



Three commentaries on the nano-segregated structure of ionic liquids

Karina Shimizu^{a,b}, Margarida F. Costa Gomes^c, Agílio A.H. Pádua^c, Luís P.N. Rebelo^b,
José N. Canongia Lopes^{a,b,*}

^a Instituto de Tecnologia Química e Biológica, ITQB 2, Universidade Nova de Lisboa, Apartado 127, 2780-901 Oeiras, Portugal

^b Centro de Química Estrutural, Instituto Superior Técnico, 1049-001 Lisboa, Portugal

^c Laboratoire Thermodynamique et Interactions Moléculaires, CNRS/Université Blaise Pascal, Clermont-Ferrand, France

ARTICLE INFO

Article history:

Received 31 July 2009

Received in revised form 12 November 2009

Accepted 19 November 2009

Available online 5 December 2009

Keywords:

Molecular dynamics simulation

Ionic liquids

Nano-segregation

Structure

ABSTRACT

The concept that ionic liquids are nano-segregated fluids has allowed the rationalization at a molecular level of many of their complex and unusual properties, either as pure substances or as solvents. In this work we will use molecular dynamics simulation results to discuss in a semi-quantitative manner different aspects of such segregation: how it varies within a homologous ionic liquid family; the influence of the nature of the ions in the morphology of the segregated domains; and the interactions of those domains with molecular solutes or solvents.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Any substance that is composed essentially of anions and cations must possess some kind of short-range organization in order to fulfill local electro-neutrality conditions. In the case of ionic liquids such imposed short-range ordering does not lead to long-range structures (crystalline forms) at room temperature. This surprising fact is the defining characteristic of this amazing and complex class of compounds.

The difficulty of forming stable crystalline structures in ionic liquids is associated in most cases with the size, charge dispersion and segregation (including the existence of low-charge density molecular residues such as alkyl-side chains), asymmetrical form, and flexibility of the molecular ions that compose the ionic liquids.

With the benefit of hindsight it is not surprising that ionic liquids are presently regarded as structured, nano-segregated fluids. After all, this segregation can be regarded as the next logical step in the following state of affairs: if the ionic liquid has to order its high-charge density portions into local structures that obey electro-neutrality criteria, then the low-charge density parts that do not participate in those structures must be segregated elsewhere. It is this interplay between the two types of regions/interactions (polar versus non-polar) that eventually lead the formation of medium-range nano-scale domains and the recognition of ionic

liquids as a high-charge density (polar) network permeated by low-charge density (non-polar) regions (Fig. 1).

This situation was first identified by different computer simulation studies [1–3] and later corroborated experimentally by X-ray diffraction studies [4]. The newly born concept was then applied numerous times in different contexts in order to explain at a molecular level some of the extraordinary properties of ionic liquids either as pure substances or as solvents [5–7].

In this work we will use recent molecular dynamics simulation results to discuss in a systematic way different aspects of the nano-structured nature of ionic liquids and their mixtures. The study is semi-quantitative in character, just using snapshots and slices of different simulation boxes and the corresponding radial or spatial distribution functions to stress in a simple, visual way the different issues under discussion. Such approach also emphasizes the difficulties that still need to be overcome in order to quantify in a precise and unambiguous way the complex structures that arise from the segregated character of ionic liquids.

A final remark can be stated at this stage concerning the similarities between the structural features of ionic liquids and those displayed by some amphiphilic molecules, namely ionic surfactants that are also composed by a large organic ion with a hydrophilic head-group and a hydrophobic non-polar tail. When dissolved in a dielectric molecular solvent like water these molecules self-aggregate into micelles, vesicles or layered structures, all characterized by non-polar regions surrounded by a polar domain. Reverse micelles are also possible in some cases when the continuous medium is apolar. If the concentration of the surfactant

* Corresponding author. Address: Instituto de Tecnologia Química e Biológica, ITQB 2, Universidade Nova de Lisboa, Apartado 127, 2780-901 Oeiras, Portugal.
E-mail address: jnlopes@ist.utl.pt (J.N. Canongia Lopes).

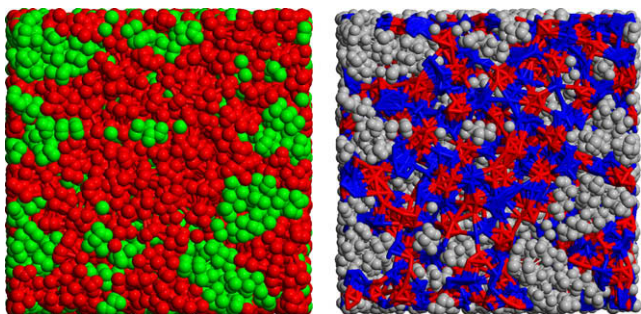


Fig. 1. Snapshot of an equilibrated simulation box containing the $[C_4mim][PF_6]$ ionic liquid. The old red–green color-coding scheme (red = polar network; green = non-polar regions) is compared with an alternative scheme where the connections (taking into account the corresponding van der Waals radii) within and between cations and anions of the polar network are emphasized (blue and red, respectively) and set against the atoms belonging to the non-polar regions (in gray). The local electro-neutrality within the polar network can be appreciated by the alternans of red and blue regions. The nano-segregation of the alkyl-side chains of the cation into the non-polar regions is evident in both cases. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

is high then lamellar, rod-like, bi-continuous, or liquid-crystal-like structures can also be found. However, and unlike ionic liquids, traditional ionic surfactants are either crystalline or amorphous solids at room temperature, and only exhibit those features when dissolved in a molecular solvent. Ionic liquids can exhibit some of those features (liquid crystalline structures for instance) in a concentration range that can go from the pure ionic liquid to dilute electrolyte solutions. This fascinating topic is also drawing a lot of attention from the scientific community but will not be discussed further in the present paper.

2. Methodology

Molecular dynamics simulations of condensed phases of different pure ionic liquids or ionic liquid mixtures were performed using the DL_POLY program [8]. All ions and molecules were modeled using a previously described atomistic force field specially suited for the systematic study of ionic liquids and their mixtures with molecular solvents [9–12]. System sizes were chosen so as to contain around 10,000 atoms, which correspond to cutoff distances above 1.5 nm. Initial low-density configurations, with ions (and molecules in the cases of mixtures) placed at random in periodic cubic boxes, were equilibrated to attain liquid like densities and structures at 300 K and 1 bar. Temperature and pressure were maintained using the Nosé–Hoover thermostat and barostat. Equilibration runs (either from new or previously obtained configurations) took up to 2 ns. In some cases temperature annealing and charge scrambling had to be performed in order to facilitate the equilibration and avoid ergodicity problems. Production runs typically took around 600 ps. Electrostatic energies were calculated using the Ewald summation method with a relative accuracy of 10^{-4} and other long-range corrections were performed above the cutoff distance. All snapshots and radial distribution functions were generated from multiple configurations taken from the production runs. Further simulation details can be found elsewhere [13].

3. Results and discussion

The results will be discussed in three different sections of increasing degree of complexity: firstly we will consider the structuration of a series of ionic liquids all belonging to the same homol-

ogous family, where the only variable is the length of the alkyl-side chain of the cation, the anion or both; secondly we will discuss different types of segregated domains that may occur in different pure ionic liquids and how they can be correlated with the morphology of the constituting ions and the number of possible interactions between them; finally we will analyze the behavior of the nano-domains when the ionic liquid is mixed with a molecular species. Both dilution regimes will be considered, with the ionic liquid acting either as a solvent or as a solute.

3.1. Nano-structures within a homologous family of a pure ionic liquid: from non-polar islands to bi-continuous phases

The first simulation studies that analyzed the possible existence of nano-segregation considered a homologous series of ionic liquids based on 1-alkyl-3-methylimidazolium cations, $[C_nmim]^+$. The studies revealed that as the alkyl-side chain of the cation increases in length, the size of the non-polar domains also increases a fact that is confirmed by the steady raise in the first peak of the pair radial distribution functions between the carbons (C_T) of the terminal methyl groups of the chain. These RDFs show that the C_T atoms tend to form clusters where the local concentration of those atoms is larger than the average concentration of C_T in the ionic liquid and that the size of the clusters increase with the length of the alkyl-side chain. This suggests that the alkyl-side chains are being segregated from the rest of the ionic liquid and that it is possible to have the formation of nanometer-scale domains, or pockets, in which the alkyl-side chains exist in an alkane-like domain, separated from the rest of the ionic liquid, that forms a polar network. A real breakthrough came when, in one of the studies, the domains were visualized by color-coding the polar and non-polar parts of each ion [3]. In those first systems the polar part was painted red and contained the whole anion $[PF_6]^-$, the imidazolium ring, and the groups of the cation directly linked to it. The alkyl-side chain of the cation starting from the second methylene group was painted green. The red–green color code became quite popular as an easy way to “see” the segregation and the corresponding domains in ionic liquids and their mixtures. In this work we have applied an alternative color scheme (already present in Fig. 1, and applied throughout the article) where the negative and positive parts of the polar network are differentiated - red and blue, respectively - and the non-polar alkyl-side chains are painted in a neutral gray. Moreover instead of painting the atoms we decided sometimes to emphasize and color the connections between them, in order to render more conspicuous the relations between the two segregated domains.

The topology of the non-polar domains as the alkyl-side chain becomes longer was also analyzed in those first studies. The general conclusion is that when the alkyl-side chains are small (C_2 – C_4 in the case of $[C_nmim][PF_6]$ [3]), the non-polar domains consists of hydrocarbon-like “islands” in the midst of a continuous polar network, whereas for longer alkyl-side chains those islands start to connect forming a second continuous micro-phase, establishing in this way a bi-continuous segregated phase. In the present work we have decided to represent (Fig. 2) the even more common (and stable) 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide family of ionic liquids, $[C_nmim][NTf_2]$. The most important feature to notice here is that since the anion in this case ($[NTf_2]^-$) is bulkier than the previous one ($[PF_6]^-$), the limit for the “percolation” of the islands seems to be slightly shifted to longer alkyl-side chains (around C_6 instead of C_4). This makes sense just from a topological perspective: if the polar network is larger due to bulkier ions (in this case the term “ions” refers just to the high-charge density parts of the cation or anion), one also needs larger islands before the connection between them (“percolation”) starts to happen.

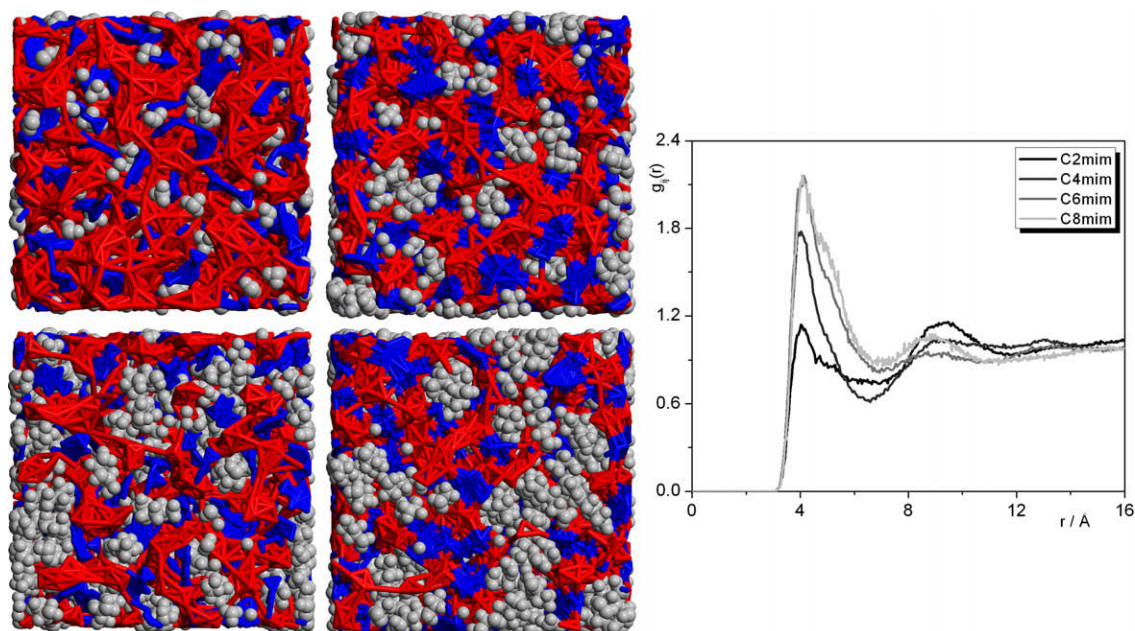


Fig. 2. Snapshots of equilibrated simulation boxes containing [C_nmim][NTf₂] ionic liquids ($n = 2, 4, 6$ and 8 from left to right; top to bottom). Color scheme as in Fig. 1b. The “growth” of the alkyl-side chains leads to a morphology change of the non-polar domains, from isolated islands to a second continuous nano-domain. The progressive “concentration” of the alkyl-side chains into larger non-polar domains can be appreciated taking into account the pair radial distribution functions of the corresponding terminal carbon atoms (CT–CT) (on the right). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Another important aspect of structuring within the same homologous family concerns the recent systematic study of ionic liquids based on 1-alkyl-3-methylimidazolium cations combined with alkylsulfonate anions [14]. In this matrix-like family the alkyl-side chains can be located in the cation, in the anion, or in both ions. Preliminary simulation runs show that the morphology of the non-polar domains is the same, irrespective of the “source” of the alkyl-side chain. This can be understood as a further proof of the segregation of the alkyl-side chains into non-polar alkane-like domains.

Finally this idea can be taken even further by considering a mixture of two homologous ionic liquids, cf. Fig. 4. In this case a situation similar to the previous case also occurs: an equimolar mixture of [C₂mim][NTf₂] + [C₆mim][NTf₂] is, from the structural point of view, very similar to pure [C₄mim][NTf₂], in other words, the origin of the alkyl-side chains (their size and point of attachment in the polar network) is not so important within the same homologous family of ionic liquids, as long as the total length of the alkyl-side chain remains constant.

3.2. Nano-structures in different pure ionic liquids: from filament to globular networks

In the previous section we have seen that the relative size (volume occupied) by the polar and non-polar parts of the ionic liquid will determine its morphology (dispersed versus bi-continuous). All those studies were based on 1-alkyl-3-methylimidazolium cations, as a convenient way to change in a systematic manner the size of the alkyl-side chain. As a matter of fact the alkyl-side chain of ionic liquids based on 1-alkyl-3-methylimidazolium cannot get much longer than C₁₄ as they will start to melt at relatively high temperatures and to form liquid crystal (smectic) phases (see also legend of Fig. 3). However many other ionic liquids are based on other cations with quite different polar/non-polar ratios. The relative distribution of the polar and non-polar parts inside a given ion can also be quite different: in 1-alkyl-3-methylimidazolium cations we can have a long alkyl-side chain that ends up in a polar “head”; in tetra-alkyl ammonium or phosphonium cations that polar “head” can be completely surrounded by long chains, occupying

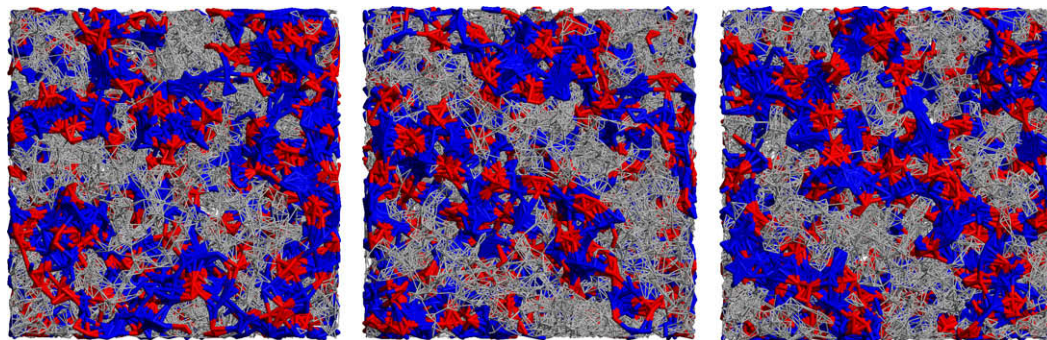


Fig. 3. Three snapshots of equilibrated simulation boxes containing [C_mmim][C_nSO₃] ionic liquids: (m, n) = (10, 2), (2, 10) and (6, 6) from left to right. Color scheme as in Fig. 2 but with the non-polar domains represented as sticks instead of space-filled atoms. This representation allows a better visualization of the polar networks. The nano-structures of the ionic liquid are similar, irrespective of the “source” of the alkyl-side chains: cationic in (10, 2), anionic in (2, 10) and from both ions in (6, 6). For long alkyl-side chains (total of 12 carbons in this case) the domains appear to start forming some kind of layered structures (which can be regarded as a prequel to the liquid crystal phases that are known to exist for longer alkyl-side chains [15]). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

in this way a more “central” position in the ion. In this section we will discuss how the morphology of the individual ions in different ionic liquids affects the topology of the ensuing nano-structured domains.

Fig. 5 shows three snapshots of three distinct ionic liquids with a quite high non-polar volume ratio. It is quite obvious that the non-polar regions occupy a considerable volume of the whole simulation box and that they form continuous phases. However the most important thing to notice in this case is the appearance of the corresponding polar networks. In the case of the tetra-alkyl ammonium ionic liquid it is not very easy to make out the contours of the polar network since its thread-like appearance is finely enmeshed within the non-polar regions. The 1-tetradecyl-3-methylimidazolium ionic liquid exhibits a quite different situation with “globules” of polar and non-polar regions quite conspicuous at the surface of the simulation box. Finally, the polar network of the tetra-alkyl phosphonium ionic liquid shows, as in the first case, a thread-like appearance. In this case the larger non-polar-to-polar volume ratio enables one to distinguish much more easily between the polar and non-polar regions. The different connectivity of the polar network – sequential in the case of the thread-like structures of the ammonium and phosphonium cations; highly branched in the case of the globular structures of the imidazolium cations – reveals how the interactions between the high-charge density parts of the anions and cations affect the morphologies of their polar networks. Apart from the obvious (and rather isotropic) electrostatic interactions, anions and cations can also interact in some

cases through other types of quite specific (and strong) interactions. A case in point is the hydrogen-bond-type interactions that the imidazolium cation can establish with different anions through its C₂ (and in a lesser degree C₄ and C₅) hydrogen atoms. These interactions allow each imidazolium to interact with more than two anions at the same time and thus form “branched” polar networks that can develop into globular structures. On the other hand the “central” tetra-alkyl phosphonium or ammonium cations do not establish such interactions and the hindered “central” atoms of phosphorus or nitrogen will be able to interact simultaneously with a limited number of counter-ions. The result will be non-branching sequences of cations and anions and the development of filament networks.

It must be stressed at this point that the notion of the existence of ionic pairs in the ionic liquid (specially in cases where specific and strong interactions are possible, like those involving the imidazolium cation and certain anions), is not conflicting with the concept of a polar network. In a condensed phase the concept of an ionic pair must be regarded as a “preferred” interaction between two ions of opposite sign: an ion will select a preferred partner from all the possible counter-ions of its first coordination shell (the one that is in a suitable position to perform a specific interaction). When such a “pair” is formed it does not mean that it will stop interacting with all the others or that the preferred counter-ion at a given instant will “fall from grace” at a later time. This means that even if such preferred interactions are very strong and the corresponding ionic pairs very stable, the polar network

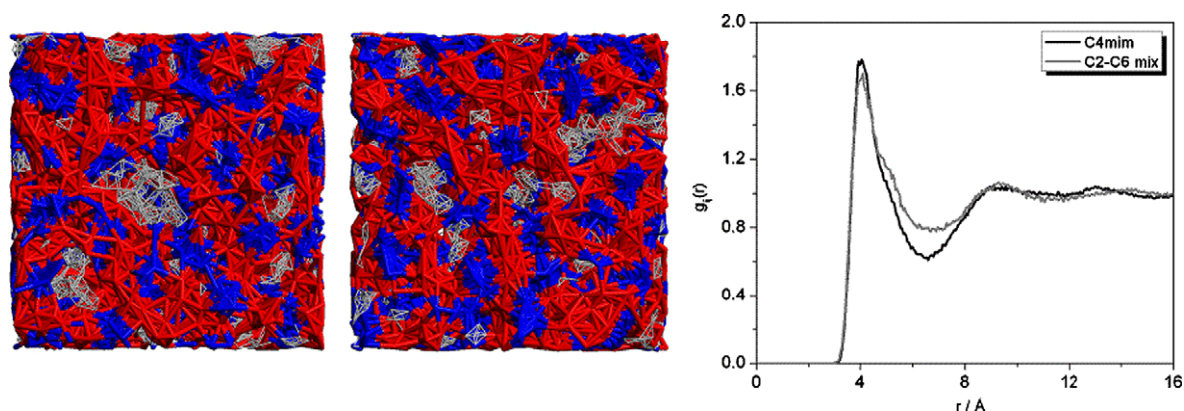


Fig. 4. From the left: Two snapshots of equilibrated simulation boxes containing an equimolar mixture of [C₂mim][NTf₂]+[C₆mim][NTf₂] and pure [C₄mim][NTf₂] ionic liquids. Color scheme as in Fig. 3. Right: Pair radial distribution functions of the terminal carbon atoms of the alkyl-side chains (CT–CT or CT–CE). The polar-to-non-polar level of segregation is very similar in both cases, although the size distribution non-polar regions is slightly different (better defined in pure C₄ than in the C₂ + C₆ mixture). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

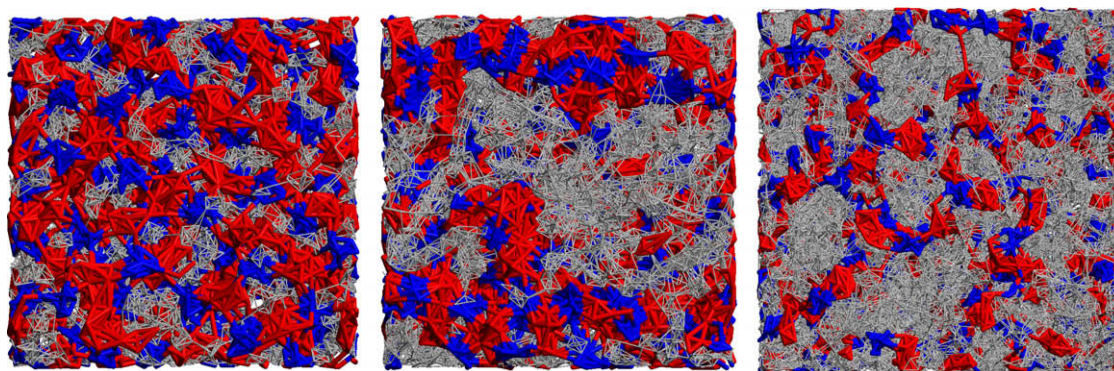


Fig. 5. Snapshots of equilibrated simulation boxes containing [N_{1 4 4 4}][NTf₂], [C₁₄mim][NTf₂] and [P_{6 6 14}][NTf₂] ionic liquids (from left to right). Color scheme as in Fig. 3. Apart from the obvious impact of the different polar-to-non-polar ratios, the morphology of the domains is also dictated by the connectivity of the polar network (see text). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

is still possible to occur through the (still) existing electrostatic interactions between ions of opposite sign. An interesting case in point is the example of task-specific ionic liquids that form very strong networks when react with CO₂ and cause a massive increase in the viscosity of these systems [16].

3.3. Nano-structures in ionic liquid plus molecular solvent/solute mixtures

The concept that ionic liquids can exhibit nano-segregated domains alters the way one can interpret the solvation properties of molecular species in those media. Different molecular solutes, according to their polarity or tendency to form associative interactions, will not only interact selectively with certain parts of the individual ions but may also be solvated in distinct local environments. In this context ionic liquids can be regarded as “two-in-one” solvents, with each domain acting as a specific solvent for a given class of solutes: molecules like *n*-alkanes will be solvated and tend to dissolve in or near the non-polar domains, whereas dipolar or associating solutes will interact with (or permeate) the polar network. These ideas were previously explored in different publications where the double (or even triple) character of ionic liquids as solvents towards different classes of solutes was analyzed [13,17]. Maybe one of the most important conclusions in this context is the notion that sometimes it is very difficult to perform comparisons between the solubility of different solutes in the same ionic liquid, just because they are experiencing different local environments and in fact it is like they are being dissolved in different solvents [17]. Another general conclusion is that solutes can be classed into three groups: those that prefer the non-polar regions of the ionic liquid – typically non-polar solutes like alkanes; those that interact strongly with the polar network – water is the obvious example of such an associative fluid that can promote hydrogen bonding, specially with specific atoms of the anion; and finally dipolar solutes that can orient themselves at the interface between the polar and non-polar regions of the ionic liquid – acetonitrile, acetone or small halogenated hydrocarbons fall into this category (Fig. 6). It is in this last group (dipolar, non-associative fluids) that one can find the best solvents for a large variety of ionic liquids, a behavior that can be rationalized in terms of the positioning of the molecules at the interface between the polar and non-

polar regions and their ability to orient their dipoles in order to interact simultaneously with the anions and cations of the polar network. The permeation of the polar network can lead to its disruption and eventual solvation of the ions that compose the ionic liquid (see below).

A special case is that of aromatic compounds like benzene and its twelve fluorinated derivatives [18]. Those that have large dipole moments (when the di-, tri- or tetra-fluorination is on the same side of the molecule) are completely miscible with ionic liquids like [C₂mim][NTf₂]. On the other hand, the five most symmetrical elements of this family (that have null dipole moment but exhibit non-null quadrupole moments) are only partially miscible with the same ionic liquid. However, they are much more soluble than non-aromatic hydrocarbons. The interesting thing is that the relative solubilities of all thirteen solutes in [C₂mim][NTf₂] can be correlated taking into account the way their dipole and quadrupole moments affect (or are affected by) the polar network of the ionic liquid (Fig. 7). In fact, the different electronic density distributions of the aromatic molecules act as templates that promote special and spatial rearrangements of the polar network around them and account for the diverse and increased solubilities of these compounds.

Finally one can also analyze the morphology of the segregated structures of the ionic liquid when they act not as solvents but as solutes in progressively more diluted mixtures of a molecular solvent. One of the most interesting aspects of ionic liquids is that if one picks a molecular fluid that is completely miscible with the ionic liquid in all proportions, then one can go from an electrolyte at infinite dilution – the (almost) pure molecular solvent – to the most concentrated electrolyte solution imaginable – the pure ionic liquid. At infinite dilution the ionic liquid ions must be necessarily solvated by the molecular solvents as discrete species or (if the specific interactions between them are very strong) as ionic pairs. At the other end of the concentration range, those same ions are part of a continuous polar network. Somewhere in the middle we must have another type of percolation limit, where the polar network starts to disrupt and starts to form isolated ionic aggregates. One of the first studies to address this problem [19] studied solutions of [C₄mim][NTf₂] in naphthalene and concluded that as the concentration of the ionic liquid diminished, the polar network started to change from a globular to a more filamentous

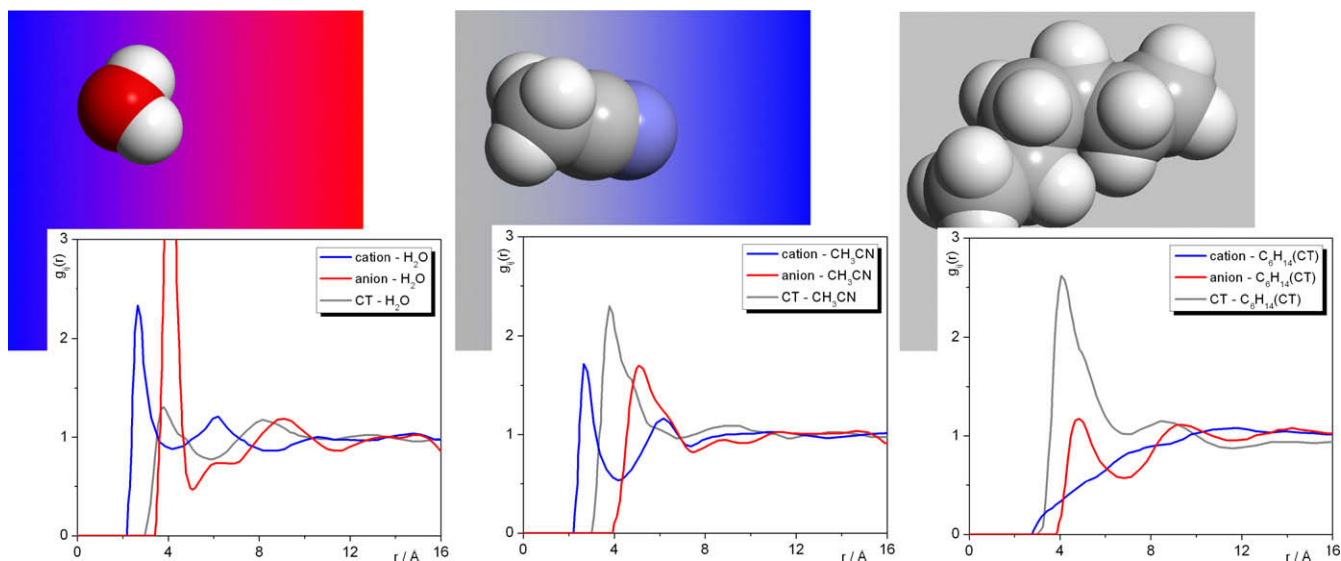


Fig. 6. Three representative types of solute and their relation to the nano-structures of an ionic liquid, as shown by the pair radial distribution functions between selected atoms of the solute and atoms of the cation, anion and alkyl-side chain of [C₄mim][NTf₂]. From left to right: associative solute (water) that interacts mainly with the polar network; dipolar solute (acetonitrile) that interacts at the polar–non-polar interface; and non-polar solute (*n*-hexane) that interacts mainly within the non-polar domains.

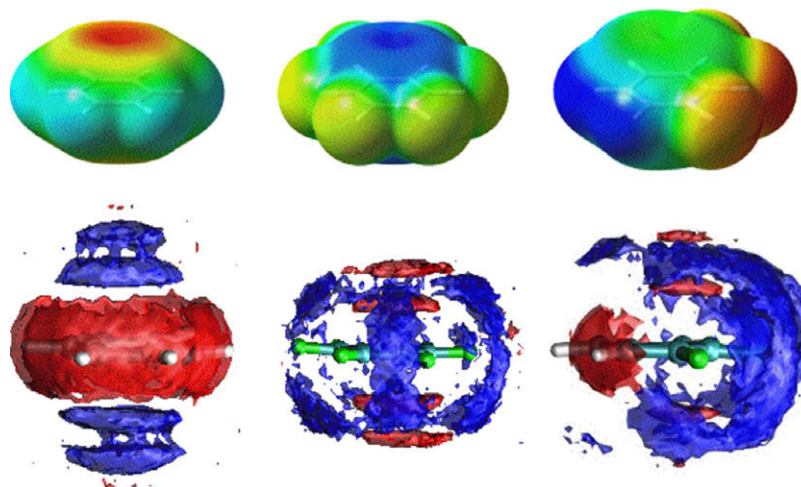


Fig. 7. Top: electrostatic potential functions (EPFs) mapped onto electron density isosurfaces around benzene, hexafluorobenzene and 1,2,3-trifluorobenzene (from left to right). Positively or negatively charged regions are indicated by color gradients changing from dark blue to red, respectively. The electrostatic potential functions were calculated ab initio on isolated molecules (Gaussian 03 at the MP2/cc-pVTZ(-f)//HF/6-31G(d) levels of theory, cf. Ref. [18]). Bottom: spatial distribution functions of the strongest interactions centres in the cations (blue) and anions (red) of the [C₂mim][NTf₂] ionic liquid around the same three aromatic molecules. The results were obtained by molecular dynamics simulation of equimolar (aromatic plus ionic liquid) mixtures. The EPFs of the aromatic molecules are used as opposite-charge templates by the polar network of the ionic liquid in order to spatially re-arrange its ions. Further details (and other aromatic molecules) are presented elsewhere [18]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

appearance (see for instance Fig. 5 of Ref. [19]). In order to rationalize this trend one must keep in mind that the solvent is not only occupying extra space (in this sense it has the same effect that using longer alkyl-side chains in homologous series of ionic liquids) but also interacting/competing with the ions of the polar network – the naphthalene of this example can interact with ionic liquids in a way similar to that of the aromatic compounds ana-

lyzed in the previous paragraph. The partial disruption of the polar network between cations and anions due to the intrusion of the aromatic molecules will in a first stage cause the collapse of the branched structures present in the concentrated [C₄mim][NTf₂] ionic liquid and produce the change from a globular to a filamentous network. At even more diluted ionic liquid concentrations (not studied in the above cited work) it would be possible to witness

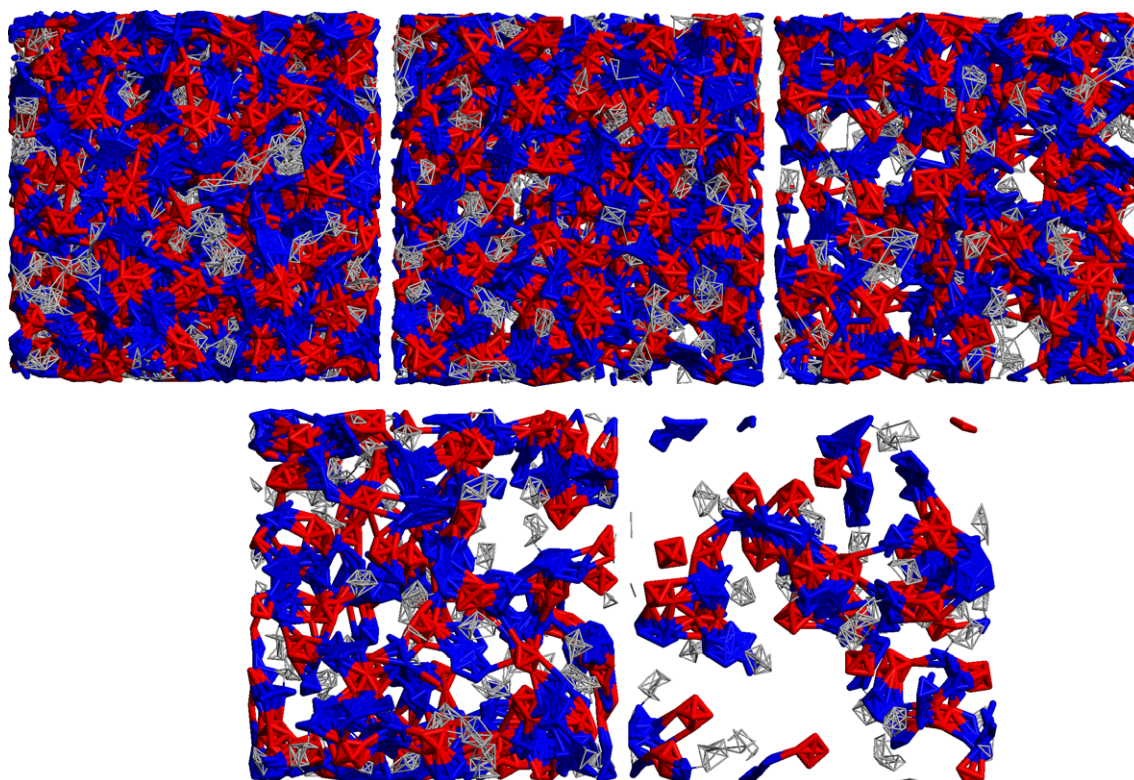


Fig. 8. Snapshots of MD simulation boxes of progressively diluted mixtures of [C₄mim][NTf₂] in acetonitrile. The mole fractions of the ionic liquid are 0.83, 0.50, 0.27, 0.14 and 0.06 from left to right and from top to bottom, respectively. The solvent (not represented) is able to permeate and finally disrupt the polar network. In the most diluted solution (bottom right) the polar network is arranged in a filamentous structure that is starting to lose its continuity (some ions or ionic aggregates are already isolated from the rest of the polar network).

the breaking apart of the continuous network into (string-like?) ionic filaments. This scenario is shown in Fig. 8, where we have simulated the [C₂mim][PF₆] system in acetonitrile.

4. Conclusions

The discussion presented in the previous section was divided into three parts. This allows the phrasing of three final commentaries regarding the nano-structured nature of ionic liquids and their mixtures:

- (a) The high-charge and low-charge density regions of the ions that compose ionic liquids tend to be segregated into a polar network and non-polar domains. The latter, depending on the relative size of the high-charge and low-charge regions in each ion, can exist as isolated (dispersed) islands or a second continuous phase. The percolation limit corresponding to the transition from a dispersed to a continuous non-polar phase can be attained with longer alkyl-side chains. It also depends on the size of the polar network. The “source” of the alkyl-side chain in homologous ionic liquids (from the cation, the anion or both) is not very important for static properties such as the relative sizes of its segregated domains.
- (b) The number of anion–cation pairs (nearest neighbours) allowed in a given ionic liquid affects the branching of the polar network and defines its morphology: filament or globular networks. Cations with a “central” positive atom surrounded by long alkyl-side chains (tetra-alkyl ammonium or tetra-alkyl phosphonium cations) will generally exhibit string-like polar networks.
- (c) The positioning of solutes within a given ionic liquid is defined by the sizes and morphology of the structures and the degree of empathy of the solute for each region. This means that different solutes are solvated in different nano-phases of the ionic liquid. The latter can be regarded as 2-in-1 solvents. Solute that interact strongly with the polar network, namely those that have a dipolar or quadrupolar nature, will re-arrange the polar network around them. They can be regarded as molecular templates that are changed by their interactions with the ions of the ionic liquid but are also capable of changing the spatial arrangement of the ions

in the polar network around them. The morphology of the domains changes (and eventually disappears) when the ionic liquid is progressively diluted in a solvent that is miscible with it in all proportions.

Acknowledgments

This work was supported by the Fundação para a Ciência e Tecnologia (FC&T), Portugal (POCI/QUI/57716/2004 and PTDC/CTM/73850/2006). KS acknowledge the Grant SFRH/BPD/38339/2007. AAHP and MFCG would like to recognize the support of the “Prof. António Xavier Excellence Award” by the Oeiras City Council.

References

- [1] S.M. Urahata, M.C.C. Ribeiro, *J. Chem. Phys.* 120 (2004) 1855.
- [2] Y. Wang, G.A. Voth, *J. Am. Chem. Soc.* 127 (2005) 12192.
- [3] A.A.H. Pádua, J.N. Canongia Lopes, *J. Phys. Chem. B* 110 (2006) 3330.
- [4] A. Triolo, O. Russina, H.-J. Bleif, E. Di Cola, *J. Phys. Chem. B* 111 (2007) 464; O. Russina, A. Triolo, L. Gontrani, R. Caminiti, D. Xiao, L.G. Hines Jr., R.A. Bartsch, E.L. Quitevis, N. Plechkova, K.R. Seddon, *J. Phys.: Condens. Matter* 21 (2009), doi:10.1088/0953-8984/21/42/424121.
- [5] Y. Wang, W. Jiang, T. Yan, G.A. Voth, *Acc. Chem. Res.* 40 (2007) 1193.
- [6] L.P.N. Rebelo, J.N. Canongia Lopes, J.M.S.S. Esperança, H.J.R. Guedes, J. Lachwa, V. Najdanovic-Visak, Z.P. Visak, *Acc. Chem. Res.* 40 (2007) 1114.
- [7] A.A.H. Pádua, M.F. Costa Gomes, J.N. Canongia Lopes, *Acc. Chem. Res.* 40 (2007) 1087.
- [8] W. Smith (Ed.), *Mol. Simul.* 32 (2006) 933.
- [9] J.N. Canongia Lopes, J. Deschamps, A.A.H. Pádua, *J. Phys. Chem. B* 108 (2004) 2038.
- [10] J.N. Canongia Lopes, A.A.H. Pádua, *J. Phys. Chem. B* 108 (2004) 16893.
- [11] J.N. Canongia Lopes, A.A.H. Pádua, *J. Phys. Chem. B* 110 (2006) 19586.
- [12] J.N. Canongia Lopes, A.A.H. Pádua, K. Shimizu, *J. Phys. Chem. B* 112 (2008) 5039.
- [13] J.N. Canongia Lopes, M.F. Costa Gomes, A.A.H. Pádua, *J. Phys. Chem. B* 110 (2006) 16816.
- [14] M. Blesic, M. Swadźba-Kwaśny, T. Belhocine, H.Q.N. Gunaratne, J.N. Canongia Lopes, M.F. Costa Gomes, A.A.H. Pádua, K.R. Seddon, L.P.N. Rebelo, *Phys. Chem. Chem. Phys.* 11 (2009) 8939.
- [15] M. Blesic, M. Swadźba-Kwaśny, J.D. Holbrey, J.N. Canongia Lopes, K.R. Seddon, L.P.N. Rebelo, *Phys. Chem. Chem. Phys.* 11 (2009) 4260.
- [16] K.E. Gutowski, E.J. Maginn, *J. Am. Chem. Soc.* 130 (2008) 14690.
- [17] L. Pison, J.N. Canongia Lopes, L.P.N. Rebelo, A.A.H. Pádua, M.F. Costa Gomes, *J. Phys. Chem. B* 112 (2008) 12394.
- [18] K. Shimizu, M.F. Costa Gomes, A.A.H. Pádua, L.P.N. Rebelo, J.N. Canongia Lopes, *J. Phys. Chem. B* 113 (2009) 9894.
- [19] M.G. Del Popolo, C.L. Mullan, J.D. Holbrey, C. Hardacre, P. Ballone, *J. Am. Chem. Soc.* 130 (2008) 7032.