Critical Properties Near the Liquid-Liquid Phase Transition of Ionic Solutions in Non-Polar Solvents

W. Schröer, M. Kleemeier, M. Plikat, L. Aberle, V. Weiss, and S. Wiegand
Institut für Anorganisehe und Physikalische Chemie
Universität Bremen
D-28359 Bremen, Germany

In ionic solutions Coulomb interactions may cause a liquid-liquid phase transition. Due to the long-range nature of the Coulomb interactions, Ising criticality, usually found in separating fluids, cannot be expected a priori. Experimentally, mean-field and Ising criticality as well as crossover have been observed.

For solutions of alkyl-ammonium picrats in higher alcohols, Narayanan and Pitzer reported an increase of the Ising-region with the dielectric permittivity of the solvent. In order to check if this observation follows a general rule we have investigated solutions of salts (NR_4^+ $S0_3R^-$) in non-protonating solvents (chloroform, toluene and cyclohexane) and also of triethyl n-hexyl ammonium triethyl n-hexyl borate (N_{2226} B_{2226}) in diphenyl ether, which seemed to be established as a system with mean field criticality.

We report measurements of the coexistence curve, light-scattering, viscosity and electric conductivity Ising criticality is found in the region of 10^{-3}K < $|T-T_c|$ < 10 K. Amplitudes of the correlation length up to ξ_o = 2.5 nm are found which is an order of magnitude larger than typically for non-ionic fluids. The location of the critical points in the corresponding state diagram is in general agreement with the theoretical results for the model system (RPM) of charged hard spheres in a dielectric continuum (ε). However, the changes of the T_c by minute variations of the solvent (toluene, xylene, ethylbenzene) cannot be explained by the RPM. The experimental results are discussed in the light of recent calculations of the Ginzberg temperature predicting an increase of the Ising region due to association to ion-pairs and solvophobic interactions.