									
[C <sub>0</sub> mim] <sup>+</sup>	[C <sub>2</sub> mim] <sup>+</sup>	[C <sub>4</sub> mim] <sup>+</sup>	[C <sub>6</sub> mim] <sup>+</sup>	[C <sub>8</sub> mim] <sup>+</sup>	[C <sub>10</sub> mim] <sup>+</sup>	[C <sub>12</sub> mim] <sup>+</sup>	[P <sub>66614</sub> ] <sup>+</sup>	[N <sub>1114</sub> ] <sup>+</sup>	[C <sub>4</sub> mpyrro] <sup>+</sup>
64.82	99.20	133.58	167.96	202.34	236.72	271.10	556.60	126.0 <sup>a</sup>	144.3 <sup>a</sup>

<sup>a</sup> From ref 40.

Similarly, aqueous biphasic systems (ABSs) in ionic liquid solutions provoked by salting-out effects<sup>37,38</sup> upon the addition of increased amounts of commonly used inorganic salts have also been witnessed. Two cases have been observed: (i) the significant broadening of a pre-existing two-phase region<sup>37</sup> and (ii) phase splitting in previously completely homogeneous mixtures (work in progress).

Cosolvent solubility is not unique to ionic liquid aqueous solutions in alcohols. Very recently, we found<sup>39</sup> for the first time that some nonaqueous ionic solutions in alcohols also exhibit cooperation solubility effects.

**Complex yet Ideal.** The inherent structured, complex nature of both liquid salts and water as well as alcohols would not *a priori* underlie quasi-ideal behavior for the binaries ionic liquid plus ionic liquid, ionic liquid plus water, and ionic liquid plus alcohol systems. Nonetheless, this is, in fact, the case. Although some binary combinations of ionic liquids present phase splitting,<sup>15,16</sup> the enthalpy and volume changes of mixing of two ionic liquids are generally quite small.<sup>15</sup> Considering that the mixture of two ionic liquids comprise an additional strategy for obtaining novel liquid salt media with unique properties, then, under the assumption of ideality, these same properties are easily and accurately estimated by mere weighed average of the values of the properties of the pure, constituent salts. This ideality was at the foundation of an extremely simple and precise methodology for the prediction of the molar volume of any ionic liquid as the combination (sum) of the effective volumes occupied by the constituent cations and anions ( $V_m = V_c^* + V_a^*$ ) (see Table 1 and refs 12 and 14 for details).

A master slope, ( $\partial V_m / \partial(2n)$ ), for the variation of the molar volume per the addition of two carbon atoms, ( $\partial V_m / \partial(2n) = (34.4 \pm 0.5) \text{ cm}^3 \text{ mol}^{-1}$ ), is obtained for the 1-C<sub>n</sub>-3-methylimidazolium-based ionic liquids, [C<sub>n</sub>mim]<sup>+</sup>, irrespective of the anion considered (Cl<sup>-</sup>, Br<sup>-</sup>, [NO<sub>3</sub>]<sup>-</sup>, [BF<sub>4</sub>]<sup>-</sup>, [PF<sub>6</sub>]<sup>-</sup>, and [NTf<sub>2</sub>]<sup>-</sup>). The typical predictive power of this algorithm is better than 0.5%.

Similarly, homogeneous solutions of ionic liquid plus water<sup>34</sup> and ionic liquid plus alcohols<sup>35</sup> also exhibit quasi-ideality. For instance, the excess heat capacities and excess volumes upon mixing are so small in comparison with the property of the mixture that a reliable prediction for the property of the solution consists of averaging the pure component values.

## Concluding Remarks

Ionic liquids can be regarded as nanoscaled, heterogeneous media composed of high- and low-charge-density domains. This distinctive characteristic is responsible for a wide variety of regimes in their interactions with distinct solutes, and in particular, it can explain their surfactant-like behavior, and their extraordinary solvent power for polar and nonpolar solutes, in short, the richness of their behavior. The relative importance of the nonpolar region is commonly manipulated by the length of alkyl side chains, which can be incorporated either in the cation or the anion.

Furthermore, the distinctive character of the interactions of a given solute toward the anionic or cationic moieties of an ionic liquid (the second facet of the dual behavior) also plays a central role in the definition of the fluid-phase behavior of ionic liquid solutions. An example is ionic liquids based on the [C<sub>1</sub>mim]<sup>+</sup> cation, which are completely soluble in water when associated with the chloride anion but, however, present liquid-liquid immiscibility domains when combined with the bistriflamide anion.

In general, the coarse tuning of their properties can be tailored by the choice of the chemical nature of the combined cation and anion, in which, as a consequence, the obtained weighed proportion of electrically charged territories versus apolar-like regions are paramount. The recognition of the doubly dual nature of ionic liquids constitutes a powerful tool for the development of future strategies aiming at a systematic interpretation and prediction of their properties.

## References

- (1) Seddon, K. R. Ionic liquids for clean technology. *J. Chem. Technol. Biotechnol.* **1997**, *68*, 351–356.
- (2) Rebelo, L. P. N.; Canongia Lopes, J. N.; Esperança, J. M. S. S.; Filipe, E. On the critical temperature, normal boiling point and vapour pressure of ionic liquids. *J. Phys. Chem. B* **2005**, *109*, 6040–6043.
- (3) 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. The distillation and volatility of ionic liquids. *Nature* **2006**, *439*, 831–834.
- (4) Smiglak, M.; Reichert, W. M.; Holbrey, J. D.; Wilkes, J. S.; Sun, L. Y.; Thrasher, J. S.; Kirichenko, K.; Singh, S.; Katritzky, A. R.; Rogers, R. D. Combustible ionic liquids by design: Is laboratory safety another ionic liquid myth? *Chem. Commun.* **2006**, 2554–2556.
- (5) (a) Baranyai, K. J.; Deacon, G. B.; MacFarlane, D. R.; Pringle, J. M.; Scott, J. L. Thermal degradation of ionic liquids at elevated temperatures. *Aust. J. Chem.* **2004**, *57*, 145–147. (b) Domanska, U. Thermophysical properties and thermodynamic phase behavior of ionic liquids. *Thermochim. Acta* **2006**, *448*, 19–30.

- (6) Holbrey, J. F. D.; Seddon, K. R. Ionic liquids. *Clean Prod. Processes* **1999**, *1*, 223–236.
- (7) *Ionic Liquids IIIA and IIIB*; Rogers, R. D., Seddon, K. R., Eds.; American Chemical Society: Washington, D.C., 2005.
- (8) (a) Deetlefs, M.; Seddon, K. R. Ionic liquids: Fact and fiction. *Chem. Today* **2006**, *24*, 16–23. (b) MacFarlane, D. R.; Seddon, K. R. Ionic liquids—Progress on the fundamental issues. *Aust. J. Chem.* **2007**, *60*, 3–5.
- (9) Najdanovic-Visak, V.; Esperança, J. M. S. S.; Rebelo, L. P. N.; Nunes da Ponte, M.; Guedes, H. J. R.; Seddon, K. R.; Szydłowski, J. Phase behaviour of room temperature ionic liquid solutions: An unusually large co-solvent effect in (water + ethanol). *Phys. Chem. Chem. Phys.* **2002**, *4*, 1701–1703.
- (10) Najdanovic-Visak, V.; Serbanovic, A.; Esperança, J. M. S. S.; Guedes, H. J. R.; Rebelo, L. P. N.; Nunes da Ponte, M. Supercritical CO<sub>2</sub>-induced phase changes in (ionic liquid, water, ethanol mixture) solutions: Application to biphasic catalysis. *ChemPhysChem* **2003**, *4*, 520–522.
- (11) Najdanovic-Visak, V.; Esperança, J. M. S. S.; Rebelo, L. P. N.; Nunes da Ponte, M.; Guedes, H. J. R.; Seddon, K. R.; de Sousa, H. C.; Szydłowski, J. Pressure, isotope, and water co-solvent effects in liquid-liquid equilibria of (ionic liquid + alcohol) systems. *J. Phys. Chem. B* **2003**, *107*, 12797–12807.
- (12) Rebelo, L. P. N.; Najdanovic-Visak, V.; Gomes de Azevedo, R.; Esperança, J. M. S. S.; Nunes da Ponte, M.; Guedes, H. J. R.; Visak, Z. P.; de Sousa, H. C.; Szydłowski, J.; Canongia Lopes, J. N.; Cordeiro, T. C. Phase behavior and thermodynamic properties of ionic liquids, ionic liquid mixtures and ionic liquid solutions. In *Ionic Liquids IIIA: Fundamentals, Progress, Challenges, and Opportunities, Properties and Structure—ACS Symposium Series*; Rogers, R. D., Seddon, K. R., Eds.; American Chemical Society: Washington, D.C., 2005; Vol. 901, pp 270–291.
- (13) (a) Gomes de Azevedo, R.; Esperança, J. M. S. S.; Visak, Z. P.; Guedes, H. J. R.; Pires, P. F.; Szydłowski, J.; Rebelo, L. P. N. Thermophysical and thermodynamic properties of ionic liquids over an extended pressure range: [bmim][NTf<sub>2</sub>] and [hmim][NTf<sub>2</sub>]. *J. Chem. Thermodyn.* **2005**, *37*, 888–899. (b) Esperança, J. M. S. S.; Visak, Z. P.; Plechkova, N. V.; Seddon, K. R.; Guedes, H. J. R.; Rebelo, L. P. N. Density, speed of sound, and derived thermodynamic properties of ionic liquids over an extended pressure range. 4. [C<sub>3</sub>mim][NTf<sub>2</sub>] and [C<sub>5</sub>mim][NTf<sub>2</sub>]. *J. Chem. Eng. Data* **2006**, *51*, 2009–2015.
- (14) Esperança, J. M. S. S.; Guedes, H. J. R.; Blesic, M.; Rebelo, L. P. N. Densities and derived thermodynamic properties of ionic liquids. 3. Phosphonium-based ionic liquids over an extended pressure range. *J. Chem. Eng. Data* **2006**, *51*, 237–242.
- (15) Guedes, H. J. R.; Cordeiro, T. C.; Lopes, J. N. C.; Esperança, J. M. S. S.; Rebelo, L. P. N.; Huq, S.; Seddon, K. R. Deviations from ideality in mixtures of two ionic liquids containing a common ion. *J. Phys. Chem. B* **2005**, *109*, 3519–3525.
- (16) Arce, A.; Earle, M. J.; Katdare, S. P.; Rodriguez, H.; Seddon, K. R. Mutually immiscible ionic liquids. *Chem. Commun.* **2006**, 2548–2550.
- (17) Łachwa, J.; Szydłowski, J.; Najdanovic-Visak, V.; Rebelo, L. P. N.; Seddon, K. R.; Nunes da Ponte, M.; Esperança, J. M. S. S.; Guedes, H. J. R. Evidence for lower critical solution behavior in ionic liquid solutions. *J. Am. Chem. Soc.* **2005**, *127*, 6542–6543.
- (18) Łachwa, J.; Szydłowski, J.; Makowska, A.; Seddon, K. R.; Esperança, J. M. S. S.; Guedes, H. J. R.; Rebelo, L. P. N. Changing from an unusual high-temperature demixing to a UCST-type in mixtures of 1-alkyl-3-methylimidazolium bis(trifluoromethyl)sulfonyl)amide and arenes. *Green Chem.* **2006**, *8*, 262–267.
- (19) Wiegand, S.; Kleemeier, M.; Schröder, J. M.; Schröder, W.; Weingärtner, H. Light-scattering investigations of the liquid-liquid phase-transition of the ionic system—Trimethylethyl-ammonium bromide in chloroform. *Int. J. Thermophys.* **1994**, *15*, 1045–1056.
- (20) Łachwa, J.; Bento, I.; Duarte, M. T.; Canongia Lopes, J. N.; Rebelo, L. P. N. Condensed phase behaviour of ionic liquid-benzene mixtures: Congruent melting of a [emim][NTf<sub>2</sub>]-C<sub>6</sub>H<sub>6</sub> inclusion crystal. *Chem. Commun.* **2006**, 2445–2447.
- (21) Holbrey, J. D.; Reichert, W. M.; Nieuwenhuyzen, M.; Sheppard, O.; Hardacre, C.; Rogers, R. D. Liquid clathrate formation in ionic liquid-aromatic mixtures. *Chem. Commun.* **2003**, 476–477.
- (22) Swatloski, R. P.; Visser, A. E.; Reichert, W. M.; Broker, G. A.; Farina, L. M.; Holbrey, J. D.; Rogers, R. D. Solvation of 1-butyl-3-methylimidazolium hexafluorophosphate in aqueous ethanol—A green solution for dissolving “hydrophobic” ionic liquids. *Chem. Commun.* **2001**, 2070–2071.
- (23) Najdanovic-Visak, V.; Rebelo, L. P. N.; Nunes da Ponte, M. Liquid-liquid behaviour of ionic liquid + 1-butanol + water and high pressure CO<sub>2</sub>-induced phase changes. *Green Chem.* **2005**, *7*, 443–450.
- (24) (a) Blanchard, L. A.; Hancu, D.; Beckman, E. J.; Brennecke, J. F. Green processing using ionic liquids and CO<sub>2</sub>. *Nature* **1999**, *399*, 28–29. (b) Scurto, A. M.; Aki, S. N. V. K.; Brennecke, J. F. CO<sub>2</sub> as a separation switch for ionic liquid/organic mixtures. *J. Am. Chem. Soc.* **2002**, *124*, 10276–10277.
- (25) (a) Wang, Y.; Voth, G. A. Unique spatial heterogeneity in ionic liquids. *J. Am. Chem. Soc.* **2005**, *127*, 12192–12193. (b) Canongia Lopes, J. N.; Pádua, A. A. H. Nanostructural organisation in ionic liquids. *J. Phys. Chem. B* **2006**, *110*, 3330–3335. (c) Lopes, J. N. C.; Gomes, M. F. C.; Pádua, A. A. H. Nonpolar, polar, and associating solutes in ionic liquids. *J. Phys. Chem. B* **2006**, *110*, 16816–16818.
- (26) Santos, L. M. N. B. F.; Lopes, J. N. C.; Coutinho, J. A. P.; Esperança, J. M. S. S.; Gomes, L. R.; Marrucho, I. M.; Rebelo, L. P. N. Ionic liquids: First direct determination of their cohesive energy. *J. Am. Chem. Soc.* **2007**, *129*, 284–285.
- (27) (a) Hu, Z.; Margulis, C. J. Heterogeneity in room-temperature ionic liquids: Persistent local environments and the red-edge effect. *Proc. Nat. Acad. Sci. U.S.A.* **2006**, *103*, 831–836. (b) Shigeto, S.; Hamaguchi, H. Evidence for mesoscopic local structures in ionic liquids: CARs signal spacial distribution of [C<sub>n</sub>mim][PF<sub>6</sub>] (n = 4,6,8). *Chem. Phys. Lett.* **2006**, *427*, 329–332.
- (28) Canongia Lopes, J. N.; Deschamps, J.; Pádua, A. A. H. Modelling ionic liquids using a systematic all-atom force field. *J. Phys. Chem. B* **2004**, *108*, 2038–2047.
- (29) Leal, J. P.; Esperança, J. M. S. S.; Minas da Piedade, M. E.; Canongia Lopes, J. N.; Rebelo, L. P. N.; Seddon, K. R. The nature of ionic liquids in the gas phase. *J. Phys. Chem. A* **2007**. ASAP on the web (DOI: 10.1021/jp073006k).
- (30) Armstrong, J. P.; Hurst, C.; Jones, R. G.; Licence, P.; Lovelock, K. R. J.; Satterley, C. J.; Villar-Garcia, I. J. Vapourisation of ionic liquids. *Phys. Chem. Chem. Phys.* **2007**, *9*, 982–990.
- (31) Zaitsau, D. H.; Kabo, G. J.; Strechan, A. A.; Paulechka, Y. U.; Zaitschich, A.; Verevkin, S. P.; Heintz, A. Experimental vapor pressures of 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imides and a correlation scheme for estimation of vaporization enthalpies of ionic liquids. *J. Phys. Chem. A* **2006**, *110*, 7303–7306.
- (32) Blesic, M.; Marques, M. H.; Seddon, K. R.; Plechkova, N. V.; Rebelo, L. P. N.; Lopes, A. Self-aggregation of ionic liquids: Micelle formation in aqueous solution. *Green Chem.* **2007**, *9*, 481–490.
- (33) van Konynenburg, P. H.; Scott, R. L. Critical lines and phase-equilibria in binary van der Waals mixtures. *Philos. Trans.* **1980**, *298*, 495–540.
- (34) Rebelo, L. P. N.; Najdanovic-Visak, V.; Visak, Z. P.; Nunes da Ponte, M.; Szydłowski, J.; Cerdeiriña, C. A.; Troncoso, J.; Romani, L.; Esperança, J. M. S. S.; Guedes, H. J. R.; de Sousa, H. C. A detailed thermodynamic analysis of [C<sub>4</sub>mim][BF<sub>4</sub>] + water as a case study to model ionic liquid aqueous solutions. *Green Chem.* **2004**, *6*, 369–381.
- (35) Łachwa, J.; Morgado, P.; Esperança, J. M. S. S.; Guedes, H. J. R.; Canongia Lopes, J. N.; Rebelo, L. P. N. Fluid-phase behavior of {1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, [C<sub>6</sub>mim][NTf<sub>2</sub>], + C<sub>2</sub>–C<sub>6</sub>n-alcohol} mixtures: Liquid-liquid equilibrium and excess volumes. *J. Chem. Eng. Data* **2006**, *51*, 2215–2221.
- (36) Saurer, E. M.; Aki, S. N. V. K.; Brennecke, J. F. Removal of ammonium bromide, ammonium chloride, and zinc acetate from ionic liquid/organic mixtures using carbon dioxide. *Green Chem.* **2006**, *8*, 141–143.
- (37) Trindade, J. R.; Visak, Z. P.; Blesic, M.; Coutinho, J. A. P.; Marrucho, I. M.; Lopes, J. N. C.; Rebelo, L. P. N. Salting out effects in aqueous ionic liquid solutions. *J. Phys. Chem. B* **2007**, *111*, 4737–4741.
- (38) Gutowski, K. E.; Broker, G. A.; Willauer, H. D.; Huddelston, J. G.; Swatloski, R. P.; Holbrey, J. D.; Rogers, R. D. Controlling the aqueous miscibility of ionic liquids: Aqueous biphasic systems of water-miscible ionic liquids and water-structuring salts for recycle, metathesis, and separations. *J. Am. Chem. Soc.* **2003**, *125*, 6632–6633.
- (39) Najdanovic-Visak, V.; Rodriguez, A.; Visak, Z. P.; Rosa, J. N.; Afonso, C. A. M.; Nunes da Ponte, M.; Rebelo, L. P. N. Co-solvent effects in LLE of 1-hydroxyethyl-3-methylimidazolium based ionic liquids + 2-propanol + dichloromethane or 1,2-dichloroethane. *Fluid Phase Equilib.* **2007**, *254*, 35–41.
- (40) Jacquemin, J. Étude thermodynamique de liquides ioniques non-aqueux. Ph.D. Thesis, Université Blaise Pascal, Clermont-Ferrand, France, 2006.

AR7000556