Morphology of 1-alkyl-3-methylimidazolium hexafluorophosphate room temperature ionic liquids

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ABSTRACT

The structural organization in selected room temperature ionic liquids, namely (a) butyl-, (b) hexyl- and (c) octyl-3-methylimidazolium hexafluorophosphate, is investigated by means of X-ray diffraction. We find novel experimental evidences of the existence of a high degree of intermediate range order that is associated to nanoscale segregation of the alkyl chains into the charged matrix. The size of these structural heterogeneities depends linearly from the alkyl chain length. A similar behaviour had been observed in other systems, such as normal alcohols. The slope of such dependence provides hints on the nature of the structural organization of these segregated domains.

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1. Introduction

Room temperature ionic liquids (RTILs) are attracting great attention as environmentally responsible replacements for many toxic solvents [1–3]. This is a consequence of their negligible vapour pressure and the tunability of their chemical–physical properties (including density, viscosity refractive index etc.) upon slight changes of their chemical architecture. They are typically built up by a bulky, asymmetric cation, such as 1-methyl-3-alkyl imidazolium, and a fluorinated anion, such as hexafluorophosphate.

Recently, Molecular Dynamics simulation studies have suggested the existence of a complex morphology in neat ILs [4–7]. This complexity is presently considered as the leading factor for many of the intriguing properties of this important class of materials. The proposed structural model considers that the charged portions of the salt (i.e. the anion and the charged imidazolium ring) are subjected to strong, long ranged coulombic interactions and, accordingly, tend to organise in a network-like fashion, similarly to what is found in conventional inorganic molten salts. On the other hand, the apolar alkyl tails connected to the imidazolium ring interact mainly through the weak, short ranged excluded volume interactions. When these tails are long enough they tend to phase segregate, building up nanometer-scale domains embedded into the charged matrix.

We recently provided a direct proof of the existence of such nanoscale segregation phenomena in a series of chloride and tetra-

fluoroborate ILs [8]. In the present Letter we provide novel experimental evidences of the existence of such a phenomenon and discuss the nature of microscopic ordering in hexafluorophosphate ILs.

In the past, we described a series of thermodynamic, structural and dynamic properties of a short chain member of the $[PF_6]^-$-based IL family, namely 1-butyl-3-methyl imidazolium $[PF_6]^-$ ([C4mim][PF_6]) [9]. In that report, no indication has been provided on the existence of longer range structural organization, as such structural heterogeneities are difficult to identify in the case of [C4mim][PF_6], as they appear as a small shoulder of a much more intense X-ray diffraction amorphous halo.

This class of RTILs has been studied by MD simulations, highlighting the existence of nanoscale heterogeneities in these salts as well. Recently, a coarse grained MD study has been reported aiming to address the issue of nanostructure in $[PF_6]^-$-based RTILs [10]. This work, together with the previous seminal paper by Canongia Lopes and Padua [6], provides calculated static diffraction patterns that can be compared with our experimental X-ray diffraction data.

In the past, some $[PF_6]^-$-based ILs have been studied using diffraction techniques. Hardacre et al. [11] used neutron diffraction to access the microscopic structural organization in 1,3-dimethylimidazolium $[PF_6]$ (i.e., [C1mim][PF_6]). The main focus of that study was on microscopic spatial scales, and the corresponding diffraction patterns qualitatively resemble our findings in [C4mim][PF_6] [9] and in [C6mim][PF_6] and [C8mim][PF_6] described in the following sections. The structure of the crystalline phase of [C2mim][PF_6] was studied earlier [12], highlighting the importance of cation–anion coulombic interactions in determining the structure. The struc-

ture of one of the two [9] crystal phases of [C4mim][PF$_6$] has been characterised using single crystal X-ray diffraction [13].

Longer ($n \geqslant 12$) alkyl chains ILs with [PF$_6$]$^-$ anion are found to have a complex phase diagram with the occurrence of many crystalline phases. They have been studied in the past [14,15] and information has been extracted on the nature of their crystalline and liquid-crystalline phases. Analogously to other long alkyl chain ILs [16], it has been proposed that the mesophase is characterised by an intermediate degree of order between the crystalline and the isotropic one.

2. Experimental

[C4mim][PF$_6$], [C6mim][PF$_6$] and [C8mim][PF$_6$] were IOLITEC products. The as-received products were kept for two days under vacuum at 40 °C, in order to remove moisture and any volatile component.

The Small-Wide Angle X-ray Scattering experiment was conducted for the three samples at the high brilliance beam line ID02, European Synchrotron Radiation Facility (ESRF), Grenoble, France [26], using an instrumental setup which allows covering the momentum range Q between 0.01 and 0.9 Å^{-1}. Measurements were collected at 25 °C, using a thermostated bath and the samples were 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 was obtained using a neat water sample in a 2 mm capillary.

3. Results and discussion

In Fig. 1 SAXS data sets for the series C4, C6, C8mim PF6 are reported at room temperature condition. Two main features can be observed in the data: (a) at high Q values a distinct upturn of the curves occurs and (b) the existence of an amorphous halo at a position (Q_{MAX}) that is dependent on the alkyl chain length. While the first feature corresponds to the tail of the high Q amorphous halos (which are related to many different spatial correlations, including alkyl chain correlations [17]), the second feature is the fingerprint of the occurrence of nanoscale structural heterogeneities in these salts.

The latter observation is similar to our previous findings in other 1-alkyl-3-methylimidazolium-based ILs [8]. Similar findings have been very recently reported by the Mizuhata group on a different class of RTILs, namely aliphatic quaternary ammonium salts (AQAS) [18].

The peak positions, Q_{MAX}, have been obtained modelling the data using a Gaussian function in the case of [C6mim][PF$_6$] and [C8mim][PF$_6$], where the peak is sufficiently well separated from the high Q upturn. For [C4mim][PF$_6$], two Gaussian functions have been used, with a high Q contribution centred at ca. 1.0 Å^{-1} (see data of Fig. 4 in Ref. [9]).

The size of these structural heterogeneities, $D \sim 2\pi/Q_{MAX}$, linearly scales for the alkyl chain length with a slope: $\partial D_{ILs}/\partial n = 2.1$ Å/CH$_2$ unit. Comparing with our previous study on similar ILs [8] (see Fig. 2), the slope of this dependence is unaffected by the anion nature (we note by passing that recently Mizuhata et al. found similar values for $\partial D_{ILs}/\partial n$ in the case of AQAS [18]); on the other hand a systematic decrease of the heterogeneities' sizes is observed upon increasing the anion size ($D_{Cl} > D_{BF_4} > D_{PF_6}$). Such dependence interestingly resembles the behaviour of the characteristic size of the mesophase in longer ($n \geqslant 12$) alkyl chains ILs [16], where the higher ability of the anions to form three-dimensional hydrogen bonding lattices (in the order Cl$^-$ > [BF$_4$]$^-$ > [PF$_6$]$^-$) leads to a larger interlayer spacing for the mesophase.

Moreover, the shape of the amorphous halo is unaltered by the anion nature, apart from differences in the amplitude. This indicates that the morphological nature of the observed structural heterogeneities is not affected by the anion nature, at least for the present anion choice.

The experimental confirmation of the MD-based proposal of structural heterogeneities in RTILs with sufficiently long alkyl chain length (ACL) is fundamental to rationalise a number of experimental evidences that so far were puzzling [19]. Watanabe and co-workers studied the diffusivity of a series of RTILs with varying alkyl chain length and found that it decreases with increasing ACL [20]. A very similar enthalpy of vaporization increment per —CH$_2$— unit has been observed for ionic liquids and solid n-alkanes, thus supporting the view of alkyl chains embedded in alkane environment [21].

The fundamental paper by Canongia Lopes and Padua [6] showed that for the cases of [Cnmim][PF$_6$] with $n = 4, 6, 8$ and 12, the corresponding static structure factors are characterised by distinct peaks with features similar to the ones that we experimen-
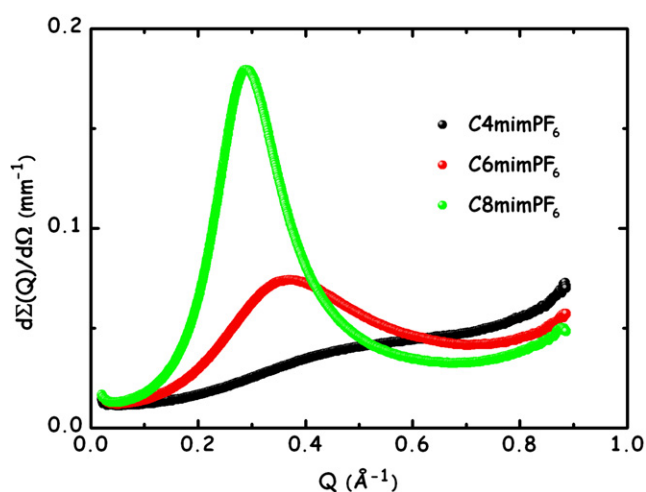

Fig. 1. X-ray diffraction patterns from the series of RTILs [Cnmim][PF$_6$], $n = 4, 6, 8$, at 25 °C (error bars are smaller than the points size).
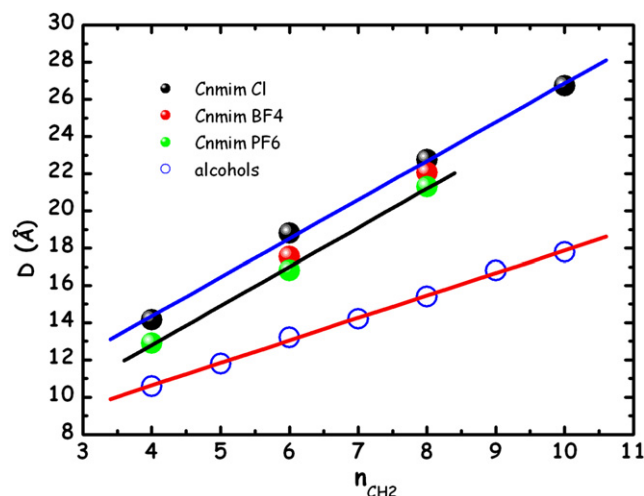

Fig. 2. Alkyl chain length dependence of the characteristic size of the structural heterogeneities observed from the SAXS data for chloride and tetrafluoroborate ILs [8], from hexafluorophosphate ILs (present study) and from linear alcohols (from butanol to decanol) (data taken from [25]). The blue line is a fit of the chloride data set with slope $\partial D_{IL}/\partial n = 2.1$ Å/CH$_2$ unit; the red line corresponds to a linear fit of the alcohol data set with a slope $\partial D_{alcohol}/\partial n = 1.2$ Å/CH$_2$ unit. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

tally described. An earlier paper by Urahata and Ribeiro high-lighted the existence of intermediate range order in similar ILs [4]. Recently coarse grained molecular dynamics simulations for selected (n = 4, 7 and 10) [Cnmim][PF$_6$] ILs have been reported, with the goal of addressing the nature of the structural heterogeneities [10]. Also in this case, in agreement with our experimental data, the two salts with n = 7 and 10 show clear indication of nano-scale segregation: by evaluating the neutron and X-ray scattering pattern from protiated salts, the authors observe an amorphous halo at Q = 0.41 and 0.29 Å^{-1}, for n = 7 and 10, respectively. The corresponding spatial sizes are ca. 15.3 and 21.6 Å, respectively.

Though these structural heterogeneities are found to have a spatial extent in the nanometer scale, their size (both in the case of Canongia Lopes and Padua [6] and Balasubramanian [10] simulations) do not fit to the linear trend that we observe experimentally for the alkyl chain dependence (see Fig. 2) and seem to be systematically smaller than expected. At the present stage, it is not clear the origin of such discrepancies between MD simulations and experimental data.

We further exploit the structural interpretation proposed by MD studies in order to rationalise our findings. In the report by Canongia Lopes and Padua [6], the diffraction peak is found to be related to the correlation between the center of mass between polar and apolar atom groups. By evaluating the partial structure factors for the system [C10mim][PF$_6$], Balasubramanian et al. find that the X-ray diffraction feature at ca. 0.29 Å^{-1} is mainly related to an intermediate range ordering between anion–anion and alkyl tail–alkyl tail pairs [10]. Given the large electron density of the [PF$_6$]$^-$ anions, the X-ray diffraction pattern at the low Q peak position was then tentatively associated to anion–anion structural correlations. The distance associated to the low Q peak is, however, characteristic also for other pairs, as indicated by [10]; this implies that
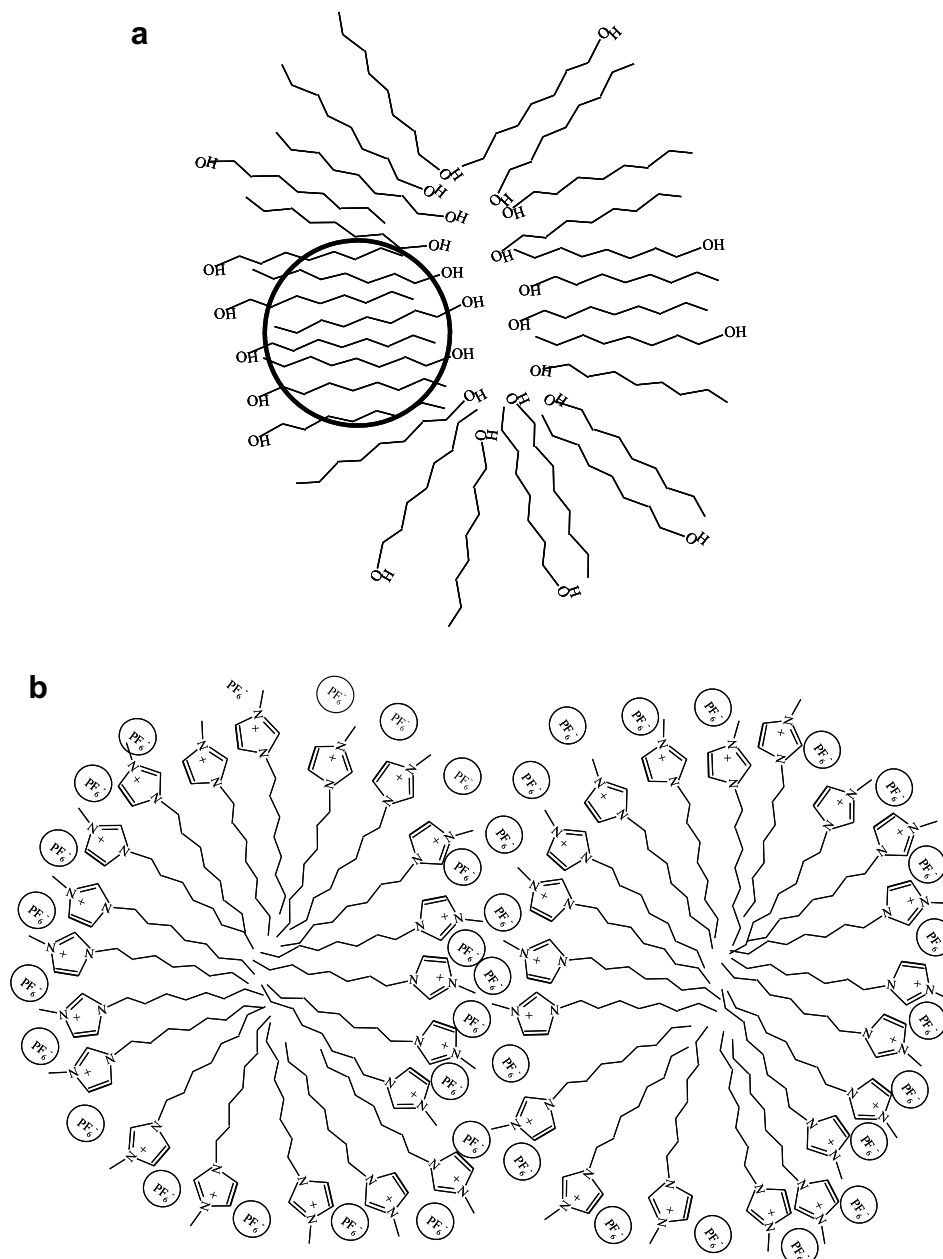

Fig. 3. Schematic bi-dimensional representation of the different morphology that characterises the liquid state of (a) *n*-alcohols and (b) 3-*n*-alkyl-1-methylimidazolium-based room temperature ionic liquids. In the case of *n*-alcohols the alkyl chains tend to interdigitate, as can be observed in the area highlighted by the circle; in the case of RTILs, this is not the case.

the peak is indicative of global degree of order and not only for the anions.

Such observations agree with the scenario proposed by other researchers on the basis of their MD studies: as a consequence of the strong and long-ranged electrostatic interactions between the anion and the head of the cation, a locally electrostatically neutral matrix will form, where nanosegregated alkyl tails are embedded. The latter interact with much weaker and short-ranged interactions (essentially van der Walls interactions).

This description corresponds to a morphology that is characterised by nano-scale domains of segregated alkyl tails in a charged network.

We then relate the experimentally observed diffraction peak to the average distance between the center of mass of two first neighbour alkyl tail pools. Due to the structural inhomogeneity of the size and shape of these domains, an analytical description of the diffraction patterns in terms of the combination of a form factor (contribution associated to the scattering from the average isolated domain) and a structure factor (contribution associated to the scattering from the structurally correlated domains) is complex and will be the subject of a following paper. By now, we can anticipate that in this framework, the characteristic distance D corresponds to the average size of the domain (considered as the sum of the alkyl tail domain size plus the thickness of the surrounding charged shell).

Such a model has been proposed in the past for similar nano-scale segregated systems such as linear alcohols, (e.g. *n*-octanol) [22]. In this case the emerging picture is describing the morphology as characterised by long and thin polar domains of hydrogen bonded hydroxyl groups and segregated non-polar regions enriched in interdigitating hydrocarbon tails, leading to the terminology 'inverted micelle', when describing this system [23]. This scenario nicely accounts for the linear dependence of the heterogeneities size from the alkyl chain length. A similar trend has been observed for the other normal alcohols, where the characteristic size depends linearly from the alcohol length (see Fig. 2), with a slope of $\partial D_{alcohol}/\partial n$ = 1.21 Å/CH$_2$ unit. This value resembles the corresponding quantity obtained by Tanford [24] for the change in chain length upon adding a CH$_2$ unit to a linear alkane: l_{CH_2} = 1.265 Å. The almost quantitative coincidence between l_{CH_2} and $\partial D_{alcohol}/\partial n$ prompts one to formulate a structural model for neat liquid linear alcohols involving an almost complete interdigitation of neighbour alkyl chains, so that upon increasing the alkyl chain length of one CH$_2$ unit (i.e., of one unit l_{CH_2}), the corresponding increasing of the domain size ($\partial D_{alcohol}/\partial n$) is $\sim l_{CH_2}$. Such a result is the consequence of the interdigitation of the hydrocarbon tails (see Fig. 3a and, in particular the area inside the circle, where such full interdigitation is highlighted) and would not be satisfied if the alkyl chains would not arrange themselves in a non-interdigitated way.

In this perspective, the structural scenario for imidazolium based ILs would be substantially different, being $\partial D_{alcohol}/\partial n \sim l_{CH_2} < \partial D_{IL}/\partial n < 2\, l_{CH_2}$. On one hand $\partial D/\partial n = l_{CH_2}$ would indicate complete interdigitation (like for the case of alcohols); on the other hand, the other extreme condition ($\partial D/\partial n = 2l_{CH_2}$) would indicate complete exclusion of adjacent alkyl tails. The observed value $\partial D_{IL}/\partial n$ = 2.1 Å/CH$_2$ unit would indicate only very limited interdigitation between adjacent tails (see Fig. 3b).

We formulate the hypothesis that such a forced structural configuration (where not all the empty space is filled by alkyl tails and which is likely to limit the potential enthalpic gain due to neighbour alkyl tails interposition) might be the consequence of the strong steric hindrance introduced by the bulky methyl-imidazolium head + anion pairs. Moreover, the high mobility of the anions, as compared to the much lower cations' one, might locally induce the formation of a net non-null positive charge at the interface between the charged network and the hydrocarbon neutral domains. Such a positive charge distribution might lead to a blowing up of the domains, as a consequence of the local repulsive interactions.

We can envisage that future detailed MD simulation might confirm this proposal and provide a microscopic description of the detailed organization of alkyl tails into the nanosegregated domains.

4. Conclusion

We reported new experimental data with the aim to characterise the morphology of a series of room temperature ionic liquids at a microscopic spatial level.

The hexafluorophosphate ILs are characterised by the occurrence of nanoscale structural heterogeneities, which has been observed in other ILs and emerged from recent Molecular Dynamics simulations. These heterogeneities are suggested to be the consequence of the nanoscale segregation of the alkyl chains into oily domains that are embedded into the charged network. By properly interpreting the alkyl chain length dependence of the domains' characteristic size, we propose that the neighbour alkyl chains in the domains do not fully interdigitate, presumably as a consequence of the local and transient net non-null charge at the interface between charged network and hydrocarbon domains and the strong steric hindrance induced by the bulky charged imidazolium ring and the neighbour anions.

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