

Aqueous Mixtures of Room-Temperature Ionic Liquids: Entropy-Driven Accumulation of Water Molecules at Interfaces

Takeshi Kobayashi,[†] Andre Kemna,[‡] Maria Fyta,[†] Björn Braunschweig,[‡] and
Jens Smiatek^{*,†,¶}

[†]*Institute for Computational Physics, University of Stuttgart, D-70569 Stuttgart, Germany*

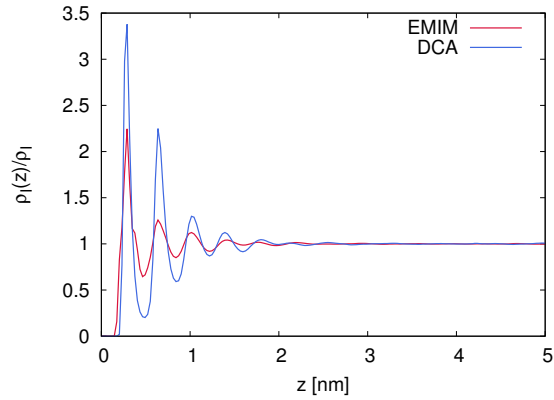
[‡]*Institute of Physical Chemistry, University of Münster, D-48149 Münster, Germany*

[¶]*Helmholtz Institute Münster: Ionics in Energy Storage (HIMS – IEK 12),*

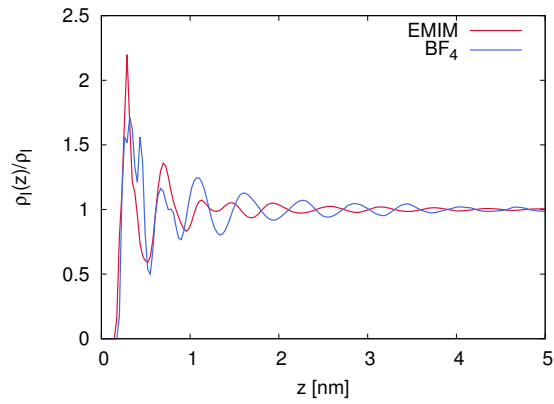
Forschungszentrum Jülich GmbH, D-48149 Münster, Germany

E-mail: smiatek@icp.uni-stuttgart.de

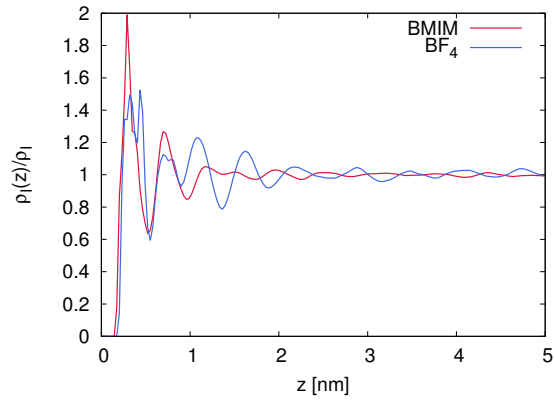
S1. Normalized number densities for neat ILs



(a) EMIM/DCA



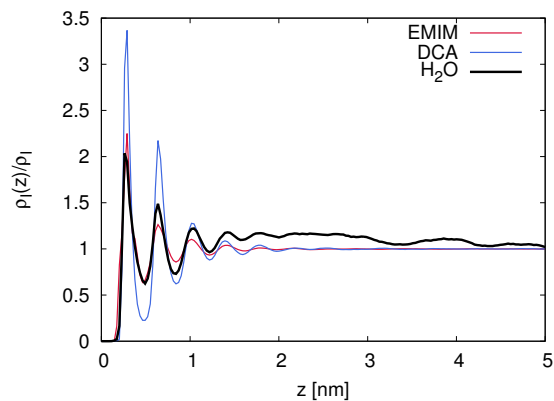
(b) EMIM/BF₄



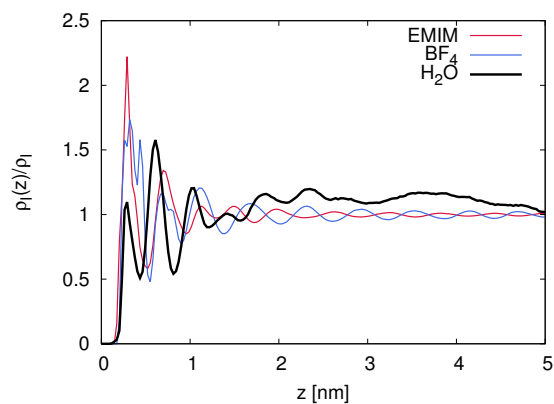
(c) BMIM/BF₄

Figure S1: Bulk-normalized number densities $\rho_I(z)/\rho_I$ for cations (red line) and anions (blue line) in front of the uncharged wall (located at $z = 0$ nm) for neat ILs with $x_{\text{H}_2\text{O}} = 0.000$. The results for EMIM/DCA are shown at the top panel, whereas the outcomes for EMIM/BF₄ and BMIM/BF₄ are shown in the middle and in the bottom panel, respectively.

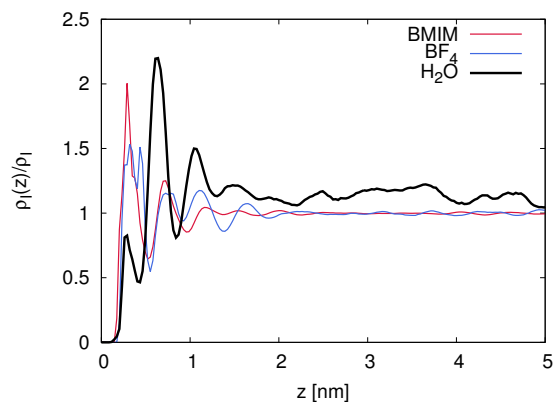
S2. Normalized number densities for $x_{\text{H}_2\text{O}}=0.125$



(a) EMIM/DCA



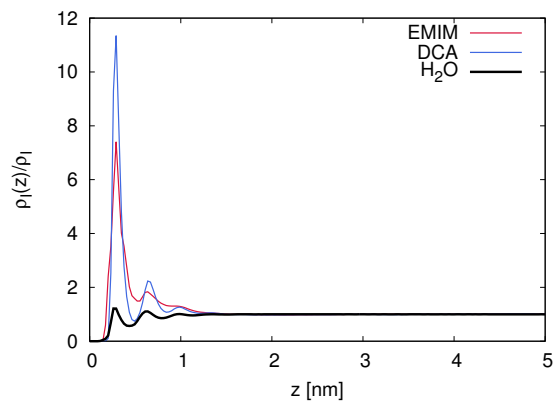
(b) EMIM/BF₄



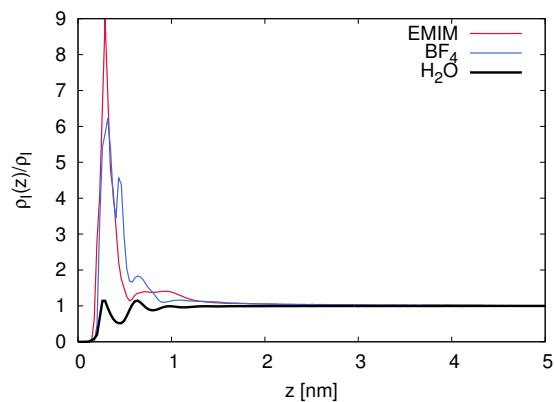
(c) BMIM/BF₄

Figure S2: Bulk-normalized number densities $\rho_i(z)/\rho_i$ of cations (red line), anions (blue line) and water molecules (black line) in front of the uncharged wall (located at $z = 0$ nm) for water mole fractions $x_{\text{H}_2\text{O}} = 0.125$. The results for EMIM/DCA are shown in the top panel, whereas the outcomes for EMIM/BF₄ and BMIM/BF₄ are shown in the middle and in the bottom panel, respectively.

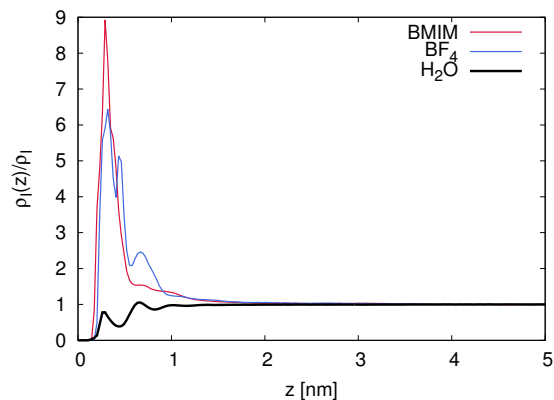
S3. Normalized number densities for $x_{\text{H}_2\text{O}}=0.98$



(a) EMIM/DCA



(b) EMIM/BF₄



(c) BMIM/BF₄

Figure S3: Bulk-normalized number densities $\rho_i(z)/\rho_i$ of cations (red line), anions (blue line) and water molecules (black line) in front of the uncharged wall (located at $z = 0$ nm) for water mole fractions $x_{\text{H}_2\text{O}} = 0.98$. The results for EMIM/DCA are shown in the top panel, whereas the outcomes for EMIM/BF₄ and BMIM/BF₄ are shown in the middle and in the bottom panel, respectively.

S4. Discussion of experimental results

Vibrational SFG spectra of EMIM/DCA, EMIM/BF₄ and BMIM/BF₄ room-temperature ionic liquids (RTIL) and their mixtures with H₂O were recorded at the liquid/gas interface and are presented in the main text. The water-free ILs show strong bands centered at 2850, 2880, and 2943 cm⁻¹. These are attributable to methylene $\nu_s(\text{CH}_2)$ and methyl $\nu_s(\text{CH}_3)$ symmetric stretching vibrations, as well as to the methyl Fermi resonance $\nu_{FR}(\text{CH}_3)$ of the alkyl side chains¹⁻⁴. Additional vibrational modes are observed at ~ 3124 and 3166 cm⁻¹ and are assigned to H-C(4)-C(5)-H stretching vibrations of the imidazolium ring^{3,5}. The shape of SFG spectra can be described with the following expression for the second-order electric susceptibility $\chi^{(2)}$

$$I_{SF} = |\chi^{(2)}|^2 = \left| \chi_{NR}^{(2)} + \sum_q \frac{A_q}{\omega_q - \omega + i\Gamma_q} \right|^2 \quad (1)$$

which is zero in the isotropic bulk solution but non-zero at the interface due the symmetry break at the interface. In equation (1), $\chi_{NR}^{(2)}$, A_q , Γ_q and ω_q are the nonresonant contribution to the second-order susceptibility, the oscillator strength, as well as the bandwidth and resonance frequency of the q -th vibrational mode. We point out that for a more rigorous treatment of the inhomogenously broadened O-H bands, the latter should be treated with a Voigt rather than with a Lorentzian line shape as indicated in equation (1)^{6,7}.

Besides the contribution of O-H stretching vibrations to the SFG spectra, we can now discuss the changes in C-H vibrational bands, which also clearly show substantial changes as a function of water concentration. These apparent changes point to structural rearrangements of the interfacial EMIM cations. In case of BMIM/BF₄ and EMIM/DCA mixtures with water, the SFG intensities of the C-H bands increase with increasing water concentration, while for EMIM/BF₄ a loss in C-H intensities is observed. Previously, Rivera-Rubero and Baldelli⁸, as well as Sung et al.⁹ studied liquid/gas interfaces from BMIMBF₄ mixtures with water and attributed the changes in the $\nu_s(\text{CH}_2)$ and $\nu_s(\text{CH}_3)$ modes to a reorientation of the

butyl chain and an increase of the alkyl chains tilt angle with respect to the surface normal, when the water concentration was increased. This will necessarily also lead to an increase in the $\nu_s(\text{CH}_2)/\nu_s(\text{CH}_3)$ intensity ratio⁹, when both good signal-to-noise and spectral resolution are paired like in our case. The changes in $\nu_s(\text{CH}_2)$ and $\nu_s(\text{CH}_3)$ modes are also associated with a decrease in the intensity of H-C(4)-C(5)-H stretching vibrations of the imidazolium ring when the water concentration was increased. Previously, Baldelli and co-workers⁸ have done a rigorous polarization analysis of the latter vibrational band and concluded that low intensities point to a close to flat lying orientation of the imadazolium ring at the interface with a tilt angle of $>70^\circ$.

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