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Coulombic and Non-Coulombic Contributions to the Criticality of Ionic Fluids. An Experimental Approach

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The recent discovery of liquid–liquid phase separations in electrolyte solutions with critical points near room temperature enables the systematic study of the critical behavior of ionic fluids. Depending on the nature of the molecular interactions, either sharp mean-field or Ising behavior is obtained in the temperature range down to $t = (T - T_c)/T_c = 10^{-4}$ or less. Mean-field-like criticality is obtained with systems which in the framework of a simple corresponding states model are fairly close to the critical point of the "restricted primitive model" (RPM) of equally-sized charged spheres in a dielectric continuum. In these cases the phase separation is driven by the Coulombic forces (so-called *Coulombic phase separations*). This type of unmixing occurs for 1:1 electrolytes in solvents of low dielectric constant. Simple mechanisms for unmixing suggested in the literature are discussed in relation to the available data. Some evidence for departures from the simple RPM prediction is found. The presence of additional short-range interactions leads to sharp Ising behavior. Examples are solutions of tetraalkylammonium salts in water and other highly structured solvents, where phase separation results from the peculiar solvophobic nature of ions (*solvophobic phase separations*). Previous speculations that this type of unmixing shows the tendency toward closed loops are confirmed by the first direct observation of a lower consolute point in an aqueous solution of propyl-tributylammonium iodide. By light scattering studies and measurements of the coexistence curve near the upper and lower consolute points Ising criticality is confirmed. A new mechanism for phase separation is reported for the system ethylammonium nitrate + octanol, where ion pairs are stabilized by hydrogen bonding beyond what is expected from the RPM. This comparatively subtle additional interaction (so-called *stricky ions*) already changes the behavior of

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otherwise RPM-like systems from mean-field to Ising criticality. The results are discussed with particular emphasis on their implications for possible scenarios for explaining a mean-field critical point or crossover from mean-field to Ising behavior beyond the accessible temperature range.

KEY WORDS: Phase separations; critical phenomena; critical exponents; ionic fluids; electrolyte solutions; light scattering; intermolecuar interactions.

1. INTRODUCTION

The molecular theory of phase transitions is complex. In the near-critical regime one finds, however, simple power laws with "universal" critical exponents, no matter what the form of the molecular interaction is. Thereby, liquid–gas and liquid–liquid phase transitions of simple fluids fall into the university class of the three-dimensional Ising model. Lars Onsager's two-dimensional analog of this model(1) is a landmark in understanding these phenomena.

In view of this universality, an exciting development has been the observation of *mean-field (classical)* critical behavior of ionic fluids with exponents $\beta = 0.5$ of the coexistence curve,(2) $\gamma = 1$ of the osmotic susceptibility,(3, 4) and $\nu = 0.5$ of the correlation length of the critical fluctuations.(3, 4) The corresponding Ising values are $\beta \cong 0.325$, $\gamma \cong 1.24$, and $\nu \cong 0.63$. Over the years, there have been repeated speculations on such a mean-field behavior of fluids with long-range interactions, partly based on coexistence curve data for molten salts(5) and liquid metals (e.g., ref. 6). However, only the recent discovery and systematic exploitation of liquid–liquid phase separations in electrolyte solutions with critical points (CP) near room temperature(7, 8) now enable measurements with the high accuracy needed in such studies. A major challenge for theory is therefore to explain the origin of this behavior. If, nonetheless, one insists on an Ising-like CP, a crossover(9–11) from mean-field to asymptotic Ising behavior must occur. However, one of the features of the experimental data is that mean-field behavior is quite sharp in the sense that no direct evidence for crossover is found in the accessible temperature range. Then, theory has to explain why this is not seen in a range where uncharged fluids are in the asymptotic Ising-like regime.

As Ising behavior is expected if the correlation lengths of the critical fluctuations are much greater than the range of the pair potential energy, it is tempting to attribute mean-field behavior to the long-range nature of the Coulombic interactions. In fact, it is known that for infinitely weak, infinitely long-range attractive forces mean-field behavior becomes exact.(12) More recent work has shown that for interaction potentials with a distance dependence of $1/r^n$ critical exponents begin to depart from Ising behavior for $n < 4.97$,(13) and become mean-field-like for $n < 4.5$.(14) The same limit for the interaction potential is obtained from a renormalization group analysis(15, 16): For an interaction potential of the form $r^{-(d+\sigma)}$ with $0 \leqslant \sigma \leqslant 2$ a generalized mean-field behavior is expected for dimensions $d \geqslant 2\sigma$ with critical exponents $\gamma = 1$, $\alpha = 0$, $\beta = 1/2$, $\delta = 3$ as expected from mean-field theory, but $\nu = 1/\sigma$ and $\eta = 2 - \sigma$, which only for $\sigma = 2$ agree with the conventional mean-field values. Hence, at a first glance, the Coulombic interaction appears to fall into the mean-field university class. However, in the presence of charges these interactions may be exponentially screened to a short range by Debye screening,[17] which should then restore an Ising-like CP. However, interestingly, $1/r^4$-independent interactions fall also into this class, which gives rise to important questions concerning the nature of these forces, their shielding, and the consequences for critical behavior.

More elaborate theories have to start with well-defined Hamiltonians that are bound to models for the intermolecular potential, but retain the skeleton of the properties of pure fluids. For ions with charges $z_i e$ and $z_j e$ in a dielectric continuum with the dielectric permittivity (dielectric constant) D a plausible form is

$$u_{ij}(r) = z_i z_j e^2/Dr + u_{ij}^*(r) \tag{1}$$

where the first term accounts for long-range Coulombic interactions, while the second one involves all short-range contributions. The simplest form for $u_{ij}^*(r)$ is the restricted primitive model which accounts for a hard-core repulsion with equal diameter a of all ions

$$u_{ij}^*(r) = \begin{cases} +\infty & r \leqslant a \\ 0 & r > a \end{cases} \tag{2}$$

As this model predicts an instability regime with an upper CP,(18–23) it has generally been assumed that it forms a natural starting point for discussing the criticality of ionic fluids. In fact, in their work on the CP of the RPM fluid, Stell and collaborators(21–23) have come to the conclusion that the CP of the RPM is Ising-like. However, some questions in its regard remain.(23, 24) On the other hand, a theory of Khodolenko and Beyerlein(25, 26) claiming spherical model (see, e.g., ref. 27) rather than Ising or mean-field critically of the RPM appears to have no sound basis.(28)

Actually, the observed critical behavior of ionic fluids is, however, richer than so far discussed. Real ions are not hard spheres and solvents do not form dielectric continua. A key question therefore concerns the role of additional contributions to $u_{ij}^*(r)$ in *real* systems which, among others, may contain terms reflecting short-range effects of the solvent. Also, one may think of various specific interactions among the ions themselves. The observation of Japas and Levelt Sengers(29) of an Ising-type liquid–liquid coexistence curve in the system tetrapentylammonium bromide (Pe_4NBr) + water shows that non-Coulombic contributions can even control criticality. In analogy to similar processes in aqueous non-electrolyte systems, immiscibilities of the latter type appear, however, to be driven by short-range interactions between solvophobic ions and water(7, 30–32) or other highly structured solvents like glycerol or ethylene glycol.(7) We have suggested the term *solvophobic unmixing* in order to discriminate this behavior from the *Coulombic unmixing* in RPM-like systems.(7)

However, long-range Coulombic forces are present in solvophobic systems as well, and in our opinion, the duality between long-range interactions is as large a mystery as is the criticality of the RPM. In fact, these observations give rise to pressing questions:

What are the relevant molecular interactions, and which parameters control criticality? Are there mechanisms not covered by this classification, and what is their universality class? Are there systems intermediate between the Coulombic and solvophobic cases? What role is played by non-Coulombic forces, necessarily in the real RPM-like systems as well? As continuously variable exponents are very unlikely on theoretical grounds, where is the borderline between Ising and mean-field behavior?

In our opinion, it is mandatory for theory to consider these questions as well. Thereby, well-designed experiments are required for guiding the theory, because one may think of various theoretical scenarios.(24) Thereby, apart from direct experiments on critical behavior, the study of the relevant intermolecular interactions is also needed. In trying to sharpen this experimental background, and seeking at least partial answers to these questions, we report here on new results on phase equilibria and criticality of ionic fluids, and reconsider the current state of the art in the experimental field, with special emphasis on the implications for theory.

2. THE CRITICAL POINT OF COULOMBIC SYSTEMS AND THE RESTRICTED PRIMITIVE MODEL

In preparation for the subsequent discussion we summarize here some (partly new) aspects of Coulombic phase equilibria in relation to the RPM. The phase diagram of the RPM is principally the same as for simple uncharged fluids with a two-phase region with an upper CP. In the following we use reduced variables defined by scaling the thermal energy

k_BT with respect to the maximum depth of the Coulomb potential, $\varepsilon = |z_i z_j| e^2/Da$, and the density with respect to the excluded volume:

$$T^* = k_B TDa/|z_i z_j| e^2 \tag{3}$$

and

$$\rho^* = \rho a^3 \tag{4}$$

where $\rho = (N_+ + N_-)/V$ is the total number density of ions. According to Fisher's analysis(24) of the Monte Carlo data of Panagiotopoulos(20) the best estimate is

$$T_c^* = 0.057 \tag{5}$$

and

$$\rho_c^* = 0.030 \tag{6}$$

While in our paper these figures will be taken as a reference, we note that new work by Caillol(33) ($\rho_c^* = 0.04$) taken along with the older analysis of Pitzer and Schreiber[19] ($\rho_c = 0.05$) indicate that there are considerable uncertainties at the upper side of this critical density, and suggest that $\rho_c^* = 0.05$ may form a reasonable upper bound. In any case, the critical temperature and the critical density are largely displaced to low T^* and low ρ^* if compared with the critical coordinates of simple uncharged systems, as exemplified by Lennard-Jones (LJ) fluids with $T_c^* = 1.35$ and $\rho_c^* = 0.35$ (e.g., ref. 34).

According to corresponding states arguments, this instability regime may (among others) be reflected by the liquid–vapor transitions of molten salts(35, 36) and liquid–liquid immiscibilities of 1 : 1 eletrolytes in solvents of low dielectric constant, $D > 10$, say.(7, 35–37) Moreover, if D is a strongly decreasing function of temperature, the upper CP may turn into a lower one, as, e.g., observed with certain 2:2 electrolytes in water at elevated temperatures.(30) Only immiscibilities of 1 : 1-electrolytes in low-D solvents occur, however, at temperatures low enough for accurate studies of critical behavior. The latter systems generally involve low-melting salts to suppress the interference of crystallization. The ions should not deviate too much from spherical shape, and have no localized interactions with the solvent or among themselves. Quaternary ammonium salts meet these criteria, and the systems used in accurate studies of critical behavior fall into this group: tetrabutylammonium picrate (Bu_4N Pic) in tridecanol(3) and *n*-hexyl-triethylammonium *n*-hexyl-triethylborate (Et_3HexN Et_3HexB) in diphenyl-ether.(2,4) Figure 1 displays the coexistence curve of $Bu_4NPic +$ tridecanol,(7) which exhibits typical features also found with other systems: a large asymmetry, and the location in the solvent-rich regime, reflecting the low critical density of the RPM.

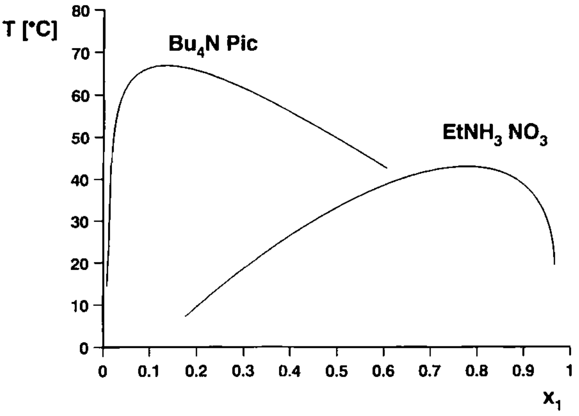

Fig. 1. Liquid–liquid coexistence curves of the systems $Bu_4NPic + tridecanol$ and $Et_3NH_3NO_3 + n\text{-octanol}$. x_1 is the mole fraction of the salt.

Figure 2 compares the CP of these and some closely related systems with the coexistence curves predicated for RPM and LJ fluids. Qualitatively, all systems map onto the RPM prediction. Interestingly, $KI + SO_2$ shows a lower CP,(38) which nevertheless appears to correspond to Coulombic unmixing. Moreover, the RPM prediction also appears to

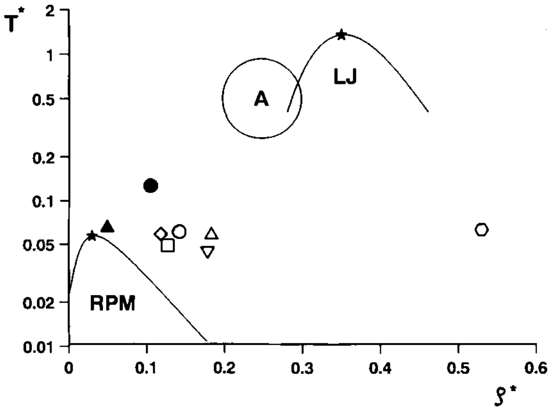

Fig. 2. Corresponding-states plot of critical points of the RPM and LJ fluids in comparison with experimental data: (○) $Bu_4NPic + 1\text{-chloroheptane}$(55) ($D = 3.8$, $a = 0.65$ nm); (△) Bu_4NPic + tridecanol(3) ($D = 4.4$, $a = 0.65$ nm); (▽) Bu_4N Pic + hexadecanol(7) ($D = 3.13$, $a = 0.65$ nm); (□) Et_3HexN Et_3HexB + diphenylether(2) ($D = 3.70$, $a = 0.7$ nm); (◇) $KI + SO_2$(38) ($D = 8.1$, $a = 0.353$ nm); (▲) NaCl; (●) $Na + NH_3$(40) ($D = 23$, $a = 0.45$ nm); (○) $EtNH_3NO_3 + n\text{-octanol}$(73) ($D = 8.4$, $a = 0.4$ nm). The circle A characterizes the location of upper and lower CP in aqueous solutions of tetraalkylammonium salts. Dielectric constants of the solvents were taken from ref. 82.

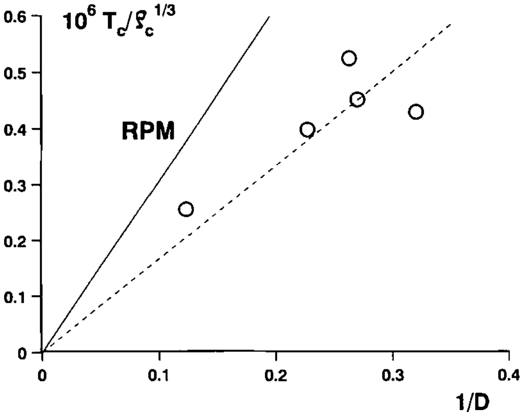

Fig. 3. Examination of Eq. (7) for liquid–liquid phase separations in electrolyte solutions. The solid line reflects the RPM prediction. The unit of $T/\rho^{1/3}$ is K m.

reproduce the liquid–liquid CP of the sodium + ammonia system at about 232 K,(39, 40) if this system is treated as an electrolyte consisting of Na^+ ions and electrons with $a = 0.4$ nm. In fact, it is known(39) that such a model is able to describe various properties of the Na + ammonia system near the dilute branch of the coexistence curve. Figure 2 would therefore suggest that this phase transition is merely a consequence of the general instability of charged systems under the peculiar conditions of temperature, density, and dielectric constant, and is not directly related to the metal–nonmetal transition occurring in this system. This is of peculiar interest, because the Na + ammonia system represents the only example for a low-molecular-weight fluid which exhibits crossover: far from T_c mean-field behavior is observed, but there are indications for a quite sharp crossover to Ising behavior about 1 K above T_c.(40–42)

At a first glance, a more quantitative analysis seems to be hampered by an insufficient knowledge of diameters of large ions with flexible alkyl chains. If, nonetheless, one uses plausible estimates, one finds the reduced temperature to be correct, but the reduced densities are by a factor of 3–6 higher than predicted (!), depending on the choice of the theoretical estimate, although lower than found with nonelectolytes. Except in ref. 36, this displacement has been overlooked in previous work. The effect is, however, too large to be ignored.

This conclusion is reinforced when eliminating the diameter from Eqs. (3) and (4), which then predicts a proportionality between $T_c/\rho_c^{1/3}$ and D^{-1},

$$T_c/\rho_c^{1/3} = A\ |z_+ z_-|/D \tag{7}$$

with the slope $A = e^2 T_c^* / \rho_c^{*\,1/3}$. The corresponding plot in Fig. 3 yields indeed a straight line with zero intercept, but the approximate slope (1.65×10^{-6} K m) differs largely from the RPM prediction based on Eqs. (5) and (6) (3.06×10^{-6} K m). Hence, independent of the uncertainties in the diameter, there is much evidence that the reduced critical density of real electrolytes is much higher than the RPM prediction, $\rho_c^* = 0.15$, say.

Is this also true for molten salts? The CP values of alkali halides are unknown, but reasonable extrapolations can be made which for NaCl yield $T_c^* \cong 0.067$ and $\rho_c^* \cong 0.05$.(35) Similar figures are obtained with KCl.(35) The difference is now scarcely outside the uncertainties of the underlying experimental and theoretical figures. Hence, there is much evidence that when treating real molten salts and solutions on a corresponding states level, there are distinct differences between the groups. Obviously, in the presence of solvents there are pronounced contributions not covered by the RPM. The critical temperature is little affected in these cases.

3. CONTINUUM MODELS BEYOND THE RPM

A first improvement is to replace the hard-core diameter by radii which differ for positive and negative ions in the "unrestricted primitive model" (UPM). This is important in the light of Stell's recent work(23): In the RPM the two quantities, charge and mass, fluctuate independently. As at the CP only the fluctuations of mass become infinite, the resulting critical behavior should be the same as that of uncharged fluids, i.e., Ising-like. A coupling between charge and mass fluctuations is, however, restored in the UPM when losing the high symmetry of the RPM. Hence, in the simple picture of the RPM just those contributions may be lost which generate the mean-field critical point.

What can be gained from experiments? While in the context of the UPM the symmetry is broken by differing sizes (or charge numbers) of anions and cations, it is obvious that in real systems symmetry can also be broken by any disparity between anion–solvent and cation–solvent interactions. An interesting question is whether such a solvent-induced symmetry breaking may explain the difference between molten salt and solution critical densities observed by us. On the other hand, no substantial differences are seen in Fig. 2 among the solutions themselves: The reduced critical density of the system containing the symmetrical salt $Et_3HexN\,Et_3HexB$ does not differ substantially from those of less symmetric systems.

Next, we consider some other possible scenarios within and beyond the RPM. As noted in the Introduction, $1/r^4$-dependent terms may play a role in determining critical behavior. First, we note that in the RPM the dielectric continuum penetrates the ions. To counterbalance this effect, a so-called "cavity term" may be introduced, so that

$$u_{ij}^{*}(r) = \mathrm{COR}_{ij}(r) + \mathrm{CAV}_{ij}(r) \tag{8}$$

Here, $\mathrm{COR}_{ij}(r)$ is any hard- or soft-core repulsion term, and $\mathrm{CAV}_{ij}(r)$ stands for the cavity term. As treated in detail by Stell,(22, 23) these cavity terms exhibit a repulsive $1/r^4$ dependence which leads to peculiar critical behavior: If not canceled by the attractive $1/r^4$-dependent ion–dipole interactions, one expects a so-called charge-density-wave instability which suppresses critical fluctuations. The effects of such charge-density waves have been described by Nabutovskii *et al.*(43) and Hoye and Stell.(44) Their work suggests that such effects may be experimentally observable in electrolyte solutions.

In more detail, even in a continuum solvent a series of further interactions may be important(22): continuum electrostatics yields for the interaction of a charge with a sphere(45, 47)

$$\varphi(r) = \frac{1}{2D}\,\frac{D - D_0}{2D + D_0}\,\frac{a^3}{r^4}\,q^2 + O\left(\frac{1}{r^6}\right) \tag{9}$$

where D and D_0 are the values of the permittivity outside and inside the sphere, respectively, a is the radius of the sphere, and q is the charge. Clearly, for $D > D_0$ the interaction is repulsive, and with $D_0 = 1$ we retain the cavity repulsion mentioned above. On the other hand, for $D = 1$, $\varphi(r)$ is the charge-induced dipole interaction in vacuum, with the polarizability α defined by

$$\frac{\alpha}{a^3} = \frac{D_0 - 1}{D_0 + 2} \tag{10}$$

In the light of the importance of shielding in scenarios of critical behavior, a prime question is then whether these terms are screened by Debye shielding. Some insight may be obtained by noting that the electric potential outside a dielectric sphere in a medium polarized by a field $\mathbf{E}$ is that of an ideal dipole $\mathbf{m}$ at the center of the sphere surrounded by vacuum(47)

$$\mathbf{m} = \frac{D - D_0}{2D + D_0}\,a^3\,\mathbf{E} \tag{11}$$

In our case $\mathbf{E} = -(q/r^2)\,\mathbf{r}/r$, so that $\varphi(r)$ represents the interaction of q with $\mathbf{m}$. The factor 1/2 in Eq. (9) results from the charging process so that

$\varphi(r)$ is a potential of the mean force. Shielding then results from the polarizing field **E** which is screened by the factor

$$(1+\kappa \cdot r)\exp(-\kappa \cdot r) \tag{12}$$

with the usual definition of the Debye length $1/\kappa$ by

$$\kappa^2 = 4\pi \cdot e^2 \sum \rho_i z_i^2 / D \cdot k_B T \tag{13}$$

While so far the arguments are based on continuum electrostatics, an answer by statistical mechanics requires the consideration of models treating the solvent as distinct particles rather than the introduction of effective Hamiltonians as in the RPM. While progress has been made for mixtures of hard-sphere dipoles and charged hard spheres,(48, 49) an exact theory for $\varphi(r)$ is not available. On may, however, note that when considering the cluster expansion of the potential of mean force of two ions in a fluid of hard-sphere dipoles ($D_0 = 1$), Jepsen and Friedman(45) found an expression which in first order of $(D-1)/(D+2)$ agrees with the result of continuum electrostatics. The question of shielding of this interaction by free ions has, however, not been addressed. On the other hand, Hoye, Stell, and collaborators have shown that the charge–dipole interaction between ions and hard-sphere dipoles becomes short range by Debye shielding.(48, 49) Then it seems reasonable to expect that this holds also for the interaction of a charge with the dipole **m** as given in Eq. (11) that is induced by a charge in a polarizable sphere immersed in a dielectric medium.

From the experimental point of view, little is known on $1/r^4$-dependent terms. In particular, there appears to be no conclusive example for effects associated with charge-density-wave instabilities, although Nabutovskii *et al.*(43) have suggested that these may be even seen in aqueous electrolyte solutions. We would, however, like to draw attention to a widely overlooked paper by Schindewolf and collaborators,(50) in which a discontinuity has been reported in the heat capacity of Na + ammonia along isotherms up to 60 K above T_c which might possibly reflect this instability. Unfortunately, the presence of a metal–insulator transition in this regime complicates the interpretation.

4. THE PARTICLE DISTRIBUTION NEAR THE CRITICAL POINT OF COULOMBIC LIQUIDS

A further important aspect to be treated here concerns the species distribution in the T^*–ρ^* regime of interest in relation to the physical origin of the phase separation. What is predicted, and what can be gained from experiment?

In seeking a simple picture which embodies the main physical effects, Fisher and Levin(24, 51) presented a comparatively simple theory in remarkable agreement with Monte Carlo results. Noting that the RPM forms the conceptional basis of the Debye–Hückel (DH) theory, they showed that DH theory predicts indeed an instability regime, but the critical density is far too low. Incorporation of Bjerrum (Bj)-type ion association known to be present in the low-D regime largely improves the results. Bjerrum's approach(52) estimates the population of ion pairs by assuming a "chemical" equilibrium between free ions and pairs. The pairs are assumed to act as ideal solutes, while free ions are treated by the standard DH procedure. Bjerrum's definition leads to an association constant of the form

$$K(T)=\int_{a}^{a/2T^*} \exp\left(\frac{a}{rT^*}\right) 4\pi r^2\,dr \tag{14}$$

This predicts indeed a CP with ρ_c^* shifted toward higher values, as now a larger ion density is needed to produce the necessary number of free ions.

However, this cannot be the full truth: large ion pairs have dipole moments up to 20 Debye, and these dipoles may interact with the remainder of the ionic fluid as with one another. So, in the context of a reliable theory, the picture of noninteracting dipolar pairs connot be retained. In fact, the coexistence curve obtained from DHBj theory is little satisfactory, although the critical coordinates are quite acceptable.(51) One scenario to deal with this defect has been discussed in detail by Fisher and Levin(24, 51): incorporating the interaction of the ion pair dipoles with the remainder of the screening ionic fluid brings the theory into satisfactory agreement with the Monte Carlo data.

Actually, there is, however, some degree of arbitrariness in the definition of ion pairs, and also in the way in which these are incorporated into (linearized) theories. Unfortunately, the critical coordinates appear to be rather sensitive to details of the theory. Thus, Fisher and Levin's choice of the Bjerrum model does not form the only option. The traditional picture of solutions in low-D solvents assumes the presence of distinct ion triplets and higher associates which may be incorporated into a chemical model of ion association.(53) Also, ion pairs may increase the dielectric constant of the solvent, which could constitute a distinct mechanism of phase separation.(54) In fact, Stell(23) notes that one has a considerable spectrum of other possible variants which lead to reasonable estimates of the CP of the RPM predicted by Monte Carlo data. While the success of the Fisher–Levin model thus indicates the importance of ion pair–free ion coupling, at the present level of understanding a good match of the coexistence curve alone may not signify that all effects have been captured.

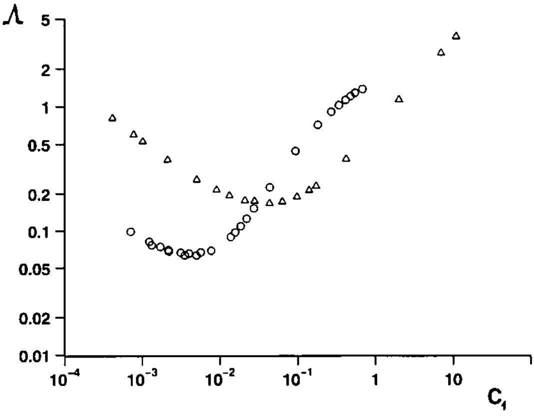

Fig. 4. Equivalent conductance of Bu_4NPic + tridecanol (○) and $EtNH_3NO_3$ + *n*-octanol (△). C_1 is in mol dm^{-3}; Λ is in S cm^2 mol^{-1}.

Can suitably chosen experiments help to resolve this question? In the absence of (neutron) scattering data, the electrical conductance is the major source of information. We have recently studied the conductance in several systems with liquid–liquid phase separation. As an example, Fig. 4 shows the equivalent conductance Λ for Bu_4NBr in tridecanol about 6 K above T_c.(7) The major feature is a rapid decrease of Λ with increasing salt concentration in the dilute regime, mainly beyond the concentration range accessible by experiments, followed by a substantial increase toward molton salt-like conductances at the CP. This conductance minimum is generally observed for $T^* < 0.12$, so it should constitute a common feature of systems with Coulombic phase separation.

Let us first consider the consequences for pair association. The evaluation of the low-concentration branch of the conductance curve yields the pair association constant $K(T)$, but at low T^* the conductance minimum is shifted to very low concentrations, so that few data points may be available, and Λ is only a small fraction of the limiting conductance Λ^0. On the basis of plausible estimates of Λ^0, we obtain $K(T_c) = 3 \times 10^9$ dm^3 mol^{-1} for this system. Schreiber *et al.*(55) reported $K(T_c) = 1.1 \times 10^8$ dm^3 mol^{-1} for another system with liquid–liquid phase separation, Bu_4N Pic in 1-chloroheptane. Both figures do not show gross discrepancies with the Bjerrum prediction.

The more interesting part of the conductance curve is, however, that above the minimum, which is directly related to effects beyond the pair approach, and which includes the CP. Conventional interpretations(53) attribute the minimum to the formation of charged triplets and larger conducting distinct species. In fact, carrying assumptions concerning the mobilities of the various charged species, the minima in both systems are well explained by ion triplets.(7, 55) This approach, however, does not cover the critical regime unless the presence of higher conducting and non-conducting aggregates is postulated. Such a cluster distribution, theoretically derived for the RPM near the critical isotherm,(19) may account for the conductance behavior,(55) but again there is some arbitrariness in the definition of the clusters.

Hence, the question remains of how far the picture of distinct ionic clusters is real. In fact, this is a long-standing problem, though ignored by most workers in the field. For example, a long time ago, Kraus and coworkers(56, 57) predicted a redissociation of ion pairs in the electric fields of other ions. A similar point of view was taken by Sukhotin.(58) This mechanism, now known as "redissociation,"(59–63) seems to correspond to Fisher and Levin's thermodynamic theory of ion pair–free ion coupling. However, a quantitative description of this effect by an elaborate conductance theory is lacking.

There is also some hope that a more subtle experimental approach may prove to be of value when discussing mechanisms for phase separation in the low-T^* regime. It is based on pair interaction coefficients $f_{ab}(a, b = +, -)$ (or in a slightly different version D^d_{ab}) derived from a combined analysis of conductance, transference, and self- and mutual diffusion data.(60–63) Essentially, diffusion and transference data are thereby used for separating the conductance into contributions from $++$, $--$, and $+-$ interactions. The latter are related to the corresponding equilibrium spatial distributions for a–b pairs by expressions of the form

$$f_{ab} \propto \int_0^{\infty} (g_{ab}(r) - 1) r \, dr \tag{15}$$

where $g_{ab}(r)$ is the usual equilibrium pair correlation function. Equation (15) predicts large positive f_{ab} when the corresponding distribution g_{ab} has a large peak, while usually the like-ion terms are negative due to Coulombic repulsion. In conjunction with model calculations, e.g., by integral equations theories,(62, 63) this approach seems to be particularly suitable for investigating the formation of larger than pairwise aggregates, because in such cases there are necessarily close like-ion encounters, causing g_{++} or g_{--} to have such a peak so that f_{++} and f_{--} become positive.

In fact, we have recently used this approach in a study of like-ion encounters in aqueous solutions of the 2:2 electrolyte $ZnSO_4$ at 298 K,(60) which is of direct relevance for the problems considered here. This system is well described by the RPM with $T^* = 0.1$–0.15 not far above T_c, and there is evidence for a lower CP in systems of this type near 500 K.(30) At 298 K, f_{++} and f_{--} are largely positive, which emphasizes the importance of larger aggregates, but the effect of ion pair–free ion coupling has not yet been considered in this context.

5. CRITICALITY OF COULOMBIC SYSTEMS

With the "Coulombic" liquid–liquid immiscibilities, it is possible to undertake measurements of critical behavior to milli–kelvin accuracy in temperature. Three studies of this type are now available.(2–4) Singh and Pitzer(2) were the first to report on accurate coexistence curve data for the room-temperature molten salt $Et_3HexN\,Et_3HexB$ dissolved in diphenylether with an upper CP near 317.17 K. In the asymptotic regime, the shape of the coexistence curve is expressed as (e.g., refs. 64 and 65)

$$\Delta x = x_1 - x_2 = Bt^{\beta} \tag{16}$$

with the reduced temperature $t = (T - T_c)/T_c$ and the order parameter Δx, where x_1 and x_2 characterize the compositions of the coexisting phases, e.g., in mole fractions or volume fractions. Beyond the asymptotic regime, a Wegner series in t allows for corrections to scaling

$$\Delta x = B_0 t^{\beta}(1 + B_1 t^{\Delta} + B_2 t^{2\Delta} + \cdots) \tag{17}$$

with $\Delta = 0.5$ exactly in mean-field systems and approximately in Ising systems. For nonionic mixtures the CP is Ising-like with $\beta \cong 0.325$, and the amplitude of the first correction term B_1 is very close to zero, so that the asymptotic regime extends, at least qualitatively, to temperatures far from T_c.(66)

Singh and Pitzer's data yield $\beta = 0.476$ down to at least $t = 10^{-3}$, which is reasonably close to 0.5 to claim mean-field behavior. Below $t = 10^{-3}$ the data are consistent with mean-field or Ising behavior, but in the latter case B_1 is anomalously large. An alternative scenario proposed by Khodolenko and Beyerlein(25, 26) claims the university class of the spherical model, which also predicts $\beta = 0.5$.(27) There are, however, severe doubts on the reliability of this analysis.(28)

To go further, static and dynamic light scattering measurements are the methods of choice. These yield the osmotic susceptibility, which diverges asymptotically as(64, 65)

$$\chi_T = \chi_0 t^{-\gamma} \tag{18}$$

and the correlation length of the critical fluctuations, which diverges as

$$\xi = \xi_0 t^{-\nu} \tag{19}$$

$\gamma = 2\nu = 1$ in the mean-field model, $\gamma = 2\nu - \eta \cong 1.24$ in the Ising model, and $\gamma = 2\nu = 2$ in the spherical model. $\eta \cong 0.04$ is the Fisher exponent.(64, 65)

As the exponents of the mean-field and spherical models are largely different, light scattering provides the desired information concerning the discrimination between the models. Such experiments have been performed by us at critical composition in the system Bu_4N Pic + tridecanol with T_c near 342 K,(3) and later by Levelt Sengers and collaborators in Pitzer's system Et_3HexN Et_3HexB + diphenylether.(4)

In detail, we have measured the scattered intensity and the time correlation function of the scattered intensity in the range $3 \times 10^{-4} < t < 3 \times 10^{-2}$, in conjunction with additional data such as turbidities and viscosities needed for data evaluation. Data evaluation has been primarily based on the intensity correlation function, giving the mutual diffusion coefficient, which, in turn enables the extraction of ξ by means of the Kawasaki mode coupling theory.(67) While the underlying theory is less rigorous than the Ornstein–Zernike theory of static scattering, contributions of double and multiple scattering can be more easily assessed in the former case. With these correlation lengths we were then able to recalculate the single- and multiple-scattering contributions to the static scattering intensity, yielding excellent agreement with the experimental data. Figure 5 shows the resulting divergence of the correlation length. Based on the

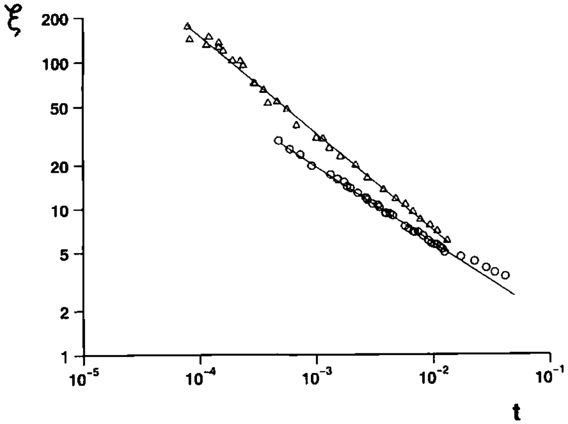

Fig. 5. Divergence of the correlation length ξ of the critical fluctuations of Bu_4NPic + tridecanol (○) and $EtNH_3NO_3$ + n-octanol (△). ξ is in nm.

Table I. Fits of Light Scattering Data to the Asymptotic Power Laws (18) and (19), assuming $\eta=0$, so that $\gamma=2\nu$

System	Method[a]	t range	$\nu=\gamma/2$	ξ_0 (nm)
Bu_4NPic + tridecanol(3)	TCF	$3\times10^{-4}<t<3\times10^{-2}$	0.525	0.5
Et_3HexN Et_3HexB + diphenylether(4)	TUR	$10^{-4}<t<10^{-1}$	0.505	1.0
$EtNH_3NO_3$ + octanol(76)	TCF	$3\times10^{-5}<t<10^{-2}$	0.61	0.45
$PrBu_3NI$ + water, upper CP[b]	TCF	$5\times10^{-4}<t<10^{-2}$	0.61	0.76
(this work)	SI	$5\times10^{-4}<t<10^{-2}$	0.58	0.93
	TUR	$5\times10^{-4}<t<10^{-2}$	0.58	0.95
$PrBu_3N$ I + water, lower CP[b]	TCF	$5\times10^{-4}<t<10^{-2}$	0.65	0.57
(this work)	SI	$5\times10^{-4}<t<10^{-2}$	0.62	0.67
	TUR	$5\times10^{-4}<t<10^{-2}$	0.65	0.56

[a] TCF, Data obtained from the time correlation function of the concentration fluctuations; SI, data obtained from measurements of the scattering intensity; TUR, data obtained from turbidity measurements

[b] Using Eq. (21) for redefining the reduced temperature.

asymptotic power law, the data yield the parameters in Table 1; in particular, we have $\gamma=2\ \nu=1.04$. A similar result has been obtained by Levelt Sengers and collaborators(4) (see Table 1). The results are sufficiently close to $\gamma=1$ to claim effective mean-field behavior, so that the spherical model is ruled out.

Moreover, we have also considered corrections to scaling, as obtained from the Wegner expansion for ξ.(3) Little is known on this expansion, but one may try(64, 65)

$$\xi=\xi_0 t^{-\nu}(1+\xi_1 t^{\Delta}+\cdots) \tag{20}$$

In doing so, our data are, in fact, consistent with an Ising-like exponent, but ξ_1 appears to be anomalously large in comparison with nonelectrolyte data. Thus our results are concordant with coexistence curve data: effective mean-field behavior is observed in a range where nonelectrolytes are in the Ising-like regime, but the possibility of crossover below $t\cong10^{-4}$ is left open.

Further interesting information concerns the correlation length amplitudes ξ_0 in Table I, which are by a factor 3–5 larger than typical figures for similar uncharged fluids. This is quite important in the context of crossover treatments, as large amplitudes might correspond to small asymptotic regimes, but we postpone a discussion until data for non-Coulombic systems have been presented.

6. COEXISTENCE CURVES OF SOLVOPHOBIC SYSTEMS

Phase separations of 1:1 electrolytes near room temperature with $T^* \cong 0.6$ have recently been discovered in aqueous solutions of higher tetraalkylammonium salts.(7, 30) Figure 2 shows the approximate location of these upper CP values in the corresponding-states plot, largely displaced from the CP of the RPM. This is particularly significant when noting that Japas and Levelt Sengers(29) have shown that a system of this type containing tetrapentylammonium bromide (Pe_4NBr) exhibits an Ising-like CP. This has led us to a detailed study of the solution thermodynamics of these systems, facilitated by a wealth of information on the thermodynamic behavior of the lower (completely miscible) homologs.(7, 30, 31) The results, not considered here in detail, show the typical features of immiscibilities in aqueous solutions of nonelectrolytes, driven by short-range forces associated with the solvophobic nature of the cations. The charges appear to be incidental to the phase separation.

Interestingly, aqueous solutions of fatty acids appear to fall into the same class: they show a fairly high conductance, but thermodynamics shows the typical features of phase separations caused by hydrophobic interactions. It has long been known that systems of this type (e.g., isobutyric acid + water(68)) show Ising-like behavior.

We have previously suggested(7, 31) that these gaps in aqueous solutions of tetralkylammonium salts may be *closed loops* with their lower parts suppressed by crystallization. By "tuning" the properties by variation of the alkyl chains, we have now indeed verified this presumption by direct observation of a lower CP in the system propyl-tributylammonium iodide

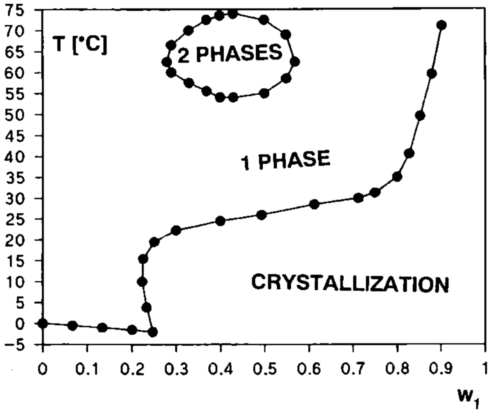

Fig. 6. Miscibility gap in the system $PrBu_3NI$ + water. The crystallization curve is also shown. w_1 is the weight fraction of the salt.

Table II. Fit of Coexistence Curve Data at the Upper and Lower CP of $PrBu_3N\,I$ + Water to the Asymptotic Power Law (16), with the Weight Fractions w_1 of the Salt as an Order Parameter[a]

	Upper CP	Lower CP
w_{1c}	0.4378	0.4457
T_c(K)	345.725	331.721
β	0.322	0.331
B	0.88	0.95
t range	$10^{-5} < t < 10^{-2}$	$5 \times 10^{-5} < t < 10^{-2}$
number of data points	18.	20.
Standard deviation χ^2	0.64	1.4

[a] w_{1c} is the critical weight fraction of the salt, T_c the critical temperature, and B the critical amplitude. Note that the reduced temperature has been redefined according to Eq. (21).

($PrBu_3N\,I$) + water. Figure 6 shows a very narrow closed gap with a lower CP at $T_c^L = 331.72$ K and an upper one at $T_c^U = 345.72$ K. The low CP make this system a promising candidate for investigations of critical behavior. (The small closed gap is also of interest in the context of "exponent doubling."(70, 71))

More accurate measurements of the coexistence curve have been performed by monitoring the transmitted light when crossing coexistence near the upper and lower CP.(69) For narrow closed gaps, the reduced temperature, however, has to be redefined: According to an appropriate form of the (mean-field) regular solution theory t is replaced by(70, 71)

$$t^* = t \pm (T_c/\delta)t^2 \tag{21}$$

with $\delta = T_c^U - T_c^L$, where the negative sign applies to the coexistence curve. This result is carried over to nonclassical behavior.(70, 71) Table II shows results obtained by fits of the upper and lower parts of the coexistence curve to Eq. (16) using the weight fraction of the salt as the order parameter. Ising behavior is obvious, but correct exponents are only obtained with t replaced by t^*, as also observed with other reentrant phase transitions.

7. MOLECULAR INTERACTIONS IN SOLVOPHOBIC SYSTEMS

As in the case of Coulombic unmixings, we may ask for the molecular picture of these phase separations. Unmixing implies (30) a strongly negative second virial coefficient $B(\kappa)$ in the virial expansion of he osmotic coefficient

$$\Phi - 1 = \Phi_{\mathrm{DH}} + B(\kappa)m + \cdots \tag{22}$$

where Φ_{DH} corresponds to the DH contribution, and m is the (molal or molar) salt concentration. In contrast to non-electrolytes, the second virial coefficient depends now implicitly on concentration, owing to Debye screening.

Standard interpretation attributes negative $B(\kappa)$ to the presence of specific short-range interactions in ion associates. A microscopic interpretation of this behavior has been discussed by Friedman and coworkers(32) in the context of model calculations using integral equation theory. To this end, Eq. (8) has been extended to the form

$$u_{ij}^{*} = \mathrm{COR}_{ij}(r) + \mathrm{CAV}_{ij}(r) + \mathrm{GUR}_{ij}(r) \tag{23}$$

The essential part of Eq. (23) is now related to the so-called "Gurney term" $\mathrm{GUR}_{ij}(r)$ which accounts for cosphere effects

$$\mathrm{GUR}_{ij}(r) = A_{ij}(V_{\mathrm{gu}}(r)/V_{H_2\mathrm{O}} \tag{24}$$

Here, $V_{gu}(r)$ is a function describing the volume of the overlapping part of the solvation spheres and $V_{H_2\mathrm{O}}$ is the molar volume of water. The "Gurney parameters" A_{ij} correspond to the change of the free energy when transferring water molecules from the bulk to the hydration sphere.

If this potential is parametrized to generate a CP, largely negative A_{++} and A_{+-} are obtained.(32) Negative A_{++} implies that close cation–cation pairs make $u_{+-}^{*}(r)$ less repulsive than resulting from the bare Coulombic repulsion. This reflects the stabilization of cation pairs driven by the peculiar conditions for hydrophobic particles in an aqueous environment. Negative A_{+-} values are perhaps more surprising, as they indicate the presence of cation–anion pairs driven by non-Coulombic interactions. We have, however, shown(7) that this result is concordant with large anion effects upon the size of the miscibility gap in the "lyotropic" series

$$F^{-} < \mathrm{Cl}^{-} < \mathrm{Br}^{-} < \mathrm{NO}_3^{-} < I^{-} < \mathrm{SCN}^{-} < \mathrm{ClO}_4^{-} < \mathrm{Pic}^{-}$$

contrary to what is expected from electrostatics. A possible picture is (32) that it costs little energy to dehydrate large anions, which are then stabilized in the environment of the cations, where D is low. Such ion pairing is also confirmed by conductance measurements in aqueous $\mathrm{Pe_4NBr}$ near the upper CP,(29) which have resulted in $K(T_c) \cong 7\ \mathrm{dm^3\ mol^{-1}}$, suggesting that at the CP 25% of the ions are associated. Moreover, widely distributed literature data indicate that $K(T)$ indeed increases with increasing cation and anion size, in agreement with the above interpretations.

8. LIGHT SCATTERING SOLVOPHOBIC SYSTEMS

Its favorable characteristics have led us to use aqueous $PrBu_3N\,I$ as a solvophobic model system in near-critical light scattering. The measurements were performed in analogy to those described above, but owing to more favorable conditions, the static light scattering intensity, the decay constant of the time correlation function of the concentration fluctuations, and the turbidity factor could be evaluated independently to obtain the correlation length ξ using standard procedures. These data evaluations are, however, intrinsically complex owing to the presence of a closed gap, and details are left to a future report.(69)

Figure 7 shows a master plot of the correlation length at the lower CP obtained by the three independent methods. Again the reduced temperature has to be redefined by t^*, but now in Eq. (16) the positive sign applies. While these measurements have been performed down to about $t = 10^{-5}$, a sensible data analysis could hitherto only be performed to $t \cong 5 \times 10^{-4}$. Beyond this range a large spread is shown by the three curves, the direction and magnitude of which are, however, consistent with what would be qualitatively expected from large double scattering contributions which could not yet be assessed in a quantitative way.

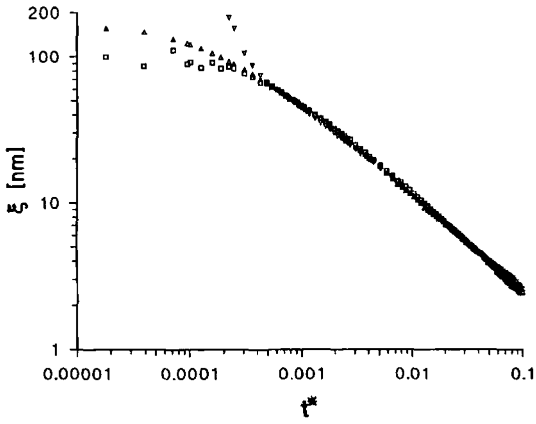

Fig. 7. Master plot of the correlation lengths deduced from the static light scattering intensity (□), the time correlation function of the concentration fluctuations (△), and the turbidity (▽). ξ is in nm.

Table I shows the results obtained by fitting the data at the upper and lower CP, respectively, to the asymptotic power law. The exponents obtained from these six independent determinations are sufficiently close to 0.63 to claim Ising behavior. Corrections to scaling are not needed, i.e., crossover phenomena are not seen.

9. A MECHANISM BEYOND THE COULOMBIC AND SOLVOPHOBIC CASES: IONS WITH STICKY INTERACTIONS

In seeking information concerning the interrelation between the intermolecular forces and critical behavior, one may ask whether there are mechanisms for phase separations beyond the Coulombic and solvophobic ones discussed so far. One idea has been to distort the Coulombic phase equilibria in solvents of low D by stabilizing ion pairs by hydrogen bonding. It is known (e.g., ref. 72) that hydrogen bonding in ion pairs has a pronounced effect upon the solution thermodynamics, resulting pair association constants up to three orders of magnitude larger than expected from Eq. (14). Appropriate systems may, e.g., contain partially substituted ammonium cations with residual protons as donors in conjunction with suitable anions. Systematic "tuning" of the alkyl substituents has resulted in an upper CP in mixtures of the room-temperature molten salt ethylammonium nitrate ($EtNH_3NO_3$) with *n*-octanol.(73)

The coexistence curve of this system in Fig. 1 is highly skewed, but in contrast to all other cases, the CP lies in the salt-rich regime at the mole fraction of the salt $x_{1c} = 0.773$, corresponding to a concentration of 7.3 mol dm^{-3}, as compared with 11 mol dm^{-3} of the pure molten salt. It is then quite difficult to estimate T^*, as certainly one cannot use D as obtained for the pure solvent. If, nonetheless, one does so, one finds T_c^* in Fig. 2 to be near the RPM prediction, but ρ_c^* is largely displaced toward higher densities. Conductance measurements in Fig. 4 show why this is so(73): $K(T_c) = 4.9 \times 10^5$ dm^3 mol^{-1} is more than an order of magnitude larger than predicted by Eq. (14). This additional stabilization appears to reflect hydrogen bonding in the pairs. As a consequence, one needs a higher salt concentration to achieve the necessary concentration of free ions to drive phase separation.

In a simple model used in integral equation theories for weak electrolytes (e.g., ref. 74) this can be accounted for by adding a *sticky interaction* between cations and anions to Eq. (2), which then reads

$$u_{ij}^*(r) = \begin{cases} \mathrm{COR}_{ij}(r) + \mathrm{STI}_{ij}(r), & i \neq j \\ \mathrm{COR}_{ij}(r), & i = j \end{cases} \tag{25}$$

where $\mathrm{STI}_{ij}(r)$ stands for a sticky interaction. While such models appear to have some physically unreasonable features,(75) it should be possible to model at least the displacement of the coexistence curve by turning on such an interaction.

In view of these results, we have performed light scattering measurements of critical behavior.(76) Figure 5 shows the correlation lengths deduced from dynamical scattering data. A fit of this curve to the asymptotic power law yields $\nu = 0.61$. Table 1 summarizes the results, which clearly show Ising criticality: no indications for crossover to mean-field behavior at large t are seen, and no corrections to scaling are needed.

10. THE ROLE OF THE CORRELATION LENGTH AMPLITUDE

As noted earlier, a key question concerns the role of the correlation length amplitude ξ_0 in determining critical behavior. Table 1 shows that the values hitherto obtained for Coulombic fluids (0.6 nm and 1 nm) are up to 5 times larger than the values typical for similar uncharged fluids (0.2 nm). Notably, when performing neutron scattering experiments in the system Na + ammonia, Chieux and coworkers also noted that in the mean-field regime, a comparatively large amplitude is found.(41, 42) To discuss the consequences of this fact in relation to our new results, it is necessary to consider crossover phenomena as predicted by Ginzburg-type theories(9–11) in some more detail.

Mean-field behavior is appropriate far from critical points. It applies when the reduced temperature distance from the critical point is much larger than the Ginzburg number

$$|t_G| = \mathrm{Gi} \equiv A \left(\frac{l_0}{\xi_0}\right)^6 \tag{26}$$

where the prefactor A is of the order of 0.01.(11) Here, l_0 is a molecular interaction length and ξ_0 is usually equated with the amplitude of the correlation length of hte critical fluctuations. In many simple fluids the asymptotic range is reached at $t < 10^{-2}$, followed by a large crossover regime roughly up to $t = 0.5$.(11) This means that mean-field exponents are never seen in simple fluids, because when crossover is complete, one is also outside the asymptotic range of mean-field theory.

Now, as, e.g., also noted by Levelt Sengers and Given,(77) the large amplitudes ξ_0 found in ionic fluids favor a small Ising regime, while large l_0 would favor a large Ising regime. In fact, the sixth power of the corresponding ratio greatly magnifies these effects. Hence, at a first glance, it appears to be straightforward to attribute mean-field behavior of Coulombic systems to ξ_0 values differing from those of nonionic fluids.

However, our data in Table I show that such unusually large amplitudes are also obtained in systems showing Ising-like criticality. (For the non-Coulombic cases ξ_0 in Table 1 refers to the nonclassical situation, but may be considered to represent a lower bound for the mean-field values.) Hence, it would appear that large ξ_0 values are a general feature of electrolytes not necessarily related to mean-field systems.

This directs attention to the other quantity in Eq. (26), as which ξ_0 values being equal for mean-field and Ising-like systems, the magnitude of the interaction length l_0 becomes crucial. Of course, one characteristic length in electrolyte solutions is the Debye screening length defined in Eq. (13). In fact, in the high-T^*, low-ρ^* regime, an exact expression exists for Debye screening, resulting in the famous Debye–Hückel limiting law for the activity coefficient. However, as is evident from Fig. 2, this is not the range where Coulombic unmixings are found. Unfortunately, little is known on screening at low T^*. If one uses the standard expression, Eq. (13), also in this regime, small l_0 values of the order of 0.2 nm or even less are found at critical concentrations. [Larger l_0 values would result when κ is replaced by κ^{free}, where κ^{free} refers to Eq. (13) with ρ being replaced by the actual concentration of free ions, i.e., $\kappa^{\text{free}} = \alpha^{1/2}\kappa$, where α is the degree of dissociation.] Hence, it remains to explain the observed Ising vs. mean-field dichotomy in terms of the shielding lengths.

11. CONCLUSIONS AND OUTLOOK

Let us come back to the questions posed at the beginning, and consider what is contributed by the above results and what consequences have to be drawn concerning future theoretical and experimental work.

It is now accepted that in contrast to normal fluid behavior, ionic fluids may show parabolic coexistence curves at least down to $t = 10^{-4}$ if Coulomb interactions determine the phase transition. Light scattering measurements rule out that this reflects the universality class of the spherical model, so that mean-field behavior appears now to be established. Fisher(24) and Stell(23) show that an alternative argument (not considered above) that the CP of ionic fluids is *tricritical* (which implies mean-field behavior) is unlikely. Hence, *the major challenge for theory is to explain the origin of this apparent mean-field behavior.*

While hitherto it has generally been assumed that the RPM forms the starting point for such theories, the work of Stell(23) would show that this model may just suppress effects of symmetry breaking which could be responsible for mean-field behavior. Such symmetry breaking can result from disparities in ion size and charges of the ions. In *real* ionic fluids it may also arise from solvation effects which may be different for anions and cations. *Is our observation of an increased critical density of electrolyte solutions as compared with that of pure ionic fluids somehow related to a larger asymmetry in solutions?*

If the CP turns out to be Ising-like, it will be mandatory for any theory to explain why no crossover is seen. Experimentally, one may hope to find such phenomena by a systematic change of state variables, similar to the situation in polymer solutions (e.g., ref. 78). At a first glance, this may include improvements in the experimental accuracy and measurements closer to the CP, to get improved upper bounds for the crossover temperature or even to enter the crossover regime. We recall, however, that the observed mean-field behavior is quite sharp, without *direct* evidence for crossover. Hence, even if in one of the existing cases crossover effects were found in the next decade closer to T_c, this would probably be marginal. *The first priority should therefore be to find cases of crossover not excessively close to T_c.* To this end, the design of new, chemically more stable systems seems to be needed. In this context, it should be recalled that crossover has indeed been observed in the sodium + ammonia system which shows a surprisingly sharp transition from mean-field to Ising behavior about 1 K above T_c.(40–42)

Another question is, of course, related to the understanding of crossover on a microscopic level. We have shown that large critical amplitudes are not necessarily related to mean-field behavior. This draws attention to the lengths scales characteristic for the intermolecular interactions in such systems. *What will the scaling lengths be, and which molecular parameters control crossover?*

In answering these questions, it is of prime importance to understand the processes driving phase separation on the molecular level. The Fisher–Levin model(51) offers such a picture in terms of a DHBj-type theory incorporating ion pair–free ion coupling, but other interpretations have been proposed. For discrimination a more extensive thermodynamic characterization of RPM-like systems may be useful. Equally interesting information could come from transport data. The electrical conductance is comparatively well characterized at low T^*. *There is lacking, however, an elaborate conductance theory which includes ion pair–free ion coupling which help to descriminate among the various possible scenarios.* Moreover, the f_{ab} formalism discussed in Section 3 may yield unique information on ionic structures. Its extension to systems at low T^* seems possible though experimentally demanding. Note, however, that in the direct vicinity of the CP, the integrals defined in Eq. (15) will diverge.

Finally, the various scenarios associated with the existence of dipolar ion pairs draw attention to the dielectric properties of such systems. Some data at low T^* are available (e.g., ref. 72), but scarcely extend to the regime where effects beyond pair formation become important. *In particular, measurements of dielectric behavior at near-critical conditions would be helpful.*

In interpreting experimental data one has, however, to be aware that there are necessarily contributions to the potential not covered by the simple RPM. We have shown that in the presence of specific interactions Ising criticality is obtained. *A more general attempt to understand the observed change from mean-field behavior in Coulombic systems to Ising behavior in systems with additional non-Coulombic interactions is therefore required.* Until now, this has been phenomenologically explained in terms of the dichotomy of Coulombic and solvophobic interactions. However, we have now reported on a mechanism beyond this classification: The stabilization of ion pairs by hydrogen bonding leads to sharp Ising behavior, although the major features of Coulombic unmixings in solvents of low dielectric constant are retained. Obviously, comparatively subtle contributions due to specific interactions can change the critical behavior profoundly. This appears to *put the borderline between mean-field and Ising criticality very close to the Coulombic limit. Hence, when examining theoretically the transition from mean-field to Ising-like criticality, it may be wiser to start with the case of sticky ions than with the complex solvophobic systems.*

The discovery of the latter mechanism opens, of course, a wide field for further experiments, as *one may think of many other specific ion-ion or ion-solvent interactions.* We quote examples presently under more detailed investigation in our laboratories: some solutions of tetraalkylammonium salts in benzene show complete miscibility in a range where large miscibility gaps are expected. Likewise some salts such as Bu_4NBr are completely miscible with carbon tetrachloride. Obviously, these CP are largely displaced from the RPM prediction, presumably due to specific interactions, in the case of benzene possibly associated with the π-electron system. What would be the critical behavior?

Another example is related to liquid–liquid phase separations in molten salt mixtures. In binary systems with a common ion such unmixings are rare. They do, however, occur for systems like $NaBr + AlBr_3$,(79) where one component is highly ionic and the second one is a rather covalently bound salt. The miscibility gaps are quite asymmetric with an upper CP at dilute concentrations of he ionized salt. We suggest that this corresponds to the RPM prediction, if the system is considered to represent a solution of an electrolyte (NaBr or $NaAlBr_4$) in an excess of the low-D environment of the covalent solvent ($AlBr_3$ with $D = 4$). On the other hand, immiscibilities are more common in reciprocal salt systems of the type $AX + BY$, such as $KBr + TlNO_3$,(80) where the gap is quite symmetric in composition. What would be the criticality in these cases?

As an alternative way to study the effect of specific interactions upon critical phenomena, one may resort to liquid–liquid phase equilibria in ternary systems. With respect to ionic fluids this is a largely uncharted territory. Exceptions are salting-out and salting-in effects caused by alkali halides and other simple salts in water + organic cosolvent mixtures. In the context of previous investigations we have also observed salting-out of the hydrophobic electrolyte Bu_4NBr in aqueous solutions by salts such as KBr. All these processes show the typical features of solvophobic phase separations. They obviously reflect a strengthening or weakening of hydrophobic interactions by added salts. Therefore Ising behavior is observed (possibly with a small renormalization effect for the special path to the CP in ternary systems).

Certainly, a more interesting problem is *to set up a ternary system composed of two subsystems with mean-field and Ising-like criticality, thus allowing one to interpolate between both situations.* Where would be the borderline? Would a sharp transition be observed at some solvent composition, or would the behavior exhibit a gradual change of the crossover temperature, thus making the crossover regime accessible. The design of such systems appears to be possible by exploiting the general trends discussed by us previously.(7) Again, it may be more favorable to interpolate between the Coulombic and "sticky-ion" cases in a common solvent than between systems with Coulombic and solvophobic interactions in binary solvent mixtures.

Finally, one should not forget that similar problems arise in metallic fluids, where the electrons screen the long-range Coulombic interactions to a short range. While also in these cases there have been speculations about a mean-field nature of the CP, more recent work for the liquid–vapor transition of alkali metals (e.g., ref. 81) and liquid–liquid transitions in alkali metal + ammonia and alkali + alkali halide systems(40–42) appear to suggest Ising-like scenarios and crossover.

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