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Using a Combined Theoretical and Experimental Approach to Understand the Structure and Dynamics of Imidazolium Based Ionic Liquids/Water Mixtures. 1. MD Simulations

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Abstract

The structural and dynamic properties of 1-butyl-3-methylimidazolium bromide ([C₄mim]Br)/water mixtures with different molar ratios have been investigated using classical Molecular Dynamics (MD) simulations, and the reliability of the results has been assessed by comparison with extended X-ray absorption fine structure (EXAFS) experimental data. The analysis of the MD trajectories has highlighted the presence of a complex network of interactions among cations, anions and water molecules even if water molecules have been found to interact preferentially with the Br[−] anion. The existence of solvent-shared ion pairs has been detected in all of the investigated mixtures with one or more water molecules acting as a bridge between the cation and the anion, also when water is present in great excess ([C₄mim]Br/water ratio of 1:200). The dynamic behavior of the systems has been characterized starting from the MD trajectories. Water molecules have been found to quicken the dynamics of the IL cations and anions, and acceleration involves all the investigated motions.

Keywords: 1-butyl-3-methylimidazolium, aqueous solution, Molecular Dynamics, Bromide, structural analysis.

1 Introduction

Ionic liquids (ILs) are chemicals entirely made by ions that show a melting point lower than 100 °C and are attracting widespread attention both by the academic and industrial communities because of their many applications in diverse scientific and technological research areas, such as synthesis, catalysis, sensoristics, electrochemistry and green chemistry in general.^{1–6} The use of these materials as solvents for a constantly increasing range of applications is motivated by their many interesting and unique properties, such as negligible vapor pressure, high thermal stability, and tunable physical properties upon slight changes in their chemical architecture.^{1–4}

Common to the most important applications are solutions and mixtures in which the IL is included as either the minor or the major component, and in this framework water plays a fundamental role. The significance of the interaction between ILs and water has been well-recognized in the last years for many reasons. Most ILs are hygroscopic and absorb water vapor from the atmosphere and, as a consequence, traces of water are thought to be ubiquitous in these materials. The presence of water can dramatically affect the physical properties of ILs, such as their polarity, viscosity and conductivity, even at low concentrations.⁷ The water content of mixtures can also modify the rate and selectivity of reactions carried out in ILs.⁸ Moreover, one of the most promising application of ILs is as green solvents and, in this respect, the solubility of these systems in water represents an important factor.⁹

A considerable number of experimental and theoretical studies have recently been published on the interaction between water and 1-alkyl-3-methyl imidazolium [C_nmim] based ILs.^{10–20} Among IL families, this class of compounds has attracted considerable interest and in general has been the most widely investigated. In ILs consisting of anions with a strong ability to form hydrogen bonds, such as [NO₃][–] and [CF₃CO₂][–], water molecules were found to be mainly hydrogen bonded to the anion,¹¹ but some authors have also inferred a weak C-H···O interaction of water with the most "acidic" ring protons of imidazolium based ILs.^{12–14} The molecular states of water in ILs have been also investigated in several papers.^{11,21–23} Cammarata et al. reported the results of an experimental investigation on the nature of molecular water within imidazolium based ILs with a large range of anions, using attenuated total reflectance (ATR) infrared spectroscopy. It has been shown that water molecules absorbed from the air are present in ILs mostly in the "free"

(not self-associated) state.¹¹ In addition, the authors suggested that in some ILs water forms complexes in which the two water protons are bonded to two distinct anions.¹¹ This behaviour has been subsequently found in several experimental and theoretical studies.^{10,16,17,22}

Despite this intensive research activity, to date a molecular level understanding of the interactions between water and ILs is still lacking, and this is because the study of the structural and dynamic properties of disordered systems represents a very complex task. Molecular Dynamics (MD) simulations play an important role in understanding how condensed phase properties of IL/water mixtures are linked to their microscopic structure and to the network of interactions formed by their components.

Among MD techniques, the use of ab initio MD simulations has serious drawbacks as these approaches are limited both in the dimension of the systems (hundreds of atoms) and in the length of the simulation (tens of picoseconds), owing to their high computational cost. The short simulation time achievable by ab initio MD is a problematic issue, since most ILs have a very high viscosity and their dynamics is much slower than conventional liquids. A proper sampling of their structural and dynamic properties can thus be obtained only with very long equilibration and simulation times (of the order of nanoseconds). As far as IL/water mixtures are concerned, even if the diffusion of the charged ions is increased to some extent when water is added to the ILs, the low mobility of the ions can still represent a limitation, especially in the IL-rich range of concentrations. In this respect, classical MD simulations are the ideal tool as they allow one to simulate the system for very long periods of time, at least three orders of magnitude longer as compared to ab initio techniques. However, classical MD simulations require analytical potentials to describe the interactions among the atoms, and this choice is crucial to obtain reliable results. A possible drawback of empirical potentials is that even if they properly reproduce the experimental properties for which they were developed, they are often not able to provide a correct description of other structural, energetic, and dynamic properties of the system. This is particularly true in the case of IL/water mixtures since both the IL^{24–26} and water^{27–29} force fields present in the literature have been obtained and tested for the pure components, and their transferability to the mixtures has not been assessed. For these reasons, in this work we have carried out MD simulations of IL/water mixtures and assessed the reliability of the theoretical structural results by comparison with extended X-ray absorption fine structure (EXAFS) experimental data (see Ref.³⁰).

The aim of this work is the study of the structural and dynamic properties of [C₄mim]Br/water mixtures as a function of water concentration up to very high dilution. A deep understanding of the complex network of interactions that are build up in these mixtures is still lacking, even if the chemo-physical properties and aggregation behaviour of [C₄mim]Br/water mixtures, as well as of aqueous solutions of [C_nmim]Br with longer alkyl chains (up to n=12), have been investigated by a number of experimental techniques, including neutron and X-ray scattering, NMR spectroscopy, surface tension, density, refractive index and conductivity measurements.^{31–35} The results of these investigations show that no aggregation occurs for [C₄mim]Br in aqueous solution, while micelle-like structures are formed with increasing chain length of the imidazolium cation starting from a critical aggregation concentration. However, a more complex picture of the bulk structure in [C₆mim]Br/ and [C₈mim]Br/water mixtures has been highlighted in a very recent NMR study, according to which the alkyl tails are not fully segregated in hydrophobic domains, as expected for spherical aggregates, but no definite conclusion about the organization of the apolar chain could be achieved.³⁶

2 Methods

2.1 Molecular Dynamics Details

Five MD simulations of [C₄mim]Br/water mixtures with different water concentrations have been carried out using the DL_POLY package.³⁷ The IL/water molar ratios of the investigated mixtures are reported in Table 1 and are the same of those used in our EXAFS experimental study of Ref.³⁰. The number of ion pairs used in each simulation depends on the mixture and computational feasibility. The ions and the water molecules were placed in a cubic box, with periodic boundary conditions, and the sizes of the simulation boxes were chosen to reproduce the experimental densities of the mixtures that were taken from Ref.³¹. The sizes of the simulated systems are given in Table 1. The force field parameters for [C₄mim]Br were taken from the Lopes and Padua force field,^{24,25} while one of the most widespread water models was employed for water, namely the SPC/E,²⁷ which provides a very good description of the structural and dynamic properties of liquid water.²⁸ The Lennard-Jones parameters for all of the different atoms were obtained from the Lorentz-Berthelot combining rules with the exception of the Lennard-

IL/water molar ratio	ion pairs	water molecules	simulation box edge (Å)
1:3	343	1029	50.28
1:6	216	1296	46.46
1:16	216	3456	54.90
1:70	64	4480	53.54
1:200	27	5400	55.36

Table 1: Molar ratios of the [C₄mim]Br/water mixtures investigated in this work together with the sizes of the simulated systems.

Jones parameters for the Br[−]-water interaction, for which the EXAFS spectroscopy has been used to assess the reliability of several interaction potentials available in the literature (see Ref.³⁰). EXAFS is a short-range-order technique that directly probes the local atomic structure around a selected atom and the advantages of EXAFS are now well recognized for the analysis of liquid samples.^{38–46} The best agreement between the EXAFS experimental spectrum of a Br[−] aqueous solution and the theoretical curve was obtained using the Br[−] ion Lennard-Jones parameters from the OPLS force field⁴⁷ to describe the Br[−]-water interaction.³⁰

Initial configurations were constructed by positioning the IL cations and anions and the water molecules on selected lattice positions within a very large cubic simulation box. Extensive equilibration runs were performed, comprising 10000 steps of initial energy minimization, a short NPT run at 500 K and 10 atm aimed at randomizing the system followed by another NPT run at 300 K and very high pressure (100 atm) to compress the box volume until the experimental density was reached. Then the systems were equilibrated under constant NVT conditions (T = 300 K) for about 3 ns. The production runs were carried out in the NVT ensemble for 6 ns, with a timestep of 1 fs and saving a configuration every 100 timesteps. The temperature was kept constant at 300 K using the Nosé-Hoover thermostat^{48,49} with a relaxation constant of 0.5 ps. A cut-off of 12 Å was used to deal with non-bonded interactions, with the Ewald summation method to treat long-range electrostatic effects.⁵⁰ All the bonds involving hydrogen atoms were constrained using the SHAKE algorithm.

2.2 Structural and dynamic analysis

The structural properties of the [C₄mim]Br/water mixtures were described in terms of radial and spatial distribution functions, and a thorough analysis of the molecular state of water and water cluster formation has been also carried out. The molecular state of water analysis and the radial distribution functions have been performed using in-house written codes, the water cluster formation has been analyzed using the GROMACS tool `g_clustsize`,⁵¹ while the spatial distribution functions have been calculated using the TRAVIS software developed by M. Brehm and B. Kirchner.⁵²

The ion and water diffusion coefficients D have been determined from the mean square displacement (MSD) using the Einstein relation:

$$D = \frac{1}{6} \lim_{t \rightarrow \infty} \frac{\langle ||\mathbf{r}(t) - \mathbf{r}(0)||^2 \rangle}{t} \quad (1)$$

where $\mathbf{r}(0)$ is the initial position of a given species and $\mathbf{r}(t)$ is its position at time t . The standard GROMACS tool `g_msdf` has been used to calculate the diffusion coefficients.⁵¹

A detailed view of the dynamics of the cation and water molecules has been obtained using reorientational correlation functions, defined as:

$$C_l^\alpha(t) = \langle P_l(\mathbf{u}^\alpha(t) \cdot \mathbf{u}^\alpha(0)) \rangle \quad (2)$$

where P_l is the l^{th} rank Legendre polynomial, and $\mathbf{u}^\alpha(t)$ is a unit vector in a certain direction α at time t . The reorientational relaxation time τ_α , defined as the rotation time of the \mathbf{u}^α vector, is given by the time integral:

$$\tau_\alpha = \int_0^\infty C_l^\alpha(t) dt \quad (3)$$

For our analyses we used $l = 1$ and, as concerns the rotation of water molecules, three different vectors: the normal to the water molecular plane passing through the center of the oxygen atom \mathbf{u}^N , a vector along the HH direction \mathbf{u}^{HH} , and the water dipole vector \mathbf{u}^D . The reorientational correlation functions have been computed using a modified version of the GROMACS tool `g_rotacf`.⁵¹

The ion pair and ion cage dynamics have been analyzed using two continuous time correlation functions $C_C^{cage}(t)$ and $C_C^{pair}(t)$ defined as:

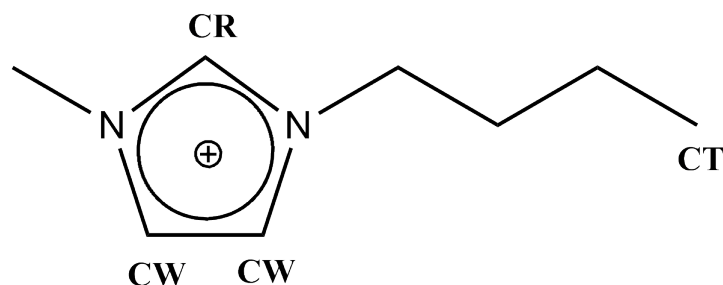


Figure 1: Atom labeling for the IL cation $[\text{C}_4\text{mim}]^+$ as used in this article.

$$C_C^{\text{cage/pair}}(t) = N \left\langle \sum_{t_0=0}^{T-t} \beta_{i,j}(t_0 + t) \beta_{i,j}(t_0) \right\rangle_{i,j} \quad (4)$$

where N is a normalization constant, T is the total simulation time, and the function β_{ij} has the value 1 as long as the criteria which define an aggregate species are fulfilled, and switches to 0 as soon as the criteria fail for the first time. The angle brackets mean the average over all ion pairs while the summation indicates the average over all starting times. The criterion for the ion cage dynamics is that a certain distance has to be smaller than or equal to the first minimum of the corresponding radial distribution function. In particular, the ion cage dynamics has been calculated using the cutoff values reported in Table 2 for the cation-anion, cation-water and anion-water interactions. On the contrary, in the ion pair dynamics analysis the cation-anion distance is calculated and the nearest neighbors are taken into account according to this distance definition. In this case the β_{ij} function goes to zero when the neighborhood relations change, i.e. if the formerly first neighbor is no longer the first neighbor. The ion pair and ion cage dynamics has been analyzed using the TRAVIS software.⁵² Note that in all of the analyses which use cutoff values for distances involving the imidazolium cation the imidazolium ring center has been taken into account in the calculations. The atom labeling used in the description of the MD results is shown in Figure 1.

3 Results

3.1 Radial distribution functions

An overall view of the structural properties of the investigated systems has been gained from the radial distribution functions $g(r)$'s of a selected subset of atoms that have been calculated from the MD trajectories. All of the calculated $g(r)$'s are depicted in Figure 2 and Figures S1-S6 of the Supporting online information, and selected first peak positions are reported in Table 2. We refer to the oxygen and hydrogen atoms of the water molecule as OW and HW. We also computed a series of coordination numbers by integration of the radial distribution function up to a selected cutoff. For each couple of atoms, the cutoff distance has been chosen as the position of the first minimum of the corresponding $g(r)$. The coordination numbers obtained from the simulations are reported in Table 2, together with the cutoff distances used in the calculations. The positions of the $g(r)$ first peaks do not show a significant shift in the different MD simulations, indicating that the first shell distances are substantially the same independently of the water concentration of the mixture. Conversely, the first shell coordination numbers are strongly dependent on the amount of water, being controlled by the relative intensity of the interactions between the different species in the mixtures.

The Br-OW and Br-HW $g(r)$'s calculated from the simulations (panel A of Figure 2) show very sharp and distinct first peaks, as strong anion-water interactions are present, in agreement with the EXAFS experimental results of Ref.³⁰. Moreover, two peaks are found in the Br-HW $g(r)$'s, the former at shorter distances, and the latter at longer distances as compared with the Br-OW $g(r)$ first maximum. This means that the first shell water molecules orient only one hydrogen atom toward the Br⁻ ion, in line with the strong ability of the Br⁻ ion to form hydrogen bonds.⁵³ The Br-OW and Br-HW $g(r)$'s calculated from the MD simulation of the Br⁻ ion in aqueous solution (see Ref.³⁰) are also shown in panel A of Figure 2 and, as it can be seen, are very similar to that obtained for the most diluted [C₄mim]Br/water mixture. Panel B of Figure 2 shows the $g(r)$'s between the ring center of the [C₄mim]⁺ cation and OW. Two distinct peaks can be observed, followed by other lower intensity peaks, showing the existence of a first hydration shell of water molecules also around the cation, even if the peaks are less pronounced than that of the Br-water $g(r)$'s, as a consequence of weaker cation-water interactions as compared to the anion-water ones.

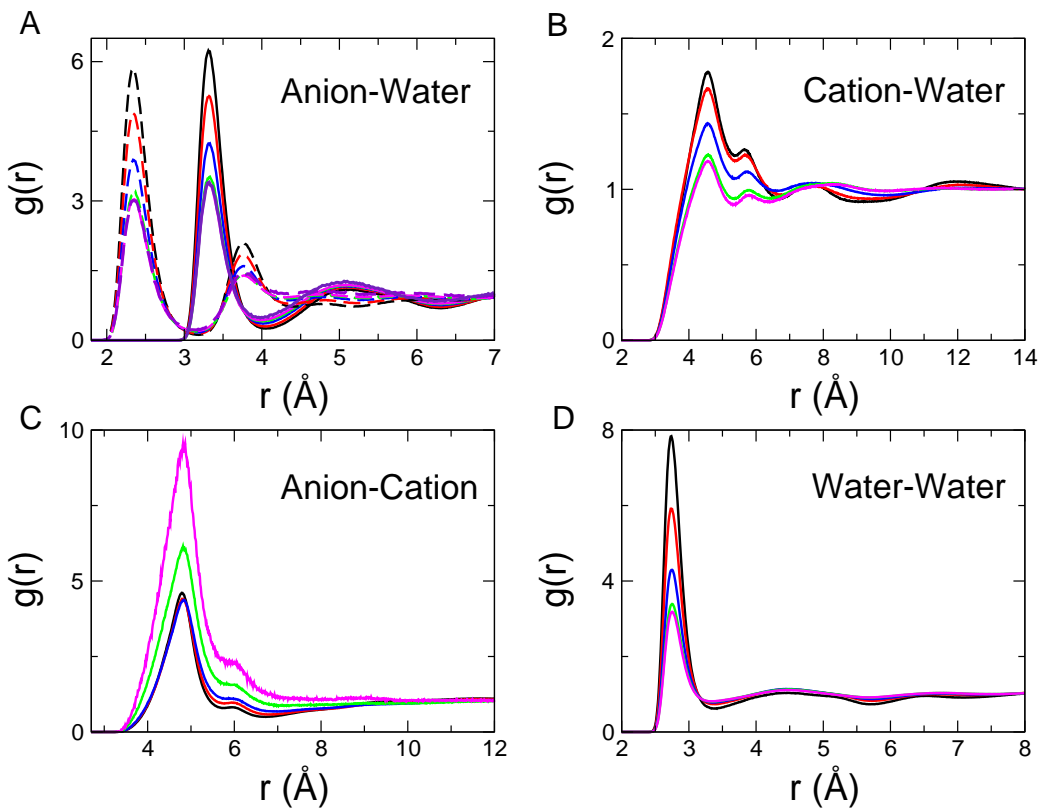


Figure 2: Radial distribution functions, $g(r)$'s, of a selected subset of atoms calculated from the MD simulations of the [C₄mim]Br/water mixtures with molar ratios of 1:3 (black lines), 1:6 (red lines), 1:16 (blue lines), 1:70 (green lines) and 1:200 (magenta lines). OW and HW are the oxygen and hydrogen atoms of the water molecules. A: Br-OW (solid lines) and Br-HW (dashed lines) $g(r)$'s. The Br-OW (violet solid line) and Br-HW (violet dashed line) $g(r)$'s calculated from the MD simulation of the Br⁻ ion in aqueous solution³⁰ are also shown. B: $g(r)$'s between the ring center of the [C₄mim]⁺ cation and OW. C: $g(r)$'s between the ring center of the [C₄mim]⁺ cation and the Br⁻ ion. D: OW-OW $g(r)$'s.

	$R(\text{\AA})$					N					cutoff(\AA)
	1:3	1:6	1:16	1:70	1:200	1:3	1:6	1:16	1:70	1:200	
Br-OW	3.32	3.32	3.32	3.32	3.32	2.9	4.0	5.4	6.4	6.9	4.00
Cat-OW	4.56	4.56	4.56	4.56	4.56	5.3	8.2	11.6	14.0	14.6	5.35
Br-Cat	4.80	4.81	4.83	4.83	4.83	3.3	2.6	1.7	0.8	0.5	5.80
OW-OW	2.74	2.74	2.75	2.75	2.75	2.2	3.0	4.0	4.8	5.0	3.50
HCR-OW	2.76	2.76	2.75	2.75	2.75	2.4	3.4	4.7	5.6	5.9	4.30
HCW-OW	2.76	2.76	2.81	2.82	2.82	2.3	3.5	5.4	6.5	6.8	4.30
CT-CT	4.03	4.03	4.03	4.03	4.03	3.0	2.5	1.2	0.3	0.2	6.50
CT-OW	3.78	3.78	3.79	3.79	3.79	5.0	8.0	13.5	17.7	18.9	5.60
HCR-Br	2.87	2.87	2.88	2.90	2.90	1.3	1.0	0.7	0.4	0.2	4.50
HCW-Br	2.88	2.89	2.94	2.96	2.98	1.1	1.0	0.6	0.3	0.2	4.50

Table 2: Structural parameters of the radial distribution functions $g(r)$'s calculated from the MD simulations of the $[\text{C}_4\text{mim}]\text{Br}/\text{water}$ mixtures with different molar ratios. R is the position of the $g(r)$ first peak and N is the coordination number calculated by integration of the $g(r)$ up to the cutoff distance. The cutoff distances used in the calculation of N are also reported.

From the analyses of cation-water site-site $g(r)$'s it has been found that the water molecules are mainly associated with the three hydrogen atoms of the imidazolium ring (the CR-OW and HCR-OW $g(r)$'s and the CW-OW and HCW-OW $g(r)$'s are depicted in Figure S1 and S2 of the Supporting online information, respectively). However, as it will be shown below, the water distribution around the cation is very broad and unstructured. The presence of three peaks in the cation-water $g(r)$'s shown in Figure 2 reflects the asymmetry of the cation: the first, second and third peaks are due mainly to water molecules in proximity of the imidazolium ring, methyl group and butyl chain, respectively.

It is well known that imidazolium based ILs having long alkyl chains ($n \geq 6$) display an amphiphilic behaviour, and the formation of micelle-like structures have been highlighted in several experimental and theoretical investigations on $[C_n\text{mim}]\text{Br}/\text{water}$ mixtures.^{32,33,35,54} In our MD simulations no evidence of a significant tail-tail aggregation has been observed as both tail-tail (represented by CT) and tail-water interactions have been found in all the investigated mixtures (see the CT-CT and CT-OW $g(r)$'s depicted in Figure S3 and S4 of the Supporting online information). Moreover, the CT-OW coordination number significantly increases with increasing dilution as the hydrophobic solvation becomes more and more important. The absence of a significant tail-tail aggregation obtained from our MD simulations is in agreement with the results of a number of experimental investigations showing that no aggregation occurs for $[C_4\text{mim}]\text{Br}$ in aqueous solution.^{32,33}

Even if the water molecules strongly interact with the Br^- anion and with the imidazolium cation, cations and anions are not completely separated, as shown by the strong cation-anion correlation that is found in all the simulations (panel C of Figure 2). The anion-cation coordination number decreases as the water concentration increases but, very interestingly, it remains different from zero also for the most dilute solution. The association between anions and cations is driven predominantly by interactions of the Br^- ion with the HCR and HCW hydrogen atoms of the imidazolium ring (the CR-Br and HCR-Br $g(r)$'s and the CW-Br and HCW-Br $g(r)$'s are depicted in Figure S5 and S6 of the Supporting online information, respectively). As far as the water-water interactions are concerned, the high and well-defined short-range peak of the OW-OW $g(r)$'s (panel D of Figure 2) suggests that the water molecules in the mixtures tend to aggregate and to form water clusters.

3.2 Spatial distribution functions

The three-dimensional organization of the anions and water molecules around the imidazolium cation can be observed looking at the spatial distribution functions (SDFs) shown in Figure 3. The SDFs have been calculated from the MD simulations with different water content using the same absolute densities for the different mixtures. The isodensity surfaces of Br^- and OW atoms are colored green and cyan, respectively. It can be clearly seen the evolution of the cation environment that progressively loses Br^- anions to accommodate more and more water molecules, going from low to high dilution conditions. The arrangement of the Br^- anions around the cations can be observed in panels A and B for 1:3 and 1:6 molar ratio MD simulations, respectively. The favourite sites of interaction of the Br^- ion are the HCR atom of the imidazolium ring, and, to a slightly lower extent, the two HCW atoms. The Br^- distribution near the CR atom is broad and symmetric with respect to the CR-HCR direction, while in the case of the HCW atoms the Br^- distributions are shifted towards the lateral chains, and the shift is more pronounced for the anions close to the methyl group, as a result of the decreased steric hindrance of the methyl group as compared to the butyl chain. In order to give an idea of the Br^- distribution in all of the investigated systems, we report in Figure S7 of the Supporting online information the SDFs of Br^- ions around the imidazolium cation calculated using the same ratio density/maximum density for all the simulations. The distributions are very similar independently of the water content of the mixture, and the Br^- ions always cluster around the positively charged hydrogen atoms of the imidazolium ring. The cation-anion SDFs calculated in the present study are similar to the functions previously reported for the pure $[\text{C}_4\text{mim}]\text{Br}$ ionic liquid.^{55–57} As far as the cation-water SDFs are concerned (see panels D and E of Figure 3 corresponding to the IL/water mixtures with 1:70 and 1:200 molar ratios), the distribution of water molecules around the imidazolium cation is much more broadened and unstructured, and less site-specific, as compared to the Br^- distribution. Similar spatial distribution functions of water molecules around the imidazolium cation have been recently obtained from a MD investigation of $[\text{C}_4\text{mim}][\text{BF}_4]/\text{water}$ mixtures.²⁰

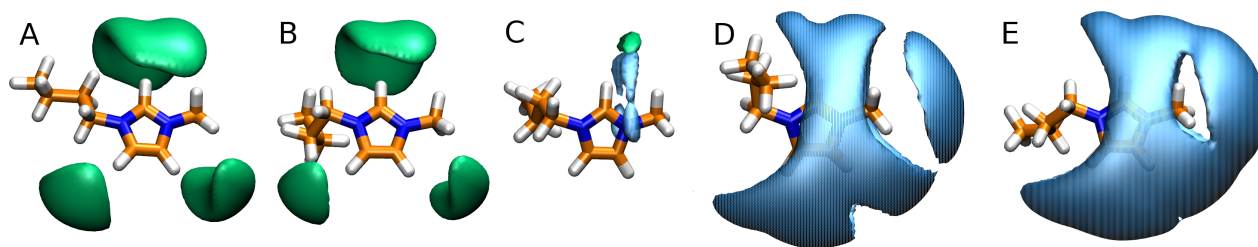


Figure 3: Spatial distribution functions (SDFs) of the anions (green) and the oxygen atom of water molecules (cyan) around the cation, calculated from the MD simulations of the [C₄mim]Br/water mixtures with molar ratios of 1:3 (A), 1:6 (B), 1:16 (C), 1:70 (D) and 1:200 (E). The SDFs have been calculated from the MD simulations with different water content using the same absolute densities.

3.3 Molecular states of water and water clustering

The picture that emerges from the analysis of the $g(r)$'s is that in IL/water mixtures a complex network of interactions among cations, anions and water molecules is formed, and among these interactions, it is interesting to analyze the molecular states of water. It is well known in the literature that in IL/water mixtures the anion-water interactions play a major role,^{11,16,17} and this is particularly true for the Br⁻ ion that possesses a strong ability to form hydrogen bonds with water molecules.⁵³ Figure 4 shows the percentage of water molecules that interact with at least one Br⁻ anion as a function of the IL/water molar ratio of the investigated mixtures. The water percentages have been calculated using as cutoff distance the position of the first minimum of the Br-OW $g(r)$'s (see Table 2). In the 1:3 mixture a huge percentage of water molecules interact at least with one Br⁻ anion, and the percentage decreases with increasing water content, as more and more water molecules gather around other water molecules and form water clusters. This result is in agreement with the EXAFS determination reported in Ref.³⁰.

Several experimental and theoretical investigations of mixtures of imidazolium-based ILs and water have suggested the presence of complexes between one water molecules and two anions (anion...HOH...anion), in which the two water protons are bonded to two distinct anions.^{10,11,16,17,22} The results of our simulations show that anion...HOH...anion complexes are present also in [C₄mim]Br/water mixtures, and in order to quantify this behaviour, the percentage of water molecules that are simultaneously bonded to two Br⁻

ions has been calculated from the MD trajectories (see Figure 4). For the less diluted mixture the percentage is about 22% and decreases with increasing dilution, becoming negligible for the mixtures with IL/water molar ratio of 1:70 and 1:200. Besides the existence of anion...HOH...anion complexes, another significant state of water which emerged from the analysis of our MD simulations is the configuration in which a single water molecule interacts simultaneously with one Br^- ion and with one imidazolium cation. The percentage of water molecules satisfying this condition is shown in Figure 4. Note that the percentages have been computed adopting for the water-cation interaction the cutoff distance between the imidazolium ring center and OW reported in Table 2. As it can be seen, a significant percentage of water molecules coordinating both the anion and the cation is found in mixtures with the lowest water content, and the percentage of water molecules involved in the anion-water-cation clusters is much higher as compared to the water molecules forming anion...HOH...anion complexes.

As mentioned above, water molecules in $[\text{C}_4\text{mim}]\text{Br}$ /water mixtures tend to aggregate and form water clusters. The cluster formation in the mixtures has been analyzed by monitoring the size of clusters of connected water molecules. A cluster is defined by molecules which are mutually connected, and we have considered two water molecules to be connected when the distance between the oxygen atoms is less than 3.50 Å, which is the position of the first minimum in the OW-OW radial distribution function. Figure S8 of the Supporting online information shows the probabilities of finding small clusters of water molecules in the mixtures. The percentage of isolated water molecules (1-clusters) decreases very rapidly with increasing water content and nearly disappears ($<0.02\%$) when the IL/water molar ratio is 1:16 and for higher water concentrations. The probabilities of finding large clusters of water molecules are shown in Figure S9 of the Supporting online information. Large water clusters appear to dominate the distribution for all of the investigated water concentrations, and both the size of clusters and the percentage of large clusters significantly increase with increasing water content. Moreover, the distributions become more and more peaked and the peak position gets closer and closer to the limit of simulation box with increasing dilution (for the 1:16 and 1:70 mixtures the peak position is exactly the total number of water molecules in the mixture). The latter result indicates that for highly diluted mixtures a single large water cluster is formed percolating through the sample. Note that the cluster analysis of the mixture with 1:200 IL/water molar ratio has not been shown since in this case a

single water cluster containing all of the water molecules has been detected in every single frame of the MD simulation. The results of the water cluster analysis obtained here are in agreement with those previously reported in the literature for mixtures of water and imidazolium-based ILs containing several anions.^{13,16,20}

3.4 Solvent shared ion pairs

The results of the radial distribution function analysis have shown that a strong cation-anion correlation is present in all of the investigated [C₄mim]Br/water mixtures, and that the anion-cation coordination number is non zero also for the most diluted solution. Additional insights into this behavior can be gained by defining an instantaneous anion-cation coordination number as the number of cations at a distance from the Br⁻ ion shorter than the cation-anion $g(r)$ first minimum and analyzing its variation along the trajectories (see Figure 5). The results of this analysis show that in the mixtures with IL/water molar ratio of 1:3 and 1:6 a dominant percentage of anion are coordinated to three cations, while the most probable ion configurations are 2-coordinated, 1-coordinated and 0-coordinated species for the mixtures with molar ratio of 1:16, 1:70 and 1:200, respectively. The very interesting result is that in the mixture with molar ratio of 1:200, a significant percentage of cations (about 35%) are still coordinated to anions. The anion-cation interactions are often mediated through water molecules that act as a bridge between counterions. This behavior has been already highlighted in section 3.3 where it was shown that water molecules coordinating both the anion and the cation are present in [C₄mim]Br/water mixtures. All together these results indicate that cations and anions do not possess a completely closed hydration shell, but rather, "solvent-shared ion pairs" are formed. The existence of solvent-shared ion pairs in IL/water mixtures has been previously pointed out in a Car-Parrinello simulation study of a 1-ethyl-3-methylimidazolium chloride/water mixture.⁵⁸ Albeit the great excess of water present in the mixture (IL/water molar ratio 1:60), it was found that the cation and anion did not separate from each other but remained in close proximity over the whole simulation time, by sharing one or more solvent molecules.⁵⁸ Moreover, the formation of solvent-shared ion pairs was also found in mixtures with water of alkylammonium chlorides, and it was shown that solvent shared ion pairs were able to survive also in conditions of very high dilution.⁵⁹⁻⁶¹ To provide visual insights, two representative snapshots of the environment seen by the

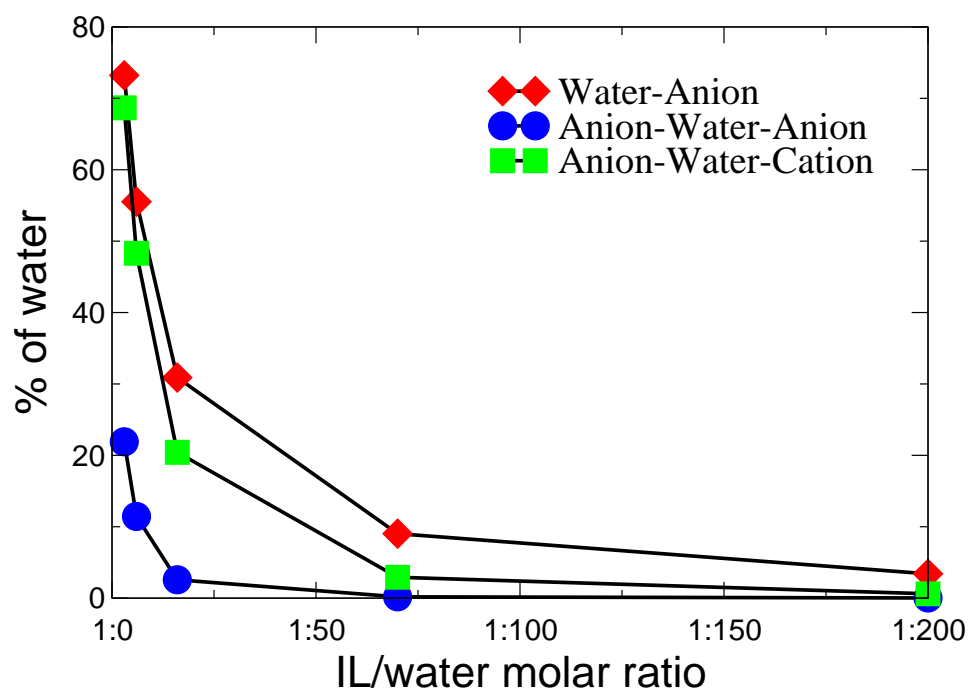


Figure 4: Percentage of water molecules that interact with at least one Br^- anion (red diamond), percentage of water molecules that are simultaneously bonded to two Br^- anions (blue circles) and percentage of water molecules that interact simultaneously with one Br^- anion and with one imidazolium cation (green squares) as a function of the $[\text{C}_4\text{mim}]\text{Br}/\text{water}$ molar ratio.

anion in the [C₄mim]Br/water mixtures with IL/water molar ratio of 1:3 and 1:200 are shown in Figure 6. It can be seen a typical neighborhood composed of three cations and three water molecules in the IL-rich solution (panel A of Figure 6), while in the highly diluted one the Br[−] ion is in contact with one cation and six water molecules (panel B of Figure 6).

3.5 Self-diffusivity

In order to elucidate the effect of water on the dynamic properties of IL/water mixtures, the translational self-diffusion coefficients can be computed. Due to the sluggish dynamics of ILs, it is important to ensure that the simulation times are long enough to probe diffusive behavior. For the present simulations, 6-ns production runs were used. One way to test if the simulations are long enough to probe diffusive behavior is to compute a linearity parameter $\beta(t)$,⁶² defined as:

$$\beta(t) = \frac{d(\log \Delta r^2(t))}{d \log(t)} \quad (5)$$

where $\Delta r^2(t)$ is the mean square displacement at time t . By definition, $\beta(t)$ must approach unity in the diffusive regime. At values below $\beta(t)=1$, the system is in the subdiffusive regime and any apparent self-diffusivity will underestimate the true self-diffusivity. We have verified that after about 1 ns of simulation time, the dynamics of different species in the mixtures becomes diffusive for all of the investigated IL/water mixtures. Therefore, the diffusion coefficients calculated from the MD simulations can be regarded as reliable.

Figure 7 shows the translational self-diffusion coefficients of both ions and water molecules as a function of water concentration (red circles). In general the diffusion coefficients increase with increasing water content. This is expected as the diffusion of the ions usually increases, and the viscosity decreases when water is added to ILs.⁷ It is fair to say that water enhances or lubricates the translational motion of this IL.

The water and cation diffusion coefficients computed from our MD simulations can be compared with the experimental diffusion coefficients obtained from a NMR study of [C₄mim]Br in D₂O³⁴ (blue squares in Figure 7). As it can be seen our results are of the same order of magnitude of the experimental determinations even if our simulations slightly overestimate both cation and water experimental diffusion coefficients for mixtures with high water

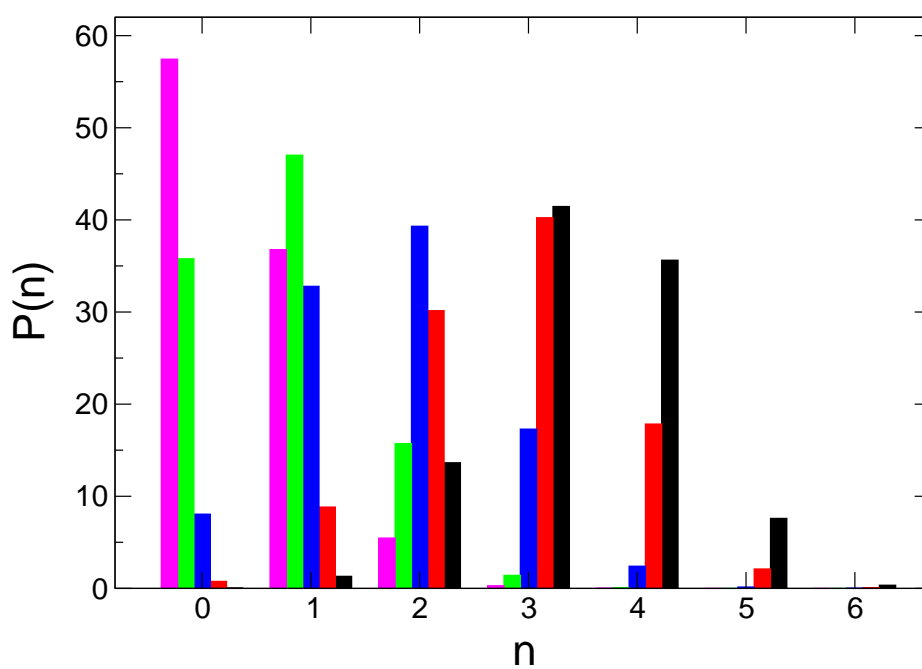


Figure 5: Instantaneous cation-anion coordination number (n) distribution calculated from the MD simulations of the [C₄mim]Br/water mixtures with molar ratios of 1:3 (black bars), 1:6 (red bars), 1:16 (blue bars), 1:70 (green bars) and 1:200 (magenta bars).

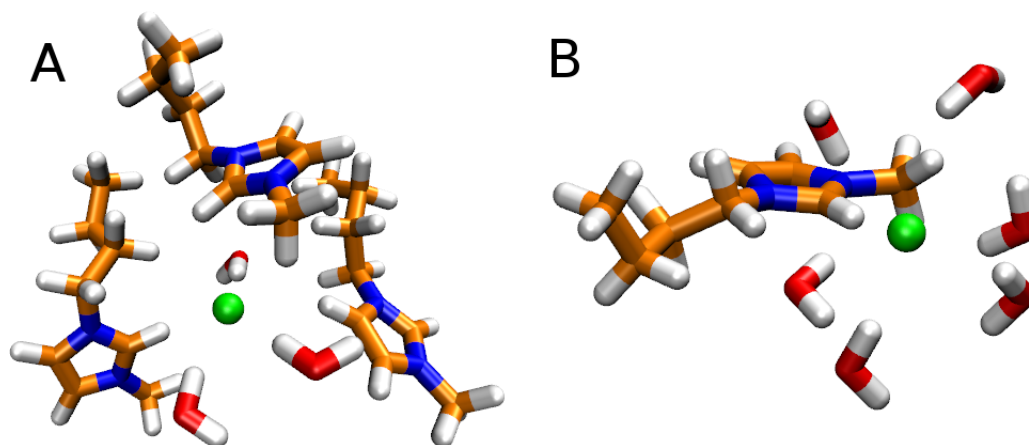


Figure 6: Simulation snapshots showing the cations and the water molecules belonging to the Br^- first coordination sphere in the $[\text{C}_4\text{mim}]\text{Br}$ /water mixtures with IL/water molar ratios of 1:3 (A) and 1:200 (B).

content, and underestimate them at low water concentration. Note that the water diffusion coefficient at high dilution calculated from the trajectories approaches the value of the water diffusion coefficient calculated from our MD simulation of Br^- in aqueous solution ($2.7 \cdot 10^{-5} \text{ cm}^2/\text{s}$).³⁰ It is useful to compare the behavior of the different diffusion coefficients within the same simulation and in all cases the same general trend is observed. The water translational mobility is always higher than that of cations and anions, in agreement with previous MD investigations of imidazolium based IL/water mixtures.^{10,13,20,63} As far as the IL diffusion is concerned, our results show that the anions exhibit faster dynamics than cations. This trend is opposite to that shown from MD simulations of pure $[\text{C}_4\text{mim}]\text{Br}$ IL carried out under high temperature, where slightly lower values of the anion diffusion coefficients were obtained as compared to the cation ones.⁵⁶ However, our results are in line with the behaviour observed for mixtures of water and other imidazolium based ILs.^{20,64} A MD study on a dilute aqueous solution of $[\text{C}_4\text{mim}][\text{PF}_6]$ has highlighted that although the IL cation diffuses faster than the anion in pure $[\text{C}_4\text{mim}][\text{PF}_6]$, the converse is true in the mixture with water.⁶⁴ Moreover, the results of another MD investigation of $[\text{C}_4\text{mim}][\text{BF}_4]$ has shown that in the pure IL the anion moves slower than the cation, while in water-rich mixtures the anion diffusion coefficient becomes higher than

the cation one.²⁰

3.6 Rotational correlation times

In addition to the translational diffusion, the reorientational motion of cations and water molecules can be investigated by computing the first rank reorientational correlation times of different vectors. For water the three vectors described in the Methods section were used, while for the imidazolium cation the normal vector to the ring plane spanned by the carbon atoms CR and CW's has been employed. The reorientational correlation times of cations and water molecules in the IL/water mixtures are reported in Table 3. Note that the time constant obtained for the cation in the less diluted mixture is of the same order of magnitude of the MD simulation time and, for this reason, should be considered only an estimate. In all the other cases the mobility of cations and water molecules is big enough that direct numerical integration of the reorientational correlation functions can be used to determine the time constants.

All of the reorientational times decrease as the water content increases, and this is the expected behavior since highly mobile water molecules have the tendency to increase the mobility of the cation, while the IL tends to inhibit the motion of water. Moreover, the rotational dynamics of the cation is significantly slower as compared to the rotation of water for all of the investigated mixtures. These results are compatible with what we have observed in terms of translational diffusion and with the results of previous MD investigations of other imidazolium-based IL/water mixtures.^{16,63,65}

The cation reorientational time obtained for the less diluted solution is significantly higher as compared to the cation reorientational time recently calculated by Kohagen et al. from MD simulations of pure [C₄mim]Br.⁵⁷ The addition of water to ILs is usually expected to increase the ion mobility but the results of Kohagen et al. were obtained at high temperature and the cation reorientational times have been found to increase dramatically as the temperature decreased.⁶³

As far as the rotation of the different water vectors is concerned, the reorientational dynamics of the \mathbf{u}^D vector is the slowest reorientation in all of the investigated mixtures. Note that for the mixture with 1:200 IL/water molar ratio the three time constants describing the water rotation approach the values obtained from our MD simulation of Br⁻ in aqueous solution (2.66, 4.2 and 4.11 ps for the rotation of the \mathbf{u}^N , \mathbf{u}^D and \mathbf{u}^{HH} vectors).³⁰ These

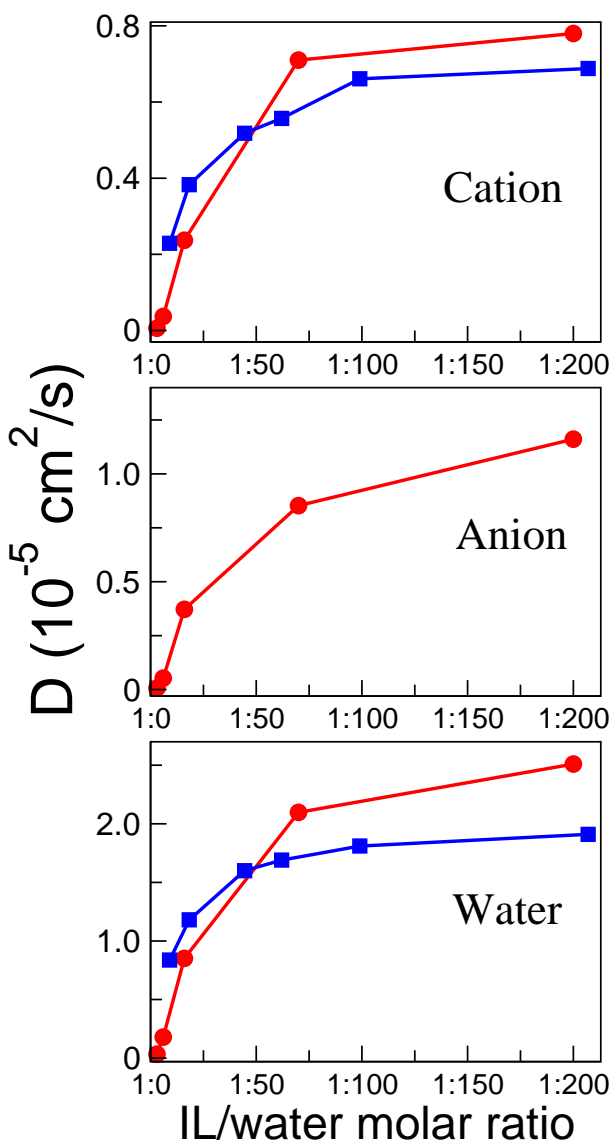


Figure 7: Self-diffusion coefficients of the cation, anion and water molecules calculated from the MD simulations of the [C₄mim]Br/water mixtures (red circles) as a function of the IL/water molar ratio of the investigated mixtures. The theoretical diffusion coefficients of cations and water molecules are compared with the experimental diffusion coefficients obtained from a NMR study of [C₄mim]Br in D₂O (blue squares).³⁴

values are similar to the one obtained from MD simulations of pure water,⁶⁶ and for bulk water molecules in aqueous solutions of metal ions.^{67,68}

3.7 Ion cage and ion pair dynamics

As described in the previous sections, a first hydration shell of water molecules is formed around both anions and cations, and Br^- and $[\text{C}_4\text{mim}]^+$ interact also among themselves in all of the investigated $[\text{C}_4\text{mim}]\text{Br}/\text{water}$ mixtures. In order to calculate the lifetime of the aggregated species existing in the mixtures we have used the continuous time correlation functions defined in the Methods section. In a recent MD investigation of pure $[\text{C}_4\text{mim}]\text{Br}$, two types of ion dynamics were studied, termed ion cage and ion pair dynamics.⁵⁷ The ion cage dynamics considers all anions surrounding the cation within a selected cutoff value and therefore describes the distortion of the ion cage, while the ion pair dynamics is given by an ion pair which is defined as cation and its next neighbor anion. The main conclusion of Ref.⁵⁷ was that in the presence of ion pairs the correlation times calculated according to both definitions should be in the same order of magnitude, which was not the case. Therefore, the ions in pure ILs exist in a fluctuating network and not as separated ion pairs. The relaxation times of correlation functions for ion cage and ion pair dynamics calculated from our MD simulations are reported in Table 3. As far as the ion cage dynamics is concerned, the relaxation times decrease with increasing water content, and this is a further evidence of the increased ion mobility caused by the addition of water. On the contrary, the ion pair dynamics becomes slower with increasing dilution. However, this is not the result of a real slowing down of the ion dynamics but is due to the fact that the number of Br^- ions surrounding each cation decreases with increasing water content (see Table 2). According to the ion pair dynamics definition, the ion pair breaks if the neighborhood relations change, i.e. if the formerly first neighbor is no longer the first neighbor, and this situation is more likely to occur in the less diluted solutions where there is a higher number of counterions around a given ion. The ion cage dynamics has been analyzed also for the cation-water and anion-water interactions and the corresponding relaxation times are reported in Table 3. Also in these cases the relaxation times decrease with increasing dilution, and our results show that water molecules around a cation translate out of the coordination shell more rapidly than those coordinated to an anion. This is probably due to the stronger anion-water interactions as compared to the cation-water

	1:3	1:6	1:16	1:70	1:200
Rotational dynamics					
τ_{Cat}	1853.9	313.0	52.5	21.4	19.6
$\tau_{\mathbf{u}^N}$	285.3	59.4	11.3	3.9	3.0
$\tau_{\mathbf{u}^D}$	697.2	126.4	21.3	7.1	5.4
$\tau_{\mathbf{u}^{HH}}$	380.0	84.3	16.1	5.8	4.6
Ion Cage Dynamics					
τ_{Cat-An}	134.0	39.1	14.5	9.6	9.5
$\tau_{Cat-Wat}$	25.2	9.9	4.3	2.8	2.6
τ_{An-Wat}	27.7	14.5	7.6	4.9	4.3
Ion Pair Dynamics					
τ_{Cat-An}	1.4	2.6	7.4	28.8	58.9

Table 3: Relaxation times of correlation functions for rotational dynamics of cations and water molecules, for the ion cage dynamics of cation-anion, cation-water and anion-water interactions and for the ion pair dynamics. See text for the definition of the different correlation functions. All relaxation times are expressed in ps.

ones. Note that the relaxation times of the ring reorientation are significantly larger than those of the cation-anion cage dynamics especially in the less diluted solutions were they are one order of magnitude higher. Therefore, the reason for the breaking of a cation-anion cage in [C₄mim]Br/water mixtures could be the translational movement and most likely not the reorientation of the imidazolium ring, at variance with the results obtained for the pure [C₄mim]Br IL.⁵⁷

3.8 Convergence analysis of the MD results

A major concern in MD simulations of IL-containing systems is represented by the slow dynamics of ILs that could hamper a proper sampling of the

phase space visited by the system. As far as IL/water mixtures are concerned, even if the dynamics of the ions is usually increased when water is added, the low mobility of the ions can still represent a limitation, especially in mixtures with low water content. When trying to gain information on these complex systems, beside ensuring that a diffusive behavior has been reached during the MD simulations (see section 3.5), it is also essential to check the convergence of the structural and dynamic properties calculated from the MD trajectories. To this end, we have focused our attention on the mixture with [C₄mim]Br/water molar ratio of 1:3, that, among the investigated concentrations, represents the most critical case in terms of slow dynamics. The convergence of the MD results has been evaluated by dividing the MD trajectory into different time slices, and monitoring the behaviour of the computed properties as a function of the time slices. As concerns all of the structural properties analyzed in this work, we have found that a MD time interval of 0.5 ns is enough to reach convergence. In Figures S10 of the Supporting online information we show, as an example, the Br-OW and [C₄mim]⁺-OW $g(r)$'s, calculated from the simulation of the [C₄mim]Br/water mixture with molar ratio 1:3, in six different time slices of 0.5 ns, and the same $g(r)$'s calculated from the entire MD trajectory. As it can be seen, all of the computed $g(r)$'s are identical, and this result ensures that convergence has been reached.

Different considerations have to be made for the dynamic properties of the mixtures, as in this case the convergence is strongly dependent on the timescale of the particular motion under investigation. As concerns rather fast motions (with relaxation times shorter than 50 ps), 1 ns of MD trajectory can be considered enough to reach the convergence of the corresponding correlation function. In Figure S11 of the Supporting online information the correlation functions of cation-water ion cage dynamics are shown as an example, and they are compared with the correlation function obtained from the entire trajectory. They have been calculated from the MD simulation of the [C₄mim]Br/water mixture with molar ratio of 1:3 in three different time slices of 1 ns. For dynamic properties with relaxation times shorter than 150 ps, 3 ns of MD trajectory are almost enough to reach convergence, while for motions that take place on longer timescales, it is not possible to make a proper convergence analysis as the corresponding correlation functions decay too slowly. As a consequence, for the latter dynamic properties the time constants obtained from our MD trajectories reported in Table 3 should be considered only estimates. In order to obtain more accurate values of

the relaxation times related to these motions, much longer MD simulations should be carried out (of several tens of ns). However, this is outside the scope of the present work as our main objective was to accurately characterize the structural properties of [C₄mim]Br/water mixtures, to be also compared with the EXAFS experimental results reported in Ref.³⁰, and to obtain a qualitative trend of some relevant dynamic properties of the systems as a function of water concentration.

3.9 Conclusions

In this work a thorough characterization of the structural and dynamic properties of [C₄mim]Br/water mixtures with molar ratios of 1:3, 1:6, 1:16, 1:70 and 1:200 has been carried out by means of classical MD simulations. The MD calculations have been performed using an "ad hoc" force field for the Br-water interaction that has been optimized on the basis of EXAFS experimental data (see Ref.³⁰). For all simulations water molecules have been found to interact preferentially with the Br⁻ anion. However, a complex network of interactions among cations, anions and water molecules emerged from the analysis of the MD trajectories. Water molecules in [C₄mim]Br/water mixtures were found to aggregate and form water clusters and a broad analysis of the molecular states of water has shown that, besides the existence of complexes between one water molecules and two Br⁻ anions, previously pointed out also in other investigations of imidazolium-based ILs/water mixtures,^{10,11,16,17,22} another significant state of water is the configuration in which a single water molecule interacts simultaneously with one Br⁻ ion and with one imidazolium cation.

A very interesting result is that, even when water is added to the IL in great excess, the imidazolium cations and the Br⁻ anions do not completely separate, but rather solvent-shared ion pairs are formed, in which one or more water molecules act as a bridge between the anion and the cation. The favourite sites of interaction of the Br⁻ ion around the cation are the protons of the imidazolium ring, while the distribution of water molecules around the imidazolium cation is much more unstructured and less site-specific, as compared to the Br⁻ distribution. Moreover, no evidence of a significant tail-tail aggregation has been observed from the analysis of our MD simulations, in agreement with the results of a number of experimental investigations showing that no aggregation occurs for [C₄mim]Br in aqueous solution.^{32,33} The dynamic behaviour of the [C₄mim]Br ions and water molecules has been

thoroughly characterized by investigating the translational self-diffusivity, the reorientational motions, and the ion cage and ion pair dynamics. As a general trend, our results show that water molecules accelerate the dynamics of the IL cations and anions, and all the investigated motions are quickened as the water content increases.

The reliability of the structural MD results, and hence the validity of the force field used in the simulations, has been assessed by comparison with the EXAFS experimental data on the same [C₄mim]Br/water mixtures and all details are reported in Ref.³⁰ This synergic experimental/theoretical procedure allowed us to gain a complete and detailed picture of the structural and dynamic properties of these complex systems.

Acknowledgments

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Supporting Information Available

Figures S1-S11, as described in the text. This information is available free of charge via the Internet at <http://pubs.acs.org>.

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