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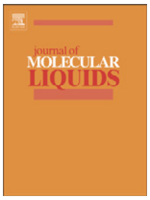

Ionic liquids at the air/water interface

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ABSTRACT

We present molecular dynamics experiments of Langmuir monolayers of iodide and chloride salts of 1-octyl-3-methylimidazolium adsorbed at water/air interfaces, covering a concentration range that spans from a dilute regime up to the experimental surface saturation for both systems. For the chloride case we observed a propensity to form monolayers with nearly equal surface concentration of both cations and anions; whereas for the iodide system, the more marked propensity to surface solvation of the anionic species leads to the appearance of quasi-double-layered structures. At the surface, the imidazolium rings remain in contact with the aqueous substrate, with a wide variety of orientations with respect to the surface normal direction. The global tilt of the hydrophobic tail of the cations was found to be $\theta_{tl} \sim 40°$and 50°, for the chloride and iodide salts, respectively. Polarization fluctuations of the interface are analyzed in terms of those describing charge distributions of the adsorbed species and the electrical response of the solvent as well. The characteristics of the local densities for the ionic species at the interface provide arguments for the microscopic interpretation of the differences observed in scattering experiments on the dependence of the surface tension with the surfactant concentration.

1. Introduction

Room temperature ionic liquids (RTIL) are molten salts with normal boiling points close or below ambient conditions. They have important practical applications in many chemical processes, most notably, those derived from their ability to host a large variety of polar and non-polar solutes. [1–5] The interest in the use of these liquid phases derives from several chemically appealing characteristics, such as minimal volatility, high thermal stability and viscosity and the wide versatility to choose "tailored" anion–cation mixtures.

Experimental and theoretical researches on RTIL have experienced a marked increment in recent years[6]. The corresponding studies include isotropic macroscopic phases [7–14] and also inhomogeneous environments, such as liquid/liquid and liquid/air interfaces[15–33]. Focusing in the latter systems, and despite of the large body of research available, there are still several important questions pertaining to the surface activity of RTIL that await proper elucidation. For example, one intriguing observation has been recently reported in a paper by Bowers et al. [22]. Using small-angle neutron scattering techniques, Bowers analyzed Langmuir monolayers of ionic liquids based on the 1-alkyl-3-methylimidazolium cation adsorbed at the water/air interface. Contrary to what is usually reported for common surfactants, the dependence of the surface tension of monolayers comprising 1-octyl-3-methylimidazolium iodide [C_8mim][Cl] versus the global concentration of the RTIL exhibits a minimum near the critical micellar concentration (cmc = 100 mmol dm^{-3}). In contrast, the surface tension of interfaces hosting the related RTIL [C_8mim][I], shows the usual behavior, characterized by a sharp drop for $c \lesssim$ cmc, followed by a flat profile beyond this critical concentration.

Subsequent investigations performed by Sung et al. [24] showed that the peculiar behavior observed by Bowers for the surface tension of [C_8mim][Cl] monolayers was also found in those comprising the shorter-chain RTIL 1-butyl-3-methylimidazolium tetrafluoroborate [C_4mim][BF_4]. As a plausible explanation of the "unexpected," non-monotonic behavior, the authors have speculated on the possibility that important surface structural modifications at the surface might occur beyond the cmc. According to Sung et al. [24], in this concentration regime, the energetics of the interface – originally dictated by interactions involving the organic tails – would be closer to that exhibited by interfaces of aqueous electrolytes, where ionic forces prevail. In a similar context, Picálek et al. [32] have recently reported molecular dynamics experiments on bulk and surface phases of [C_4mim][BF_4]-water and [C_4mim][PF_6]-water solutions at a series of solute concentrations, ranging from pure water up to the corresponding cmc. Their surface tension results, although rather noisy, provide clues that would suggest that the above justification – i.e. a net increase of the local concentration of anionic species – is physically sound. Motivated by these observations, in the present paper, we return to the analysis of the longer chain RTIL originally investigated by Bowers et al. using molecular dynamics experiments. Our objective

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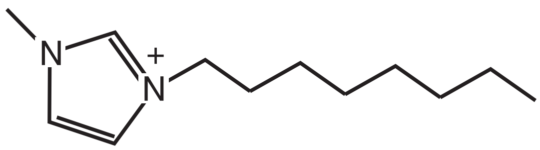

Fig. 1. Chemical structure of 1-octyl-3-methylimidazolium cation.

was to establish differences in the equilibrium solvation structures of the adsorbed monolayers at the vicinity of the cmc that, in turn, would provide additional clues to validate the previous mentioned hypothesis.

2. Model

The results presented in this paper correspond to molecular dynamics experiments performed on aqueous slabs containing $N_w = 800$ molecules. The samples were obtained from fully periodic systems, confined within a rectangular box, with linear dimensions 31.17 Å × 31.17 Å × 24.95 Å. After an initial equilibration period of ~200 ps at $T = 298.15$ K and $p = 1$ bar, periodic boundary conditions were suppressed along the z-axis. In addition, equal numbers N_α of 1-octyl-3-methylimidazolium [C$_8$mim] cations (see Fig. 1) and simple anions such as Cl$^-$ and I$^-$, were distributed in the vicinity of one of the free surfaces of the slabs, in a random fashion. In what follows, systems with Cl$^-$ and I$^-$ will be referred to as of type A and B, respectively. The initial intramolecular configurations of the octyl chains in the [C$_8$mim] corresponded to fully *trans* conformers, with their head-to-tail vectors aligned parallel to the z-direction. For each system three different number of RTIL ion pairs were placed at the surface of the water substrate in that way. These amounts were chosen in order to obtain surface concentrations that roughly correspond to 0.5, 1.0 and 1.5 times those experimentally reported for the corresponding saturated monolayers: $\Gamma_A = 1.3 \times 10^{-2}$ Å^{-2} and $\Gamma_B = 8.5 \times 10^{-2}$ Å^{-2}[22]. It is important to remark that our objective was focused in reproducing the reported surface excesses corresponding to different bulk concentrations at the vicinity of the cmc. In doing so, no efforts were made in analyzing the characteristics and the eventual influence of the bulk states on the surface states of the RTIL.

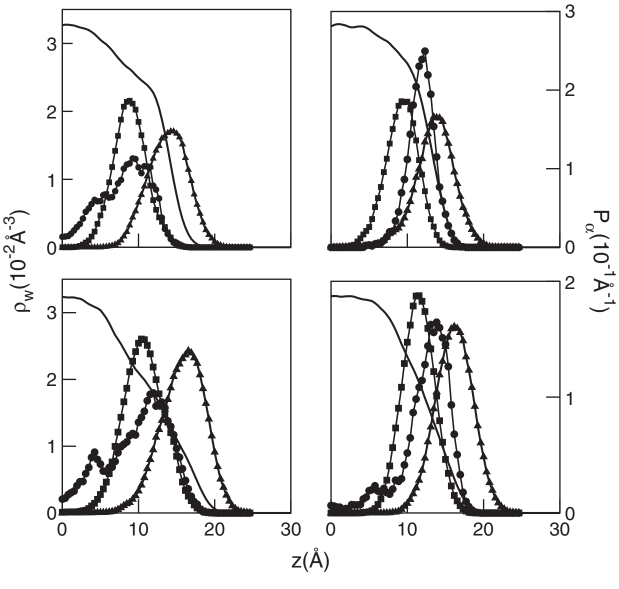

Fig. 2. Water local density (solid line, left axis) and probability densities (solid line, right axis) for the [C$_8$mim][Cl] (left panels) and the [C$_8$mim][I] (right panels). The upper panels correspond to the lower concentrations analyzed; whereas the lower panels show results from the higher concentrations. For the sake of clarity, results for the intermediate concentrations are not shown. Tail and head distributions are shown with black squares and triangles, respectively. The anion distribution is presented with black circles.

The Hamiltonian employed corresponded to the classical, non-additive, polarizable, RPOL model developed by Dang[34]. In addition to the direct interactions between partial charges, Coulomb forces in Dang's model also include interactions involving induced dipoles, centered at the positions of the atomic sites. Length, energy and polarization parameters for interactions involving anionic species were taken from Ref. [35]. Interactions involving the cationic species were modeled using the GROMACS force field[36–38]. For these species, polarization effects were not taken into account, since previous simulation studies have shown that the explicit incorporation of such fluctuations in these molecules can be safely disregarded at least, in what to its structural behavior concerns. A detailed analysis of the relevance of the incorporation of polarization of cations and anions to the force field for the determination of dynamical and equilibrium properties of ionic liquids can be found in Refs. [39] and [40].

The simulation experiments corresponded to microcanonical runs performed at a temperature close to $T = 298$ K. Statistical averages were collected from trajectories lasting typically ~3 ns. Long-range Coulomb interactions were treated using Ewald sums specially adapted for systems with a slab geometry and include interactions between partial charges and induced dipoles[41,42]. For additional technical details pertaining to our simulation procedure, we refer the interested reader to Ref. [43].

3. Results

The first aspect that we will address concerns the structure of the aqueous interfaces. Results for the water local density profiles,

$$\rho_w(z) = \frac{1}{A}\left\langle \sum_{i=1}^{N_w} \delta(Z_i - Z_{CM} - z) \right\rangle \tag{1}$$

for both systems, are shown in the four panels of Fig. 2. In the previous equation, the angular brackets denote an equilibrium ensemble average, whereas Z_i and Z_{CM} refer to the z-coordinates of the i-th water oxygen and the center of mass of the water slab, respectively. In Eq. (1), $\rho_w(z)\mathrm{d}z$ represents the number of water molecules per unit of area, A, at the xy-plane, with their oxygen sites lying between z and $z + \mathrm{d}z$.

The corresponding density profiles look rather asymmetric, so we estimated the position of the Gibbs dividing surfaces ($\bar{z}_G$) and the corresponding interface widths (Δz) by adopting the usual criterion based on the positions of the 10% and 90% of the bulk density. The results for these magnitudes appear in Table 1a and reveal that the localizations of the interfaces remain practically unchanged, regardless of the system, or concentration, considered. The corresponding widths are somewhat narrower for systems of type B, while polarization fluctuations do not modify the geometrical characteristics of the aqueous interface in a sensible fashion either. A comparison between the overall interface widths in the presence of the RTIL monolayers and in those hosting a prototype cationic surfactant, say tetradecyltrimethylamonium bromide, shows comparable scenarios. [44,45].

For the rest of the species, we computed site probability distributions of the type:

$$P_\alpha \propto \left\langle \sum_i \delta(z_i^\alpha - Z_{CM} - z) \right\rangle; \tag{2}$$

where z_i^α refers to the z-coordinate of site α in the i-th molecule. The anionic distributions look both asymmetric and differ at a quantitative level. Interestingly, these distributions can be reasonably well