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Pressure-responsive mesoscopic structure in room temperature ionic liquids

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Among the most spectacular peculiarities of room temperature ionic liquids, their mesoscopically segregated structural organization keeps on attracting attention, due to its major consequences for the bulk macroscopic properties. Here we use Molecular Dynamics simulations to explore the nm-scale architecture in 1-octyl-3-methylimidazolium tetrafluoroborate, as a function of pressure. This study reveals an intriguing new feature: the mesoscopic segregation in ionic liquids is characterized by a high level of pressure-responsiveness and progressively vanishes upon application of high enough pressure. These results are in agreement with recent x-ray scattering data and are interpreted in terms of the microscopic organization. This new feature might lead to new ways to develop designer solvents for enhanced solvation capabilities and selectivity.

Room temperature ionic liquids (RTILs) represent one of the hottest research fields in the last couple of decades. The interest towards these compounds, which are composed solely of ionic species, stems from a variety of reasons, including their negligible volatility, high electrochemical and thermal stability and the possibility of fine-tuning their physico-chemical properties by slight modifications of their chemical composition (e.g. alkyl chain length, anion or cation nature etc.). One of the most stimulating RTILs's peculiarities is the enhanced level of their structural organization at mesoscopic level[1–12] that is the direct consequence of their intrinsic amphiphilicity. Being composed by charged moieties covalently bound to alkyl tails, most of the existing RTILs show a distinct tendency to separate into nm-scale domains of their polar and apolar moieties that tend to mutually exclude each other. Such a specific architecture is fingerprinted in a clear-cut, experi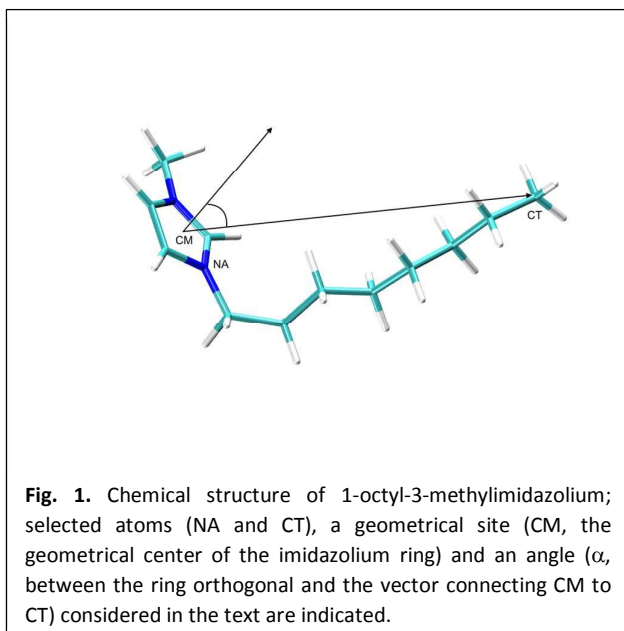mental way by X-ray or neutron diffraction, as a distinct low Q peak reflects the length scale of polar-apolar alternation. These evidences are detected whenever a RTIL bears a long enough alkyl tail, whose polarity is distinctly different from the charged moieties' one. In particular together with a variety of experiments conducted at ambient conditions on pure compounds[3,13–17], the low Q scattering feature was also detected in binary mixtures of RTILs either with other ionic species[18,19] or with molecular compounds[20,21], as well as in neat RTILs as a function of temperature[4,22]. So far however not much is known on the mesoscopic organization in RTILs at high hydrostatic pressure conditions. Most of the studies were conducted using spectroscopic techniques (e.g. Raman or IR spectroscopies) aiming at characterizing the existence of liquid-crystal transitions as a function of pressure/temperature.[23–36] Here we explore the fundamental issue of mesoscopic organization in RTILs (namely in [C_8mim][BF_4], 1-octyl-3-methylimidazolium tetrafluoroborate, see Fig. 1) under hydrostatic pressure, by using Molecular Dynamics simulations.

Not many studies tackled this issue using computational approaches: recently Zhao and co-workers[37] simulated [C_4mim][PF_6] extracting interesting results related to this present study, although the butyl tail in their chosen compound is at the limit to probe mesoscopic order effects in RTILs; to our knowledge only the study by Maginn and coworkers[38] computationally described the structure in RTILs bearing long enough alkyl tails to develop the nm-scale segregation effects. Recently an experimental study focused on a series of 1-alkyl-3-methylimidazolium tetrafluoroborate that were investigated as a function of pressure and temperature, using Small Angle X-ray scattering (SAXS).[39] This study shows that the above mentioned low Q feature slightly shifts towards higher Q values upon pressure increase; more interestingly, its amplitude progressively decreases and eventually the feature disappears when high enough pressure is reached (above 1 GPa). These observations prompt for a high level of pressure-responsiveness of the mesoscopic architecture in RTILs and deserve an in depth exploration of its intimate mechanism at atomistic level. As a matter of fact,

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Fig. 1. Chemical structure of 1-octyl-3-methylimidazolium; selected atoms (NA and CT), a geometrical site (CM, the geometrical center of the imidazolium ring) and an angle (α, between the ring orthogonal and the vector connecting CM to CT) considered in the text are indicated.

Fig. 2. Calculated x-ray weighted static structure factors for [C_8mim][BF_4], S(Q), at different values of hydrostatic pressure between 1 and 10,000 atm (namely, in order of decreasing amplitude of the peak centered at 0.28 Å^{-1}: 1, 300, 1000, 3000 and 10000 atm) and 320 K. In the inset the experimental SAXS data collected by Yoshimura et al. on the same IL as a function of pressure (please note the different abscissa scale)[39] (Reprinted with permission from [39]. Copyright (2015) American Chemical Society.

several of the smart properties of RTILs have been related to the existence of segregated polar and apolar domains that facilitate the simultaneous dissolution of as dissimilar compounds as ionic or oily ones in the same medium or enhance the catalytic properties of neat RTILs. Accordingly a rationalization of the disappearing of the low Q peak, fingerprinting the dissolving of the mesoscopically segregated structure, is necessary in order to be able to exploit the mechanism triggering such major structural rearrangements as a response to pressure changes.

It has been shown by us[4,5,40,41] and others[42] that the low Q peak is not detected in those RTILs where the side chain is characterized by polarity comparable to the one of the ionic moieties, thus removing the driving force to the mutual segregation of the incompatible moieties. For example, chains where one methylene group is replaced by an oxygen atom behave in such a way and no segregation has been found for these compounds. On the other hand in the case of [C_8mim][BF_4], the alkyl tail is known to deliver polar-apolar differentiation; accordingly, the reason for the disappearing of the segregated morphology must be found elsewhere.
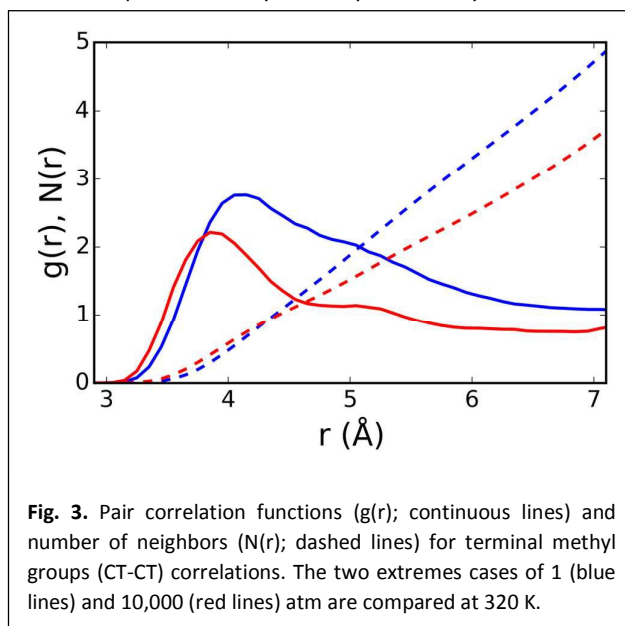
Aiming at rationalizing these evidences, we developed a series of Molecular Dynamics simulations of [C_8mim][BF_4] at 320 K and under different values of hydrostatic pressure. While computational details are provided in the ESI, here we mention that we used cubic simulation boxes with large enough sides to allow for an accurate determination of the mesoscopically segregated nature of the morphology in this compound. In Fig. 2, we show the pressure dependence of the low Q portion of the computed diffraction pattern, together with the experimental SAXS results obtained by Yoshimura et al.[39]

The calculated diffraction pattern, S(Q), at ambient pressure is in very good agreement with the experimental SAXS data collected by us[4] and by Yoshimura[39]: the pattern is characterized by two major peaks centered at ca. 0.28 and
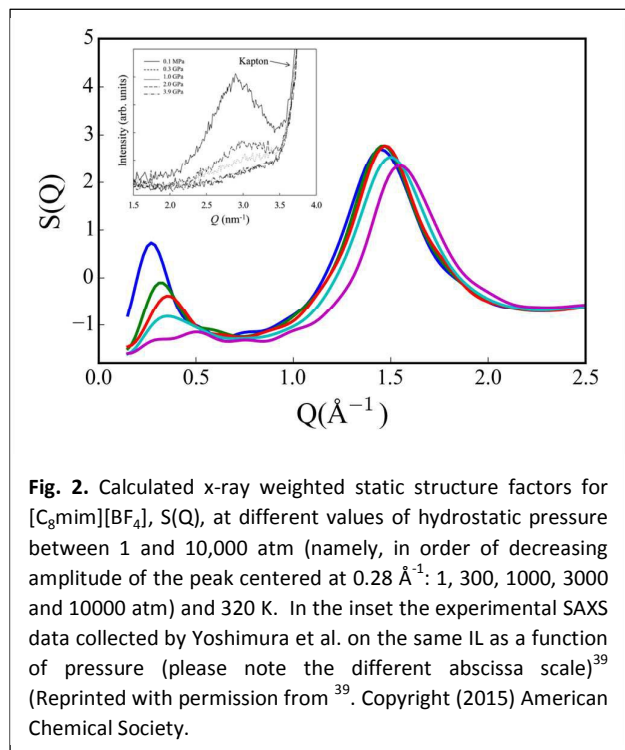
1.43 Å^{-1} (peak I and II, respectively). Upon pressure increasing, a progressive shift of peak I is observed towards higher Q values and, concomitantly, its amplitude decreases and almost disappears at the highest pressure that we studied (ca. 10,000 atm=1 GPa), consistently with the experimental observations by Yoshimura et al.[39] This indicates that our simulations are realistic enough to provide a description for the mechanism underlying the disappearing of the polar-apolar alternations at atomistic level.

Aiming to elucidate the structural properties of these systems, we now discuss the pair distribution functions (pdfs). Pdfs from ionic species are only limitedly affected by the increase in

Fig. 3. Pair correlation functions (g(r); continuous lines) and number of neighbors (N(r); dashed lines) for terminal methyl groups (CT-CT) correlations. The two extremes cases of 1 (blue lines) and 10,000 (red lines) atm are compared at 320 K.

pressure: Figure S1 in the ESI describes cation-cation, cation-anion and anion-anion pdfs at the two extreme pressures (1 and 10,000 atm). Similarly to what had been reported in previous studies conducted on RTILs under pressure, structural correlations between ionic species are not particularly influenced by increasing pressure, as these moieties interact through strong coulombic correlations that maintain relatively unchanged the mutual distances between ions.[37,38] Overall, across the whole pressure range that we explored, the ionic species tend to organize in a typical onion like fashion where opposite sign ions tend to form a first shell, and then similar sign ions create a following shell and so on over the distance of a few nm. On the other hand, it can be expected that, as alkyl tails interact through weaker dispersive interactions, pressure changes will largely affect their conformations. In figure 3 we report the pdf and the N(r) (number of neighbors) for CT-CT correlations between the terminal methyl groups: We observe that upon increasing pressure, mutual correlations between CT's progressively decrease: the closest approach distance decreases but the number of neighbors decreases. This is somehow at odd with previous MD studies where it was
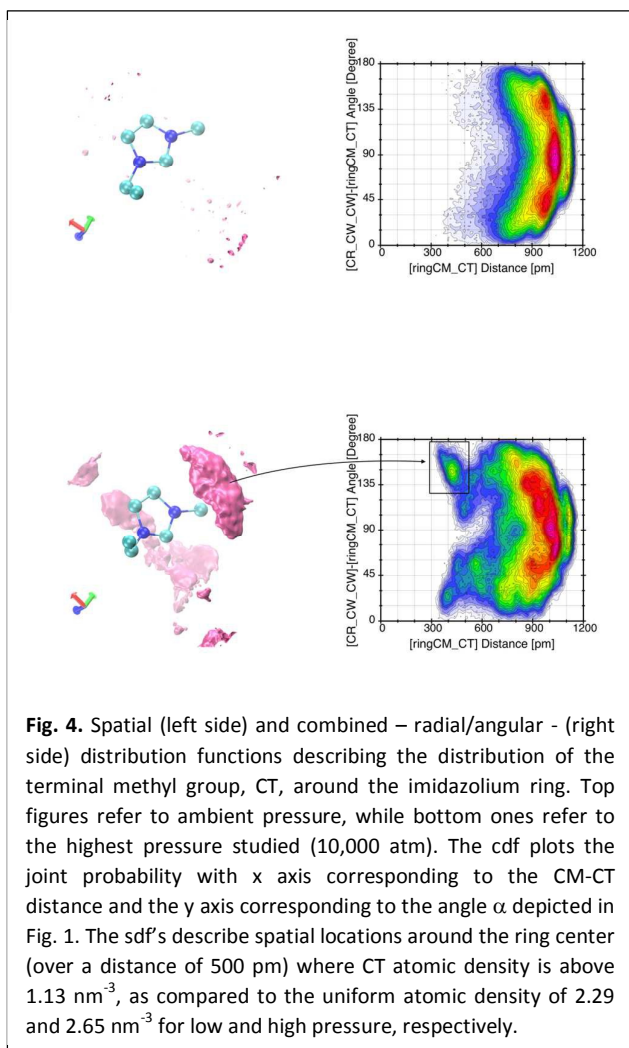
proposed that high pressure results in an enhancement of the tail-tail aggregation in $[C_{18}mim][Tf_2N]$.[43] Indeed, the mentioned pdf is commonly considered to represent a reliable indicator of the existence of segregated apolar domains and its pressure evolution prompts for progressive disappearing of this segregation.

We also evaluated the combined distribution function (cdf; data treatment was done using the TRAVIS analysis tool package[44]) built up by following two channels: a) in the abscissa there is the distance between the imidazolium geometric ring and the terminal methyl group (CM-CT, see Fig. 1) and in the ordinate the angle (hereinafter indicated as α, see Fig. 1) between the two vectors orthogonal to the imidazolium plane and connecting CM and CT, respectively. This cdf is plotted in figure 4 for the two extreme pressures explored in this study (1 and 10,000 atm, right top and bottom panels, respectively): it can be appreciated the approach of the terminal methyl group to the imidazolium ring, when pressure increases. In fact together with a large distribution at distances between 600 and 1200 pm (that is essentially similar to the behavior at ambient pressure), there is also a hot lobe centered at 400 pm and α=150° that is not found at lower pressure. This indicates an enhanced probability of finding the terminal methyl group close to the imidazolium ring, as a consequence of the tail curling. This evolution of the intramolecular structural organization is confirmed by the spatial correlation functions (scf) reported in figure 4 (left top and bottom panels for 1 and 10,000 atm, respectively) depicting the spatial distribution of CT around the imidazolium ring that confirms the enhanced level of probability of finding the terminal CT group in the close neighborhood of the imidazolium ring, upon pressure increasing.

Overall this whole trend is resembling the observations done by Margulis[42] and Canongia Lopes[41], when dealing with RTILs, where the alkyl tail is replaced with a polar tail containing ether groups. In those situations, the tendency of tails to segregate from the charged moieties, leading to the low Q diffraction peak, vanished due to the comparable polarity of charged moieties and tails. In the present case we observe similar structural effects, despite the fact that the polar and apolar moieties in the RTIL are maintained. Mere application of hydrostatic pressure succeeds in determining such an outstanding structural change.

These results are confirmed by the pressure evolution of the dihedral angles along the octyl chain: while at ambient conditions the alkyl tail is characterized by a high fraction of trans conformation for all the dihedrals, raising the pressure leads to an increase of gauche conformers, in agreement with several experimental and computational studies. In Figure S3 of the ESI, the fraction of gauche conformers along a given octyl chain is reported for the two extreme pressures, highlighting their increased number upon pressure increase.

Such a change in the dihedral populations leads to a collapsing of the alkyl tail, as witnessed by the length distribution for the distance between imidazolium nitrogen and terminal methyl (see Figure S5 in ESI). As a matter of fact it has been proposed that the increasing number of gauche bonds in alkanes leads

Fig. 4. Spatial (left side) and combined – radial/angular - (right side) distribution functions describing the distribution of the terminal methyl group, CT, around the imidazolium ring. Top figures refer to ambient pressure, while bottom ones refer to the highest pressure studied (10,000 atm). The cdf plots the joint probability with x axis corresponding to the CM-CT distance and the y axis corresponding to the angle α depicted in Fig. 1. The sdf's describe spatial locations around the ring center (over a distance of 500 pm) where CT atomic density is above 1.13 nm^{-3}, as compared to the uniform atomic density of 2.29 and 2.65 nm^{-3} for low and high pressure, respectively.

to a more globular shape for which the excluded volumes are smaller than for more extended conformations: this explains the tendency for the tail collapsing upon increasing pressure.[45–48]
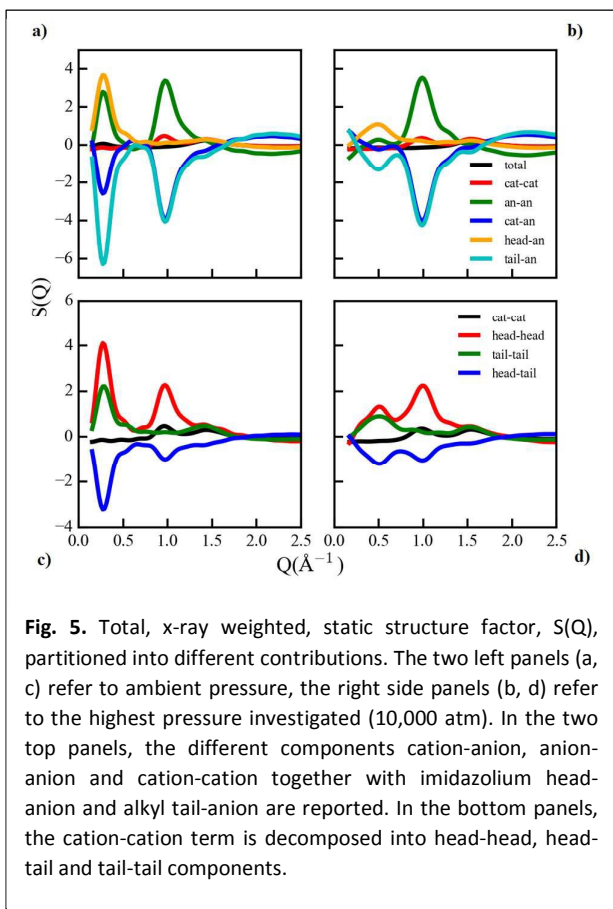

Fig. 5. Total, x-ray weighted, static structure factor, S(Q), partitioned into different contributions. The two left panels (a, c) refer to ambient pressure, the right side panels (b, d) refer to the highest pressure investigated (10,000 atm). In the two top panels, the different components cation-anion, anion-anion and cation-cation together with imidazolium head-anion and alkyl tail-anion are reported. In the bottom panels, the cation-cation term is decomposed into head-head, head-tail and tail-tail components.

Finally, we partitioned the calculated S(Q) plotted in Figure 2 in terms of different components arising from moieties of the ionic liquid, following the formalism introduced by Margulis in a series of papers.[6,7,42,50] In Figure 5, following Margulis' approach we decomposed the total static structure factor into different ionic and sub-ionic components[51]: the pre-peaks and anti-pre-peaks observed at ca. 0.28 $Å^{-1}$ correspond to the structural correlation associated to the polar–apolar alternation.[6,7]

We find that while, similarly to other cases, at ambient pressure the plots of Figure 5 a) and c) indicate the existence of in-phase polar-polar and apolar-apolar correlations as well as out of phase polar-apolar ones, in the case of high hydrostatic pressure (Figure 5 b) and d)) there is only very limited sign of the polar-apolar alternation fingerprints.

We can now conclude rationalizing the observed pressure-responsiveness of the mesoscopic architecture in RTILs on the basis of atomistic considerations. The polar vs apolar segregated landscape in bulk RTILs at ambient conditions is characterized by alkyl tails that tend to avoid the charged moieties: this is achieved by means of pretty much stretched alkyl tail that leads to preferential van der Waals interactions

between neighbor tails with an average environment around each tail resembling the liquid alkane one. Upon application of hydrostatic pressure this scenario soon begins to be altered: while, on one hand, polar moieties that interact through strong coulombic interactions are quite unaffected by the pressure, on the other hand the conformation of the alkyl tail is influenced. An increase of the gauche conformations along the tail is observed that leads to a reduction of the excluded volume and induces a characteristic tail curling towards the imidazolium ring, despite of the polar vs apolar incompatibility. This resembles the scorpion configuration that was proposed by Canongia-Lopes in the case of ethers bearing tails[41]. In the present situation, however it is the hydrostatic pressure that drives the cation structure towards a more compact, globular conformation, with the effect of breaking up the highly organized architecture of segregated polar-apolar domains. It can be envisaged that these findings will provide a new perspective in the exploitation of RTILs as designer solvent, prompting for a new variable (namely pressure) towards which the mesoscopic polar-apolar diversification is responsive.

Acknowledgements

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