Structure and Criticality in Ionic Solutions

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In the last decade the criticality of ionic solutions was a major topic in the field of critical phenomena [1], because, it was questioned if phase transitions driven by long-range Coulomb interactions also belong to the Ising-universality class, generally found in phase-transitions of fluids. In this report we review the experimental work dedicated to this problem, which includes thermodynamic and light-scattering measurements. In order to rationalize the experimental results a connection is made to the theoretical work on the mean field theory of charged hard spheres in a dielectric continuum (RPM). The location of the critical points is estimated in fair agreement with experiments on ionic solutions, but modifications due to specific interactions are noticeable. Concerning the nature of the critical point, experiments yielding mean-field and Ising criticality as well as crossover have been reported. Ising criticality was found in most cases, in agreement with theoretical work. However, the Ginzburg temperature derived from RPM theory comes out so high that the mean-field region appears not accessible in the experiments, which is in variance to the observations of crossover and apparent mean field behavior in ionic fluids. Theoretical work and simulations of the RPM suggest the possibility of a crossover between an Ising and a tri-critical point in analogy to observations on polymer solutions [2]. Impurities may play an important role but are difficult to assess experimentally. In this connection investigations of ternary mixtures of solutions of NaBr in mixtures of water and 3-methyl pyridine [3] are of interest. Reports of a tri-critical point in this system, however, are not confirmed [4]

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