

Invited Review

Nanostructural Organization of Ionic Liquids: Theoretical and Experimental Evidences of the Presence of Well Defined Local Structures in Ionic Liquids

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Summary. From an overview of the different theoretical and experimental methods it was possible to evidence the presence of aggregates in ionic liquids (ILs), and to specify their role in determining the unique physical-chemical properties of these media. An understanding of the structure of ILs, as pure compounds or in the presence of dissolved species, is fundamental if the reactivity and selectivity in ILs mediated reactions is to become predictive.

Keywords. Ionic liquids; Interionic interactions; Ionic network; Solid-like.

Introduction

Room temperature ionic liquids (ILs), which are organic salts having melting points below 100°C, have attracted in the last decade much attention in applied chemistry as alternative green solvents [1]. This is because of some advantages presented by these compounds when used as reaction media: thermal stability, nonvolatility, non-combustibility, amphiphilicity, and so on. The most commonly used ionic liquids are the ones based on nonsymmetrically substituted *N,N'*-dialkylimidazolium cations and bulky anions, such as PF_6^- , BF_4^- and $[(\text{CF}_3\text{SO}_2)_2\text{N}]^-$, although also the corresponding pyridinium, pyrrolidinium, and phosphonium salts have been widely investigated. Recently, also new ILs based on different cations (sulfonium, triazolium, guanidinium, morpholinium, and so on), or bearing specific functional groups

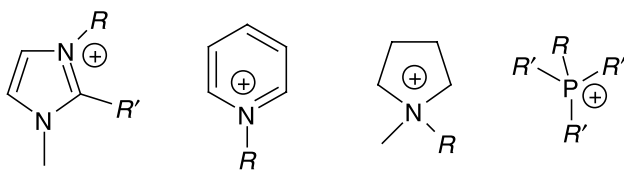
on the cation or anion, are receiving increasing attention as designer media in catalysis and material sciences [2].

ILs are considered as “designer solvents” as one has the ability to, in principle, fine-tune solvent properties, such as viscosity, melting point, density, refractive index, polarity, or water miscibility by using an appropriate combination of the cationic and anionic constituents [3]. Far from being each ionic liquid a solution for all problems, it is becoming apparent that specifically tailor-made ILs can improve a lot of processes by virtue of the fact that each IL presents peculiar features although, and fortunately, not all ILs present exactly the same properties. For example, many solutes are poorly soluble in many ILs but they are soluble in some specific liquid salts; some reactions take place slowly or not at all in many common ionic liquids, but this not necessarily implies that they cannot occur in some selected ILs. A deeper knowledge of ILs and their properties is desirable for a rational design and subsequent application of new ionic solvents having improved properties.

Apart from a large number of studies directed towards the characterization of the various physico-chemical properties, ILs have been investigated as solvent systems in organic and inorganic synthesis, catalysis, and electrochemical studies [4]. With the aim to understand their structural and dynamic properties, more recently, single-crystal X-ray diffraction

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Common cations



Common anions

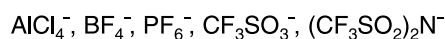


Fig. 1. Common ionic liquids cations and ions

studies, IR and Raman spectroscopy investigations, and computer simulations have been performed on common ILs, mainly imidazolium salts.

In chemical reactions, viscosity and polarity are two properties of the solvent that can affect reaction rates and product yields [5]. To investigate the polarity of ILs several approaches have been applied and consequently several scales have been developed [6] including the static dielectric constants [7]. But, in addition to these physical properties, the fate of a chemical reaction is strongly correlated to the mutual interactions between the reacting molecules and the solvent molecules surrounding them. A chemical reaction is a function of the motions that occur in the surrounding liquid on a time scale similar to the rate of the reaction. Slow reactions will depend mostly on the diffusive behavior of the solvent whereas a very fast reaction will depend predominantly on inertial motions.

In very general terms, the role of the solvent in promoting a chemical reaction is to alter the energies of the reactant and product states in order to optimise the probability of jumping from one electronic state to another [5]. In a purely static view, this implies a rearrangement of charges in the solvent, described by the dielectric constant, in response to an altered charge distribution on the solute. From a dynamic point of view, states with different charge distributions are solvated by solvent modes occurring on a femtosecond to picosecond timescale.

The environment constituted by ILs is completely different from that of apolar and polar molecular solvents. Ionic liquids are constituted exclusively by ions and hence experience strong coulombic interactions in addition to possible hydrogen bonds and/or other dispersive forces due to the alkyl chains. The interionic interactions determine the physico-chemi-

cal and spectroscopic properties of ILs and their nanostructural organization. More than a decade ago it was proposed that in the solid state 1-ethyl-3-methylimidazolium chloride should be considered a three dimensional network of anions and cations linked together by weak interactions, mainly hydrogen bonds [8]. Subsequently, it was suggested that 1-alkyl-3-methylimidazolium salts have a similar structure both in solid and liquid states [9]. In recent years, it has become clear that ILs, and their mixtures with other molecules present a supramolecular structural organization and this organization is a fundamental peculiarity able to determine the majority of the unusual features of these media.

Here, by an overview of the different theoretical and experimental methods, throughout it was possible to collect evidences of the presence of aggregates in ILs, and their role in determining the unique physical and chemical properties of these media, will be described. An understanding of the structure of ILs, as pure compounds or in the presence of dissolved species, is fundamental if the reactivity and selectivity in ILs mediated reactions is to become predictive.

Interionic Interactions and Nanostructural Organization

Determination by OHD-RIKES, Neutron Diffraction, ESI-MS, and NMR Measurements

Signals in optical heterodyne-detected Raman-induced Kerr effect spectroscopy (OHD-RIKES) result from intermolecular librations and intramolecular vibrations. In principle, the optical Kerr effect (OKE) spectrum will have contributions from a molecular term, and an interaction-induced term and a molecular-interaction-induced-cross term. The OKE spectrum of most liquids, however, tends to be dominated by the molecular term, which arises from collective librational motions of the molecules in the liquid [10]. Libration describes the “rocking” of molecules in the field of neighbouring molecules and raises the issue of the local structure. For example, in the case of cyclohexane, a molecule with no permanent dipole moment and very low polarisability, the (OHD-RIKES) signal is due to the libration of an interaction-induced dipole moment [11]. The weak intermolecular interactions in cyclohexane determine the relatively low frequency of the two Brownian oscillators, at 25 and 53 cm^{-1} . At variance, DMSO

has a permanent dipole moment and shows higher librational frequencies (21, 54, and 91 cm^{-1}) consistent with the expected stronger intermolecular interactions. Using optical heterodyne-detected Raman-induced Kerr effect spectroscopy (OHD-RIKES), Giraud *et al.* evidenced [11] that the intermolecular part of the OKE spectrum of ILs can be viewed as a reflection of the librational motion of the imidazolium ring. All the investigated ILs were characterized by spectra broader than those of non-polar, weakly interacting molecular liquids, such as cyclohexane, but comparable in width to those of polar, strongly interacting molecular liquids. Really, the spectra of ILs present libration bands at frequencies slightly higher than *DMSO*, suggesting even stronger intermolecular interactions and a high degree of association. On the other hand, the large number of functions required to fit these spectra (for *[bmim][Tf₂N]*, the signal is fitted with three functions at 15, 56, and 95 cm^{-1}) has been considered an evidence of the inhomogeneous nature of the sample on very short time scales. The librational bands observed in the OKE spectra have been attributed [11] to the three types of preferred location of the anion with respect to the cation, as shown in Fig. 2, and the relative amplitudes of these bands have been considered proportional to the probability of finding an anion in these locations. The probability is significantly higher for the position closer to the C2 atom, intermediate for the opposite position (between C4 and C5), and lower for the remaining two positions (between nitrogen atoms and C4 or C5).

The fact that the three peaks are separated by approximately 30 cm^{-1} , and they are resolved in the spectrum rather than merged into a single peak, indicates that if the anion can change its position relative to the cation, this must occur on a timescale longer

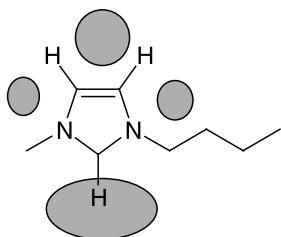


Fig. 2. Possible location of anion (grey spots) with respect to the imidazolium cation. The dimensions of the spots are qualitatively related to the probability to find the anion in that position

than 1 ps. The lifetime of the ion in its environment is therefore quite long.

Subsequently, Shirota and Castner provided [12] evidences, through a comparative study of the ionic liquid 1-methoxyethylpyridinium dicyanoamide (*[MOEPy][DCA]*) and a 1:1 binary neutral mixture of 1-methoxyethylbenzene and dicyanomethane (*MOEBz/DCM*), that interionic interactions cause ILs to be different from molecular liquids. Although the neutral mixture and ionic liquid are similar in molecular shape, charge distribution, and mass, the presence of charges increases the density and viscosity of *[MOEPy][DCA]* with respect to *MOEBz/DCM* and modifies the OKE spectrum of IL which is higher in frequency and broader than that of *MOEBz/DCM*.

However, the sole presence of interionic interactions is not sufficient to explain all the features of the OHD-RIKES spectra of ILs. It is necessary to assume that these interactions are responsible for a nanostructural organization of these liquids, an aspect which has found, as discussed below, several experimental and theoretical supports.

As evidenced by Xiao *et al.* [13], the presence of a nanostructural organization inside ILs provides a conceptual framework to understand the intermolecular dynamics of ILs. Xiao *et al.* found indeed that at the low-frequency ($<200\text{ cm}^{-1}$) intermolecular optical Kerr effect (OKE) spectra of binary ionic liquid mixtures of 1-pentyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (*[C₅mim][Tf₂N]*) and 1-pentyl-3-methylimidazolium bromide (*[C₅mim]Br*) are additive. Additivity in physical properties is usually indicative of ideal behavior, where interspecies interactions are absent. Given their molecular complexity, ILs are far from being ideal systems and the fact that the OKE spectrum of a binary ionic liquid mixture is simply given by the sum of the OKE spectra of the neat ionic liquids is quite surprising. In particular, if we consider that the reported OHD-RIKES spectra of mixtures of molecular liquids are nonadditive, even for nonassociating molecular liquids. The additivity in the OKE spectra of ILs has been therefore explained [13] by assuming that mixtures are nanostructurally organized as neat ILs, with three-dimensional ionic networks probably permeated by nonpolar regions, and the structure of the ionic networks in the mixtures is such that there are “blocks” along the network ordered in the same way as in the neat liquids, with

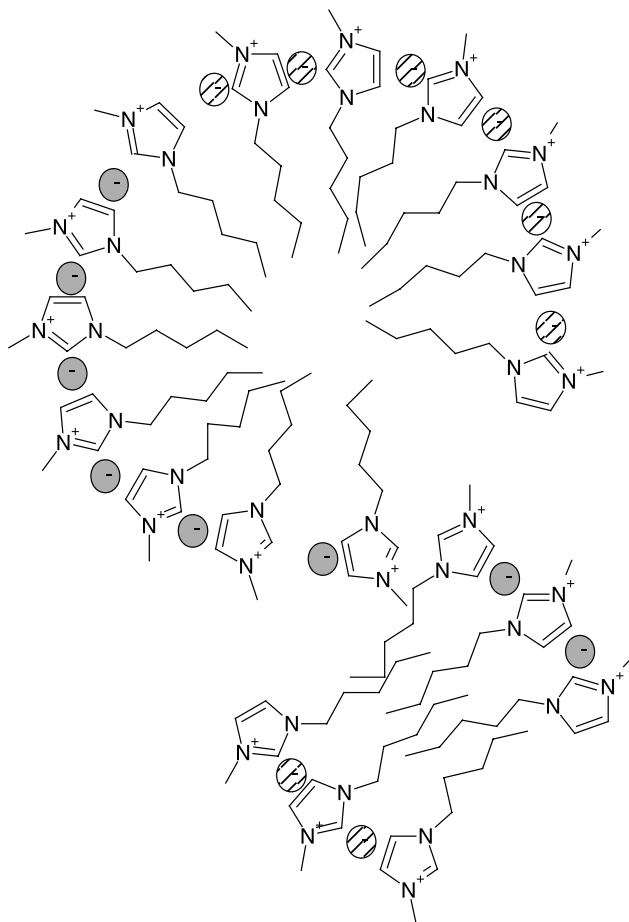


Fig. 3. Schematic representation of the nanostructural organization in binary mixture of $[C_5mim][Tf_2N]$ and $[C_5mim]Br$. The two anions are evidenced using different colours. The ionic network should be a multistranded chain instead of a single-stranded chain, for simplicity it has been represented in this way

clustering of the alkyl groups into nonpolar domains (Fig. 3).

More recently, to explore further the role of interionic interactions in determining the OKE spectra and the nature of nanostructural organization in ILs, the same authors have investigated [14] the effect of anion size on the temperature dependence of the OKE spectra of three imidazolium ionic liquids having as cation 1-pentyl-3-methylimidazolium ($[C_5mim]Br$, $[C_5mim][PF_6]$ and $[C_5mim][Tf_2N]$). Whereas the OKE spectrum of $[C_5mim][Tf_2N]$ is temperature-dependent, the OKE spectra of $[C_5mim]Br$ and $[C_5mim][PF_6]$ are temperature independent. It is to note that the bulk densities of all these ILs are temperature-dependent. The temperature independence of the OKE spectra and the

temperature dependence of the bulk density in $[C_5mim]Br$ and $[C_5mim][PF_6]$ has been therefore rationalized on the basis of the presence of inhomogeneities in the densities of these liquids. The existence of these inhomogeneities may be considered a consequence of the nanostructural organization of ILs characterized by nonpolar regions and ionic networks. On the basis of this representation, differences in the temperature dependences of the OKE spectra must be attributed to the degree of charge ordering in the polar regions of the ILs. The stability to charge ordering in the ionic network of $[C_5mim]Br$ and $[C_5mim][PF_6]$ makes these ILs less prone to temperature changes and the OKE spectra are in the examined temperature range independent of this parameter. In contrast, the temperature dependence of the OKE spectrum of $[C_5mim][Tf_2N]$ is a manifestation of the presence of ions in the network with significantly less charge ordering. Because of this charge ordering, the ionic networks will be more closely packed or more “solid-like” in $[C_5mim]Br$ and $[C_5mim][PF_6]$ than in $[C_5mim][Tf_2N]$. They will have higher cohesive energy densities than $[C_5mim][Tf_2N]$ and the less charge ordering characterizing this latter makes this ionic network more “liquid-like”.

OKE measurements are therefore able to evidence some peculiarities of ILs: 1) the interaction between anions and cations produces ionic organized networks; 2) inhomogeneities are present in these media when cations bear sufficiently long alkyl groups, which determine the existence of unpolar domains besides the polar ones; 3) the nature of cation and anion determines the degree of charge ordering.

Related to this latter feature, neutron diffraction measurements performed on ionic liquids with 1,3-dimethylimidazolium as cation ($[dmim]^+$) confirm that there is significantly less charge ordering in salts with Tf_2N^- anion in comparison to salts with PF_6^- or Cl^- [15]. The larger cation–cation and cation anion separation, characterizing $[dmim][Tf_2N]$, is indicative of an expansion of the liquid structure in this salt with respect to $[dmim]Cl$ and $[dmim][PF_6]$. In addition it is noteworthy that, whereas two-dimensional NOE-experiments (NOESY) on neat imidazolium salts having as anion BF_4^- show both intra- and intermolecular contacts, no intermolecular contacts have been detected in neat $[bmim][Tf_2N]$ and $[bm_2im][Tf_2N]$ [16]. Considering the data arising from neutron diffraction and OKE spectra, *Mele*

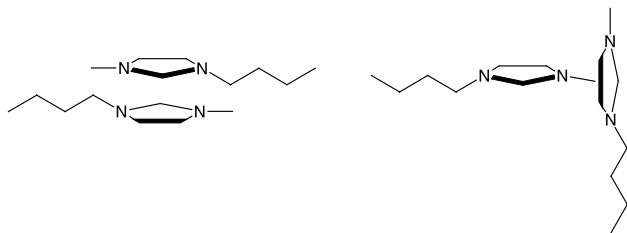


Fig. 4. Representation of the head-to-head aggregation of $[bmim]^+$ as evidenced by NOESY measurements

et al. attributed [16] this behavior to the increased interaction distance in the Tf_2N^- salts, rather than to unfavorable correlation times. The NOESY experiments, however, evidence primarily the aggregation inside the ILs due to cation–cation interactions. Quantitative NOE interaction data and average internuclear distances of the head-to-head interactions were reported, showing that the distances are consistent with the presence of some type of aromatic-ring association, either stacking or perpendicular T-shaped assembly (Fig. 4).

The comparison of these data with those related to the solid state evidences that cation–cation distances obtained by NOESY measurements are in the range of the homologous short contacts observed in the crystals of $[bmim]^+$ and $[bm_2im]^+$ with different anions. Imidazolium cations are close in space despite the coulombic repulsion, and the NMR data provide further support to the existence of polar domains in pure ILs. At variance, the formation of non-polar domains due to the aggregation of the alkyl chains seems not to be consistent with the observed NOE interactions [16].

On the other hand, information on the size of these local structures due to the alkyl chains in imidazolium salts, including also the $[bmim]^+$ cation, have been reported on the basis of the spatial distribution measurement of the coherent anti-*Stokes Raman* scattering (CARS) signals [17]. The measurements, carried out on three common imidazolium ILs $[C_nmim][PF_6]$ ($n=4, 6, 8$), seem to evidence the presence of local domains, with a size in the range of 10–100 nm, which increases with the alkyl chain length.

Similarly, X-ray diffraction studies carried out on other 1-alkyl-3-methylimidazolium-based salts have provided further experimental evidences of the existence of structural organization in neat liquid and supercooled ILs [18]. The characteristic size of these

structural heterogeneities is found to linearly scale with the alkyl chain length. This behavior has been attributed to the fact that the domains are due to the aggregation of the alkyl tails which are surrounded by charges whose distribution is determined by the strong electrostatic forces.

A further support for the concept that ILs are micro-biphasic systems composed of polar and unpolar domains can be found also in the values of standard molar enthalpies of vaporization, determined for a series of 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonylimides), $[C_nmim][Tf_2N]$ using a high-precision vacuum-vaporization drop microcalorimetric method [19]. The cohesive energy increases with the length of the alkyl chain on cation, although the computed *Coulomb* energy is constant along the homologous series. The increase of cohesive energy has been therefore attributed to an increase in the *van der Waals* interactions.

Analogously, a similar conclusion can be gained considering the molar conductivity ratios (A_{imp}/A_{NMR}), calculated from the molar conductivity determined by the electrochemical impedance method (A_{imp}) and that estimated by the use of pulse-field-gradient spin-echo NMR ionic self-diffusion coefficients and the *Nerst-Einstein* relation (A_{NMR}). If this ratio may be considered a quantitative evaluation of the formation of ionic aggregates, as suggested by *Tokuda et al.* [20], the observed decrease in the ratio A_{imp}/A_{NMR} with increasing number of carbon atoms in the alkyl chain for the $[C_nmim][Tf_2N]$ series has to be attributed to the increased contribution of the *van der Waals* interactions. However, these latter interactions can increase the ratio A_{imp}/A_{NMR} if the IL is an organized structure. More in particular, in a non-organised liquid, the presence of longer alkyl chains should separate the charged parts of the cation and anion and consequently the electrostatic forces would decrease along the series. The decrease in these forces should determine an increase in the A_{imp}/A_{NMR} , with this ratio being a measure of the ionic association. On the other hand, if ILs are three-dimensional polar networks permeated by nonpolar domains, as the alkyl chains become longer the unpolar regions increase in size but the ionic network remains intact. Thus, while the *van der Waals* interactions increase, the intensity of the *Coulomb* forces is kept constant; the sum of these two effects determines the decrease in the ratio A_{imp}/A_{NMR} .

Recently, also the Terahertz-time-domain spectroscopy (THz-TDS) has been used to obtain information about the ultrafast processes in ILs [21]. The dielectric values of the investigated ILs ([*emim*][*TfO*], [*emim*][BF_4], [*bmim*][*TfO*], and [*bmim*][BF_4]), which are related to subpicosecond-to-picosecond dynamics, are similar to those of short-chain alcohols, in between to those of nonpolar liquids and water. At variance with alcohols, however, ILs show structured lineshapes which reflect the low-frequency motions of interion and/or intramolecular vibrations. By comparison of the spectra obtained from different imidazolium based ILs, containing the same anions as counterions, it has been evidenced that the THz spectra do not originate from the intramolecular vibrations of the imidazolium cations. The interion vibrations dominantly contribute to the THz dielectric spectra, strongly suggesting that also in the liquid phase the ILs have local structures similar to their solid-phase structures.

Although the ionic network characterizing ILs is generally represented, as reported in Fig. 3, as a single-stranded chain of ions it should be thought as a three-dimensional structure, *i.e.* as superimposed multi-stranded chains. Experimental and MD calculations show that there are several anions in the first coordination shell around a given cation. Considering the three-dimensional structure, it is possible that the aromaticity of the imidazolium cation, through the π - π interaction, may play an important role in the local structure formation. Although no systematic investigation has been performed on nonaromatic ILs, a recent picosecond time-resolved fluorescence study on solute-solvent interaction of 2-aminoquinoline in aromatic and nonaromatic ILs seems to suggest that, whereas imidazolium based ionic liquids can be considered nanostructured fluids, nonaromatic ILs seem not able to form a specific local structure [22]. Imidazolium based ILs, due to the aromaticity of cation, may have peculiar properties inside the wide and unexplored world of ILs.

The pronounced supramolecular self-organization characterizes not only the solid and liquid state but also the gas phase. Information on the ability of ILs to give supramolecules has been obtained for the gas phase by tandem mass spectrometric experiments. Mass spectrometry was successfully applied to ionic liquids more than two decades ago [23]; however, only recently it has been possible to

prove and characterize the existence of aggregates with electrospray ionization mass spectrometry (ESI-MS) [24]. ESI-MS has been applied to investigate ILs assemblies and to compare and measure, *via* collision-induced dissociation (CID), the *intrinsic* “solvent-free” strengths of the anion-cation interaction, defined by the authors as hydrogen bond ability [25]. The observation that ionic liquids formed cationic $[\text{C}_{q+1}\text{X}_q]^+$ and anionic $[\text{C}_q\text{X}_{q+1}]^-$ supramolecular aggregates, which are efficiently transferred into the gas phase by the electrospray ionization process, induced *Gozzo et al.* [25] to investigate the possible formation of mixed supramolecular networks formed by different cations coordinated to a selected anion or by different anions bonded to a given cation of composition $[\text{C}1 \dots \text{X} \dots \text{C}2]^+$ and $[\text{X}1 \dots \text{C} \dots \text{X}2]^-$. From these experiments, the intrinsic solvent-free magnitude of the hydrogen bond of five ions (CF_3COO^- , BF_4^- , PF_6^- , InCl_4^- , and BPh_4^-) to the 1-butyl-3-methylimidazolium ion was evaluated. More recently, ESI-MS in both positive and negative modes have been applied by *Bini et al.* [26] to measure the relative strength of anion-cation interaction inside different ionic liquids. Low-energy collision dissociation of loosely bonded homologous and mixed complexes have provided important and complementary information about the magnitude of these interactions. Based on the relative abundances of fragment ions originating from the MS/MS decompositions of mixed complexes ($[\text{C}1 \dots \text{Br} \dots \text{C}2]^+$) it was possible to infer a qualitative order of intrinsic bond strength to Br^- : $[\text{emim}]^+ > [\text{bmim}]^+ > [\text{mor}1,2]^+ > [\text{hmim}]^+ > [\text{omim}]^+ > [\text{mor}1,4]^+ > [\text{bupy}]^+ > [\text{bpyrr}]^+ > [\text{picol}]^+ > [\text{bm}_2\text{im}]^+ > [\text{TBA}]^+$. Analogously, the formation, isolation, and dissociation of mixed gaseous $[\text{X}1 \dots \text{bmim} \dots \text{X}2]^-$ supramolecules has allowed to envisage two classes of anions: anions tightly coordinated to the cationic moiety, that include CF_3COO^- , Br^- , $\text{N}(\text{CN})_2^-$, and BF_4^- and anions loosely interacting with the alkyimidazolium species such as OTf^- , PF_6^- , and Tf_2N^- . The measurements evidence that Tf_2N^- is absolutely the least interacting anion among the investigated ILs.

Theoretical Studies

In the last years also theoretical studies on clusters of ILs have been performed and cooperative effects have been evidenced. Recent molecular dynamics

(MD) simulations have shown [27, 28] that ILs based on the 1-alkyl-3-methylimidazolium cation ($[C_n\text{mim}]^+$) with alkyl chains C4 and longer are spatially heterogeneous. Using a united-atom MD method, *Urahata* and *Ribeiro* [27a] showed that a low wave vector peak appears in the partial structure factor. They attributed this peak to the occurrence of an intermediate range order for C4 and C8 but not for shorter chains. *Wang* and *Voth* [29] using a multiscale coarse-grain MD method showed that heterogeneous domains are formed by the aggregation of alkyl groups for C4 and longer, with the cation rings and anions homogeneously distributed. The tail groups of cations aggregate forming spatially heterogeneous domains, due to the competition between the long range electrostatic interactions between charged head groups and anions and the collective short range interactions between the mutual tail groups. Contemporaneously, *Lopes* and *Padua* [28a] using an all-atom MD method showed by color coding the nonpolar and polar regions, that the polar regions are not isolated, but they are interconnected in such a way as to form a three-dimensional, charge-ordered ionic network permeated by nonpolar regions. As the length of the alkyl chain increases, the nonpolar domains become larger and more connected and cause swelling of the ionic network, in a manner analogous to systems exhibiting microphase separation. *Lopes* and *Padua* coined the phrase “nanostructural organization” to describe this spatial heterogeneity in ionic liquids.

The presence of voids inside the ILs can contribute to the heterogeneity of the system. Previously, *Margulis* had calculated the distribution of cavities in imidazolium based ILs with different alkyl chains and found the existence of long-lived cavities for long chained imidazolium salts [30]. Although these cavities are small they can accommodate even not spherical molecules, such as CO_2 , since the small cavities can reorganize into a smaller number of larger voids upon introduction of CO_2 [31]. This phenomenon of reorganization of “empty space” in the liquid has been considered the cause for the small change of volumes as CO_2 is added to the ionic liquid. Specific interactions however, can play in the solubility of CO_2 in ionic liquids. Specific interactions between CO_2 and the anion of $[bmim][\text{PF}_6]$ have been evidenced through X-ray diffraction measurements [32], whereas recent *ab initio* molecular dynamic simulation studies of the $[bmim][[\text{PF}_6]]$ -

CO_2 mixture confirming that CO_2 is primarily solvated by the anion suggest that also specific interactions, such as the hydrogen bond between the CO_2 and the ring hydrogen H(C3), could contribute to the solubility of CO_2 in this IL [33].

Effect of Nanostructural Organization on ILs Physico-Chemical Properties

The fact that ILs exhibit medium range ordering, *i.e.* they present persistent microscopic domains, typical of the glassy state has important consequence on the physico-chemical properties of ILs, such as viscosity, diffusion, conductivity, and spectroscopic features. Moreover, presence of microphase segregation between polar and nonpolar domains in imidazolium based ILs bearing sufficiently long chains can significantly affect the mechanism throughout ILs are able to solvate polar and unpolar solutes. This gives a rational support to the fact that ILs possess a dual behavior when used as a stationary phase in gas chromatography. They act as a low-polarity phase with unpolar compounds, while molecules with strong proton donor groups are strongly retained [34].

Structural analysis on the solvation of nonpolar, polar, and associating solutes in $[bmim][\text{PF}_6]$ have been performed by *Lopes et al.* [28b]. Whereas *n*-hexane and water represent the two extreme situations where the solute is concentrated either in the nonpolar domain or in the charged domain, acetonitrile and methanol represent intermediate situations. Interaction with both domains were evidenced for these solutes, although in different proportions [28]. Methanol and acetonitrile seem to interact strongly with the anion; in methanol, hydrogen bonding occurs between the hydroxy group and the fluorine atoms of the anion. On the other hand, the interactions of the hydrogen atoms of imidazolium are stronger with acetonitrile than with methanol [28]. Also water interacts strongly with the anion, and the interactions are dominated by hydrogen bonding (two hydrogen bonding in the case of water). Moreover, the oxygen of water much more than that of methanol is able to give a stronger interaction with the hindered H2 atom of imidazolium. Due to the strong binding of water to the anion, water molecules tend to be isolated from each other and this may explain the lower reactivity of water when dissolved in ILs.

The influence of water on the nanostructural organization of ILs has been a central focus in the last years due to its potential application to synthetic chemistry and catalysis. Starting from the work of Schröder *et al.* [35], who studied water induced acceleration of ion diffusion and proposed for the first time that imidazolium-based ILs are supermolecular structures characterized by polar and unpolar regions, numerous experimental and theoretical studies have been performed [36] to investigate the water effect on the IL structure. Despite the intensive activity, the interaction between water and ILs remains somewhat controversial. For example, quantum chemical calculations have been used to investigate the interaction between water molecules and some imidazolium based ionic liquids (*[emim]Cl*, *[emim]Br*, *[emim][BF₄]*, and *[emim][PF₆]*) [37]. The predicted geometries and interaction energies evidence that the water molecules (*W*) interact with Cl^- and Br^- to form $X^- \dots W$ or $2X^- \dots W$ complexes (where X^- is Cl^- or Br^-) and with BF_4^- anion *via* $\text{BF}_4^- \dots W$ and $W \dots \text{BF}_4^- \dots W$ models. Moreover, the same study indicates that also the cation forms a strong interaction with the water molecules. However, at variance with the data arising from molecular dynamic simulation [28], the hydrophobic PF_6^- anion seem not able to form a stable complex with the water molecules at the density functional theory level. On the other hand, far-infrared spectra probing intermolecular interactions in water/ILs mixtures evidence a strong interaction between water and BF_4^- , whereas the spectral contribution of the stretching bands between water molecules and PF_6^- cannot be unambiguously detected, suggesting a weaker interaction between water molecules and this anion [38].

The amount of water added to the IL is surely a fundamental parameter determining the structural organization of the whole system. Recently, molecular dynamic simulations have been carried out on mixtures of 1-octyl-3-methylimidazolium nitrate and water at multiple water concentrations [39]. Evolution of the cations-anions network, water network, and micelle structures has been visualized and analyzed *via* partial radial distribution functions. The turnover in evolution of the IL structure as a function of the water content has been explained considering the competition between the persistent hydrophobic interaction of the nonpolar groups and the breakup of the cation head-groups-anion electro-

static network, after the introduction of water. As the amount of water increases the polar network is continuously dissolved by the intruding water, while the structural organization of the water network and the micelle exhibits a turnover. At the turnover point, the most ordered micelle (cation–cation) structure and water network (anion–water–anion) are formed. Thereafter, the structural organization abates drastically and only loose micelle structure exists due the dominant water–water interactions.

Conclusions

In conclusion, in spite of the extensive interest towards ILs the structural studies of these media are recent and still in a developing stage. Experimental and theoretical investigations performed primarily on imidazolium ILs suggest that these salts form at the liquid state local structures. The interaction between anions and cations produces ionic organized networks in the solid, liquid, and gas phase, with the charge ordering degree determined mainly by the nature of cation and anion. Moreover, the presence of sufficiently long alkyl groups on imidazolium cation determines the existence of polar and unpolar domains. The role of aromaticity, as well as of the hydrophobic alkyl chains, however, deserve further investigation.

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