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Solvation in aqueous binary mixtures: Consequences of the hydrophobic character of the ionic liquids and the solvatochromic probes

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Description of the solvation model applied for treating the data in binary solvent mixtures

The equations below describe the solvent-exchange equilibria in the solvation shell of the probe:

$$IL + W \rightleftharpoons IL\text{-}W \qquad (1)$$

$$Probe(IL)_m + m\,(W) \rightleftharpoons Probe(W)_m + m\,IL \qquad (2)$$

$$Probe(IL)_m + m\,(IL\text{-}W) \rightleftharpoons Probe(IL\text{-}W)_m + m\,IL \qquad (3)$$

$$Probe(W)_m + m\,(IL\text{-}W) \rightleftharpoons Probe(IL\text{-}W)_m + m\,W \qquad (4)$$

Where (m) represents the *average* number of solvent molecules whose exchange in the probe solvation shell affects E_T(probe); usually $m \leq 2$; (m) should not be confused with *the total number* of solvent molecules that solvate the probe. An important consequence of this model is that the mole fractions that we have employed in our calculations are *"effective" not analytical* ones.[1] The formation of hydrogen-bonded complexes between ILs, e.g., $BuMeImBF_4$ or AlBuImCl and water has been demonstrated by IR,[2a,b] NIR,[3], ^{1}H NMR,[4] and predicted by theoretical calculations.[5,6]

The equilibrium constants of Eqs. (5) to (7) are termed solvent "fractionation factors, φ", defined on the mole fraction scale, after rearrangement, as:

$$\varphi_{W/IL} = \frac{x_W^{Probe} / x_{IL}^{Probe}}{(x_W^{Bk;\,Effective} / x_{IL}^{Bk;\,Effective})^m} \qquad (5)$$

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$$\varphi_{\text{IL-W/IL}} = \frac{x_{\text{IL-W}}^{\text{Probe}} / x_{\text{IL}}^{\text{Probe}}}{(x_{\text{IL-W}}^{\text{Bk; Effective}} / x_{\text{IL}}^{\text{Bk; Effective}})^{m}} \qquad (6)$$

$$\varphi_{\text{IL-W/W}} = \frac{x_{\text{IL-W}}^{\text{Probe}} / x_{\text{W}}^{\text{Probe}}}{(x_{\text{IL-W}}^{\text{Bk; Effective}} / x_{\text{W}}^{\text{Bk; Effective}})^{m}} \qquad (7)$$

Where (Bk,Effective) refers to the effective concentration of a solvent species (IL, W, IL-W) in bulk solvent.

Calculation of the effective concentrations of the solvent species present requires knowledge of the association constant, K_{assoc}, between IL and water. These data were previously showed in a recent study. [7]

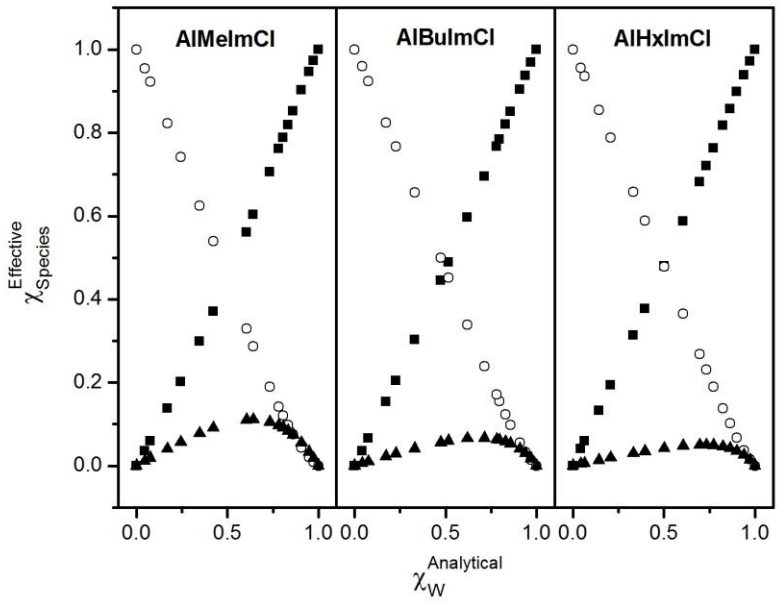

Figure *ESI*-1: Representative dependence of the concentrations of the species in the IL-W binary mixtures on the length of R of AlRImCl. The data shown are for 25 °C; the symbols employed are ○, ■, ▲ for IL, W, and the IL-W 1:1 complex, respectively. Data reproduced from reference 7.

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