

Criticality of the Liquid-Liquid Phase Transitions in Ionic Solutions

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The critical properties of phase transitions of fluids and fluid mixtures are known to agree with that of the 3d-Ising model because short-range r^{-6} interactions drive the phase transition. Because of the long-range nature of the Coulomb forces it was suspected that the universal validity of the 3d-Ising model may not apply for phase transitions of ionic systems; mean-field critical behavior was reported for the liquid-liquid phase transition discovered by Pitzer in the ionic solution of $N_{2226}B_{2226}$ (n-hexyl-triethylammonium n-hexyl-triethylborate) in biphenyl ether. However, later work [1] could not reproduce those results. Ising behavior was found instead. The investigations suggested experimental shortcomings in the earlier work [2]. However, it is very hard to draw firm conclusions from the work on Pitzer's system because of the chemical instability of the salt. Experiments with other, more stable salts are therefore desirable. Recently low melting salts, termed Ionic Liquids became a major object of research because of their wide perspective of applications. Those salts are rather stable and a great variability is commercially available in good quality. In this paper we report measurements of the viscosity, of the coexistence curve and the static and dynamic light scattering of three systems: C18mim NTF₂ (1-Octadecyl-3-methylimidazolium bis(trifluoromethylsulfonyl)-imide) in cyclohexane, C12mimCl in benzene, and C5mim triflat (trifluoromethyl-sulfonat) in water. The experiments reveal Ising criticality in all cases and all properties. The critical part of the viscosity data reaches a plateau, when approaching the critical point. Correcting for shear gives the temperature dependence predicted by the mode-coupling theory. Mode coupling theory is also applied for the analysis of the dynamic light scattering. The light-scattering data are corrected for multiple scattering, and background scattering caused by dynamical processes that are slow or fast if compared to the timescale of the scattering experiment. Relaxation of non-equilibrium inhomogeneities and stability of the location of the critical temperature are ensured. Coexistence curves and light scattering intensity both indicate crossover to mean-field criticality described by the crossover theory, where the solution in water shows inhomogeneous crossover.

[1] S.Wiegand, M.E. Briggs J.M.H. Levelt Sengers, M. Kleemeier, W.Schröer, J. Chem. Phys. 109 9038-9051 (1998)

[2] W. Schröer, M. Wagner, O. Stanga, J. Mol.Liquids 127 (2006) 2-9