Corresponding States Analysis and Criticality of the Liquid-Liquid Phase Transition of Ionic Liquids in Solution

W. Schröer[C, S] and D. Saracsan
Institute of Inorganic and Physical Chemistry, University Bremen, Bremen, Germany
schroer@uni-bremen.de

A systematic study of the phase diagrams and other critical properties as viscosity and light-scattering of binary solutions of Ionic Liquids (IL) is presented. The ILs considered are salts with different cations (tetra alkyl phosphonium and 1-alkyl 3-methyl imidazolium cation ($R_n mim^+$) with different lengths of the side chains). The anions are Cl^-, Br^-, BF_4^-, PF_6^- and $(CF_3SO_2)_2N^-$. The solvents considered include non-polar hydrocarbons, the weakly polar higher alcohols and polar solvents as methanol and even water. The concept of corresponding states has proved to be a powerful tool in order to reduce the data and also to enlighten general aspects of the systems under consideration. As the result of the analysis it can be concluded that the phase diagrams satisfy the principle of corresponding states: the coexistence curves of the different systems reduce to a master plot, when reduced variables are used. Furthermore, for the non polar solvents the critical temperatures agree with the predictions for the simple model of equal sized charged hard spheres in a dielectric continuum: the reduced temperatures defined by this model agree with the experimental findings. Considering polar solvents it is found that the reduced critical temperatures depend almost linearly on the dielectric permittivity of the solvent. This observation indicates a continuous change from phase separations caused by Coulomb interactions in non-polar solvents to a mechanism based on solvophobic interactions in solvents of high dielectric constant. Measurements of the viscosity, the phase diagrams and of static and dynamic light-scattering with mK accuracy state that all phase transitions belong to the Ising universality class. No difference in the nature of the critical point can be found between the phase transitions that are driven by Coulomb interactions and such driven by solvophobic interactions.