

## Structure and criticality of ionic fluids\*

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*Abstract:* Two properties render electrolyte theories difficult, namely the long-range nature of the Coulomb interactions and the high figures of the Coulomb energy at small ion separations. In solvents of low dielectric constant, where the Coulomb interactions are particularly strong, electrical conductance and dielectric spectra suggest that the ion distribution involves dipolar ion pairs, which then interact with the free ions and with other dipolar pairs. The dipole–dipole interactions between ion pairs lead to an increase of the dielectric constant, which in turn stabilizes the free ions, thus leading to redissociation at high salt concentrations. An equation of state that accounts for ion pairing, ion–ion pair, and ion pair–ion pair interactions rationalizes the basic features of the ion distribution. It also predicts a fluid-phase transition at low reduced temperatures, which closely corresponds to simulation results and to experimentally observed liquid–liquid phase transitions. The long-range nature of the Coulomb potential driving these transitions raises questions concerning their universality class. Experiments suggest that the Ising universality class applies, but there is cross-over to mean-field behavior rather close to the critical, not yet well explained by theory.

### INTRODUCTION

Electrolyte solutions have ever been of central interest in physical chemistry and many other fields such as chemical engineering or geology. Two properties render electrolyte theories difficult, namely the long-range nature of the Coulomb interactions and the high figures of the Coulomb energy at small ion separations.

The long-range nature of the  $r^{-1}$ -dependent Coulomb interaction does not only cause technical problems in theory and simulations, but also challenges the hypothesis that all liquid–gas and liquid–vapor phase transitions belong to the Ising universality class [1–5]. We recall that the Ising model assumes only nearest-neighbor interactions, and applies only to  $r^{-n}$  potentials with  $n > 4.97$  [3,4]. Thus, ionic criticality has received wide attention from experimentalists and theoreticians alike [1–5]. More recent experiments [6] and simulations [7] seem to point toward an Ising-like nature of the critical point, but there remain open problems, because there are strong indications for cross-over from Ising to mean-field behavior close to the critical point [6], and there is some possibility for tricritical behavior [8] which in three-dimensional systems is mean-field like.

The second striking aspect is the strength of the interionic forces. While in normal fluids at ambient conditions the size of the intermolecular interactions at small separations is only a few times the thermal energy  $k_B T$ , Coulomb interactions are much stronger. We are particularly interested in solutions in solvents of low dielectric constant  $\epsilon$ , where liquid–liquid phase transitions driven by Coulomb inter-

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actions are expected [1,9,10]. Then, interionic interactions may even reach the strength of a chemical bond.

These strong interactions have distinct consequences for the structure of ionic liquids. While ordinary liquids can in good approximation be described in the van der Waals picture as hard-core bodies in a sea of an average potential, the interionic interactions generate long-living ion aggregates. In particular, ion pairs may be formed as molecule-like entities which, however, may separate into free ions by rather mild conditions, e.g., by a change of solvent. In a “chemical” picture we may therefore regard ionic solutions as systems comprising free ions, ion pairs, and higher ion clusters in equilibrium. In a “physical” picture, these aggregates are just consequences of large values of the Mayer  $f$ -functions that characterize the interionic interactions. The technical consequence is, however, a major complication of electrolyte theory, because the popular approximations in liquid-state statistical mechanics such as the mean spherical approximation (MSA) use high-temperature approximations of these functions. Even the hypernetted chain theory (HNC), which applies the Mayer functions in full, seems to fail, because under such conditions the neglect of the bridge graphs in this theory is inadequate.

The usual way out of these difficulties are hybrid models in which ion configurations of high energy are considered separately by a chemical model, while other configurations are treated by the Mayer functions, for example, at the level of the MSA [11]. The same concept can, however, also be applied to Debye–Hückel (DH) theory. Surprisingly, in spite of its often-quoted deficits, DH theory led to reasonable agreement with results of simulations [12]. In many cases, DH theory provides analytical expressions, which are physically more transparent than those of the MSA, which has to be solved numerically.

The present paper aims at discussing some new experimental results on the structure and criticality of ionic fluids and their theoretical interpretation along the lines outlined above.

## MODELS FOR IONIC FLUIDS

In comparing experiment, theory, and simulations, we resort to the hard-sphere ionic fluid in the “restricted primitive model” (RPM), which pictures the fluid as equal-sized and equal-charged hard ions with diameter  $a$  and charges  $q = z_+e = |z_-|e$  immersed in a medium with dielectric constant  $\epsilon$ . Then, all thermodynamic states are specified by a reduced temperature and reduced density, respectively. The reduced temperature

$$T^* = 4 \pi k_B T \epsilon \epsilon_0 a / q^2 \quad (1)$$

characterizes the ratio of the thermal energy  $k_B T$  to the depth of the interionic potential which is given by the Coulomb energy  $q^2/(4\pi\epsilon\epsilon_0 a)$  at contact distance  $a$ .  $\epsilon_0$  is the permittivity of the vacuum. The reduced density is given by

$$\rho^* = \rho a^3, \quad (2)$$

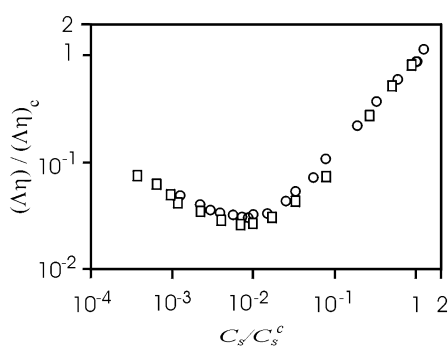
where  $\rho = (N_+ + N_-)/V$  is the ion density. Because this model predicts a fluid-phase transition, it has served as a generic model for discussing ionic criticality [1–5,12]. The RPM satisfies the corresponding states principle [9,10]. Obviously,  $T^*$  is mainly affected by the dielectric constant of the medium which can vary over a particularly large range. Most results considered here concern solutions in low- $\epsilon$  solvents, which typically implies  $T^* < 0.1$ . Then, the strength of the Coulomb interactions at small separations is more than an order of magnitude larger as the thermal energy. It can be argued that under such conditions, the neglect of specific short-range interactions in the theory is fairly adequate [9,10]. On the other hand, gross deviations in the behavior of real fluids from the RPM predictions can be used to single out systems, where specific interactions dominate [5,13].

## PARTICLE DISTRIBUTION IN SOLVENTS OF LOW DIELECTRIC CONSTANT

In the absence of X-ray or neutron scattering data, the electrical conductance offers a major source of information. At very low salt concentrations, the conductance is well described by Debye–Onsager theory, which assumes free ions, but takes into account long-range interionic interactions, thus yielding the famous square-root law. However, in low- $\epsilon$  solvents this regime is at too low concentrations to be reached. Rather, at the lowest concentrations, where experiments are feasible, the conductance is determined by ion pair association, thus yielding information on the association constant  $K(T)$  for ion pair formation which, in turn, allows us to test theoretical predictions such as Bjerrum association theory [11].

At higher concentrations, if  $\epsilon$  is low enough, one observes a conductance minimum, indicating the reappearance of charged species at higher concentrations due to redissociation to free ions and/or the formation of charged species.

Figure 1 shows conductance isotherms for tetra-*n*-butyl ammonium picrate ( $\text{Bu}_4\text{NPic}$ ) dissolved in tridecanol [13] and 1-chloroheptane [14]. The isotherms are recorded at largely different temperatures (346 and 419 K), but in each case only slightly above a liquid–liquid critical point observed in these systems. It is then intriguing to normalize the data relative to the values at the critical points. Both sets of data fall onto a common curve, which clearly indicates that corresponding states' behavior of the degree of dissociation controls the conductance.

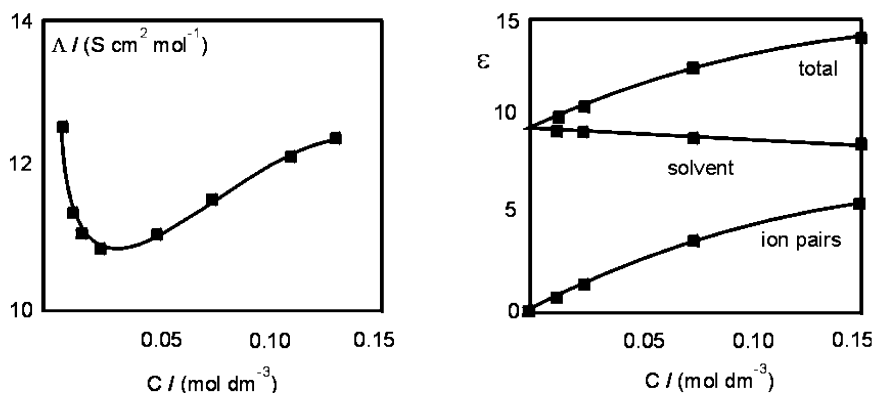


**Fig. 1** Conductance for tetra-*n*-butylammonium picrate ( $\text{Bu}_4\text{NPic}$ ) dissolved in tridecanol (circles) and 1-chloroheptane (squares) along isotherms slightly above the liquid–liquid critical points of these systems. The molar conductance and molar salt concentrations are normalized to their values at the critical points.

The origin of this conductance minimum has been of long-standing and controversial debate. In light of more recent theoretical studies, it is now known that the interaction of ion pairs with free ions stabilizes the free ions [12], thus favoring redissociation [15]. Furthermore, the presence of ion pairs is expected to increase the dielectric constant of the solution that thus also lowers the association constant [15–17]. The popular Fuoss–Kraus mechanism of triple ion formation [18] seems to play a minor role.

The crucial role of the dielectric properties in these interpretations led us to consider dielectric behavior of such systems. As the solutions are conducting, the static dielectric constant can only be determined by determining the frequency-dependent complex permittivity  $\epsilon^*(\omega)$ , followed by zero-frequency extrapolation of the real part which defines  $\epsilon$ . However, the information provided by dielectric spectroscopy is more rich, because ion pair dipoles and solvent dipoles reorient at different time scales, so that  $\epsilon$  can be separated into ion pair and solvent contributions.

Figure 2 shows such data for tetra-*n*-butyl ammonium iodide in dichloromethane [9];  $\epsilon$  increases with increasing salt concentration. The increase results solely from the formation of dipolar ion pairs. The decrease of the solvent contribution reflects a decrease in the solvent density. The increase of the



**Fig. 2** Concentration dependence of the electrical conductance and static dielectric constant of solutions of tetra-*n*-butylammonium iodide in dichloromethane near the conductance minimum.

ion pair contribution is not linear. The decreasing slope may indicate the disappearance of dipoles by redissociation, but estimates show that this cannot account for the total effect. Correlations between ion pairs may serve as a tool for describing the data. In non-electrolytes, such dipole correlations are described by the famous Kirkwood factor, for example, evaluated by the Kirkwood–Fröhlich theory [19]. A recent generalization of this theory to dipole–dipole interactions screened by a sea of free ions [20] allows us to describe ion pair correlations by the same formalism. The resulting Kirkwood factors  $g < 1$  for ion pair–ion pair interactions indicate a tendency for antiparallel dipole arrangements. In cluster pictures this result can be rationalized as the formation of quadruple ions formed by antiparallel pairs.

The findings are well in accordance with some results by Monte Carlo simulations of the RPM [21]. Defining clusters by somewhat arbitrary critical distances, species populations may be obtained from an analysis of particle separations found in the simulated box which indicate that, when lowering  $T^*$  in the regime  $0.05 < T^* < 0.1$ , free ions rapidly disappear at the expense of pairs, and higher ion clusters become noticeable. It is remarkable that such changes become less sharp with increasing ion density.

## COEXISTENCE CURVES

Perhaps the most exciting property of electrolytes at low reduced temperatures is a fluid-phase transition with an upper critical point. This is true even for the simple RPM which according to more recent simulations possesses a critical point at [22]

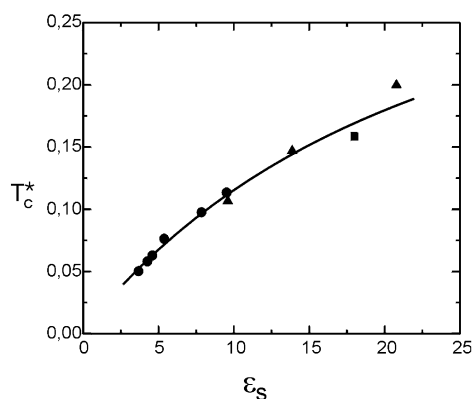
$$T_c^* = 0.048\text{--}0.05; \quad \rho_c^* = 0.07\text{--}0.08. \quad (3)$$

The figure for  $T_c^*$  is by more than an order of magnitude lower than that of the Lennard–Jones fluid ( $T_c^* \cong 1.31$ ), and  $\rho_c^*$  is about one-fourth of that of the Lennard–Jones fluid ( $\rho_c^* \cong 0.32$ ). According to corresponding states arguments, this should correspond to the liquid–vapor transition of the molten salt, which in general is not reached by experiments, and to a liquid–liquid transition in electrolyte solutions of low dielectric constant. In recent years, many such liquid–liquid transitions have been discovered, above all in solutions of low-melting tetraalkylammonium salts [1,2,5,6,9,13]. Many of these transitions occur in the regime predicted by the RPM, so that these coexistence curves and critical points are sensitive targets for testing theories.

However, there are systems with gross deviations of the coexistence curve from RPM behavior [5,13]. Clear examples of the importance of such non-Coulombic effects are aqueous solutions of some tetraalkylammonium salts, where closed miscibility loops are observed [13]. Furthermore,  $T_c^* \cong 0.5$  is one order of magnitude higher than predicted by the RPM, and therefore the ionic forces are not ex-

pected to cause phase separation. We have ascribed this behavior to solvophobic effects of salts with large ions in solvents of high cohesive energy density [5,13].

Instructive examples for the interplay of Coulomb and solvophobic forces are tetraalkylammonium picrates dissolved in homologous alcohols. For this purpose, we calculate  $T_c^*$ , defined in eq. 1, for the experimental critical temperatures. The characteristic separation  $a$  of the ionic charges is estimated from the van der Waals radius of the oxygen (1.4 Å), which is assumed to be the center of the charges in the picrate anion and the Stokes radius of the cation (5.2 Å) [9]. As the charge and the ion diameter are fixed, the RPM predicts  $T_c^* \cong 0.05$  to be constant. In view of the uncertainty of the estimate of  $a$  one expects the product  $\epsilon \cdot T_c^*$  to be constant [6,10]. Figure 3 shows that  $T_c^*$  is of the magnitude expected but increases with  $\epsilon_s$ . However, for long chain lengths of the alcohols, when the solvent becomes almost nonpolar, one approaches indeed this ‘‘Coulombic limit’’ of  $T_c^* \cong 0.05$  predicted by the RPM.



**Fig. 3** Reduced critical temperature vs. dielectric constant of the solvent of tetra-*n*-butylammonium picrate (circles), 1-butyl-3-methylimidazolium hexafluorophosphate [24] (triangles) and tetrafluoroborate (square) in homologous alcohols.

Interestingly, there are now observations of liquid–liquid coexistence in solutions of some newly designed room-temperature molten salts, e.g., based on imidazolium cations. These ‘‘ionic liquids’’ have prospects for engineering applications [23]. At present, these systems are mostly treated by typical non-electrolyte equations of state that ignore the long-range terms associated with Coulombic interactions. In seeking for molecular-based interpretations, one should, however, not forget that in such systems Coulomb interactions may form the major driving force for phase transitions. As an illustrative example, we show in Fig. 3 the location of the critical point in the corresponding-states plot derived from literature data [24] for 1-butyl-3-methylimidazolium hexafluorophosphate and own data 1-butyl-3-methylimidazolium tetrafluoroborate in the lower normal alcohols. The effective ion diameter of this salt should be markedly smaller than that of the picrate, where the center of charge in the cation is buried by the alkyl groups. We simply estimate the characteristic separation of the ions from the bond lengths of the B-F bond (1.4 Å), of the P-F bond (1.73 Å) and from van der Waals radii of the thickness of an aromatic nucleus (1.85 Å) and of the fluorine (1.35 Å). The reduced critical temperatures of the imidazolium-based salts practically fall onto the same line as those of the tetraalkylammonium salts, impressively showing the need for including Coulombic effects in data analysis.

## EQUATION OF STATE AT LOW REDUCED TEMPERATURES

In developing such an equation of state (EOS) that is consistent with the observed features of the ion distribution, a crucial part is played by ion pair formation, as described by the mass action law

$$2(1 - \alpha) / (\rho \alpha^2) = \rho_p / (\rho_+ + \rho_-) = K(T) (\gamma_+ + \gamma_-) / \gamma_p, \quad (4)$$

where  $\alpha$  is the degree of dissociation,  $K(T)$  is the pair association constant, the  $\rho_i$  are the number densities of the free ions and pairs ( $p$ ), and the  $\gamma_i$  are the activity coefficients of the various species.

Pairing theories based on eq. 4 require the modeling of the activity coefficients of both the free ions and of the pairs, but most theories treat the pairs as thermodynamically ideal species with  $\gamma_p = 1$ . Such an assumption is obviously inadequate at low  $T^*$ , where high dipole moments of the pairs lead to strong interactions with free ions [12] and other dipolar pairs [25]. If the equation of state is formulated in terms of the reduced Helmholtz free energy density

$$\Phi = A\sigma^3/k_B TV = \Phi_{id} + \Phi_{ex}, \quad (5)$$

where  $A$  is the Helmholtz energy and  $\Phi^{id}$  is the ideal gas contribution, the excess part for a system comprising free ions and dipolar pairs then reads in the most general form [25]

$$\Phi_{ex} = \Phi_{hc} + \Phi_{ii} + \Phi_{id} + \Phi_{di} + \Phi_{dd} - \rho_p^* \ln K(T), \quad (6)$$

where  $\Phi_{ex}$  is summed over the hard-core ( $hc$ ), ion-ion ( $ii$ ), ion-dipole ( $id$ ), dipole-ion ( $di$ ) and dipole-dipole ( $dd$ ) contributions. By symmetry,  $\Phi_{id} = \Phi_{di}$ . The last term in eq. 6 reflects the internal partition function of the ion pair which depends on the pair equilibrium constant  $K(T)$ .  $\rho_p^*$  is the reduced density of the pairs. One major challenge for theories that incorporate dipole-dipole interactions between pairs is then an adequate incorporation of a state-dependent dielectric constant [25], because, as shown, dipole-dipole interactions between pairs cause  $\epsilon$  to increase. Reported equations of state for ionic fluids can be classified according to the terms retained in eq. 6 and the approximations for these terms [1].

For obtaining a simple and internally consistent treatment of the screened interactions in the complete equation of state (eq. 6), one has to resort to DH-type approaches [12], although there are many current efforts to obtain the same level for MSA-based theories [1,4]. Extending a theory by Levin and Fisher based on DH theory and a Bjerrum-type association model [12], Weiss and Schröder [25] have analyzed the role of the various terms in the complete eq. 6. The theory accounts for the essential features of the RPM deduced from simulation data. The coexistence curves [25] and conductance minima [15] are predicted, but it is fair to say that there is still a lack of quantitative agreement both with simulations and experimental data.

The detailed theoretical analysis clearly pinpoints the role of interactions of the pairs with free ions and with other dipolar pairs. With regard to the conductance behavior, the shielding of pairs by the free ions can already cause the conductance to increase, but this simple picture fails at lower  $T^*$ , where DI and DD interactions become increasingly important. There is no need for invoking triple ions in the explanation of the conductance minimum. In contrast, the increase of the dielectric constant by the increasing number of ion pairs seems to form an important ingredient. It is also found that the mechanisms responsible for the conductance minimum cause phase separation at higher concentrations.

## CRITICAL BEHAVIOR OF IONIC FLUIDS

The observation of phase transitions driven by Coulomb forces raises questions regarding the universality class of such systems [1–5]. It is known since a long time that near critical points liquid-vapor and liquid-liquid phase transitions of nonionic components exhibit an Ising-like critical behavior rather than mean-field criticality implied by the popular analytical expressions of the free energy in powers of temperature and density. These anomalies are describable by power laws of the form [26]

$$X = X_0 t^\mu + \dots \quad (7)$$

Here,  $X_0$  is a nonuniversal amplitude and  $\mu$  a universal critical exponent. The reduced temperature  $\tau = [(T - T_c)/T_c]$  describes the temperature distance from the critical temperature  $T_c$ . Among others, the

Ising-like universality rests on the short-range nature of the interaction potentials, which for  $r^{-n}$  potentials in three-dimensional systems implies  $n > 4.97$  [3,4].

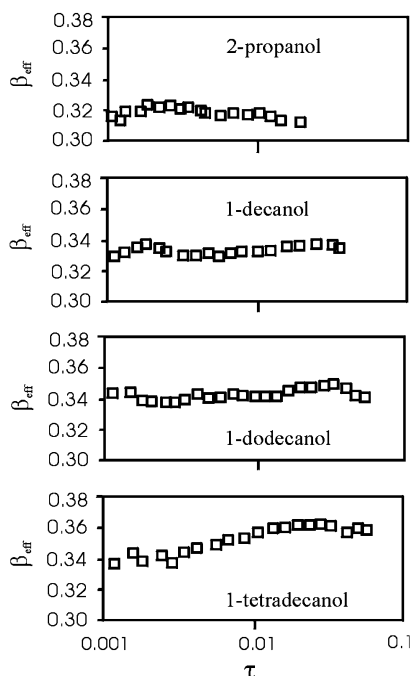
Clearly, this condition is not fulfilled by the bare Coulomb interaction, which may then give rise to mean-field critical behavior. This was just the result of remarkable experiments of Pitzer and coworkers [2]. On the other hand, in real fluids Coulomb interactions are screened to short-range, which may restore an Ising-like criticality [3,4]. This crucial role of screening puts the problem at the very heart of electrolyte theory. Unfortunately, an RG treatment of the RPM or other model electrolytes seems still to be some way ahead, and thus, the problem of ionic criticality has stimulated intense experimental activities, for example, summarized in ref. [1]. It seems now that some experiments indicating mean-field like criticality cannot withstand closer examination [1].

However, there are still many open problems. In particular, more recent accurate experiments [6] seem to indicate a cross-over scenario to mean-field behavior with cross-over temperatures much closer to the critical temperature than observed with normal fluids. Focusing on the behavior of the coexistence curve, the key quantity is the order parameter  $M$  that obeys the scaling law

$$M = B_0 \tau^\beta (1 + B_1 \tau^\Delta + \dots) \quad (8)$$

where  $B_0$  is the critical amplitude and  $\beta$  is a universal critical exponent. The parentheses contain corrections to scaling, as represented here by the first term of a Wegner series with an amplitude  $B_1$  and the universal exponent  $\Delta \cong 0.5$ . In liquid mixtures,  $M$  reflects the difference in compositions of the coexisting phase, often expressed in terms of volume fractions. Ising-type universality implies  $\beta = 0.326$ , while mean-field criticality exhibits  $\beta = 0.5$ . Deviations from asymptotic behavior are often illustrated by an effective exponent defined by  $\beta_{\text{eff}} = d \ln M / d \ln \tau$ , which reflects the local slope in the double logarithmic plot of  $M$  vs.  $\tau$ .

Figure 4 shows effective exponents  $\beta_{\text{eff}}$  of tetra-*n*-butylammonium picrate dissolved in several alcohols as a function of the reduced temperature based on volume fractions as an order parameter. When



**Fig. 4** Effective exponents  $\beta_{\text{eff}}$  of tetra-*n*-butylammonium picrate dissolved in several alcohols as a function of the reduced temperature based on volume fractions as an order parameter.

approaching the Coulombic limit by increasing the chain length  $n$  (see also Fig. 3) deviations from Ising-like behavior become visible such indicating a trend toward mean-field behavior comparatively close to  $T_c$ .

Far away from the critical regime mean-field theory should apply, and there is a well-known criterion by Ginzburg that predicts the range of validity of mean-field theory, as characterized by the Ginzburg temperature  $T_{Gi}$  [27]. This type of analysis, subsequently worked out in many other versions, works well for nonionic fluids. In accordance with experimental observations it predicts the cross-over to occur far away from the critical temperature. According to the experimental results,  $T_{Gi}$  for ionic fluids should differ substantially from that of nonionic fluids. Several studies [1], including extensive calculations based on models conforming to the EOS (6) [28,29], have shown that  $T_{Gi}$  of ionic systems becomes even larger than that of normal fluids. In this respect, the theory is clearly in variance to what is expected from the experiments.

Because cross-over from these arguments cannot be explained, there is the pressing question what else may be responsible for the observed effects. Calculations of ionic systems that include dispersion interactions [30], such as the RPM lattice [31], both yield a tricritical point suggesting the existence of some real or virtual tricritical point in ionic fluids, which in three-dimensional systems is mean-field-like. Experimental evidence for tricriticality has come from light-scattering data for the ternary system NaBr/water/3-methylpyridine [8]. For such ternary systems, tricritical behavior forms a more natural scenario than in binary systems. However, recent experiments for this system do not confirm this observation [32,33].

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