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Liquid–liquid phase separation of ionic liquids in solutions: Ionic liquids with the triflat anion solved in aryl halides

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ABSTRACT

After a short review of the research concerning the nature of the critical point in ionic systems, the phase behavior is reported and analyzed for five solutions of ionic liquids with the 1-alkyl-3-methyl imidazolium cation ($C_n$mim, n = 6,7,8) and the triflat anion ($SO_3CF_3^+$, TFO) in aryl halides (C_6H_5 X, X = Cl, Br, J). The phase diagrams are determined by the synthetic method and visual observation of the cloud points. Depending on the length of the side chain and the dielectric permittivity of the solvent, partial miscibility with an upper critical solution point (UCSP) at ambient pressure conditions is observed in the polar aprotic solvents. The phase diagrams are analyzed presuming Ising behavior and taking into account the asymmetry of the phase diagrams. Corresponding state behavior is observed. Comparison with the predictions of the model system of charged hard spheres (CHS) is made using structural information from Monte Carlo simulations for C_2mimTFO. The critical temperatures are in remarkable good agreement with the simulation results of the CHS-model, which cannot be said for solutions in alkanols and non-polar hydrocarbons, where the critical temperatures are either above or below that of the CHS model, respectively. The corresponding state phase diagrams in the variables of the CHS model show an UCSP and are in fair agreement with the results for this model. When taking into account the temperature dependence of the dielectric permittivity of the solvents in the CHS-corresponding state variables the critical points remain UCSPs, which is different to the phase diagrams of ionic solutions in alcohols.

1. Introduction

1.1. Criticality of Coulomb systems

Phase diagrams of liquid mixtures are basic information for chemical engineering processes and for this reason measured for many systems [1]. Thus, knowledge of the phase behavior of Ionic liquids (IL) in solution is of actual interest, because ILs that are salts with melting temperatures below 100 °C, are expected to be useful as solvents and other applications in chemical technology, e.g., for separation processes [2–4]. Besides that, the phase behavior of ionic solutions is of interest for fundamental research concerning the nature of the critical point in systems determined by Coulomb forces, termed Coulomb systems [5–8]. While Ising criticality is found in all non-ionic systems, where short-range interactions, e. g., van der Waals interactions determine the properties, this is not necessarily true in ionic systems because of the long-range nature of Coulomb interactions. We first give a short review of this topic because the work reported here is strongly related to this problem, which is important for understanding the phase behavior of IL-solutions, but is not so well known in the IL scientific community.

The very fact that the same compound can exist in different states, although the molecular interactions are independent of the state, was a challenge for theory since the early days of natural sciences. The van der Waals theory for the liquid–gas phase transition explains the two-phase region, where the liquid and the gas are in equilibrium, and the one-phase region above the two phase region, and also the critical point, where the two regions merge, by the interplay of attractive and repulsive interactions. Similar theories for the liquid–liquid phase transition of binary mixtures and the transition from paramagnetic to ferromagnetism have been developed in the years near1900 [9,10]. All those theories, which are now the standard theories taught in Physical Chemistry courses, describe the basic molecular mechanism causing phase-transitions. The theories are termed mean-field theories because the average thermodynamic potential of the particles is modeled. However, in the vicinity of the critical temperature T_c such mean-field theories and their sophisticated refinements [1] predict universal relations for properties e.g. a parabolic shape for the coexistence curves; meaning that the reduced temperature $t = |T - T_c|/T_c$ is a quadratic function of the density difference of the two coexisting phases. Unfortunately, like other predictions of mean-field theories, this prediction is wrong [9,10]. Near the critical point the reduced density $\Delta\rho = |\rho - \rho_c|/\rho_c$ is described by a power law of the form $\Delta\rho \sim t^{\beta}$. While in mean-field theories $\beta = 0.5$ in real fluids holds β=0.326, which is a property of the Ising model in d = 3 dimensions [9,10]. Similar power laws that are

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different from the predictions of the mean-field theories hold for the correlation length, the susceptibility, the viscosity and the surface tension [9,10]. This flaw of the mean-field theories, which was already known to van der Waals [11,12], was exposed by Guggenheim [13], who showed that for simple gases the liquid–gas coexistence curves map on a master curve of cubic shape, thus demonstrating not only the applicability of the principle of corresponding states, but also the fundamental flaw of the mean-field theories. The fundamental error of the classical theories, which cannot be corrected by refining the molecular model, is founded in the neglect of fluctuations that become essential in the vicinity of a critical point. In order to take fluctuations into account special techniques are required as power expansion [9], elaborate simulations [14] or the renormalization group theory [15], which provides a recipe to transform a mean-field theory into a theory, which is correct in the critical region. Solving a fundamental problem of natural science, which stayed for 100 years, the renormalization group theory was honored by a Nobel-price in 1982.

The validity of the 3d-Ising model in real fluid systems is remarkable, as this model is the crudest cartoon of intermolecular interactions. It considers the molecules as spins with two orientations, takes into account next neighbor interactions only, and describes the interactions by just one energy parameter *J*, which differs in sign for the interactions between two spins oriented parallel or anti-parallel. It has been proven that in 3d-space all systems, which are determined by interactions that depend on the separation *r* of the particles by a power law r^{-n} with $n < 4.97$ [16,17] are in agreement with the properties of the Ising model. Much experimental work was devoted verifying the universality of the Ising model and determining the critical exponents accurately [18].

Naturally, the extraordinary agreement between the critical properties of the Ising model and experiments provokes searching for systems in which – as in some theoretical models – the critical properties may be different [19]. For rods in a one-dimensional system interacting with the potential $J \cdot \lambda \cdot \exp[-\lambda \cdot r]$ the van der Waals equation is the exact solution in the long-range limit $\lambda \rightarrow 0$ [20]. Therefore, for phase transitions determined by the long-range r^{-1}-Coulomb potential mean-field criticality [5,21] was discussed among other possibilities [6]. In fact, Buback and Franck [22] reported mean-field behavior for the phase diagram of the ammonium salts $NH_4^+Cl^-$ and $NH_4^+HF_2^-$ with critical points near $T_c = 1150$ K [22], while for $BiCl_3$ [23], which near $T_c = 1178$ K is a molecular liquid, Ising behavior was found as in water [24] and metallic fluids [25]. Because critical temperatures of typical inorganic salts as NaCl are expected near 3000 K [26,27] accurate measurements in the critical region of such salts are impossible till now. During a discussion of the work of Buback and Franck, Friedman suggested that electrolyte solutions with a liquid–liquid phase-transition at ambient conditions may be more suitable for studies of ionic criticality than molten salts [21]. He also referred to an unpublished remark of Widom, who guessed that mean-field criticality may be expected for phase transitions that are driven by Coulomb forces.

According to the correspondence principle [10] the liquid–liquid transition in ionic solutions can be expected to show the same critical properties as the liquid–gas transition of pure salts.

First measurements of the coexistence curve [28] of $N_{2226}B_{2226}$ (triethyl-hexylammonium triethyl-hexylborate) in biphenylether and of the critical opalescence [29] appeared to corroborate the hypothesis of mean-field criticality in a Coulomb system. However, later work could not state those reports [30]. Possible flaws in the experiments as changes of the critical temperature with time [31] and other uncertainties in the measurements [31,32] were noted. Ensuring equilibration of the samples, Ising criticality was consistently observed in subsequent investigations of the viscosity [33–36], of the phase diagrams [30,37–39], and in light-scattering investigations of the critical fluctuations [30,32,40–42] of the liquid–liquid phase transition of the mentioned system and solutions of ammonium picrates in alcohols. Clearly, chemical stability is always an issue in investigations of critical properties, particularly in ionic systems; now, investigations of solutions of ILs are expected to allow for decisive experiments.

Can theory provide some guide for such experiments? Unfortunately, a rigorous theoretical proof of the Ising criticality for Coulomb systems is not available. Furthermore, simulations near the critical point even of simple model fluids require particle numbers that are beyond the present possibilities. However, extrapolations that are based on finite size scaling techniques [14] are a possibility for estimating critical properties. Such very demanding simulations have been carried out for simple model fluids including charged hard spheres (CHS) in a dielectric continuum [43,44]. The notation CHS was introduced in [45] because the commonly applied notation "restricted primitive model" (RPM) appears to be less instructive. The potential of this model system is

$$\varphi = \frac{q_\alpha q_\beta}{\varepsilon \cdot r}, \quad \text{if } r > \sigma \text{ and } \varphi = \infty \text{ if } r \leq \sigma, \tag{1}$$

where ε is the dielectric permittivity of the medium and σ is the diameter of the ions with the charges $q_{\alpha,\beta}$. The dimensionless corresponding state variables are the reduced temperature

$$T^* = kT\varepsilon \cdot \sigma / q^2, \tag{2}$$

which is the ratio of the thermal energy to the Coulomb energy of two ions in contact and the reduced number density of the ions.

$$\rho^* = 2\rho \cdot \sigma^3. \tag{3}$$

As result of those simulations the critical data of the CHS system are determined to $T_c^* = 0.049$ and $\rho_c^* = 0.07$ [43]. The critical exponents are found to be consistent with Ising criticality [44] quite as for other model fluids.

While simulations may be regarded as experiments with the computer, theory provides a physical picture of the ionic solutions and allows visualizing the thermodynamic space. A remarkable simple mean-field theory was developed by Fisher and Levin (FL) [46]. This theory predicts a coexistence curve, which agrees rather well with the results of early simulations [47] for the CHS system that did not use finite size scaling techniques and may be regarded as "mean-field" simulations. The theory is based on macroscopic electrostatics. It extends the Debye–Hückel (DH) theory, which accounts for electrostatic interactions among the ions by incorporating ion pairing (following the ideas of Bjerrum) and accounting for the interactions of free ions and ion pairs. The critical data are located in the correct region of the temperature-density plane, while the original DH theory, which yields a rather good figure for the critical temperature [6,48], underestimates the critical density by an order of magnitude. The agreement of the FL theory and its generalization to charge asymmetric fluids [49] with the simulations is better than that of apparently more advanced theories as the mean-spherical approximation (MSA) [50]. Based on the FL-theory the Ginzburg temperature was estimated, which is the temperature, where a mean-field theory becomes inconsistent, when approaching the critical region. It turns out that the estimates of the Ginzburg temperature are further apart from the critical point than expected for non-ionic fluids, which excludes the possibility of mean-field behavior for the CHS fluid [51,52]. Thus, the FL theory explains the fact that, in spite the long-range nature of the Coulomb interactions, mean-field criticality is not observed: the Coulomb-interactions are shielded by the charge distribution surrounding an ion, so that the correlations become effectively short ranged and Ising criticality may result.

1.2. Critical properties of ionic solutions

Clearly, the model system of charged hard spheres is no realistic molecular model for the liquid–liquid phase transition in solutions of ionic