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Critical behaviour of ionic solutions in non-polar solvents with a liquid–liquid phase transition

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Abstract. Turbidity measurements showing crossover from mean-field to Ising criticality have been reported by Narayanan and Pitzer for the liquid–liquid phase transition in ionic solutions of alkyl-ammonium picrates in higher alcohols. The Ising region was found to increase with the dielectric permittivity D for solvents with $4 < D < 8$. It was conjectured that the Ising region becomes too small to be observed for lower values of D , which is in accordance with the finding of mean-field criticality in the system triethylhexylammonium triethylhexylborate ($N_{2226}B_{2226}$) in diphenyl ether (Ph_2O), where $D \approx 3.7$. In order to check this hypothesis, we investigate solutions of salts in non-protonating solvents with $D < 2.5$. The systems are tetrabutylammonium naphthyl sulphonate ($N_{4444}NS$) in toluene and tributylheptylammonium dodecyl sulphate ($N_{4447}DS$) in cyclohexane. The location of the critical points in the corresponding state diagram is in general agreement with the model system of charged hard spheres in a dielectric continuum, i.e. the restricted primitive model (RPM). However, changes of T_c by minute variations of the salt and of the solvent (toluene, xylene, ethylbenzene) cannot be explained by the RPM. We report measurements of the phase diagram and light-scattering results. The amplitudes of the correlation length are up to an order of magnitude larger than those typically found in non-ionic fluids. For the new systems, but also for the solution of $N_{2226}B_{2226}$ in Ph_2O , Ising criticality is found in the region of $1 \text{ mK} < |T - T_c| < 10 \text{ K}$.

1. Introduction

The criticality of ionic fluids is an unsolved fundamental problem in statistical physics and is of great interest in many applied fields such as chemical engineering and geophysics [1–4]. The theory is complicated due to the long-range nature of the Coulombic interactions, suggesting a criticality eventually different from the Ising behaviour generally found in fluids and fluid mixtures for which thermodynamical properties are determined by short-range interactions. Furthermore, the energies of ions at contact are similar to those of chemical bonds so that ion pairs and higher associates may exist. Much insight in understanding ionic fluids is gained by analytical liquid theory [3], generalized van der Waals (vdW) theory [2, 5, 6], and Monte Carlo simulations [7–9]. A theory detailed enough to give quantitative thermodynamic results beyond the mean-field (MF) level, however, is not available for phase transitions (PTs) driven by Coulombic interactions. The rediscovery of the liquid–liquid (l–l) PT in ionic solutions [1], first reported in 1903 by Walden and Centnerszwer [10], stimulated this research, as l–l PTs are observed at ambient temperatures, allowing for measurements of critical properties of ionic fluids with an accuracy in the mK range.

The simplest model for ionic fluids is the restricted primitive model (RPM), consisting of charged hard spheres of equal size immersed in a dielectric continuum. In this model criticality is founded in Coulombic interactions and it is expected that in a corresponding

state representation [11] the phase diagrams of the RPM and of real ionic fluids coincide if the PT is driven by Coulombic forces. The appropriate reduced temperature and density variables are $T^* = kT Da/q^2$ and $\rho^* = \rho a^3$. D is the dielectric permittivity of the solvent and ρ , a , q are the number density, the diameter and the charge, respectively, of the ions.

The critical point (CP) is located at a temperature and a density which are about an order of magnitude below the corresponding values typical for normal fluids. The simulation results seemed to converge to $T_c^* \approx 0.056$ and $\rho_c^* \approx 0.030$ [7, 8], recent calculations, however, yield somewhat different figures $T_c^* \approx 0.049$ and $\rho_c^* \approx 0.065$ [9]. On the basis of the Debye–Hückel (DH) theory, taking into account shielded charge–dipole interactions of ions and ion pairs, but neglecting the dipole–dipole interactions, Levin and Fisher [2, 12] developed a generalized vdW theory, which is in remarkable agreement with simulation results. The nature of the CP, however, is not clear *a priori* because of the long-range Coulombic interactions. For r^{-n} potentials with $n < 3$ the thermodynamic limit may not exist and specific properties such as the energy per particle may depend on the size of the system. However, for ionic fluids and crystals electroneutrality and electric (Debye) shielding ensure the existence of the thermodynamic limit. Nevertheless, the long-range nature of the Coulombic interactions suggests MF criticality as a possibility, if the range of the interactions is larger than the correlation length ξ of the thermodynamic fluctuations. However, characterizing the range of the potential by the Debye shielding length $1/\kappa$, the condition $\xi \leq 1/\kappa$ can hardly be satisfied near the CP of a Coulombic system as elucidated by Stell [3] on very general grounds. This conclusion may also be drawn from the Levin–Fisher theory [12] yielding $\kappa a \approx 1$ at the CP which implies $\xi \leq a$, while ξ is certainly diverging in reality. Furthermore, the order parameter for the PT in the RPM is the number density, not the charge density, and the density correlation function is proved to be a short-range function. Therefore, Stell [3] predicts Ising criticality for the RPM; however, he expects different behaviour if the symmetry is broken, e.g. by a different size and shape of the ions (but see [33] in this regard).

An important tool for judging the range of applicability of a MF theory is the Ginzburg temperature (G_i). First estimates of G_i for the RPM have recently been reported. In the generalized mean spherical approximation, Leote de Carvalho and Evans [13] found similar values for G_i of a square-well fluid and of the RPM ignoring ion pairing. Fisher and Lee [14] reached the same conclusion for an extension of the Levin–Fisher approach [12] taking into account density fluctuations in the DH theory [15]. Hence, even in respect of the crossover no substantial difference to argon-like systems is predicted. However, as G_i results from the coefficients of the Landau–Ginzburg Hamiltonian, it may be sensitive to the approximations involved in the underlying MF theory and the method of estimating the coefficient of the square-gradient term [16].

The location of the CP in the RPM has guided the search for l–l PTs [17] and led to the discovery of different types of PTs in ionic solutions. For systems with a CP in agreement with the RPM, the PT is expected to be driven by Coulombic interactions and termed accordingly. For a different kind of system, termed solvophobic, demixing is driven by short-range interactions of ions, ion pairs and higher clusters with the solvent. The location of the CP is very different from that predicted for the RPM and normal Ising behaviour is observed [18–20]. Two groups of solvophobic demixing may be distinguished: (a) in strong electrolytes the salt is widely dissociated (e.g. in solutions of organic salts in water) and the PT is driven by solvophobic interactions of the ions with the solvent [18, 19]; (b) in weak electrolytes (e.g. butyric acid in water or ethylammonium nitrate in octanol [20]) ion pairs are stabilized additionally by other interactions as H bonds (sticky ions). In this case interactions of the ion pairs with the solvent drive the PT, similar to the PT in mixtures of

a polar and a non-polar compound.

Comparing real ionic solutions with the RPM is problematic since in the model fluid interactions with the solvent as well as specific properties of the ions such as size, shape and internal flexibility are neglected. Inevitably, the assessment of the ionic diameter a in the RPM variables is to some extent arbitrary [4, 17]. As Coulombic forces are the most important interactions, adopting the distance of charges in the configuration with maximal electrostatic attraction seems to be appropriate [4, 21]. In fact, by taking the shortest distance between the centres of charge, a mapping of critical data of ionic solutions with those of the RPM is achieved. This approach appears to be superior to attempts based on vdW radii of the ions. Experimentally, this charge distance may be obtained from x-ray analysis or from the dipole moment of ion pairs determined by dielectric measurements. The mapping of the critical data of real fluids is reasonable but by no means perfect. The ratio $\rho_c^{*1/3}/T_c^*$, which is independent of a , yields the value 5.5 for the RPM, but varies strongly among the systems. For solutions in non-polar solvents this ratio is slightly above the RPM value, but is far below it for solutions in water.

We now review the experiments concerning the nature of the CP of Coulombic systems. MF criticality in Coulombic fluids was concluded quite definitely from the phase diagram [22] and turbidity measurements [23] on solutions of $N_{2226}B_{2226}$ in Ph_2O ($D = 3.6$ at $44^\circ C$). First light-scattering investigations on tetrabutylammonium picrate ($N_{4444}Pic$) in tridecanol ($C_{13}OH$, $D = 4.2$) also seemed to yield MF exponents [24]. However, systematic turbidity measurements [25] on this salt and other picrates in various alcoholic solutions indicate a crossover from MF to Ising criticality also observed in viscosity measurements [26]. The crossover appears to happen more sharply than in non-ionic fluids which is conceivable with the crossover theory of Anisimov *et al* [27]. The Ising region is found to increase with D of the solvent, and Pitzer argued [25] that the Ising region may become too small to be observable in low- D solvents somewhere below $D = 4$ as reported for $N_{2226}B_{2226}$ in Ph_2O ($D = 3.7$), while for $N_{1112}Br$ in chloroform with $D = 4.7$ Ising behaviour without any indication of crossover is observed [21]. The obvious question to ask now is: is this D dependence of the crossover from MF to Ising criticality a general rule for Coulombic systems or merely a specific property of the systems investigated?

In order to answer this question we have started a systematic search for l-l demixing in solutions of salts in solvents with $D < 4$, such as toluene ($D \approx 2.4$) and cyclohexane ($D \approx 2.0$). Demixing in benzene was reported for $N_{4444}Cl$ [28] but appears to have been caused by traces of water [17]. The first requirement to be met by the salt is sufficient solubility in the low- D solvent. This calls for lipophilic ions. Unequal size and non-spherical shape of the ions lead to low melting points and an increase of the solubility. The systems found are $N_{4444}NS$ in toluene and $N_{4447}DS$ in cyclohexane. We have determined phase diagrams and carried out light-scattering measurements in the range $1 \text{ mK} \leq T - T_c \leq 10 \text{ K}$. Other properties such as viscosities, densities and electric conductivities were also determined. Since we find Ising criticality in both cases we also performed light-scattering measurements on $N_{2226}B_{2226}$ in Ph_2O in order to check the earlier results.

2. Experimental details

The salts were prepared by standard methods [29], recrystallized and carefully dried under reduced pressure. Care was taken to exclude humidity. Purity and stability of the compounds were checked by nuclear magnetic resonance (NMR) spectroscopy. The critical

concentrations were determined using the equal volume criterion. Critical temperatures may vary among samples but have been checked to be stable for the sealed samples. Phase diagrams were obtained by determining the refractive index in the two phases in a sealed sample of critical composition as a function of temperature. For this purpose the deflection of two parallel laser beams passing through the two phases in a square 1 cm sample was monitored using the method of 'minimum deviation' [30]. The intensity and the time correlation function have been measured in a 90° scattering geometry. The incident and the transmitted light of a 5 mW HeNe laser were monitored by photodiodes in order to normalize the intensity of the scattered light and also to determine the turbidity. Details of the experimental set-up have been described elsewhere [20, 21].

3. Results and discussion

The salt $N_{4444}NS$ is colourless and not hygroscopic. In toluene ($D = 2.4$) the upper critical consolute point is located at a weight fraction of $w_c = 0.1061 \pm 0.0003$ and $T_c \simeq 46$ °C. Among samples T_c may vary by 0.5 °C. By NMR it was found that the salt is a mixture of two isomers differing in the position of the sulphonate group. The investigated sample consisted of 65% 1-isomer. The sulphonic acid used in the synthesis had the same ratio of isomers, which was checked to see that it remained unchanged during the synthesis and in the prepared solutions. The properties of the isomers are similar, so that the solution is treated as a pseudo-binary mixture. The system is identified as a Coulombic one: assuming the distance between the centres of charge on the nitrogen and the sulphur to be the RPM diameter a , and assuming the nitrogen–sulphur distance to be given by the sum of the vdW radii of the N_{4444}^+ ion (0.414 nm [31]) and of the SO_3^- group (estimated to be 0.287 nm), the CP is located at $\rho_c^* = 0.086$ and $T_c^* = 0.032$, which is in the region predicted by the RPM. In Ph_2O ($D = 3.7$) we find complete miscibility, corresponding to a shift of T_c towards smaller values, while in p-xylene ($D = 2.3$) T_c is too high to be observable by us. These trends are in accordance with the RPM. However, replacing toluene by similar solvents with slightly larger values of D (ethylbenzene $D = 2.4$, o-xylene $D = 2.6$, tetrahydronaphthene $D = 2.8$), T_c is shifted to higher values contrary to expectation. A decrease of the content of the 2-isomer causes a linear shift of T_c towards lower values without changing ρ_c , which might be rationalized by assuming a smaller value of a for the 2-isomer. Clearly, more specific solvation properties, e.g. steric effects, not assessed by the RPM influence the location of the CP.

The phase diagram (figure 1) is symmetric for the volume fraction ϕ , the weight fraction w and the mole fraction x . The analysis yields the critical exponent $\beta = 0.345 \pm 0.003$. On approaching T_c , the intensity of the scattered light (figure 2) passes through a maximum at $t = (T - T_c)/T_c \simeq 0.001$ as losses due to scattering reduce the intensity of the light in the scattering volume. The scattering intensity is normalized appropriately and evaluated applying the Ornstein–Zernike theory. The amplitude of the correlation length is determined as $\xi_0 = 2.55 \pm 0.04$ nm and the critical exponents as $\nu = 0.618 \pm 0.003$ and $\gamma = 1.259 \pm 0.008$. The amplitude ξ_0 is the largest value ever observed in ionic solutions and is about 10 times what is typically found in non-ionic fluids. Similar results are obtained from the analyses of the turbidity data ($\xi_0 = 2.74 \pm 0.07$ nm, $\nu = 0.625$ (fixed)) and of the intensity time correlation function using the Kawasaki theory ($\xi_0 = 1.97 \pm 0.04$ nm, $\nu = 0.656 \pm 0.004$). The investigation of the other systems mentioned above also yields critical exponents close to the Ising values. For $N_{4447}DS$ in cyclohexane the CP is located at $w_c = 0.1404$ and $T_c = 82.49$ °C. The analysis of the scattered intensity gives $\xi_0 = 0.96 \pm 0.01$ nm, $\nu = 0.609 \pm 0.002$ and $\gamma = 1.235 \pm 0.005$. The system $N_{2226}B_{2226}$

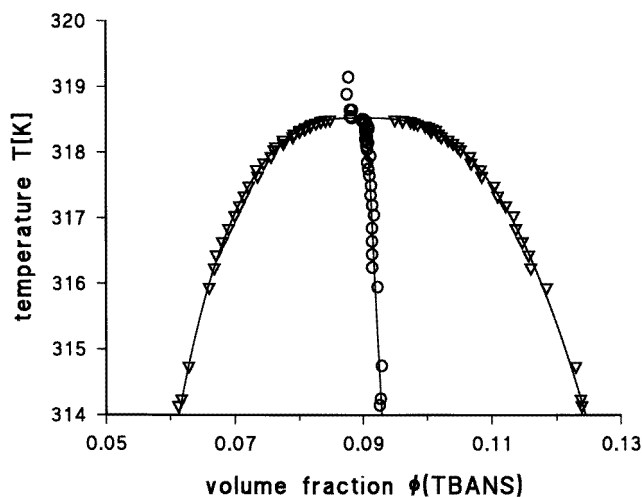


Figure 1. The coexistence curve of tetrabutylammonium naphthylsulphonate ($N_{4444}NS$) in toluene. The transition temperatures are plotted as a function of the volume fraction ($\phi_c = 0.0899$, $T_c = 318.53 \pm 0.01$).

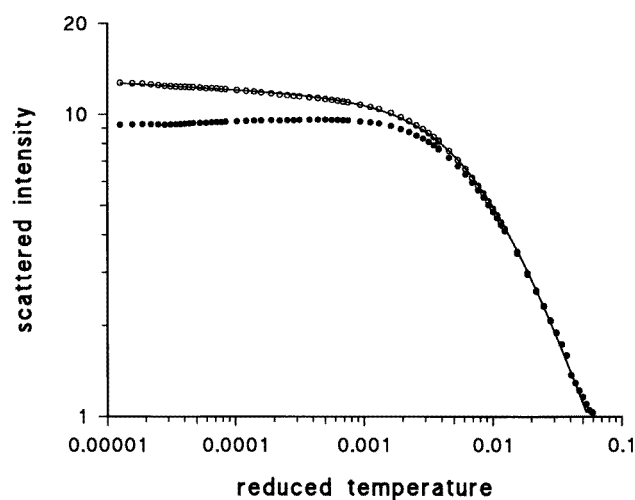


Figure 2. The scattering intensity $I(t)$ of a sample of $N_{4444}NS$ in toluene at critical composition ($w_c = 0.106$), as a function of the reduced temperature $t = (T - T_c)/T_c$ ($T_c = 319.179 \pm 0.001$ K) in a log-log plot. The experimental intensity is represented by filled circles (●), the intensity corrected for turbidity by open circles (○). The solid line shows the fit yielding $\nu = 0.618 \pm 0.003$, $\gamma = 1.259 \pm 0.007$ and $\xi_0 = 2.55 \pm 0.04$ nm.

in Ph_2O , which consists of ions of very similar size and shape, is up to now the only ionic system reported to display MF criticality. It is notorious for large variation of the critical data in different samples [22, 23]. Our sample (provided by the National Institute of Standards and Technology (NIST), Gaithersburg, MD) has its critical point at $x_c = 0.049$ and $T_c = 308.694$ K. Here the analysis of the scattering intensity gives $\xi_0 = 1.46 \pm 0.04$ nm, $\nu = 0.638 \pm 0.002$ and $\gamma = 1.31 \pm 0.01$ in perfect agreement with the new turbidity

measurements carried out by Wiegand at NIST [32] which also yielded Ising behaviour and $\xi_0 = 1.4$ nm. In conclusion, we cannot confirm earlier reports of MF criticality in this system. The reason for this discrepancy remains mysterious. All the exponents determined from the phase diagram and the light-scattering experiments prove Ising criticality for the investigated ionic solutions in solvents with $D < 4$. No differences in the criticality are found among ionic solutions containing ions equal or different in size and shape. Within the accuracy of our measurements we see no indications of crossover in any of the systems investigated, while, extrapolating the results reported for the solutions of alkyl-ammonium picrates in higher alcohols [25], a small Ising region was to be expected.

One might argue that in low- D solvents the ions are almost completely paired and that the criticality is therefore determined by the ion pairs. However, conductivity measurements show that the solutions contain ions as well as non-conducting associates. In short, the light-scattering investigations of the l-l PT of ionic solutions in non-polar solvents yield no indication of a crossover. The amplitudes of the critical fluctuations are larger than those typically found in non-ionic fluids, the exponents, however, are in agreement with Ising criticality.

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References

- [1] Pitzer K S 1990 *Acc. Chem. Res.* **23** 333
- [2] Fisher M E 1994 *J. Stat. Phys.* **75** 1
- [3] Stell G 1995 *J. Stat. Phys.* **78** 197
- [4] Harvey A, Wiegand S and Levelt Sengers J M H 1996 *Ionic and Chemically Reacting Fluids near Critical Points (IUPAC Volume on Equation of State for Fluids and Fluid Mixtures)* ed J V Sengers et al (New York: AP) at press
- [5] Yeh S, Zhou Y and Stell G 1996 *J. Phys. Chem.* **100** 1415
- [6] Guillot B and Guissani Y 1996 *Mol. Phys.* **87** 37
- [7] Orkoulas G and Panagiotopoulos A Z 1994 *J. Chem. Phys.* **101** 1452
- [8] Caillol J M 1994 *J. Chem. Phys.* **100** 2161
- [9] Caillol J M, Weis J J and Levesque D *preprint*
- [10] Walden P and Centnerszwer M Z 1903 *Phys. Chem.* **42** 432
- [11] Friedmann H L and Larsen B 1979 *J. Chem. Phys.* **70** 92
- [12] Levin Y and Fisher M E 1996 *Physica A* **225** 164
- [13] Leote de Carvalho R J F and Evans R 1995 *J. Phys. Condens. Matter* **7** 575
- [14] Fisher M E and Lee B P 1996 *Phys. Rev. Lett.* submitted
- [15] Lee B P and Fisher M E 1996 *Phys. Rev. Lett.* **76** 2906
- [16] Weiss V C and Schröder W 1996 *J. Chem. Phys.* at press
- [17] Weingärtner H, Merkel T, Maurer U, Conzen J-P, Glasbrenner H and Käshammer S 1991 *Ber. Bunsenges. Phys. Chem.* **95** 1579
- [18] Weingärtner H, Kleemeier M, Wiegand S and Schröder W 1995 *J. Stat. Phys.* **78** 169
- [19] Japas M L and Levelt Sengers J M H 1990 *J. Phys. Chem.* **94** 5361
- [20] Schröder W, Wiegand S and Weingärtner H 1993 *Ber. Bunsenges. Phys. Chem.* **97** 975
- [21] Wiegand S, Kleemeier M, Schröder J M, Schröder W and Weingärtner H 1994 *Int. J. Thermophys.* **15** 1045
- [22] Singh R R and Pitzer K S 1990 *J. Chem. Phys.* **92** 6775
- [23] Zhang K C, Briggs M E, Gammon R W and Levelt Sengers J M H 1992 *J. Chem. Phys.* **97** 8692
- [24] Weingärtner H, Wiegand S and Schröder W 1992 *J. Chem. Phys.* **96** 848

- [25] Narayanan T and Pitzer K S 1995 *J. Chem. Phys.* **102** 8118
- [26] Kleemeier M, Wiegand S, Derr T, Weiss V, Schröer W and Weingärtner H 1996 *Ber. Bunsenges. Phys. Chem.* **100** 27
- [27] Anisimov M A, Povodyrev A A, Kulikov V D and Sengers J V 1995 *Phys. Rev. Lett.* **75** 3146
- [28] Barker C and Yarwood J 1977 *J. Chem. Soc. Faraday Discuss.* **64** 1322
- [29] Gordon J E 1965 *J. Am. Chem. Soc.* **87** 4347
- [30] Jacobs D T, Anthony D J, Mockler R C and O'Sullivan W 1977 *J. Chem. Phys.* **20** 219
- [31] Krumgalz B S 1982 *J. Chem. Soc. Farad. Trans. 1* **78** 437
- [32] Wiegand S, Levelt Sengers J M H, Zhang K J, Briggs M E and Gammon R W 1996 submitted
- [33] Stell G 1996 *J. Phys.: Condens. Matter* **47** 9329