Criticality of the Liquid-Liquid Phase Transition in Solutions of the Ionic Liquids with the Triflat Anion

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The phase behaviour of solutions of ionic liquids with the 1-alkyl-3-methyl imidazolium cation ($C_n$mim) and the triflat anion ($SO_3CF_3^+$, TFO) is reported. The triflat anion has Janus – character because of its hydrophobic and hydrophilic sides. Depending on the length of the side chain partial miscibility with an upper critical solution point at ambient conditions is observed in the non-polar solvent dioxan, aprotic polar halo arenes, and water. The 22 phase diagrams are analysed presuming Ising behaviour and the temperature dependence predicted by the theory of complete scaling. Corresponding state analysis, which is based on the model of charged hard spheres (CHS) and uses structural information from simulations for C_2mimTFO, reveals general agreement with the predictions for the CHS-model. Deviations scale with the dielectric permittivity of the solvent pinpointing the distinction between Coulomb demixing in weakly polar solvent and hydrophobic demixing in water and diluted dioxan solutions. For accurate measurements of the viscosity, of the coexistence curve and the static and dynamic light scattering with mK accuracy the mixtures C_5mimTFO/water, C_6mimTFO/chlorbenzene, C_8mimTFO/4–chlortoluen are selected. Approaching the critical temperature viscosity measurements show a plateau, which caused by shear effects, is quantitatively explained by the theories of Oxtoby and Onuki. All data show Ising critical behaviour with indications of homogeneous crossover to mean-field criticality for the solutions in aprotic solvents and inhomogeneous crossover for the solutions in water. In variance to the predictions for mixtures of incompressible fluids the diameter of the phase diagrams shows the 2ß-anomaly for all concentration variables including the number density. The analysis of light scattering measurements is complicated by the presence of long living concentration inhomogeneities.