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Unveiling the complex network of interactions in Ionic Liquids: a combined EXAFS and Molecular Dynamics approach

A Serva[1]**, V Migliorati**[1]**, A Lapi**[1] **and P D'Angelo**[1]

[1] Dipartimento di Chimica, Università di Roma "La Sapienza", P.le A. Moro 5, 00185 Roma, Italy

E-mail: `alessandra.serva@uniroma1.it`

Abstract. The structural properties of geminal dicationic ionic liquids ($[C_n(mim)_2]Br_2$)/water mixtures have been investigated by means of extended X-ray absorption fine structure (EXAFS) spectroscopy and Molecular Dynamics (MD) simulations. This synergic approach allowed us to assess the reliability of the MD results and to provide accurate structural information about the first coordination shell of the Br^- ion. We found that the local environment around the anion changes as a function of the water concentration, while it is the same independently from the length of the bridge-alkyl chain. Moreover, as regards the long-range structural organization, no tail-tail aggregation occurs with increasing alkyl chain length.

1. Introduction

Ionic liquids (ILs) are an emerging class of solvents, showing a melting point near room temperature. Recently, a special class of "high stability" ILs, geminal dicationic ionic liquids (DILs), has been obtained [1]. DILs represent a very interesting variation of the cationic partner with various advantages over the traditional monocationic ILs when used as lubricants, catalysts, solvents, and separation media. Up to now, only few experimental and theoretical studies of pure DILs [2, 3] and mixtures of DILs and water [4] have been reported in the literature, thus the complex molecular organization taking place in DIL/water solutions is still lacking.

Here, we present a combined Molecular Dynamics (MD) and extended X-ray absorption fine structure (EXAFS) study of the structural properties of 1,3-bis[3-methylimidazolium-1-yl]alkane bromide ($[C_n(mim)_2]Br_2$)/water mixtures (see Figure 1). In particular, we investigated $[C_3(mim)_2]Br_2$/water mixtures as a function of water concentration (DIL/water molar ratios of 1:16, 1:70 and 1:400) and $[C_n(mim)_2]Br_2$/water mixtures, obtained by changing the alkyl-bridge chain length (n= 3, 6, 9) with constant water concentration (DIL/water molar ratio of 1:70). The synergic use of EXAFS and MD is particularly well suited to provide a global structural picture of DIL/water solutions both in proximity of the anion, and in the longer distance range.

2. Methods

The $[C_n(mim)_2]Br_2$/water mixtures were prepared by adding the proper amount of bidistilled water to pure $[C_n(mim)_2]Br_2$. X-ray absorption spectra above the Br K-edge were collected at room-temperature in transmission mode at the Elettra Synchrotron (Trieste, Italy) on the
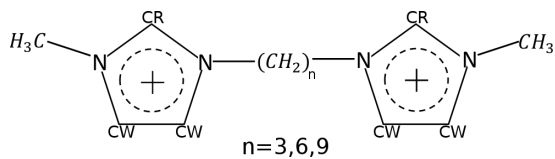
Figure 1. Molecular structure of 1,3-bis[3-methylimidazolium-1-yl]alkane dication, $[C_n(mim)_2]^{2+}$.

beamline 11.1. The storage ring was operating at 2 GeV with an optimal storage beam current between 300 and 30 mA. EXAFS data have been analyzed with the GNXAS program. Five MD simulations of $[C_n(mim)_2]Br_2$/water mixtures have been carried out using the DL_POLY package [5]. The ions and the water molecules were placed in a cubic box, with periodic boundary conditions. The number of ion pairs used in each simulation depends on the mixture and computational cost. The force field used for $[C_n(mim)_2]Br_2$ was taken from Lopes and Pádua [6, 7], with a minor modification introduced by Yeganegi et al. for the $[C_3(mim)_2]^{2+}$ cation [2], while the SPC/E forcefield was employed for water [8]. As regards the Br^--water interaction, the Lennard-Jones parameters were taken from the OPLS force field [9], that in a combined EXAFS-MD study has been shown to provide a reliable description of the structural properties of a Br^- aqueous solution [10]. Each system was first equilibrated in the NPT ensemble for 1 ns to obtain an almost constant density and subsequently the production runs were carried out for 6 ns in the NVT ensemble.

3. Results
The EXAFS spectra of the $[C_3(mim)_2]Br_2$/water mixtures with molar ratio of 1:16, 1:70 and 1:400 are shown in Figure 2 (a), together with the experimental data of pure $[C_3(mim)_2]Br_2$ and the corresponding Fourier transform calculated in the interval k=0.7-12.0 $Å^{-1}$ (b). The first evidence is the difference between the EXAFS spectra of the $[C_3(mim)_2]Br_2$/water mixtures and that of pure $[C_3(mim)_2]Br_2$: the experimental spectrum of pure $[C_3(mim)_2]Br_2$ is characterized by a lower amplitude as compared to the mixtures. These results suggest that water molecules have a high affinity with the anion and enter its coordination sphere, also for the most diluted solution. Moreover, the EXAFS and FT signals change as a function of the water concentration: going from the DIL/water mixture with molar ratio of 1:16 to 1:400, the EXAFS amplitudes become higher and there is an increase in intensity of the FT signals, indicating a progressive crowding of the Br^- ion coordination environment. After studying the effect of the water concentration on the $[C_3(mim)_2]Br_2$/water mixtures, we then analyzed the structural arrangement around the Br^- ion as a function of the alkyl chain length linking the two imidazolium rings. In this case the water concentration was kept fixed. Figure 2 (d, e) shows the EXAFS spectra of the 1:70 $[C_n(mim)_2]Br_2$/water mixtures (with n=3, 6, 9) and the corresponding Fourier transform calculated in the interval k=0.7-12.0 $Å^{-1}$. Both the EXAFS and FT signals are almost identical for the three members of the series, thus meaning that the local coordination around the bromide ion is the same independently from the length of the alkyl-bridge chain. To better understand these results, we calculated the Br-O and Br-H radial distribution functions, g(r), from the MD simulations of the DIL/water mixtures under investigation (O and H are the oxygen and hydrogen atoms of the water molecules, respectively.) Figure 3 shows the g(r)s, that have been multiplied by the numerical density of the observed atoms, ρ, in order to compare DIL/water mixtures with different densities. In all cases the Br-O and Br-H g(r)s show a first distinct and sharp peak at 3.33 and 2.35 Å, respectively. Moreover, as regards the Br-H g(r)s, two distinct peaks, at shorter and longer distances as compared to the Br-O first peak, can be observed: only one hydrogen atom of the water molecules belonging to the first shell is oriented toward the Br^- ion, due to the ability of the bromide ion to make hydrogen bonds [11]. When considering the effect of the water concentration (Figure 3 (a,c)) on the $[C_3(mim)_2]Br_2$/water mixtures, the position of the g(r) first peak does not change with

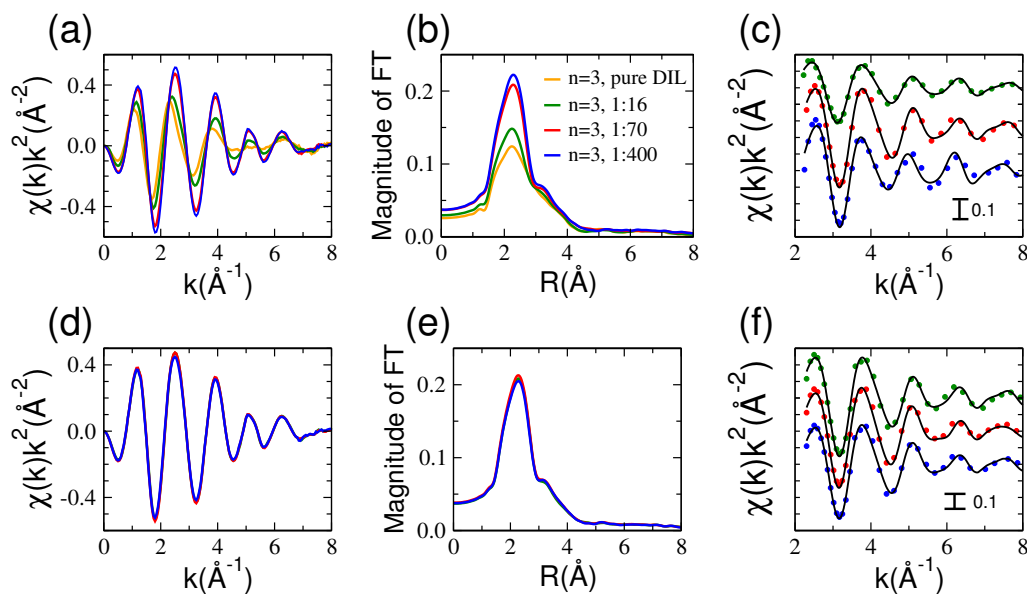**Figure 2.** a,d: Experimental EXAFS spectra of the $[C_3(mim)_2]Br_2$/water mixtures with different molar ratios and of the $[C_n(mim)_2]Br_2$/water mixtures with different alkyl-bridge chain lengths, respectively. b,e: Non-phase shifted corrected Fourier tranforms of the experimental data. c,f: Comparison between the experimental spectra (dotted line) and the theoretical signals (solid black line) calculated from the simulations.

increasing water content, while the intensity of the peak becomes higher, meaning that the bromide coordination sphere becomes more populated. Note that the Br^- hydration number is 4.4, 6.0 and 6.5 for the 1:16, 1:70 and 1:400 $[C_3(mim)_2]Br_2$/water mixtures, respectively. Conversely, if we look at the Br-O and Br-H g(r)s obtained by fixing the amount of water and changing the alkyl chain length from n=3 to n=9, they are almost identical with a Br-O coordination number of 6.0. These results are in agreement with the EXAFS experimental spectra and confirm that the local structural environment seen by the Br^- ion is not influenced by the alkyl-bridge chain length of the imidazolium dications. The Br-O first-shell bond lengths and the coordination numbers obtained in our work are comparable to that found in an MD-EXAFS study of monocationic $[C_4mim]Br$/water mixtures with different molar ratios [10]. Moreover, for the most diluted solution (DIL/water molar ratio of 1:400), the Br-O coordination number is similar to that obtained in theoretical studies of bromide aqueous solutions [10, 12].

The Br-O and Br-H g(r)s, obtained from the MD trajectories for all of the DIL/water mixtures under investigation, have been used to calculate $\chi(k)$ theoretical signals. Comparison of the EXAFS experimental spectra with the MD results allows one on the one hand to carry out a reliable EXAFS analysis, that represent a non trivial task when the EXAFS technique is applied to the study of disordered systems. On the other hand it allows us to prove that the force field used is able to correctly describe the structural properties of the investigated systems. The comparison between the experimental EXAFS spectra and the corresponding theoretical signals for all of the $[C_n(mim)_2]Br_2$/water mixtures is shown in Figure 2 (c,f). In all cases, a very good agreement between the theoretical and experimental data has been obtained. It is important to stress that non-polarizable force fields like those used here usually provide a good description of the structural properties of ILs, while failing to predict dynamic properties, such as diffusion coefficients and conductivities. However, this is outside the scope of this work.

From the analysis of the MD trajectories it is also possible to explore the long-range structural
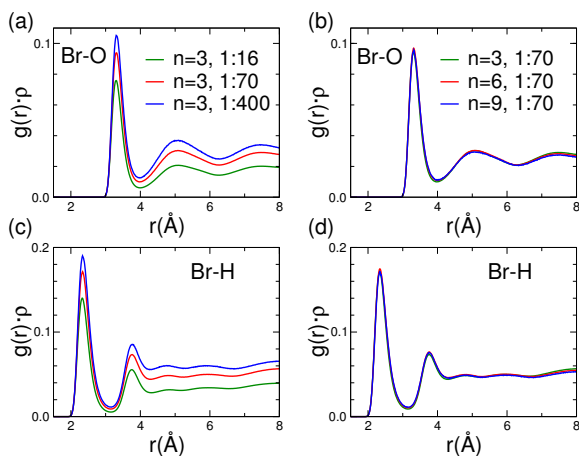
Figure 3. Br-O and Br-H g(r)s, multiplied by the numerical density ρ for the $[C_n(mim)_2]Br_2$/water mixtures.
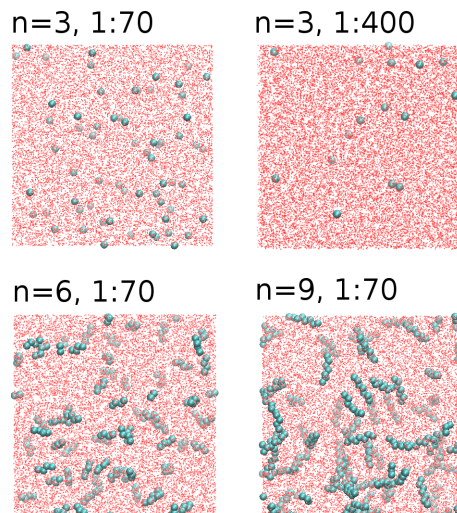

Figure 4. MD snapshots of the DIL/water mixtures, with the polar regions in red and the alkyl-bridge chains in cyan.

properties of the investigated mixtures. Figure 4 shows some MD snapshots of the simulation boxes, where the polar regions (imidazolium cations, water molecules and Br^- ions) and the alkyl-bridge chains are colored red and cyan, respectively. In particular, no evidence of the aggregation of linkage alkyl chains has been found with increasing alkyl chain length. These results are in good agreement with a previous study of $[C_n(mim)_2](Tf_2N)_2$, where aggregation occurs only when n is 12 [3]. This behaviour differs from that of monocationic ILs: several theoretical and experimental studies on $[C_n mim]Br$/water mixtures show the segregation of the alkyl tails and the formation of polar and apolar domains occurs with long enough alkyl chains $(n \geq 5)$ [13].

4. Conclusions

In this paper we presented a detailed investigation of $[C_n(mim)_2]Br_2$/water mixtures as a function of the water concentration and of the alkyl-bridge chain length. Our combined EXAFS-MD approach allowed us to provide direct structural information of the systems both in proximity of the anion and in the longer distance range.

References

[1] Anderson J L, Ding R, Ellern A and Armstrong D W 2005 *J. Am. Chem. Soc.* **127** 593-604
[2] Yeganegi S, Soltanabadi A and Farmanzadeh D 2012 *J. Phys. Chem.* B **116** 11517-26
[3] Li S, Bañuelos J L, Zhang P, Feng G, Dai S, Rother G and Cumming P T 2014 *Soft. Matter.* **10** 9193-9200
[4] Barghava B L and Klein M L 2010 *J. Chem. Theory Comput.* **6** 873-79
[5] Smith W and Forester T 1996 *J. Mol. Graphics* **14** 136-41
[6] Canongia Lopes J N, Deschamps J and Pádua A H H 2004 *J. Phys. Chem.* B **108** 2038-47
[7] Canongia Lopes J N and Pádua A H H 2006 *J. Phys. Chem.* B **110** 19586-92
[8] Berendsen H J C, Grigera J R and Straatsma T P 1987 *J. Phys. Chem.* **91** 6269-71
[9] Jorgensen W L, Ulmschneider J P and Tirado-Rives J 2004 *J. Phys. Chem.* B **108** 16264-70
[10] D'Angelo P, Zitolo A, Aquilanti G and Migliorati V 2013 *J. Phys. Chem.* B **117** 12516-24
[11] D'Angelo P, Migliorati V and Guidoni L 2010 *Inorg. Chem.* **49** 4224-31
[12] Migliorati V, Sessa F, Aquilanti G and D'Angelo P 2014 *J. Chem. Phys.* **141** 044509
[13] Zhao Y, Gao S, Wang J and Tang J 2008 *J. Phys. Chem.* B **112** 2031-39