Chemical Science

Heterogeneous nanoscale structure in alkyl-methylimidazolium bromide ionic liquids: a step towards greener solvents?

Ionic liquids, organic salts with low melting points (<100°C), are receiving increasing attention in the chemical industry due to their interesting properties. In particular they are considered as promising environmental-friendly replacements for conventional organic solvents [1]. A remarkable feature of ionic liquids is their large tunability, since they can be obtained by the combination of a large number of possible cations based on several main groups with many different anions ranging from simple halides to complex organic groups. As a result it is theoretically possible to design a liquid adapted to a particular application by combining the appropriate cation and anion. Unfortunately, the basic understanding needed to achieve such a goal is still lacking, due to the high complexity of the molecular interactions leading to the macroscopic properties of the resulting liquid. As a step in this direction, we have combined the high-energy synchrotron X-ray diffraction (XRD) technique with atomistic Molecular Dynamics (AMD) simulations to explore the atomic structure of imidazolium-based ionic liquids with three different alkyl chain lengths, 1-alkyl-3-methyl-imidazolium bromide ($C_{n=2,4,6}$mimBr, Fig. 1).

High-energy XRD experiments were carried out at the high-energy X-ray diffraction beamline **BL04B2** with a photon energy of 61.5 keV in symmetric transmission geometry over the scattering vector Q ($=4\pi\sin\theta/\lambda$, 2θ: scattering angle, λ: wavelength of photons) range of 0.15–22 Å^{-1}. Classical AMD simulations were carried out with the DL_POLY 2.18 code employing the same conditions that proved to reproduce well both the structure and dynamics of C_2mimBr [2,3].

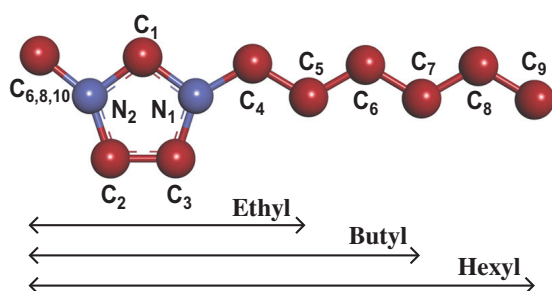Figure 2 shows the $S(Q)$s for the three liquids

measured at temperatures close to that of the simulations, 360 K. Five major features can be identified, indicated by the labels I–V. Only Peak I, at Q = 0.44 and 0.33 Å^{-1} for C_4mimBr and C_6mimBr, respectively, corresponding to correlation lengths D = 14 and 19 Å, shows a strong dependence on alkyl chain length; this feature appears to resemble the first sharp diffraction peak (FSDP) seen in molecular and network liquids and glasses, but its amplitude decreases with temperature unlike the increase generally observed with FSDPs. The AMD simulations reproduce well the total static structure factor of the three systems [4], including the low-Q peak that proved problematic in previous work in the literature. Therefore we have employed them to characterize in real space the structural heterogeneity implied by this feature, by defining a density heterogeneity order parameter (DHOP):

$$H_i(R) = \exp\left(\frac{\delta_i(R)}{d_i} - 1\right)$$

where $\delta_i(R)$ is the density of atoms of type i lying within a sphere of radius R about a reference atom of type i, making allowance for the periodic boundary conditions, d_i is the density of those atoms averaged over the entire system, and the angular brackets represent an average over all saved configurations.

The DHOPs for four types of atoms in C_6mimBr are shown in Fig. 3. An atom type dispersed homogeneously would be characterized by a DHOP gradually rising to one as R increases, while one dispersed heterogeneously would rise rapidly to a value higher than one and then decrease. Figure 3 shows that the distribution of the methylene groups next to the ring is rather homogeneous, while those of the ring centers and anions are slightly heterogeneous, with the DHOP reaching a maximum around 9 Å, a value close to $D/2$. In contrast, the tail distribution is extremely heterogeneous, with the DHOP reaching a maximum value of 1.2 at 6 Å.

Our results are consistent with the concept of a nanoscale heterogeneity with small, crystal-like moieties similar to that elaborated by Annapureddy et al. [5]. As the authors point out, there is no justification in either the experimental or simulation literature for more complex structural motifs such as micelles or strands. The similarity between the liquids and corresponding crystals on the nanoscale is supported by our detailed XRD and AMD comparison
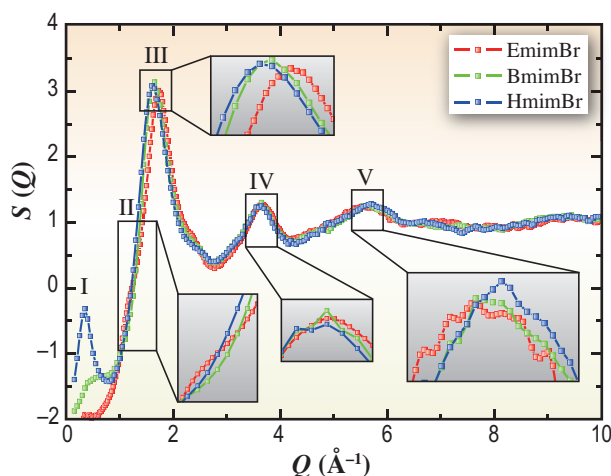
Fig. 1. 1-alkyl-3-methylimidazolium [$C_n$mim] cation. The carbon of the methyl group is named as C_6 for the ethyl- (n = 2), C8 for the butyl- (n = 4), and C10 for the hexyl- (n = 6) methylimidazolium cation.

Fig. 2. X-ray structure factors for the three liquids, C_2mimBr (EmimBr), C_4mimBr (BmimBr), and C_6mimBr (HmimBr), at 360 ± 2 K. The lines joining the points are a guide to the eye.

of the structure [2] and dynamics [3] of liquid and crystalline C_2mimBr. A better understanding of the origin and the extension of nanoheterogeneities in ionic liquids is a crucial step towards a better comprehension of their unusual properties and will hopefully lead to the design of new ionic liquids having the required properties to replace standard solvents by more ecologically friendly substitutes.
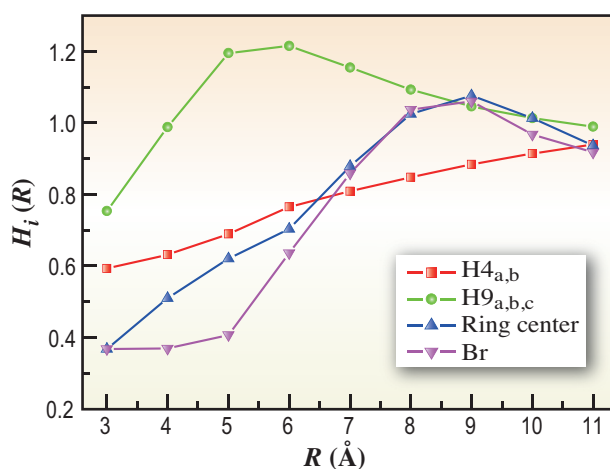

Fig. 3. Density heterogeneity order parameters [Eq. (1)] in C_6mimBr as a function of sphere radius for methylene group hydrogen atoms next to the ring, tail group hydrogen atoms, ring centers and anions. The labels $H4_{a,b}$ and $H9_{a,b,c}$ refer to hydrogen atoms on the C4 and C9 carbons, respectively (Fig. 1).

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