International Journal of Thermophysics, Vol. 15, No. 6, 1994

Light-Scattering Investigations of the Liquid–Liquid Phase Transition of the Ionic System: Trimethylethyl-Ammonium Bromide in Chloroform[1]

S. Wiegand,[2] M. Kleemeier,[2] J.-M. Schröder,[2] W. Schröer,[2,3] and H. Weingärtner[4]

Phase diagrams and light-scattering measurements of solutions of trimethylethyl-ammonium bromide in chloroform ($\varepsilon = 4.72$ at 25°C) with an ethanol content of 1% are reported. The system has a lower critical point near $T = 25$°C. The critical mole fraction is $x_c = 0.0503 \pm 0.0002$, which corresponds to the reduced variables $T_c^* = 0.036$ and $c_c^* = 0.029$ of the *restricted primitive model* (RPM) and is slightly below the values predicted by the RPM for the critical parameters. The analysis of the scattering intensity at critical composition gives $\nu = 0.621 \pm 0.003$ for the critical exponent of the correlation length ξ with an amplitude of $\xi_0 = 0.87 \pm 0.01$ nm. The system, a solution of a salt of essentially spherical ions of almost equal size in a simple low-dielectric polar liquid, with critical parameters very close to predictions of the RPM, nevertheless has an Ising critical point.

KEY WORDS: chloroform; critical phenomena; ionic solution; light scattering; liquid–liquid phase transition; ternary mixture; trimethylethyl-ammonium bromide.

1. INTRODUCTION

The phase transitions in nonionic fluids are governed by short-range van der Waals interactions, resulting in Ising criticality. In contrast, the strong

---

[1] Paper presented at the Twelfth Symposium on Thermophysical Properties, June 19–24, 1994, Boulder, Colorado, U.S.A.

[2] Institut für Anorganische und Physikalische Chemie, Universität Bremen, Leobener Strasse, D-28334 Bremen, Germany.

[3] To whom correspondence should be addressed.

[4] Institut für Physikalische und Elektrochemie, Universität Karlsruhe, Kaiserstrasse 12, D-76128 Karlsruhe, Germany.

0195-928X/94/1100-1045$07.00/0 © 1994 Plenum Publishing Corporation

long-range Coulomb forces present in ionic fluids may lead to a different critical behavior [1, 2].

In the experimental investigations of the liquid–liquid phase transition of ionic solutions, mean-field [3–5] as well as Ising behavior [6–8] has been found. Most recently, crossing over from mean-field to Ising criticality has been reported [9].

The so-called restricted model (RPM) has proved to be a useful guide for describing the phase separation in ionic fluids and localizing the critical point in the diagram of corresponding states [10]. In this model the ions are treated as charged hard spheres with identical diameter a in a homogeneous dielectric. The dimensionless variables are the reduced concentration $c^* = ca^3$ and the reduced temperature $T^* = 4\pi\varepsilon_0(kT\varepsilon a/Z^2e^2)$, which is the ratio of thermal and Coulomb energy of the ions in contact. Simulations [11–13] and analytical theories [14, 15] predict phase separation at low concentration and low temperature. The results of the Monte Carlo calculations [11, 13] seem to converge to a critical point at $T_c^* = 0.056$ and $c_c^* = 0.040$. The most recent simulation, which takes into account the exchange of ion pairs between boxes, gives even lower values ($T_c^* = 0.053$, $c_c^* = 0.03$ [16]). The agreement with $T_c^* = 0.055 \pm 0.002$ and $c_c^* = 0.026 \pm 0.008$ obtained from the Levine–Fisher model [2, 15] is remarkable. This model is a van der Waals theory modified for ionic systems by taking into account the Debye–Hückel contribution to the free energy, as well as those of Bjerrum ion pairs and charge–dipole interactions. With respect to ionic solutions, $T_c^* = 0.05$ implies that phase separation is expected at ambient temperatures in solvents of a low dielectric constant ($\varepsilon < 10$) [2, 17]. Such systems are termed Coulombic systems [2].

While the basic physics which determines the phase diagram of the RPM now seems to be reasonably understood, the nature of the critical point in ionic fluids is still a subject of controversy [2, 18]. Measurements of the coexistence curve [3] and of the turbidity [4] obtained from a solution of triethylhexyl-ammonium triethylhexyl-borate (short-hand notation, $N_{2226}B_{2226}$) in diphenylether ($\varepsilon = 3.7$) prove mean-field behavior in the entire temperature range investigated. Static and dynamic light-scattering measurements on the system tetra-n-butyl-ammonium picrate (N_{4444}Pic) in 1-tridecanol ($\varepsilon = 4.2$) yield an effective critical exponent $\nu = 0.523$ for the correlation length, slightly above the mean-field value. Thus, the experiments reported so far [3–5] support the conclusion that mean-field behavior, with perhaps a small Ising-like region, is observed, if the location of the critical point is in agreement with that predicted by the RPM.

Ising criticality is observed in ionic solutions with effective critical temperatures and densities much higher than those predicted by the RPM. In such cases short-range interactions are the driving forces for the phase transition. Hydrogen bonds between the ions [6] can enhance the ionic association by orders of magnitude, so that the solution of the salt in a low-dielectric solvent can almost be regarded as a polar/nonpolar mixture. In solvents of high dielectric permittivity, hydrophobic interactions [8, 19, 20] between the ions and the solvent cause the phase transition.

Clearly, the RPM appears to be a very artificial model for real ionic fluid mixtures. The RPM, treating the solvent as a continuum, is a model for the liquid–gas phase transition and cannot take into account details of the interactions with the solvent. Furthermore, the ions, and thus the charge distribution, in the systems reported are not spherical; neither are the solvent molecules, and these may even by hydrogen-bonded. Therefore, the agreement of experimental critical data with the RPM prediction may be fortuitous and deviations can be expected. In order to assess this problem, we have designed a new system, which corresponds much closer to the RPM model, and in a next step of approximation, may be represented as a mixture of charged and dipolar hard spheres [21]. The system is trimethylethyl-ammonium bromide ($N_{1112}Br$) dissolved in chloroform ($\varepsilon = 4.72$). The ions are almost spherical and of similar size and the solvent is a simple low dielectric liquid. Therefore, this system should be a good candidate for testing predictions of the RPM or more realistic models.

To characterize the criticality of this system we have initially determined the phase diagram and located the critical point. We report measurements of static light scattering for the determination of the correlation length and deduce the corresponding critical exponent ν. Measurements of dynamic light scattering, viscosity, and X-ray diffraction are reported elsewhere.

2. EXPERIMENTS

2.1. Sample Preparation

Trimethylethyl-ammonium bromide ($N_{1112}Br$) was synthesized [22] by reacting trimethylamine (Fluka, purum, 98%) with ethylbromide (Fluka, purum, 99%) in acetone (p.a., Fluka, 99.5%) for 3 days at −78°C. The salt, which is extremely hygroscopic, was recrystallized twice from boiling nitromethane (p.a., Fluka, 99%). Finally, it was dried for 48 h under vacuum between 60 and 80°C. We found a melting point of 347.5°C, which lies 9°C above the melting point in the literature [3]. Humidity lowers the melting temperature.

The samples have been prepared using the following procedure. A small amount of salt was dried for 2 h at 70°C under a pressure of $5 \cdot 10^{-3}$ mbar and was then quickly filled and weighted into glass tubes with a diameter of 8 mm. The tubes were then connected to a vacuum line and the salt was dried again for 1 h at 70°C. Chloroform (Fluke, pa., 99%), which contains 1% ethanol (mass fraction) for stabilization, was used without further purification. The required amount of chloroform was filled into a spherical flask and was degassed by repeated pumping and freezing with liquid nitrogen. The chloroform was then condensed onto the salt, which was cooled by liquid nitrogen as well. Finally, the frozen samples were sealed. The mole fraction of the samples has an uncertainty of $\Delta x = 2 \times 10^{-4}$.

2.2. Determination of Coexistence Curve and Critical Concentration

For determination of the coexistence curve we used the fact that the intensity of the transmitted light decreases sharply when the phase separation temperature is reached. In ternary mixtures the extrema of the coexistence curve are not necessarily equivalent with the critical point [24]. To locate the critical point, which is characterized by maximum scattering intensity, we used a simplified 90°-scattering setup [5], with a sensitive photodiode instead of a photomultiplier. This setup allows the determination of transmitted and scattered light intensity simultaneously. For each of the 28 samples, we started the measurement approximately 10 K below the expected phase separation temperature. The cell is heat at a rate of 10 mK/min, while scattered and transmitted intensities are continuously recorded. The phase transition temperature is determined with an accuracy of $\Delta T = 30$ mK.

2.3. Measurement of the Scattering Intensity

The light-scattering experiment was performed at a $\vartheta = 90^\circ$ scattering geometry with an experimental setup described before [6]. The intensity of the incident beam was internally recorded by a photodiode. Furthermore, the intensity of the transmitted light was measured using a large-size photodiode. In order to obtain a high degree of temperature stability the temperature was controlled in two stages in an improved cell. This cell contains an inner and an outer copper cylinder, thermally isolated by an air gap of 15 mm. The outer cylinder is fed by a thermostat (Lauda, KP-20D), controllable to 5 mK. The sample is mounted inside the inner copper block, which is filled with 100 ml water to ensure homogeneous thermal contact. By an electrical heating of the inner copper block a temperature stability of 0.5 mK was achieved. The actual temperature was measured by a small-size calibrated precision thermistor, placed in the water bath very close to the sample.

3. RESULTS

3.1. Coexistence Curve

The coexistence curve is shown in Fig. 1. The $N_{1112}Br$/chloroform system shows a lower consolute temperature curve. The actual transition temperatures are extremely sensitive to the ethanol content, present in the commercially available chloroform for stabilisation. An ethanol content of 2% leads to a phase separation temperature above 50°C. If the alcohol is removed the liquid–liquid unmixing is suppressed by crystallization in the critical region.

The commercial chloroform 1% ethanol, turned out to be convenient for investigation the phase separation at ambient temperature, well separated from the crystallization of the salt and the boiling point of chloroform. The high sensitivity to small changes in the alcohol content and water is the reason for the scatter of the phase separation temperatures. Investigations of three-component mixtures are complicated by the fact that in such systems the critical point and the extremum of the observed curve of phase separation in general do not coincide. Therefore

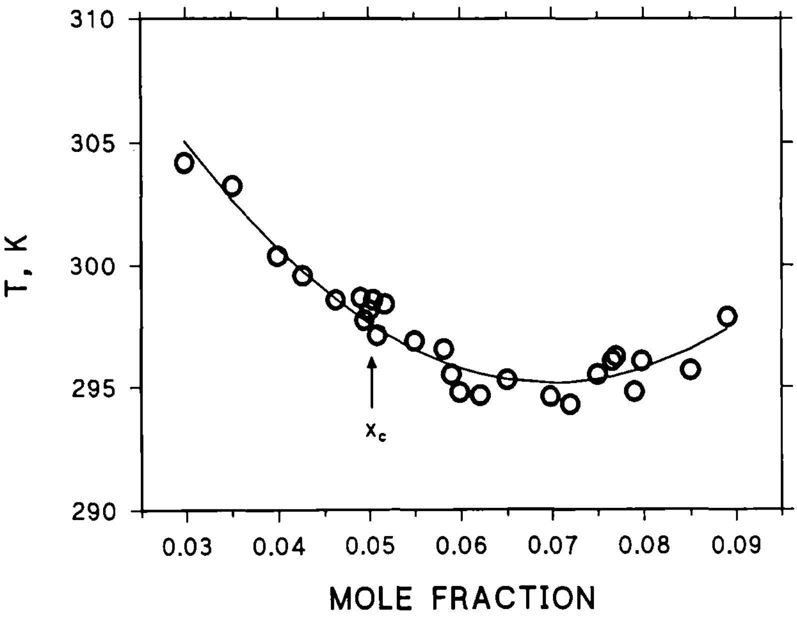

Fig. 1. Coexistence curve of trimethylethyl-ammonium bromide in chloroform (+1% ethanol) in the critical region. The observed transition temperatures are plotted as a function of the mole fraction.

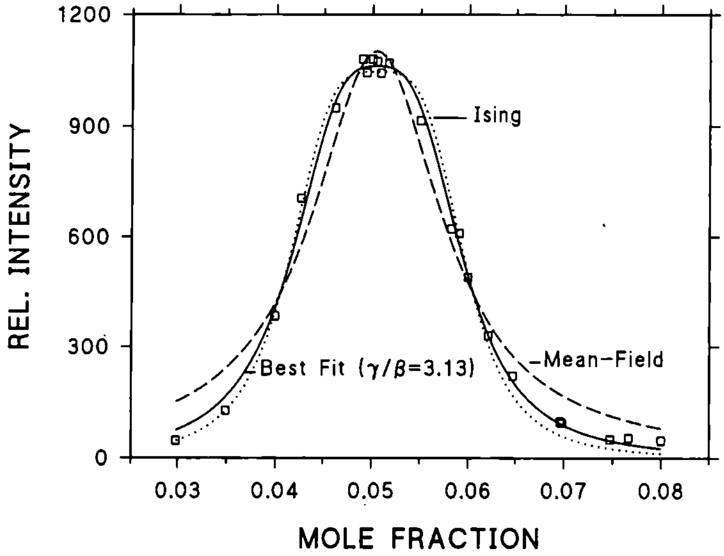

Fig. 2. Maximum scattering intensity $I(x)$ close to the phase separation temperature as a function of the mole fraction. The solid line represents the best fit taking γ/β as the fitting parameter. The dotted and dashed lines give the fits presuming Ising and mean-field exponents, respectively.

the critical point had to be located by light scattering. Figure 2 shows that the maximum scattering intensity close to the phase separation temperature varies smoothly with the mole fraction, allowing precise determination of the critical composition. The samples with mole fractions near $x = 0.07$, with the lowest phase separation temperatures, are noncritical (Fig. 2). In contrast, the highest scattering intensities are observable for concentrations close to $x_c = 0.0503$. We mention that the scattering intensities of samples with nearly the same concentration are always similar, while their separation temperatures may be quite different. The relative scattering intensity I/I_0 at the phase separation temperature is well described as function of the composition by Eq. (1)

$$\frac{I(x)}{I_0} = A \frac{1}{B(x - x_c)^{\gamma/\beta} + q^2} \tag{1}$$

obtained from the Ornstein–Zernike equation with the assumption that $\gamma = 2 \cdot \nu$ and $\tau \propto (x - x_c)^{1/\beta}$, where $\tau = (T - T_c)/T_c$ is the reduced temperature, q is the amplitude of the scattering wave vector, A is a constant which depends on the system and the optical setup and B depends only on the system, and γ and β are the critical exponents for susceptibility and the coexistence curve. The experimental intensities $I(x)$ are best described by Eq. (1) if a ratio $\gamma/\beta = 3.13 \pm 0.14$ (solid line) is used. This value of γ/β lies between the Ising value of 3.8 and the mean-field value of 2.0. In Fig. 2 the dotted line represents the fit for the fixed Ising exponent; the dashed line describes the best mean-field curve. In the last case the value obtained for mean-square derivation χ^2 is twice as big as in the Ising case. The value for the critical mole fraction $x_c = 0.0503 \pm 0.0002$ is almost independent of the choice of γ/β. The slight asymmetry in the measured scattering intensities may be reduced by a more suitable choice of the order parameter instead of the molar fraction. The volume fraction does not lead to a more symmetric curve.

3.2. Scattering Intensity

The scattering intensities of the critical sample with $x = 0.0504$ as a function of the reduced temperature $\tau = (T - T_c)/T_c$ are shown in Fig. 3. The critical temperature $T_c = 298.840$ K is determined experimentally and kept fixed in the fitting procedure. The correlation length is calculated from

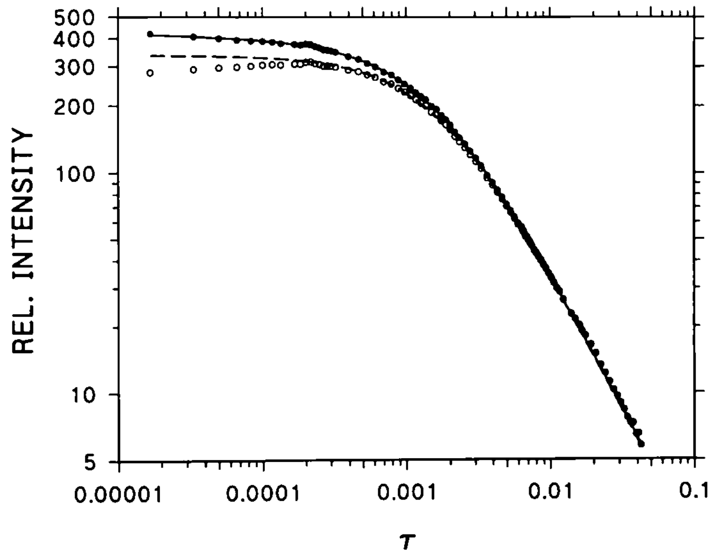

Fig. 3. Relative scattering intensity $I(\tau)$ as function of reduced temperature $\tau = (T - T_c)/T_c$ in a log-log plot. The dashed line gives the fit with I_0, the uncorrected intensity (○), and the solid line represents the fit with I_0 corrected for turbidity (●).

the relative scattering intensity by using the Ornstein–Zernike approximation in the form

$$\frac{I(\tau)}{I_0} = \frac{A}{\xi_0^{-2}\tau^{2\cdot\nu} + q^2} + \Delta \tag{2}$$

which implies a Fisher exponent $\eta = 0$. A is treated as a constant depending on the geometry of the scattering experiment and system properties, Δ is the background term for noncritical density fluctuations, and the correlation length is given by $\xi = \xi_0 \tau^{-\nu}$. The parameters of Eq. (2) are determined in two steps. In a first approximation we fitted the experimental scattering intensities in the temperature range $\tau = 5 \times 10^{-2} \ldots 5 \times 10^{-4}$, where corrections due to the turbidity are almost negligible, being below 10%. The fit obtained is given in Fig. 3 (dashed line), showing deviations for $\tau < 5 \times 10^{-4}$. The background intensity is found to be insignificant. The resulting values for the amplitude and exponent of correlation length ξ_0 and ν allow calculation of the temperature dependence of the turbidity by means of the Ford–Puglielli [5] expression. The amplitude of the turbidity, which depends on the amplitude of the susceptibility and the concentration dependence of the refractive index, is the only experimental parameter connecting the light scattering and the turbidity measurements. In the next step I_0 is corrected for the loss of intensity due to turbidity. The fit describes the experimental data over the entire temperature range, yielding: $\xi_0 = 0.87 \pm 0.01$ nm and $\nu = 0.621 \pm 0.003$. The value obtained for ν is in good agreement with the theoretical Ising value, $\nu \approx 0.63$. Contributions of the Fisher renormalization [26] are not measurable due to a low content of ethanol. This is surprising, as this small amount of ethanol leads to a significant shift of the critical point.

3.3. X-Ray Analysis

In order to get a reliable experimental value for the averaged ionic diameter a, we carried out x-ray analysis. Single crystals were obtained from a solution in chloroform. The x-ray analysis yielded 0.425 nm for the shortest distance between the nitrogen of the ammonium ion and the bromide ion. Furthermore it should be mentioned that the crystal contained chloroform at a stoichometric ratio (1:1) and that the hydrogen atom of the chloroform points into the direction of the bromide ion. Both facts indicate that there could be some specific interation between the salt and the solvent.

4. DISCUSSION

In this work we report on light-scattering measurements near the liquid–liquid phase transition of the ionic solution trimethylethylammonium bromide ($N_{1112}Br$) in chloroform. The chemical structure of this ionic system seems to correspond much closer to the model of charged hard spheres considered in the RPM than other systems investigated before. It is a solution of a salt with essentially spherical ions in a simple low-dielectric solvent. However, it has a lower critical solution point and Ising criticality is observed in the entire temperature region investigated. This provokes two questions to be addressed here: (i) Is the critical point of this system in the corresponding state diagram of the RPM located in the region predicted by the RPM? (ii) If yes, why is it that the criticality of this system may be different in comparison to that of other Coulombic systems?

At first glance the lower critical solution point seems to contradict the expectation for Coulombic fluids, as the RPM predicts an upper critical point. Lower critical points and closed loops are expected in cases of solvophobic demixing [19]. This discrepancy is easily resolved. By taking into account the temperature dependence of the dielectric constant of chloroform [7] and rescaling the temperature accordingly, the sign of the curvature is changed. The coexistence curve in terms of the RPM variables is shown in Fig. 4.

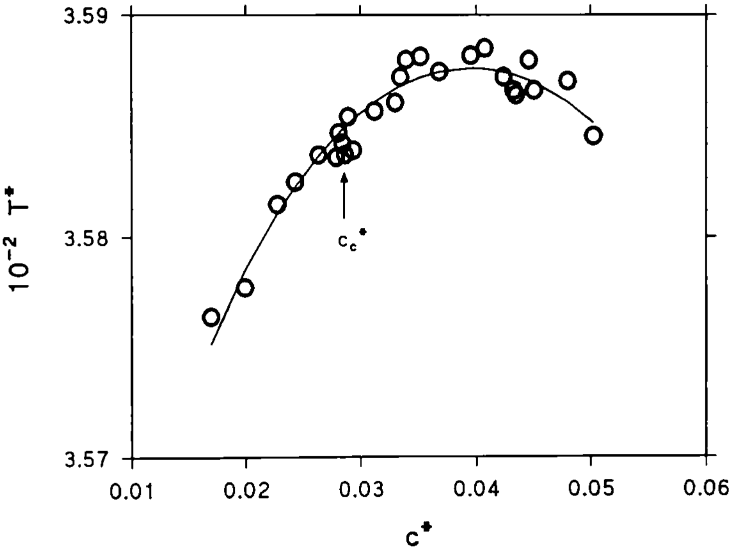

Fig. 4. Coexistence curve in reduced variables as defined by the RPM model.

The localization of the critical point in the RPM variables depends strongly on the actual estimation of the ionic diameter a, which for charged hard spheres is also the distance of the charges in the ion pair. We identify the distance between the nitrogen of the ammonium ion and the bromide ion (0.425 nm) with a, which was determined by x-ray analysis from single crystals of the salt. This value is in reasonable agreement with an estimate (0.48 nm) based on van der Waals radii. Therefore, the assumption that the distance of the ions in the crystal can be identified with a seems most reasonable. Note that in this case the averaged ionic diameter and the distance between the charges are almost the same, as the anion is exactly spherical and the cation in very good approximation. This is different from other demixing ionic systems mentioned in Section 1. Those consist of nonspherical ions with an asymmetric charge distribution. However, for these systems the distance between the charges determines the stability of the ion pair. Therefore, for the calculation of reduced variables mapping the phase diagram of a real system onto the phase diagram of the RPM, this distance can be expected to represent a more appropriate estimate of a than the averaged van der Waals diameter.

In terms of the RPM variables, with the x-ray result of a, the critical point is located at $T_c^* = 0.036$ and $c_c^* = 0.029$. A similar result ($T_c^* = 0.04$, $c_c^* = 0.04$) is obtained from van der Waals radii. The critical point is in the region expected for Coulombic systems as modeled by the RPM. While c_c^* agrees almost perfectly with the theoretical predictions [15, 16], T_c^* is almost 40% lower. It is difficult to judge the significance of this close agreement of c_c^* and the deviation in T_c^*. Predictions by theoretical methods are sensitive to approximations applied in the calculation [14, 28], and so far critical fluctuations have not yet properly taken into account in the theoretical work on the RPM.

Looking at the critical data of other ionic mixtures regarded as Coulombic systems [3–5], we find that those also deviate from the theoretical predictions, but toward higher values ($c_c^* = 0.06 - 0.15$, $T_c^* = 0.05 - 0.07$). These values involve estimates for the diameter a, based on van der Waals radii. For the system N_{4444} Pic/tridecanol [5], e.g., we have $a = 0.76$ nm giving $c_c^* = 0.15$ and $T_c^* = 0.066$. Approximating instead a by the charge distance in the ion pairs (0.41 nm), known from dielectric measurements [9], the location of the critical point is shifted toward smaller values ($c_c^* = 0.023$ and $T_c^* = 0.038$), similar to that found for N_{1112}Br/chloroform. Taking into account the uncertainties of the theoretical estimates of the critical point as well as the arbitrariness of the value of a chosen to map the phase diagram of real systems on the corresponding state diagram of the RPM, we conclude that the critical point of the N_{1112}Br/chloroform system is in the region predicted by the RPM. The critical point of the N_{1112}Br/chloroform system agrees reasonably with that of other systems regarded as Coulombic. Therefore, we conclude that the N_{1112}Br/chloroform system can be regarded as a Coulombic system too.

This provokes the second question raised above, Why, for this system, Ising criticality is observed over the entire temperature region investigated, while all other Coulombic systems show at least a mean-field region, with perhaps a crossing-over to an Ising criticality? As the criticality of the RPM is still a matter of controversy, we are far away from understanding real ionic solutions. However, comparing experimental results can nevertheless give some insight. Till now Ising criticality was observed in ionic solutions in highly polar solvents such as water [7, 19], where short-range solvophobic interactions of the solvent with the salt determine the phase transition. Ising criticality was also found in systems with ion association enhanced [6], e.g., by hydrogen bonding, so that dipole interactions determine the phase transition. For the N_{1112}Br/chloroform system neither model is applicable, so that the observed Ising criticality is unexplained. However, other explanations are suggested by the recent work, which need to be investigated in detail in future work. So we just mention that an investigation of crossing-over by varying the solvent has led to the hypothesis [9] that the value of the dielectric constant, ε, is an independent parameter determining the criticality, and a region with mean-field criticality well accessible for light-scattering experiments requires $\varepsilon \leqslant 4.6$, while for chloroform $\varepsilon = 4.72$. From a theoretical analysis it is also suggested [18] that the actual criticality and crossover behavior are determined by the relative size of the ions. However, a theory that takes into account more specific properties such as the nonspherical shape and charge distribution of the ions, but also the structure of the solvent and the specific interactions with the ions, is not yet available. The reported observation, that N_{1112}Br crystallized from chloroform contains chloroform at a stochiometric ratio (1:1), indicating specific interaction between the ion and the solvent, as well as the shape and the charge distribution of the ions, may turn out to be important facts to be considered in a theory able to explain criticality of real ionic systems.

ACKNOWLEDGMENTS

We are grateful to E. Lork, T. Bornemann, and R. Mews for x-ray spectrum. J. M. H. Levelt Sengers, M. E. Fisher, G. Stell, K. S. Pitzer, and T. Narayanan provided prepublication results and shared insights. This work was supported by the Fond der Chemischen Industrie and of the Deutsche Forschungs Gemeinschaft.

REFERENCES

1. K. S. Pitzer, *Acc. Chem. Res.* **23**:333 (1990).
2. M. Fisher, *J. Stat. Phys.* **75**:1 (1994).
3. R. R. Singh and K. S. Pitzer, *J. Chem. Phys.* **92**:6775 (1990).
4. K. C. Zhang, M. E. Briggs, R. W. Gammon, and J. M. H. Levelt Sengers, *J. Chem. Phys.* **99**:8692 (1992).
5. H. Weingärtner, S. Wiegand, and W. Schröer, *J. Chem. Phys.* **96**:848 (1992).
6. W. Schröer, S. Wiegand, and H. Weingärtner, *Ber. Bunsenges. Phys. Chem.* **97**:975 (1993).
7. M. L. Japas and J. M. H. Levelt Sengers, *J. Phys. Chem.* **94**:5361 (1990).
8. H. Weingärtner, M. Kleemeier, S. Wiegand, and W. Schröer, *J. Stat. Phys. Onsager Issue* (in press).
9. T. Narayanan and K. S. Pitzer, *Int. J. Thermophys.* **15**:1037 (1994).
10. H. L. Friedmann and B. Larsen, *J. Chem. Phys.* **70**:92 (1979).
11. A. Z. Panagiotopoulos, *Fluid Phase Equil.* **76**:97 (1992).
12. J. P. Valleau, *J. Chem. Phys.* **95**:584 (1991).
13. J. M. Caillol, *J. Chem. Phys.* **100**:2161 (1994).
14. G. Stell, K. C. Wu, and B. Larsen, *Phys. Rev. Lett.* **37**:1369 (1976).
15. M. E. Fisher and Y. Levine, *Phys. Rev. Lett.* **71**:3826 (1993).
16. G. Orkoulas and A. Z. Panagiotopoulos, private communication.
17. H. Weingärtner, T. Merkel, U. Maurer, J.-P. Conzen, H. Glasbrenner, and S. Käshammer, *Ber. Bunsenges. Phys. Chem.* **95**:1579 (1991).
18. G. Stell, *J. Stat. Phys. Onsager Issue* (in press).
19. W. Schröer, S. Wiegand, M. Kleemeier, and H. Weingärtner, *J. Phys. Condensed Matter* **6**:A157 (1994).
20. H. Weingärtner, *Ber. Chem.* **93**:1058 (1989).
21. G. Stell, G. N. Patey, and J. S. Høye, *Adv. Chem. Phys.* **48**:183 (1981).
22. E. Grovenstein, E. P. Blanchard, D.A. Gordon, and R. W. Stevenson, *J. Am. Chem. Soc.* **81**:4842 (1959).
23. M. J. McDowell and C. A. Kraus, *J. Am. Chem. Soc.* **73**:2170 (1951).
24. C. M. Knobler and R. Scott, in *Phase Transitions and Critical Phenomena, Vol. 9*, C. Domb and J. L. Lebowitz, eds. (Academic Press, London, 1984), p. 214.
25. V. G. Puglielli and N. C. Ford, *Phys. Rev. Lett.* **25**:143 (1970).
26. M. E. Fisher and Scesney, *Phys. Rev.* **A2**:825 (1970).
27. A. A. Maryott and E. R. Smith, *Table of Dielectric Constants of Pure Liquids* (National Bureau of Standards, Circ. 514, Washington, DC, 1951), p. 5.
28. S. de Leew, J. S. Perram, and E. R. Smith, *Proc. Roy. Soc.* **A373**:27 (1980).
29. M. Davies and G. Williams, *Trans. Faraday Soc.* **56**:1619 (1960).