

Chapter 2

Structural Organization in Neat Ionic Liquids and in Their Mixtures

Olga Russina, Barbara Fazio, Gaetano Di Marco, Ruggero Caminiti
and Alessandro Triolo

Abstract Room temperature ionic liquids (RTILs) represent a class of materials whose employment in several applications is considered as a green alternative to toxic chemicals. Their potentialities are deemed to grow the more we understand their chemical-physical behaviour. As a matter of fact properties as basic as structural organization or microscopic interactions turn out to play a major role in many of their chemical-physical features, such as diffusive properties or solvation capabilities. Their being complex solvent media is a direct consequence of the chemical composition that leads to as diverse interactions as dispersive, coulombic, H-bonding, just to mention the most commonly encountered in conventional RTILs. The degree of comprehension of the structure in neat and mixed RTILs is steadily growing thank to the use of several complementary techniques such as diffraction and spectroscopic techniques and the link between their chemical details and the structure at microscopic as well as mesoscopic level is being unravelled by these studies. That opens the way to the rationalisation not only of basic chemical-physical properties but also of their bulk performances as solvent media. In this contribution we present experimental results aiming provide a structural description of two classes of samples. A first selection of diffraction experiments will aim to address the now well-known issue of mesoscopic structural organization in medium chain length RTILs. We will report original diffraction data from the family of 1-alkyl,3-methylimidazolium tetrafluoroborate as a function of the side alkyl chain length, highlighting the role of this parameter in affecting the mesoscopic order in the neat RTIL. We will also show experimental data highlighting the role of polar versus apolar interactions in determining this

O. Russina · R. Caminiti
Chemistry Department, La Sapienza University of Rome, Rome, Italy

B. Fazio · G. Di Marco
Istituto Processi-Chimico-Fisici, C.N.R., Messina, Italy

A. Triolo (✉)
Istituto Struttura della Materia, Rome, Italy
e-mail: triolo@ism.cnr.it

phenomenology describing results from a sample whose side chain is not an alkyl one. In the second part of this contribution, experimental results will be reported on binary mixtures of selected tetrafluoroborate salts and water. By the use of complementary techniques such as Raman and infrared spectroscopies, X-Ray and neutron diffraction we will provide a detailed overview of the phase diagram, nature of interactions as well as structural properties of these binary mixtures, expanding the current level of description for these systems. Overall we aim to provide a description of how the proposed experimental techniques can be successfully used to provide useful information in exploring the exciting, complex issue of RTILs and their mixtures.

2.1 Introduction

Room temperature ionic liquids are attracting a great attention as green compounds to progressively replace noxious volatile solvents in several applications. They are composed solely of ionic species and are characterised by a low melting point, conventionally lower than 100 °C. Most of RTILs are characterised by the presence of one or more (alkyl) side chains connected either to the cation's or the anion's head: for a given choice of the polar, charged heads, it is possible to obtain several RTILs, by simply changing the chain length or its chemical nature. This introduces a wide tunability of their chemical physical properties, as these reliably depend on the side chain length. Another way to modulate chemical-physical properties is to mix RTILs with other molecular compounds, such as water or alcohols. Due to their inherently amphiphilic nature, RTILs are characterised by large compatibility with both polar and apolar compounds, thus making binary and ternary solutions homogeneous over wide thermodynamic (concentration, temperature, pressure) conditions. Accordingly mixing RTILs with other compound that lead to homogeneous mixtures is a valuable approach to finely modulate properties and performances without the necessity of introducing and developing new materials.

In this contribution we will describe how the micro- and meso-scopic morphology of RTILs is affected by either the alkyl chain length or the addition of a molecular compound (in this case, water).

Changing the side alkyl chain length will be found to affect the mesoscopic structure of RTILs, as the balance between coulombic and dispersive interactions will progressively change the larger the amount of CH₂ units in the chain. Accordingly it will be observed a tendency to develop a segregation of the side chains, mostly interacting through dispersive interactions, from the charged moieties, namely the anions and the cations heads. In this case we will show an example from a series of tetrafluoroborate-based salts, namely 1-alkyl,3-methylimidazolium [BF₄], [C_nmim][BF₄], with alkyl = ethyl-decyl, n = 2–10.

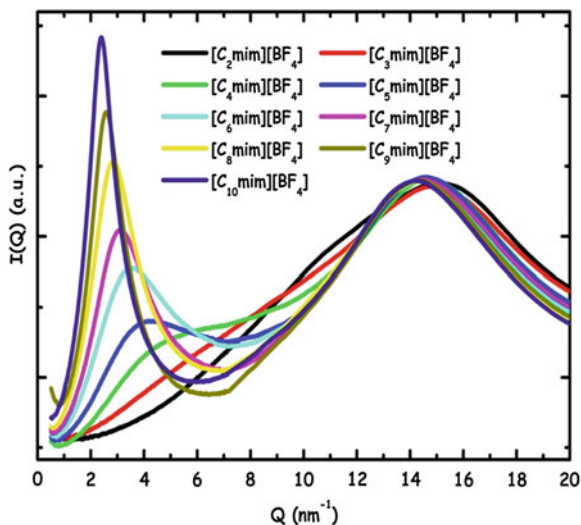
This microphase segregated morphology turns out to affect several properties of RTILs, including their ability to dissolve simultaneously both polar and apolar compounds. When polar compounds are dissolved into RTILs, they will tend to selectively distribute into the charged portion of the structure; while apolar compounds will prefer to localise into the oily domains. Of course this distribution will affect the structure and in this contribution we will explore binary mixtures of two selected tetrafluoroborate-based salts, $[C_4mim][BF_4]$ and $[C_8mim][BF_4]$, mixed with water, in order to probe the effect of water additions.

2.2 Mesoscopic Structural Organization in Neat 1-alkyl,3-methylimidazolium Tetrafluoroborate

1-alkyl,3-methylimidazolium tetrafluoroborate, $[C_nmim][BF_4]$, RTILs have been studied largely in the past. Salts bearing an intermediate length alkyl chain ($n = 2-10$) have been found to be liquid over a wide temperature range [1]. The authors observed that these salts show complex phase behaviour as a function of the alkyl chain length. The first two members of the series ($n = 0, 1$) are solid at ambient conditions, while the medium chain members ($n = 2-9$) are liquid at ambient temperature and can be supercooled to obtain the glassy state, without intervening crystallization. The longer chain members are characterised by the occurrence of a crystalline phase whose melting point is above ambient conditions and for $n > 11$ the existence of liquid-crystalline mesophases has been reported. The structural properties of the LC mesophases have been explored also in other reports [2]: these systems are characterised by a pseudo lamellar morphology, where the characteristic spacing is determined by layers of ordered charged heads that are separated by the molten alkyl chains. This organization leads to well-known diffraction features, namely to a low Q peak that closely resembles the ones from crystalline phases. When temperature is high enough, a LC $\rightarrow$ Isotropic phase transition occurs and the LC phase low Q peak disappears, while a broad, low intensity amorphous peak remains. This diffraction halo is ubiquitous in RTILs as it is found also for those RTILs that do not possess LC morphology. It is the fingerprint of some short-range associative structural ordering in the isotropic liquid state [2]. As a matter of fact even RTILs bearing short chains that were considered to be structurally homogeneous are characterised in their liquid state by a considerable degree of order that is the consequence of the occurrence of covalently bound polar and apolar moieties in their ions that tend to mutually exclude each other, thus developing a microscopically segregated morphology.

In the case of $[C_nmim][BF_4]$, this behaviour was observed in 2007 in the first experimental report highlighting the existence of such diffraction features [3]. In that paper the occurrence of a low Q amorphous halo was reported and its dependence from the side alkyl chain length described for the case of a few members (namely for the case of $n = 4, 6$ and 8). In Fig. 2.1, we show new Small

Fig. 2.1 Small-Wide Angle X-Ray Scattering (SWAXS) patterns from a series of 1-alkyl,3-methylimidazolium tetrafluoroborate, $[C_n\text{mim}][\text{BF}_4]$, (alkyl = ethyl-decyl) at ambient conditions

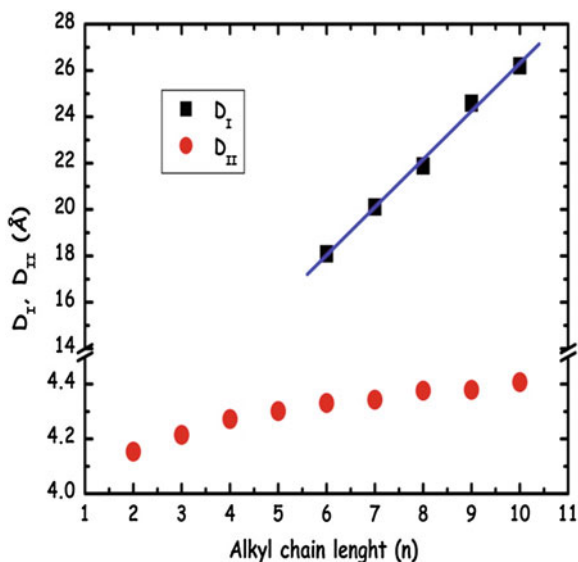


Angle X-Ray diffraction data collected on a more complete series of $[C_n\text{mim}][\text{BF}_4]$ salts ($n = 2-10$). X-Ray scattering data from $[\text{BF}_4]$ -based RTILs have been previously reported for $[\text{C}_2\text{mim}][\text{BF}_4]$ [4, 5] and for $[C_n\text{mim}][\text{BF}_4]$ ($n = 2, 4, 6$) [3].

The low Q portion of these data is characterised (see Fig. 2.1) by the presence of two amorphous halos, one centred at approximately $Q_{\text{II}} = 1.45 \text{ \AA}^{-1}$ (corresponding to a characteristic periodicity, $D_{\text{II}} = 2\pi/Q = 4.3 \text{ \AA}$) and another whose amplitude and position strongly depend on the alkyl chain length and is centred between $Q_{\text{I}} = 0.2$ and $0.7 \text{ \AA}^{-1}$, depending on n (corresponding to characteristic periodicities, $D_{\text{I}} = 14-30 \text{ \AA}$). While peaks at Q values larger than ca. $3 \text{ \AA}^{-1}$ are mainly of intramolecular origin, the amorphous halos observed in Fig. 2.1 stem mainly from intermolecular interactions. In related systems it has been verified that the higher Q value peak (peak II) is originating from oppositely charged nearest neighbour ions [6]. It is therefore rather intuitive that its position (and consequently the average distance between these nearest neighbours) only slightly depends upon the alkyl chain length. In Fig. 2.2, we show the characteristic distance associated to this spatial correlation, D_{II} : it can be noticed that it slightly changes from 4.15 to 4.45 $\text{\AA}$, upon increasing the alkyl chain length. This behaviour can be rationalised in terms of an entropic role played by the conformational isomerism associated to the long alkyl tails that limits the approach of neighbour oppositely anions.

The low Q peak is on the other hand much more complex to be rationalised, although at present a great deal of efforts, both experimental and computational [7–11], have been paid in this direction and now the matter is much better understood. We note first of all that at Q values lower than the low Q peak the scattering intensity tends to the thermodynamic limit, without further evidences of

Fig. 2.2 Alkyl chain length dependence of the characteristic sizes (D_I and D_{II} , $D_I = 2\pi/Q_I$) associated to the peaks detected in the SWAXS patterns from the series of 1-alkyl-3-methylimidazolium tetrafluoroborate, $[C_n\text{mim}][\text{BF}_4]$, (alkyl = ethyl-decyl) at ambient conditions. The *blue line* is a linear fit with slope $dD_I/dn = 2.07 \text{ \AA}/\text{CH}_2$ unit. Note the different vertical scale for the two data sets

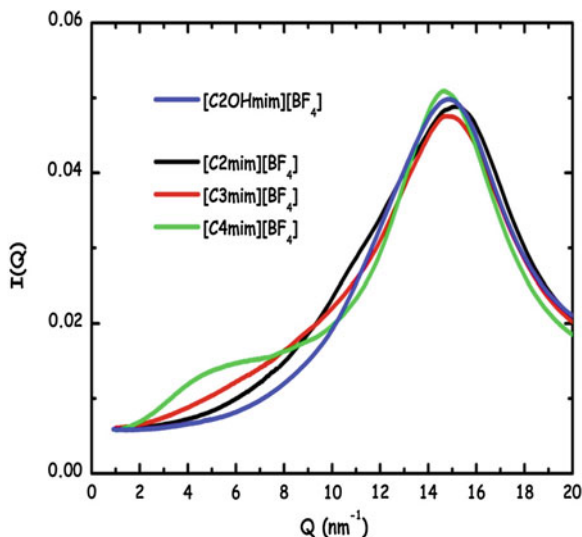


excess scattering that might be due to other characteristic distance of large aggregates present in the sample. Accordingly the low Q peak fingerprints the largest characteristic size occurring in the neat RTILs and it corresponds to dimensions of the order of several ($\approx 2\text{--}3$) nm. In Fig. 2.2 these characteristic sizes, D_I , are plotted as a function of the alkyl chain length. For chain lengths shorter than $n = 6$ it is hard to quantitatively determine the position of the low Q peak as it is very broad and partially merged with the higher Q features; however the determination of its position is quite robust in the case of longer alkyl chains and error bars in these cases are smaller than the symbol size in Fig. 2.2.

The trend described by these data has been found in the past for several families of RTILs to be linear, at least for chains shorter than ca. $n = 12$ [3, 12–15]. In this case we determine the slope of the trend to be $dD_I/dn = 2.07 \text{ \AA}/\text{CH}_2$ unit, in excellent agreement with our previous determination, over a narrower data set [3]. The value obtained for the latter parameter prompts for a structural model consisting of clustered cations building up a nano-pool with a size that grows of approximately twice the van der Waals size of a CH_2 unit ($1.265 \text{ \AA}$) [16], thus indicating limited interdigitation between oppositely oriented cations in the cluster. The model arising from these evidences as well as from a range of other experimental and computational studies is the one where the alkyl tails tend to segregate into an oily domain, maintaining apart from the charged moieties.

Recently we reported sound experimental evidences of the nature of the driving force of such a phenomenology as due to the inherent amphiphilicity of the ions in RTILs [9, 10, 17, 18]. As a matter of fact we showed that the existence of polar versus apolar moieties covalently bound in the ions is responsible for the occurrence of the segregation.

Fig. 2.3 Comparison between the SWAXS patterns from the short chained members of the family of 1-alkyl,3-methylimidazolium tetrafluoroborate, $[C_n\text{mim}][\text{BF}_4]$, (alkyl = ethyl-butyl) and from a sample of 1-(2-hydroxyethyl)-3-methylimidazolium tetrafluoroborate, $[\text{C2OHmim}][\text{BF}_4]$ at ambient conditions



When the chemical nature of the side alkyl chain is changed in the direction of decreasing the polar versus apolar contrast between the different moieties, the tendency to segregation consequently drops. In Fig. 2.3 we show the SWAXS data collected on a sub-set of the data reported in Fig. 2.1 (namely the shorter chains members of the family), together with the data collected on a sample of 1-(2-hydroxyethyl)-3-methylimidazolium tetrafluoroborate, $[\text{C2OHmim}][\text{BF}_4]$.

In the latter sample an hydroxyl group replaces the terminal CH_3 group of the alkyl side chain. The introduction of a polar group in the chain leads to the capability of the latter to interact with other polar moieties in the sample, thus destabilising the formation of alkyl tails aggregates. This can be observed in the data of Fig. 2.3, where the $[\text{C2OHmim}][\text{BF}_4]$ sample is characterised by an extremely low amplitude in the region $0 < Q \text{ (nm}^{-1}\text{)} < 10$ where the other samples, although bearing a short alkyl chain, still show some excess intensity that is related to the above mentioned segregation process. The $[\text{C2OHmim}][\text{BF}_4]$ sample accordingly, due to the diminished polar versus apolar contrast between its moieties does not tend to structurally organise in a segregated morphology. We mention also that a similar behaviour has been recently observed by other groups when dealing with Protic Ionic Liquids. In particular Atkin reported the strong decrease of the low Q peak amplitude upon replacement of the terminal alkyl group with an hydroxyl moiety in ethylammonium nitrate (EAN) [19]. Similarly Drummond and coworkers observed analogous effects when considering longer members of the family of alkyl-ammonium nitrates (where alkyl arrives up to pentyl). These authors also probed the role played by the replacement of the terminal methyl group with a methoxy group, $-\text{O}-\text{CH}_3$, and found that the latter substitution leads to a decrease of the low Q peak amplitude but not as pronounced as in the case of the hydroxyl group, thus suggesting that either more extended

intergratation occurs, or, more probably, the methoxy groups tend to shorten the chain length as a consequence of their affinity to reside close to the ammonium moiety [20]. Such a phenomenology is presently attracting a great deal of interest and several groups are active in providing additional experimental and computational evidences to validate these observations and better rationalising them.

2.3 Structural Organization in Binary Mixtures of 1-butyl,3-methylimidazolium Tetrafluoroborate/Water Mixtures

Of course this structural scenario opens the way to major implications in the field of catalysis, separation, synthesis and similar, due to the existence of an highly compartmentalised morphology where both polar and apolar can be efficiently dissolved and maintained in solution being only a few Å apart from each other.

Several computational studies have been devoted to this issue, highlighting the role of the existence of such potentialities and recently also structural studies begun to approach this issue [10, 21–23]. RTIL can dissolve a wide range of molecules, providing new perspectives to realize chemicals reactions or industrial separations. Then, the comprehension of the behavior of these systems when mixed with other liquids, for example a polar and green liquid such as water turns out to be fundamental to optimize processes. In the following we will present results from a careful study of binary mixtures of a $[\text{BF}_4]$ -based RTIL, namely $[\text{C}_4\text{mim}][\text{BF}_4]$, and water. The role of water addition to RTILs has been widely explored in the past, especially considering that water is among the most common contaminant in commercial RTILs and, accordingly a sound understanding on the influence of this compound in affecting structural, dynamic and thermodynamic properties in RTILs is mandatory. Despite their ionic nature, as a matter of fact, several RTILs show only limited solubility towards water. For example aqueous mixtures of $[\text{C}_n\text{mim}][\text{BF}_4]$ salts with long enough alkyl chains ($n \geq 6$) show a miscibility gap; in the case of $[\text{C}_4\text{mim}][\text{BF}_4]$, however, its binary mixtures with water are homogeneous over all the concentration range, at ambient temperature. Accordingly this is an ideal system where to investigate the correlations between RTILs and water.

Several Molecular Dynamics investigations provided a detailed description of structural and dynamic properties of $[\text{C}_4\text{mim}][\text{BF}_4]$ /water mixtures at atomistic level [24–27].

From the experimental point of view, a plethora of studies focused on these mixtures. This survey is not supposed to be exhaustive, but is limited to reports that are related to the presently reported studies. Among the most illuminating works on $[\text{C}_4\text{mim}][\text{BF}_4]$ /water (but discussing molecular states of water in a variety of other RTILs), the report from Cammarata et al. [28] highlighted (using ATR-IR) the existence of strong anion-water interactions. The mixtures were studied also by other groups using spectroscopic techniques: Jeon et al. used

ATR-IR to explore the complete concentration range [29], Fazio et al. used Raman and IR spectroscopies to explore the whole concentration range at ambient temperature [30], Danten et al. focused on water diluted solutions [31, 32], Hatano et al. studied the conformational changes in $[\text{C}_4\text{mim}][\text{BF}_4]/\text{D}_2\text{O}$ using Raman spectroscopy [33], Chang et al. investigated the mixtures at high pressure with IR spectroscopy [34, 35].

$[\text{C}_4\text{mim}][\text{BF}_4]/\text{water}$ mixtures were studied using Small Angle Neutron scattering techniques [36] aiming to detect the existence of micellar aggregates. A subsequent report from Perera et al. highlighted the existence of large density fluctuations due to the vicinity to a phase separation [37] to rationalise neutron scattering data [38]. This complex behaviour was further studied using surface tension measurements by Turmine et al. [39], light scattering by Chen et al. [40] and other physico-chemical properties by Wang et al. [41]. Mele and coworkers investigated these mixtures using NOE-NMR techniques [42, 43].

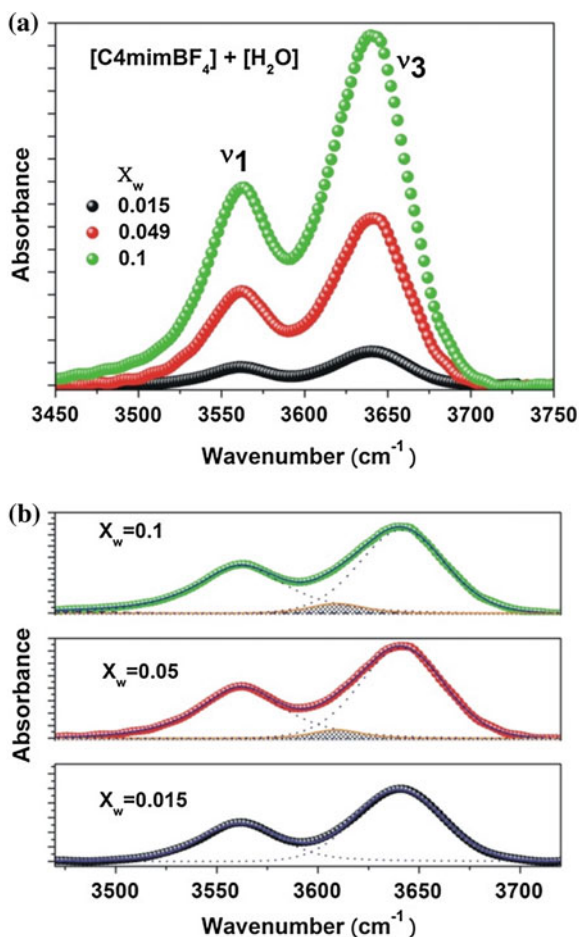
As discussed earlier, imidazolium based cations are composed by a non polar alkyl side chain and a polar imidazolium headgroup that are covalently bonded, thus leading to a bulky asymmetric cation that opposes the strong charge ordering, preventing crystallization as in a conventional salt and allowing for a wide liquid range. The polar headgroup is hydrogen bonded typically with a fluorinated anion, as in the case of the $[\text{C}_n\text{mim}][\text{BF}_4]$ family. When a small amount of water is added to imidazolium based ILs it preferentially interacts with the charged portion of the ionic liquid, the anion and the positively charged head, and has repulsive interactions with the alkyl chain, due to the amphiphilic nature of the RTIL. This selective interaction leads to complex morphological scenarios as water content increases in the mixtures.

In order to monitor the evolution of water aggregation state in the mixtures at increasing water content over the whole concentration range, we made use of FTIR and Raman spectroscopies, for low and high water content respectively. The O–H stretching modes of water, lying in the spectral region between 3000 and 3800 cm^{-1} , are very sensitive to the organization of water molecules in clusters and network and to the presence of any compounds that interact with water via H-bonding [44–49].

When a small amount of water is added to $[\text{C}_4\text{mim}][\text{BF}_4]$, most of water molecules tend to associate to the anions rather to self-aggregate. In Fig. 2.4a, b, FTIR spectra of the mixtures $[\text{C}_4\text{mim}][\text{BF}_4]/\text{H}_2\text{O}$ for water molar fraction (X_w) 0.015, 0.05, 0.1 in the O–H stretching region and the corresponding fits are shown. Two dominant spectral features can be distinguished, centred at 3560 and 3640 cm^{-1} respectively, that do not change in terms of intensities ratio and peaks' positions until $X_w = 0.1$. These bands are centred at the same frequency shifts of the symmetric (ν_1) and antisymmetric (ν_3) stretching modes of the single water molecule when it is interacting with the $[\text{BF}_4]^-$ anion, as found by ab initio calculation from Wang et al. [50].

In these mixtures, the $[\text{BF}_4]^-$ anion could interact with the water molecules via anion...water or water...anion...water [50] or as suggested by Cammarata et al., forming symmetric complexes anion...water...anion [51]. Then we assume that

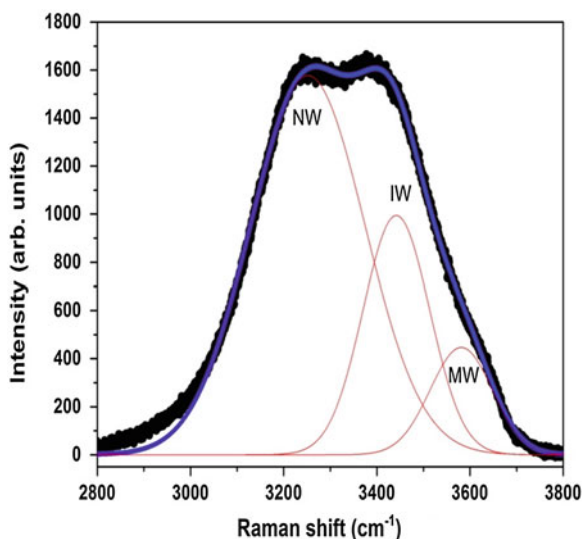
Fig. 2.4 **a** FTIR spectra of $[\text{C}_4\text{mim}][\text{BF}_4]/\text{H}_2\text{O}$ mixtures at $X_w = 0.015$ (*black circle*), $X_w = 0.05$ (*red circle*), $X_w = 0.1$ (*green circle*) and **b** the relative fits (*blue continuous lines*). These latter curves has been obtained by the convolutions of the Gauss-Lorentz bands to take into account the different contributions to the symmetric (ν_1) and antisymmetric (ν_3) O–H stretching modes of free water molecules coordinated with the BF_4 anions (*blue dotted lines*) and the Gaussian band of the MW organization (*yellow line, dense pattern*)



bands ν_1 and ν_3 in Fig. 2.4 represent respectively the symmetric and antisymmetric O–H modes relative to the distribution of single molecules coordinated with the anions in their different possible configurations, but not yet aggregated with other water molecules. The analysis of the O–H stretching region in the IR spectra of the $[\text{C}_4\text{mim}][\text{BF}_4]/\text{H}_2\text{O}$ mixtures, as a function of the water content, indicates that starting from $X_w = 0.05$ a small band centred at 3600 cm^{-1} develops (Fig. 2.4b). To better understand the origin of this band and the local organization of water molecules when mixed with $[\text{C}_n\text{mim}][\text{BF}_4]$, it is appropriate to comment the vibrational spectrum (Raman) of neat liquid water (shown in Fig. 2.5).

In pure liquid water, the dominating O–H stretching features are identified in terms of the main degrees of connectivity established between water molecules: accordingly the spectrum is fitted with three Gaussian distributions. The Gaussian band centred at higher energy (about 3580 cm^{-1}) corresponds to water molecules free or forming dimers and small aggregates, so that their vibration frequencies are

Fig. 2.5 Raman spectrum of liquid water (black circle) and relative fit curve (blue continuous line) obtained by taking into account the three O–H stretching Gaussian distributions that identify the main degrees of connectivity established between the water molecules, NW, IW and MW (red continuous lines)

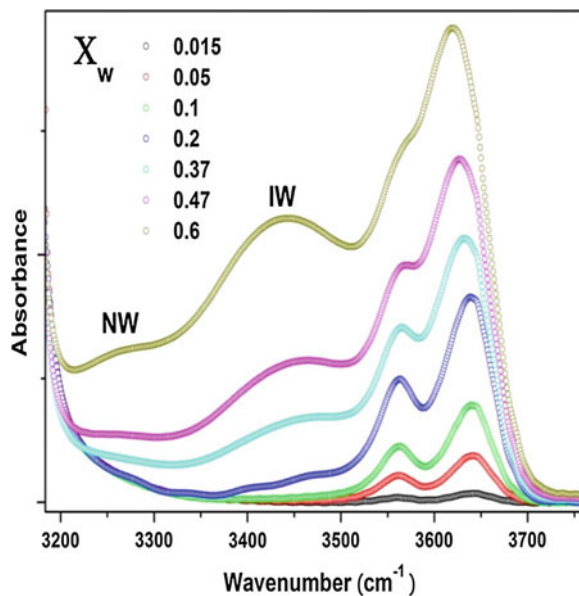


close to those found in vapour phase. This band is indicated as *Multimer Water* (MW) and corresponds to water molecules with a low degree of connectivity. The intermediate energy Gaussian (*Intermediate Water*, IW—centred at 3455 cm^{-1}) accounts for all those water molecules that do not form all four H-bond with neighbouring molecules and are not able to develop a fully connected network, but are involved in a so called distorted network. The lower energy band (about 3250 cm^{-1}) corresponds to those water molecules that exhibit high connectivity degree, forming four H-bonds with other water molecules and creating transient networks (*Network Water*, NW band) that constantly break and form [52, 53].

According to this scheme we interpret the O–H band appearing in Fig. 2.4b, and centred at 3600 cm^{-1} , as due to small water clusters, resembling the *multimer water band* (MW) that appears in the vibrational spectrum of neat liquid water. The blue shift (ca. 20 cm^{-1}) observed in dilute $[\text{C}_4\text{mim}][\text{BF}_4]/\text{H}_2\text{O}$ mixtures with respect to the stretching frequency of the MW O–H groups in liquid water (where it is centred at about 3580 cm^{-1}) can be interpreted as due to the fact that these small aggregates are not properly embedded in a network organized environment (like in liquid water), as they are forming in close proximity with the anion.

Above $X_w = 0.1$, the water molecules get involved in super-molecular connectivity scheme and are found to self-aggregate in a distorted network giving rise to a Gaussian-shaped band centred at 3470 cm^{-1} (see Fig. 2.6). This band is considered to be the fingerprint of the hydration water solvating the RTIL polar region. Upon further water addition, it shifts its position systematically to lower wavenumbers, up to ca. 3455 cm^{-1} at $X_w = 0.7$: this is a clear indication of its shape evolution towards the analogous band in liquid water called *intermediate water* (IW).

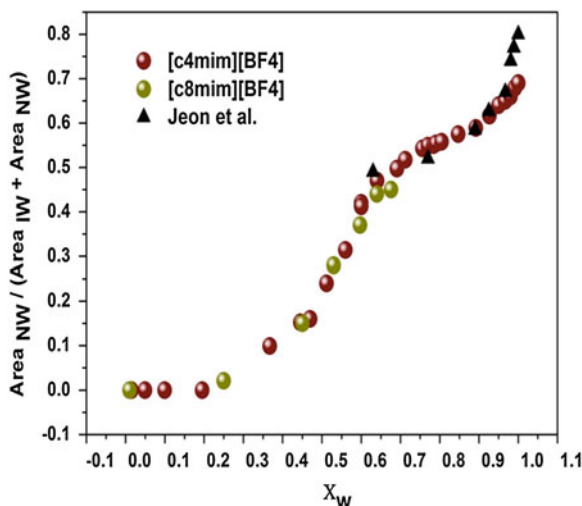
Fig. 2.6 FTIR spectra of [C₄mim][BF₄]/H₂O mixtures at different water molar fractions in the range of the O–H stretching vibrational modes



Upon increasing the water content in the range between $X_w = 0.2$ and 0.37 , the water molecules tend to organize in a tetrahedrally coordinated transient network that continuously breaks and forms, similarly to the behaviour found in bulk liquid water. Those molecules, acting as bulk-like inner part of the water aggregates, are responsible of the appearance of a broad Gaussian shaped band centred at 3250 cm^{-1} , named *Network Band* (NW). Despite this bulk water like behaviour, we notice that a non-negligible amount of water molecules are yet strongly involved in H-bond driven complexes with the anions until $X_w \sim 0.75$, as indicated by the strong bands centred at 3550 and 3650 cm^{-1} .

In Fig. 2.7 the trend of the fraction of *network water* with respect to the total network aggregated O–H stretching population (Area NW/Area IW + Area NW) is plotted as a function of water molar fraction; the present results are in good agreement with the findings from Jeon and coworkers [29], who explored the same mixtures in a narrower range of mixture concentrations. The trend is obtained by merging the results from both IR and Raman spectra, at low and high water content respectively [30]. In the same figure, data corresponding to mixtures of 1-octyl,3-methyl-imidazolium tetrafluoroborate (hereinafter indicated as [C₈mim][BF₄]) and H₂O are also shown for concentrations up to $X_w \sim 0.7$ (more concentrated solutions lead to phase separation). We clearly distinguish three regimes in the *network water* fraction trend as a function of X_w : a first one ($0 < X_w < 0.25$) where water molecules are not yet self-aggregated in a bulk liquid water fashion, but just form an hydration shell around the polar regions, principally the anions; a second regime ($0.25 < X_w < 0.75$) where the water molecules self-organize in a transient network whose population rapidly increases up to $X_w \sim 0.75$. The plateau region

Fig. 2.7 Trend of NW fraction plotted as a function of water molar fraction for $[C_4mim][BF_4]/H_2O$ (red circle) and $[C_8mim][BF_4]/H_2O$ (green circle) mixtures; the black triangles represent the results obtained by Jeon et al. that show a good agreement with our findings. NW fraction is calculated as “ $Area_{NW}/Area_{IW} + Area_{NW}$ ” and the trend is obtained by merging FTIR and Raman results

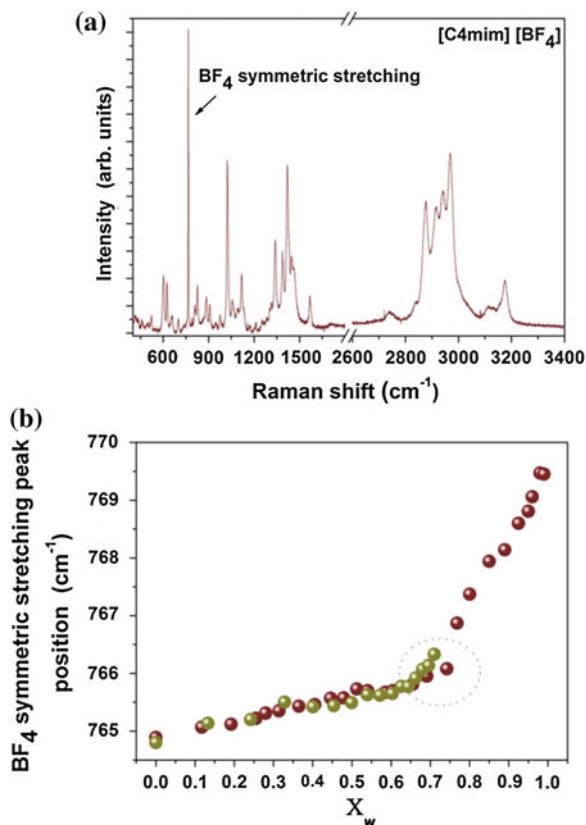


at $0.75 < X_w < 0.85$ is interpreted as a competition between NW and IW populations when water is added. Here water molecules take their place no more inside the polar sites, but start to diffuse outside, forming novel hydration shells and then novel coordinations around the IL molecules. This occurrence certainly affect the structural segregation of the cations alkyl chains at higher X_w , then giving rise to a different scenario on the structural organization of the mixtures at $0.85 < X_w < 1$ (third regime).

Many studies highlighted the role that the weak hydrogen bonds between anions and the imidazolium ring C–H groups, specially the acidic one in position C2 (the one between the two imidazolium nitrogen atoms), play in determining and affecting the peculiar structure of RTILs [54]. The proposed scenario for the evolution of the water molecules organization that gets triggered around the anion can affect the hydrogen bonded ion pairs between the acidic CH group of the imidazolium rings and the fluorine of the tetrafluoroborate anions [55]. A detailed study of the B–F symmetric stretching (BF_4 breathing mode) of the anion as a function of water content was presented in a previous paper, where a progressive shift of the B–F stretching band had been reported [30]. A similarly low but systematic shift of the B–F symmetric stretching to higher wavenumbers is found also for $[C_8mim][BF_4]/H_2O$ mixtures, as shown in Fig. 2.8. In the past we proposed that this is due to the progressive weakening of hydrogen-bonded ion pairs interactions, while the drastic change of slope around $X_w \sim 0.75$, observed in $[C_4mim][BF_4]/H_2O$ mixtures, prompts for a more efficient screening of this interaction, due to the water molecules that strongly solvate the anion, and a consequent major structural reorganization of the mixtures.

Here we confirm our original hypothesis proposing the same scenario for the $[C_8mim][BF_4]/H_2O$ mixtures; moreover, it is noteworthy that $X_w \sim 0.75$ is very close to the concentration range where phase separation occurs at room

Fig. 2.8 **a** Raman spectrum of neat $[\text{C}_4\text{mim}][\text{BF}_4]$, the arrow indicates the BF_4 breathing mode at 764.8 cm^{-1} . **b** Trend of the BF_4 breathing mode peak position as a function of water molar fraction in $[\text{C}_4\text{mim}][\text{BF}_4]/\text{H}_2\text{O}$ (red circle) and $[\text{C}_8\text{mim}][\text{BF}_4]/\text{H}_2\text{O}$ (green circle) mixtures

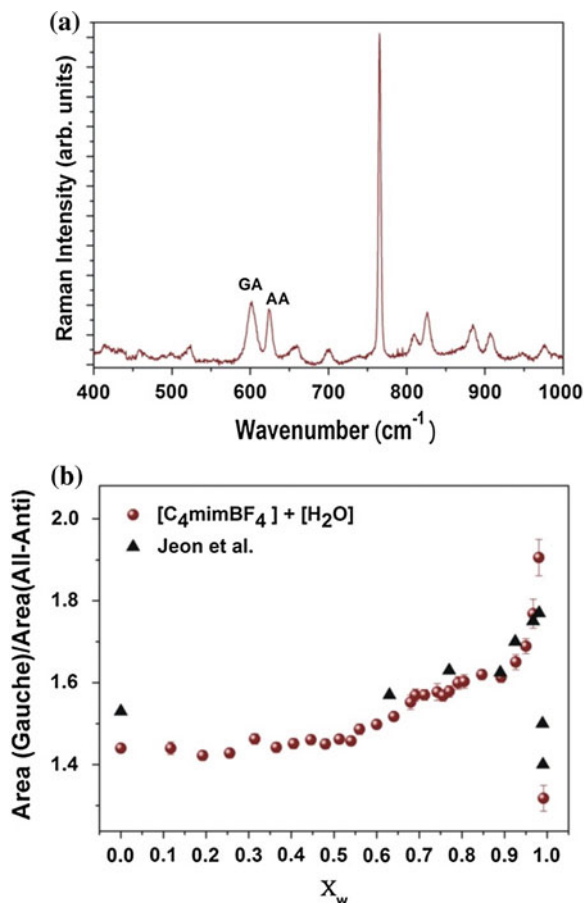


temperature in these mixtures. Accordingly it can be proposed that the demixing of the components in $[\text{C}_8\text{mim}][\text{BF}_4]/\text{H}_2\text{O}$ mixtures might be activated by the mentioned screening and consequent structural reorganization.

The analyses of the Raman data sets indicate a more complex scenario for the mixtures at water high content. In the range $0.9 < X_w < 1$, we noticed a peculiar behaviour of both network water fraction (Fig. 2.7) and the B–F symmetric stretching (Fig. 2.8b) versus water content, as already observed by Jeon and coworkers [29]; these observations suggest a further possible structural change in the systems organizations and a possible explanation for these observations will be provided in the following sections.

We further analysed the Raman bands of $[\text{C}_4\text{mim}][\text{BF}_4]$ ascribed to C–H bending modes N–C(7)–C(8) (centred at $\sim 602\text{ cm}^{-1}$) and of C(7)–C(8)–C(9) (centred at $\sim 625\text{ cm}^{-1}$) that reflect the *Gauche* (GA) and the *All-Anti* (AA) conformations around the C(7)–C(8) bond of the $[\text{C}_4\text{mim}]$ cation, respectively (see Fig. 2.9a). These two conformers coexist in the liquid state [56–58]. When water is added to the RTIL, the ratio between their populations varies as a function of water content and this is a valid indicator of changes in the alkyl chain conformation and

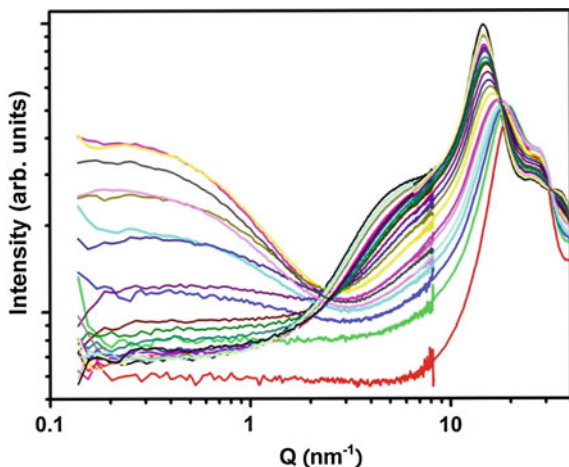
Fig. 2.9 **a** Raman spectrum of neat $[\text{C}_4\text{mim}][\text{BF}_4]$ where the labels GA and AA indicate the Raman bands ascribed to the Gauche and the All-Anti conformations around the C(7)–C(8) bond of the $[\text{C}_4\text{mim}]$ cation, centred at ~ 602 and $\sim 625\text{ cm}^{-1}$ respectively. **b** Plot of the the complex evolution of the GA/AA bands areas ratio as a function of water molar fraction; the *black triangles* represent the results obtained by Jeon et al. that are in good agreement with our findings



deviations from the chemical organization found in the bulk IL. Figure 2.9b shows a rapid increment of the area ratio between the GA and AA forms starting at about $X_w = 0.9$ to reach a maximum at $X_w = 0.98$. Above that concentration the mentioned ratio rapidly decreases. Our data, in agreement with the ones from Jeon and co-workers [29], confirm the possible occurrence of a structural change in this range of water content that is fingerprinted by the complex evolution of the GA/AA areas ratio. Aiming to clarify all the different regimes that were detected by vibrational spectroscopy (either IR or Raman), we further analyzed $[\text{C}_4\text{mim}][\text{BF}_4]/\text{H}_2\text{O}$ mixtures using X-Ray and neutron diffraction. These are very valuable tools in exploring condensed matter at micro- and meso-scopical spatial level, as they can probe the existence of structural correlations over distances between fraction of Angstrom and several nm.

In Fig. 2.10 the Small-Wide Angle X-Ray Scattering data sets are shown over the whole range of concentration; a complex scenario appears at different Q ranges. One of the most impressive feature observed occurs in the low Q portion

Fig. 2.10 Small-Wide Angle X-Ray Scattering data sets of the $[\text{C}_4\text{mim}][\text{BF}_4]/\text{H}_2\text{O}$ mixtures over the whole water molar fraction range



($Q < 3 \text{ nm}^{-1}$), where, in the range $0.9 < X_w < 1$, one detects a peculiar behaviour characterised by high scattering intensities (see Fig. 2.11). This behaviour is essentially the same detected by Perera and coworkers using Small Angle Neutron Scattering in the same mixtures [38]. The mentioned Q range is the one associated typically to structural heterogeneities with size of the order of several nm. In the past Bowers et al. described these features in terms of the diffraction pattern arising from the form factor of an ensemble of polydisperse micelle-like aggregates [36]. Of course such a description might be reasonable for the case of longer alkyl chain RTILs, but at least in the present case some doubt can be raised on the exact nature of the observed structural heterogeneities leading to the strong scattering at low Q in the present case. Data in the low Q portion could be reasonably well accounted for, by using a minimalistic model consisting of a Lorentzian

Fig. 2.11 Small X-Ray Scattering data sets of the $[\text{C}_4\text{mim}][\text{BF}_4]/\text{H}_2\text{O}$ mixtures in the concentration range of high water molar fraction and for neat $[\text{C}_4\text{mim}][\text{BF}_4]$ (red open circle) and neat H_2O (blue open circle)

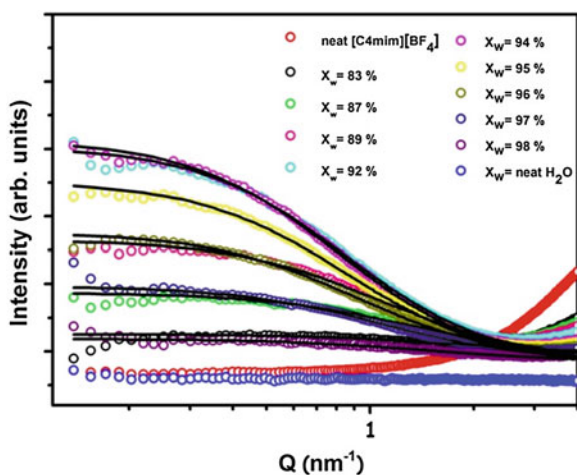
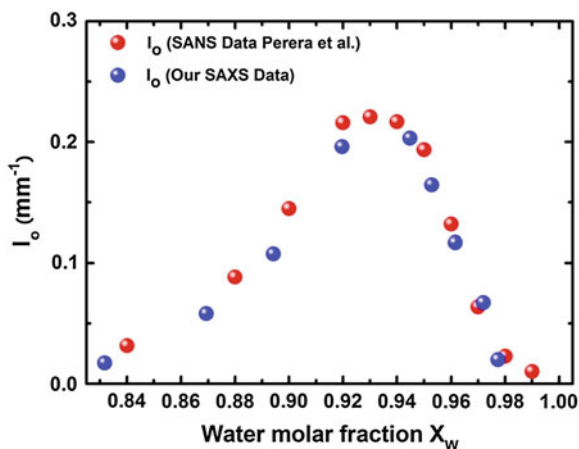


Fig. 2.12 Plot of the amplitude of the low Q Lorentzian feature in the SAXS spectrum as a function of the water content (*blue circle*). Data are in agreement with Small Angle Neutron Scattering (SANS) data from Alamy and coworkers here plotted as *red circles*



function, without imposing the existence of any aggregates and implying instead an Ornstein-Zernicke trend, that accounts for statistical concentration fluctuations arising from the close vicinity of the system to a phase separation boundary. The amplitude of this contribution strongly depends on the water content and in Fig. 2.12 such a trend is shown, exhibiting a maximum at X_w about 0.93. This finding is in agreement with Small Angle Neutron Scattering (SANS) data from Alamy and coworkers [59], and suggests that, at this concentration range, the system is close to phase separation [37].

The strong amplitude of the quasi critical scattering, shown in Fig. 2.11, does not allow the determination of further structural features that might be related to the formation of micellar aggregates, as originally proposed by Bowers et al. [36] and as suggested by the structural scenario depicted by Raman data shown in Fig. 2.9b.

At higher Q spectral range we observe further interesting behavior: (a) at the intermediate Q range the intensity of peak that identifies the alkyl tail nano-segregation decreases adding water in the mixtures (see Fig. 2.13b), while at high Q values a well-defined band related to a number of short range intermolecular spatial correlations that shifts its maximum with water content, as shown in Fig. 2.14a.

This latter feature gently shifts its position towards higher Q values until $X_w = 0.75$ and then more rapidly slopes up, as shown in the Fig. 2.14b.

We find again that $X_w = 0.75$ is a key concentration value where the intermolecular correlations are strongly weakened by the water presence, confirming what previously guessed on the basis of vibrational spectroscopy. Indeed, at this turnover concentration, the water solvation shells have a kind of saturation, strongly weakening the ion pairs interactions between anions and imidazolium rings, as a consequence a repulsive action between the positive polar head break the slack segregation in $[\text{C}_4\text{mim}][\text{BF}_4]$. In the case of aqueous solutions of $[\text{C}_8\text{mim}][\text{BF}_4]$, the water molar fraction at which the systems phase-separate is just

Fig. 2.13 Small X-Ray Scattering data sets of the $[\text{C}_4\text{mim}][\text{BF}_4]/\text{H}_2\text{O}$ mixtures over the whole concentration range showing the characteristic low Q peak that identifies the alkyl tails nano-segregation in the IL

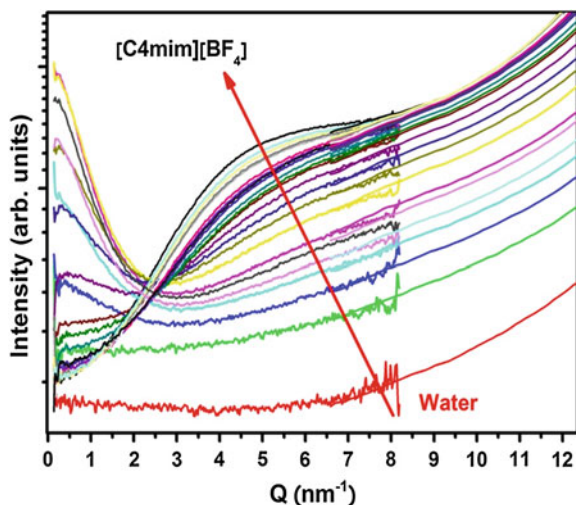


Fig. 2.14 a Wide angle X-Ray Scattering data sets of the $[\text{C}_4\text{mim}][\text{BF}_4]/\text{H}_2\text{O}$ mixtures in the whole concentration range of water molar fraction showing the band related to the short range intermolecular spatial correlations. **b** Evolution of the peak position of this band with water content

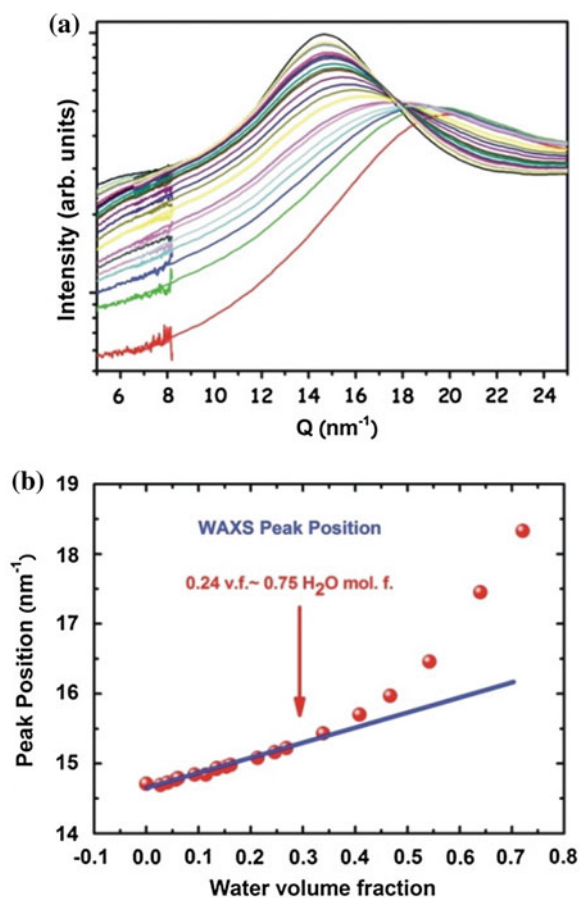
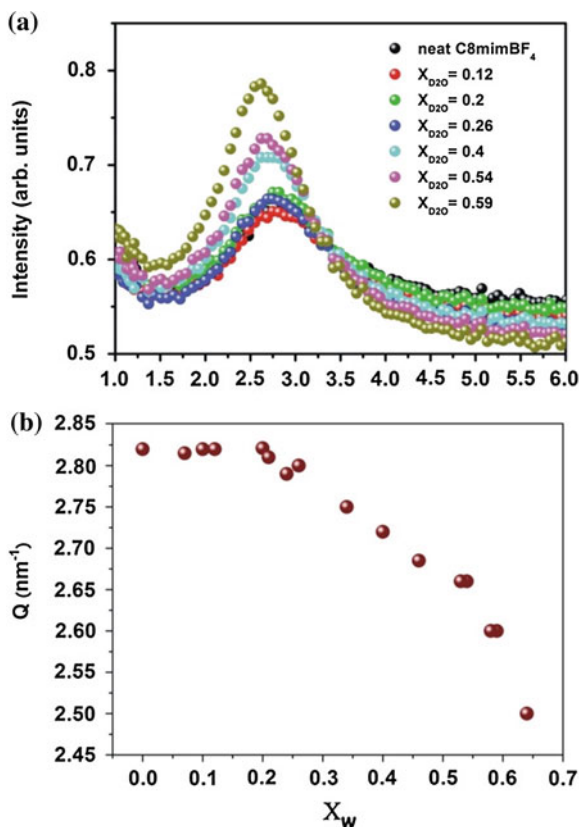


Fig. 2.15 **a** Small Angle Neutron Scattering data sets of the $[\text{C}_8\text{mim}][\text{BF}_4]/\text{H}_2\text{O}$ mixtures over the concentration range where mixtures are homogeneous. In the spectra are well visible the peak related to the alkyl tails nano-segregation in the IL, **b** Evolution of the peak position of this band with water content



before $X_w = 0.75$ and we interpret this occurrence considering the overcoming tendency of the octyl chains to segregate that predominates on the ion-pairing disruptive water action.

Due to the defective segregation of the short alkyl chain of $[\text{C}_4\text{mim}][\text{BF}_4]$ the SAXS peak associated to the tail segregation nanodomains in the neat IL looks slack and not well defined (Fig. 2.13); moreover, it is slightly covered by the WAXS band. On the contrary, the corresponding feature for the same salt having an octyl tail is centred at lower Q values and appears well distinct, as shown in Fig. 2.15a where Small Angle Neutron Scattering (SANS) data sets of aqueous solutions of $[\text{C}_8\text{mim}][\text{BF}_4]$ are plotted for different D_2O content. A qualitative analysis of these data shows that upon increasing the heavy water content, after a starting concentration range where no major changes are observed, above $X_w = 0.25$ the peak shifts to lower Q s (see Fig. 2.15b), the observed concentration threshold corresponds to the value where bulk-like network water begins to form as shown in Fig. 2.7.

The morphological scenario that we deduce from all these experimental finding is definitively complex and the existence of nanodomains, formed by segregated alkyl chains in the neat ILs investigated, looks to be the main reason for this

complexity. In this context, the presence of a polar solvent such as water has a strong effect on the stability of the polar network.

Introducing very small quantities of water in our system, the water molecules preferentially interacts with the charged portion of the RTIL and remain trapped as single molecules in the polar network forming H-bond driven complexes with the $[\text{BF}_4]^-$ anions. The increment of water portion in the mixtures slowly brings to a more efficient hydration of the polar regions that partially weakens the interactions between cation and anion: when water molar fraction exceed 0.25, the H_2O molecules start to self-organize in puddles embedded in the charged matrix, still strongly coordinating the $[\text{BF}_4]^-$ anions.

With the continuous addition of water in the mixtures, these puddles increase their spatial dimensions, enlarging the volume taken up by the polar network and then increasing the distances between domains. In spite of the presence of the water puddles, the segregated alkyl chains domains are still preserved until $X_w \sim 0.75$; at this water content, however, the hydration shells of the anions get efficient in screening the ion pairs interactions that support and maintain unaltered the domain-like structure. As a consequence, the repulsive action between the positive polar heads is no more screened and leads to the breakup of the segregated domains. We deduce that $X_w \sim 0.75$ is a turnover concentration above which the 1-alkyl-3methyl-imidazolium tetrafluoroborate and water mixtures tend to re-organise themselves in a structural arrangement that strongly differs from more water-dilute mixtures; a similar behaviour has been observed from Voth and co-workers in molecular dynamic simulations performed in ionic liquids and water mixtures [25, 60]. We propose that above this threshold water content, water is able to ‘dissolve’ the segregated domains, which are no longer stabilised by the neutralised charge on the domains surface, as a consequence of the mentioned breaking of ion pairing. However, in the case of long alkyl chains, such as $[\text{C}_8\text{mim}][\text{BF}_4]$, the oily tails tend to maintain their segregated nature, thus expelling additional water and leading to phase separation.

In the $[\text{C}_4\text{mim}][\text{BF}_4]/\text{H}_2\text{O}$ mixtures, above $X_w \sim 0.75$ water starts to diffuse outside the IL polar regions and above from $X_w \sim 0.9$, the salt tends to self-organize in micelle like aggregates that seems to reach a conformational stability at $X_w \sim 0.98$, as indicated by the trend of the butyl chain conformation. Further increasing of the water content leads to the disruption of the micelles. We put also in evidence that at high dilution in water, this effect superimposes with strong concentration fluctuations that have a maximum at $X_w \sim 0.93$, due to the vicinity to the phase demixing.

2.4 Conclusion

Room temperature ionic liquids are one of the most exciting and promising class of materials in the last decades. Their performances are strongly determined by chemical features such as side alkyl chain and cation/anion head nature, for the

neat ILs, and by the polar/apolar nature of the additives and their content in binary mixtures.

The full understanding of their physical–chemical properties upon changing these parameters is a key tool to rationalise and improve macroscopic performances.

In this contribution we showed the valuable contribution that experimental techniques such as X-Ray and neutron diffraction as well as Raman and IR spectroscopies can provide in this direction, exploring micro and mesoscopic structural organization in neat ILs and in their binary mixtures with water.

Of course strong interplay between experimental techniques and computational ones is a major tools to fully exploit the advantages of the different approaches.

2.5 Experimental Section

The as-received $[\text{C}_n\text{MIM}][\text{BF}_4]$ samples, purchased from Solvent Innovation/IO-LITEC (purity > 99 %), were kept under vacuum (10^{-3} bar) at 60 °C for 3 days, in order to purify them and remove the moisture. The residual water amount, estimated using infra-red spectroscopy (according to literature [51]) was ca. 0.015 in molar fraction.

The $[\text{C}_4\text{MIM}][\text{BF}_4]/[\text{C}_8\text{MIM}][\text{BF}_4]$ and deionised H_2O mixtures, covering all the solubility range, were prepared in a glove box, using dry N_2 as inert atmosphere and kept there before the measurements.

Fourier Transform Infrared spectroscopy was carried out using a Spectrum GX Perkin spectrophotometer, recording the spectra with a resolution of 4 cm^{-1} . A specific cell (201 μm thick) with ZnSe windows was used as sample housing.

Room temperature Raman spectra were excited by the 632.8 nm line of an He–Ne laser, focused on the sample with an Olympus BX-40 accessorised for macro-investigation ($4\times$ magnification objective lens). The incident power was ca. 3 mW. The scattered light was collected in a backscattering geometry by an Horiba-Jobin–Yvon HR460 monochromator, equipped with a 1800 line mm^{-1} grating and detected by a charge-coupled device array sensor at 77 K. Elastically scattered light was rejected by a notch filter. The Raman spectra were acquired in the $250\text{--}3900\text{ cm}^{-1}$ spectral region.

The Small-Wide Angle X-Ray Scattering (S-WAXS) experiment was conducted at the high brilliance beam line ID02, European Synchrotron Radiation Facility (ESRF), Grenoble, France, using an instrumental setup which allows covering the momentum range Q between 0.1 and $2\text{ \AA}^{-1}$, with a wavelength $\lambda = 0.75\text{ \AA}$ (Energy = 16.5 keV). Measurements were collected at 25 °C, using a thermostated bath and the sample was kept inside a temperature controlled flow-through cell, with internal diameter of 1.9 mm. The corresponding empty cell contribution was subtracted. Calibration to absolute units (mm^{-1}) was obtained using a neat water sample in a 2 mm capillary.

Small Angle Neutron Scattering measurements were conducted at the LOQ SANS instrument at ISIS (UK). Mixtures of the ILs with D₂O were kept in 1 mm thickness quartz cells that were maintained at 25 °C using a thermostated bath. Corrections were conducted using the standard procedures using the software available at the beamline.

Acknowledgements We acknowledge the European Synchrotron Radiation Facility for provision of synchrotron radiation facilities and would like to thank Dr. T. Narayanan for his valuable assistance in exploiting beamline ID02. We thank the Rutherford Appleton Laboratory for provision of beam time at LOQ with the financial support from CNR and Dr. R. K. Heenan, for his valuable support during the beam time. A.T. acknowledges support from FIRB-Futuro in Ricerca (RBF086BOQ) and PRIN (2009WHPHRH). A.T. warmly remembers the SANS measurements round as one of the last that he could enjoy with the late Prof. R. Triolo.

References

1. Holbrey J.: J. Chem. Soc. Dalton. Trans. 2133–2139 (1999)
2. Bradley, A.E., Hardacre, C., Holbrey, J.D., et al.: Chem. Mater. **14**, 629–635 (2002). doi: [10.1021/cm010542v](https://doi.org/10.1021/cm010542v)
3. Triolo, A., Russina, O., Bleif, H.-J., Di Cola, E.: J. Phys. Chem. B **111**, 4641–4644 (2007). doi: [10.1021/jp067705t](https://doi.org/10.1021/jp067705t)
4. Takamuku, T., Kyoshoin, Y., Shimomura, T., et al.: J. Phys. Chem. B **113**, 10817–10824 (2009). doi: [10.1021/jp9042667](https://doi.org/10.1021/jp9042667)
5. Kanzaki, R., Mitsugi, T., Fukuda, S., et al.: J. Mol. Liq. **147**, 77–82 (2009). doi: [10.1016/j.molliq.2008.10.003](https://doi.org/10.1016/j.molliq.2008.10.003)
6. Santos, C.S., Annapureddy, H.V.R., Murthy, N.S., et al.: J. Chem. Phys. **134**, 064501 (2011). doi: [10.1063/1.3526958](https://doi.org/10.1063/1.3526958)
7. Pádua, A.A.H., Costa Gomes, M.F., Canongia Lopes, J.N.A.: Acc. Chem. Res. **40**, 1087–1096 (2007). doi: [10.1021/ar700050q](https://doi.org/10.1021/ar700050q)
8. Greaves, T.L., Drummond, C.J.: Chem. Soc. Rev. (2012). doi: [10.1039/c2cs35339c](https://doi.org/10.1039/c2cs35339c)
9. Russina, O., Triolo, A., Fazio, B., et al.: Faraday Discuss. 97–109 (2012). doi: [10.1039/c1fd00073j](https://doi.org/10.1039/c1fd00073j)
10. Russina, O., Triolo, A., Gontrani, L., Caminiti, R.: J. Phys. Chem. Lett. **3**, 27 (2012)
11. Annapureddy, H.V.R., Kashyap, H.K., De Biase, P.M., Margulis, C.J.: J. Phys. Chem. B **114**, 16838–16846 (2010). doi: [10.1021/jp108545z](https://doi.org/10.1021/jp108545z)
12. Russina, O., Triolo, A., Gontrani, L., et al.: J. Phys. Condens. Matter **21**:424121. doi: [10.1088/0953-8984/21/42/424121](https://doi.org/10.1088/0953-8984/21/42/424121)
13. Santos, C.S., Murthy, N.S., Baker, G.A., Castner, E.W.: J. Chem. Phys. **134**, 121101 (2011). doi: [10.1063/1.3569131](https://doi.org/10.1063/1.3569131)
14. Martinelli, A., Marechals, M., Östlund, Å., Cambedouzou, J.: Phys. Chem. Chem. Phys. (2013). doi: [10.1039/c3cp00097d](https://doi.org/10.1039/c3cp00097d)
15. Hardacre, C., Holbrey, J.D., Mullan, C.L., et al.: J. Chem. Phys. **133**, 074510 (2010). doi: [10.1063/1.3473825](https://doi.org/10.1063/1.3473825)
16. Tanford, C.: J. Phys. Chem. **76**, 3020–3024 (1972)
17. Triolo, A., Russina, O., Caminiti, R., et al.: Chem. Commun. **48**, 4959–4961 (2012). doi: [10.1039/c2cc31550e](https://doi.org/10.1039/c2cc31550e)
18. Kashyap, H.K., Santos, C.S., Daly, R.P., et al.: J. Phys. Chem. B **117**, 1130–1135 (2013). doi: [10.1021/jp311032p](https://doi.org/10.1021/jp311032p)

19. Hayes, R., Imberti, S., Warr, G.G., Atkin, R.: *Phys. Chem. Chem. Phys.* **13**, 3237–3247 (2011). doi: [10.1039/c0cp01137a](https://doi.org/10.1039/c0cp01137a)
20. Greaves, T.L., Kennedy, D.F., Mudie, S.T., Drummond, C.J.: *J. Phys. Chem. B* **114**, 10022–10031 (2010). doi: [10.1021/jp103863z](https://doi.org/10.1021/jp103863z)
21. Yang, P., Voth, G. A., Xiao, D., et al.: *J. Chem. Phys.* **135**, 034502 (2011). doi: [10.1063/1.3601752](https://doi.org/10.1063/1.3601752)
22. Bardak, F., Xiao, D., Hines, L.G., et al.: *ChemPhysChem*, 1–15 (2012). doi: [10.1002/cphc.201200026](https://doi.org/10.1002/cphc.201200026)
23. Greaves, T.L., Kennedy, D.F., Kirby, N., Drummond, C.J.: *Phys. Chem. Chem. Phys.* **13**, 13501–13509 (2011). doi: [10.1039/c1cp20496c](https://doi.org/10.1039/c1cp20496c)
24. Moreno, M., Castiglione, F., Mele, A., et al.: *J. Phys. Chem. B* **112**, 7826–7836 (2008). doi: [10.1021/jp800383g](https://doi.org/10.1021/jp800383g)
25. Feng, S., Voth, G.A.: *Fluid Phase Equilib.* **294**, 148–156 (2010). doi: [10.1016/j.fluid.2010.02.034](https://doi.org/10.1016/j.fluid.2010.02.034)
26. Zhong, X., Fan, Z., Liu, Z., Cao, D.: *J. Phys. Chem. B* **116**, 3249–3263 (2012). doi: [10.1021/jp3001543](https://doi.org/10.1021/jp3001543)
27. Schröder, C., Rudas, T., Neumayr, G., et al.: *J. Chem. Phys.* **127**, 234503 (2007). doi: [10.1063/1.2805074](https://doi.org/10.1063/1.2805074)
28. Cammarata, L., Kazarian, S.G., Salter, P.A., Welton, T.: *Phys. Chem. Chem. Phys.* **3**, 5192–5200 (2001). doi: [10.1039/b106900d](https://doi.org/10.1039/b106900d)
29. Jeon, Y., Sung, J., Kim, D., et al.: *J. Phys. Chem. B* **112**, :923–928 (2008). doi: [10.1021/jp0746650](https://doi.org/10.1021/jp0746650)
30. Fazio, B., Triolo, A., Di Marco, G.: *J. Raman Spectrosc.* **39**, 233–237 (2008). doi: [10.1002/jrs.1825](https://doi.org/10.1002/jrs.1825)
31. Danten, Y., Cabaço, M.I., Besnard, M.: *J. Mol. Liq.* **153**, 57–66 (2010). doi: [10.1016/j.molliq.2009.07.001](https://doi.org/10.1016/j.molliq.2009.07.001)
32. Danten, Y., Cabaço, M.I., Besnard, M.: *J. Phys. Chem. A* **113**, 2873–2889 (2009). doi: [10.1021/jp8108368](https://doi.org/10.1021/jp8108368)
33. Takekiyo, T., Imai, Y., Hatano, N., et al.: *Chem. Phys. Lett.* **511**, 241–246 (2011). doi: [10.1016/j.cplett.2011.06.022](https://doi.org/10.1016/j.cplett.2011.06.022)
34. Chang, H.-C., Jiang, J.-C., Liou, Y.-C., et al.: *J. Chem. Phys.* (2008). doi: [10.1063/1.2958256](https://doi.org/10.1063/1.2958256)
35. Chang, H.-C., Jiang, J.-C., Liou, Y.-C., et al.: *Anal. Sci.* **24**, 1305–1309 (2008)
36. Bowers, J., Butts, C.P., Martin, P.J., et al.: *Langmuir* **20**, 2191–2198 (2004)
37. Rebelo, L., Najdanovic-Visak, V.: *Green Chem.* **6**, 369–381 (2004)
38. Almásy, L., Turmine, M., Perera, A.: *J. Phys. Chem. B* **112**, 2382–2387 (2008). doi: [10.1021/jp076185e](https://doi.org/10.1021/jp076185e)
39. Malham, I.B., Letellier, P., Turmine, M.: *J. Phys. Chem. B* **110**, 14212–14214 (2006)
40. Chen, Y., Ke, F., Wang, H., et al.: *ChemPhysChem* **13**, 160–167 (2012). doi: [10.1002/cphc.201100782](https://doi.org/10.1002/cphc.201100782)
41. Wang, J., Wang, H., Zhang, S., et al.: *J. Phys. Chem. B* **111**, :6181–6188 (2007). doi: [10.1021/jp068798h](https://doi.org/10.1021/jp068798h)
42. Mele, A., Tran, C.D., De Paoli Lacerda, S.H.: *Angew. Chem. Int. Ed. Engl.* **42**, 4364–4366 (2003). doi: [10.1002/anie.200351783](https://doi.org/10.1002/anie.200351783)
43. Mele, A., Romanò, G., Giannone, M., et al.: *Angew. Chem. Int. Ed. Engl.* **45**, 1123–1126 (2006). doi: [10.1002/anie.200503745](https://doi.org/10.1002/anie.200503745)
44. De Benedetti, P.G.: *Metastable liquids : concepts and principles*. Princeton University Press, Princeton (1996)
45. Eisenberg, D., Kauzmann, W.: *The structure and properties of water*. Oxford University Press, London (1969)
46. Walrafen, G.E., Fisher, M.E., Hokmabadi, M.S., Yang, W.H.: *J. Chem. Phys.* **85**, 6970 (1986)
47. Saito, S., Ohmine, I.: *J. Chem. Phys.* **125**, 84506 (2006)
48. Pieniazek, P.A., Stangret, J.: *Vib. Spectrosc.* **39**, 81 (2005)
49. Lindgren, J., Hermansson, K., Wójcik, M.J.: *J. Phys. Chem.* **97**, 5254 (1993)
50. Wang, Y., Li, H., Han, S.A.: *J. Phys. Chem. B* **110**, 24646 (2006)

51. Cammarata, L., Kazarian, S.G., Salter, P.A., Welton, T. *Phys. Chem. Chem. Phys.* **3**, 5192–5200 (2001). doi: [10.1039/b106900d](https://doi.org/10.1039/b106900d)
52. Brubach, J.B., Mermet, A., Fiabozzi, A., et al.: *J. Phys. Chem. B* **105**, 430 (2001)
53. Boissière, C., Brubach, J.B., Mermet, A., et al.: *J. Phys. Chem. B* **106**, 1032 (2002)
54. Mele, A., Tran, C.D., De Paoli Lacerda, S.H.: *Angew. Chem. Int. Ed. Engl.* **42**, 4364–4366 (2003). doi: [10.1002/anie.200351783](https://doi.org/10.1002/anie.200351783)
55. Köddermann, T., Wertz, C., Heintz, A., Ludwig, R.: *ChemPhysChem* **7**, 1944–1949 (2006). doi: [10.1002/cphc.200600034](https://doi.org/10.1002/cphc.200600034)
56. Ozawa, R., Hayashi, S., Saha, S., et al.: *Chem. Lett.* **32**, 948–949 (2003)
57. Hayashi, S., Ozawa, R., Hamaguchi, H.-O.: *Chem. Lett.* **32**, 498–499 (2003). doi: [10.1246/cl.2003.498](https://doi.org/10.1246/cl.2003.498)
58. Hamaguchi, H.-O., Ozawa, R.: *Adv. Chem. Phys.*, 85–104 (2005)
59. Almásy, L., Turmine, M., Perera, A.: *J. Phys. Chem. B* **112**, 2382–2387 (2008). doi: [10.1021/jp076185e](https://doi.org/10.1021/jp076185e)
60. Jiang, W., Wang, Y., Voth, G.A.: *J. Phys. Chem. B* **111**, 4812–4818 (2007). doi: [10.1021/jp067142l](https://doi.org/10.1021/jp067142l)

The Structure of Ionic Liquids

Caminiti, R.; Gontrani, L. (Eds.)

2014, XI, 193 p. 92 illus., 30 illus. in color., Hardcover

ISBN: 978-3-319-01697-9