Why Do Liquids Mix? The Effect of Hydrogen Bond Redistribution on the Mixing Behavior of Protic Ionic Liquids

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We study hydrogen bond (HB) redistribution in mixtures of two protic ionic liquids (PILs) sharing the same cation: triethylammonium-methanesulfonate ([TEA][OMs]) and triethylammonium-triflate ([TEA][OTf]). The mixture is exhibiting large negative excess energies of mixing. Based on results obtained from atomic detail molecular dynamics (MD) simulations, we derive a lattice model, discriminating between HB and nonspecific intermolecular interactions. We demonstrate that due to the ordered structure of the PILs, mostly the HB interactions contribute to the mixing energy. This allows to us to connect the equilibrium of HBs to each of the two anion species with the excess energies and entropies of mixing. The entropy associated with HB redistribution is shown to be negative, and even overcompensating the positive entropy associated with a statistical distribution of the ions in the mixture (see Figure 1). This is suggesting that the mixing process is driven by enthalpy, not entropy. In addition, we use a combination of calorimetry, and 1H-NMR chemical shift measurements to determine the difference in HB strength favouring the [TEA]-[OMs] interaction. Both, the results from MD-simulation and from experimental calorimetry and 1H-NMR chemical shift data show a qualitatively similar behaviour and can be explained within the same theoretical framework.

FIGURES

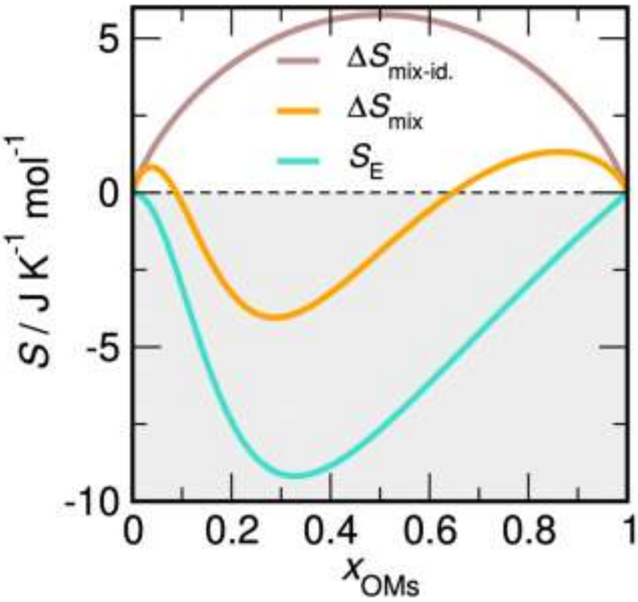

Figure 1: The excess entropy S_E due to HB redistribution is negative, even overcompensating the positive ideal contribution $\Delta S_{\text{mix-id.}}$ due to the statistical distribution of the anions in the mixture in the range $0.1<x_{\text{OMs}}<0.65$.