Experimental Evidence for Crossover to Mean-Field Tricritical Behavior in a Concentrated Salt Solution

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We have discovered a mean-field multicritical point on the critical locus in an aqueous solution of 3-methylpyridine and sodium bromide. Light-scattering measurements indicate Ising-like asymptotic critical behavior at the lower salt concentrations. However, the temperature range of Ising critical behavior shrinks with increasing salt concentration and the critical behavior becomes mean-field-like at a concentration of about 17% mass fraction of NaBr. Emergence of a new characteristic length scale diverging at this point and a simultaneous pronounced increase in the background scattering suggests mean-field tricritical behavior associated with the formation of a microheterogeneous phase due to clustering of ions and molecules.

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While it is believed that the asymptotic critical behavior of fluids conforms to that of the three-dimensional Ising universality class, the nature of the critical behavior of ionic solutions is still unclear. Theoretically, ionic fluids, regardless whether the phase separation is driven by Coulombic or solvophobic interactions, should exhibit Ising-like critical behavior either due to screening effects (low dielectric constant) or to short-ranged forces (high dielectric constant) [1]. In practice, Ising-like critical behavior [2], classical mean-field behavior [3], or a crossover between these two regimes [4] has been observed experimentally in ionic solutions. The question—what physical feature tunes the crossover—"becomes vital" [5].

To further investigate the nature of critical crossover behavior in ionic solutions, we have found it of interest to study the critical fluctuations in a ternary mixture of water (H_2O), 3-methylpyridine (MP), and sodium bromide (NaBr) near the locus of lower consolute points as a function of the salt concentration [6]. At the lower salt concentrations the measurements show a sharp crossover from mean-field critical behavior to Ising critical behavior upon approaching the critical temperature. However, the temperature range of Ising critical behavior shrinks as more salt is added and we now have found that it indeed vanishes at a concentration of about 17% mass fraction of NaBr, where complete mean-field critical behavior of the susceptibility is observed. Moreover, a simultaneous pronounced increase of the background scattering appearing at the higher salt concentrations suggests that this is to be interpreted as mean-field tricritical behavior associated with the appearance of a microheterogeneous phase due to clustering of ions and molecules.

The binary liquid solution MP + H_2O is miscible at all temperatures at atmospheric pressure. A miscibility gap with a closed-loop two-phase region appears in this system with the addition of 0.4% mass fraction of NaBr. The locus of critical points as a function of the mass fraction X of NaBr is shown in Fig. 1. With the addition of the electrolyte (NaBr), the polar groups in MP and H_2O become increasingly shielded from each other, reducing the strength of the hydrogen-bond forces, and the lower consolute critical temperature decreases. Note that the locus of lower consolute points exhibits a dip at a mass fraction of NaBr between 16.5% and 17%. Such a dip may be an indication of the presence of an actual multicritical point of some kind [7] or the near vicinity of a virtual multicritical point depending on whether the dashed curve (to be discussed below) in Fig. 1 does or does not correspond to a locus of second-order phase transitions.

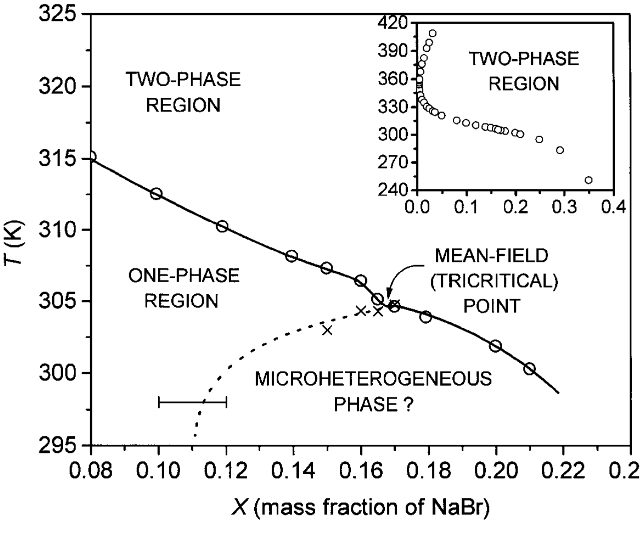

FIG. 1. Phase diagram of the 3-methylpyridine + water + NaBr system. The solid curve represents the critical phase-separation line and the dashed curve bounds the temperature and salt concentrations where a microheterogeneous phase exists. The symbols indicate experimental data. The critical-temperature curve over the entire range of experimental salt concentrations is shown as an inset.

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We have measured the intensity of scattered light as a function of the temperature T upon approaching the critical temperature T_c for a variety of salt concentrations. In Fig. 2 we have plotted the light-scattering intensity I as a function of $\tau = (T_c - T)/T$ obtained at seven different salt concentrations ranging from $X = 8\%$ to $X = 17\%$. The light scattering intensity I is expected to consist of a contribution I_c from critical concentration fluctuations and a background scattering contribution I_0. The critical scattering contribution can be represented by

$$I_c = \frac{C\chi}{1 + (q\xi)^2}, \tag{1}$$

where χ is the susceptibility, C is an experimental constant, ξ is the correlation length, and q is the wave number of the critical concentration fluctuations, related to the scattering angle θ (90° in our experiments) as $q = 4\pi n/\lambda_0 \sin(\theta/2)$, where $\lambda_0 = 632.8$ nm is the vacuum wavelength of the incident light and n is the refractive index. We have found the noncritical background scattering I_0 to be negligibly small for all measurements at the lower salt concentrations ($X \leq 0.14$). However, at the higher salt concentrations an enhanced background scattering appears at the lower temperatures, starting marginally at the edge of the experimental temperature range $\tau \simeq 2 \times 10^{-2}$ for the sample with $X = 0.15$ but rapidly increasing for the samples with higher salt concentrations.

In applying Eq. (1) we have represented both χ and ξ by expressions from a crossover theory which recovers Ising asymptotic behavior with Wegner corrections close to the critical point and mean-field behavior far away from the critical point and accounts for the temperature dependence of the effective values of the exponents γ and ν for χ and ξ [8,9]. Since in a ternary mixture the path $X =$ const does not correspond exactly to a path of zero-ordering field, we also have taken into account the effect of Fisher renormalization of the critical exponents as described by Jacob *et al.* [6]. Basically, the effect of the renormalization depends on the slope of the critical temperature as a function of the salt concentration. Furthermore, Fisher renormalization must disappear in the mean-field limit. In previous publications [8–10] we have demonstrated that the crossover to mean-field behavior is generally controlled by two physical parameters, namely, a rescaled coupling constant and a so called "cutoff." In simple fluids the cutoff is related to the molecular length scale and the trend to mean-field critical behavior is controlled by the coupling constant only. In complex fluids the cutoff is associated with the characteristic supramolecular length $\xi_D = v_0^{1/3}\Lambda^{-1}$ representing a crossover length scale [9], with v_0 being a molecular volume ($v_0^{1/3} \simeq 3.5$ Å for our samples [6]) and Λ is a dimensionless characteristic cutoff wave number. If ξ_D is large enough, it competes with the correlation length of the critical fluctuations and controls a crossover to mean-field tricritical (or, more generally, multicritical) behavior. If ξ_D diverges, one will recover a mean-field tricritical point. One may define an empirical crossover temperature $\tau_\times$ as the value of τ where a plot of the variation of the effective susceptibility exponent from its asymptotic Ising value $\gamma = 1.24$, recovered after accounting for Fisher renormalization, to its mean-field value $\gamma = 1.00$ as a function of τ exhibits an inflection point [6,10]. We have fitted the crossover model for the critical light-scattering intensity I_c to the experimental light-scattering data in the temperature ranges where the noncritical background scattering is negligible ($\tau \leq 7 \times 10^{-3}$ at $X = 0.16$; $\tau \leq 2 \times 10^{-3}$ at $X = 0.165$). At $X = 0.17$ we did not find any trend to Ising behavior near the critical point and the observed susceptibility retained mean-field behavior upon the approach to T_c. We determined the background scattering I_0 (observed at $X \geq 0.16$) as the difference between I_c as represented by our crossover model and the observed total scattering intensity and represented this background scattering by a "virial-type" relation suggested by the formation of "clusters" emerging at certain $\tau = \tau_0(X)$ [11].

$$I_0 = m_1(\tau - \tau_0) + m_2(\tau - \tau_0)^2 \tag{2}$$

with τ_0, m_1, and m_2 as adjustable parameters.

We have found crossover behavior from Ising critical behavior asymptotically close to the critical temperature to mean-field critical behavior at all salt concentrations up to and including $X = 0.165$. However, the range of Ising critical behavior shrinks with increasing salt concentration. In Fig. 3 we compare the deviations from Ising behavior at the higher salt concentrations with those at the lowest salt concentration $X = 0.08$. At $X = 0.08$ all experimental data are in the crossover regime, at $X = 0.16$ a substantial fraction of the experimental data exhibits mean-field critical behavior, at $X = 0.165$ the experimental data

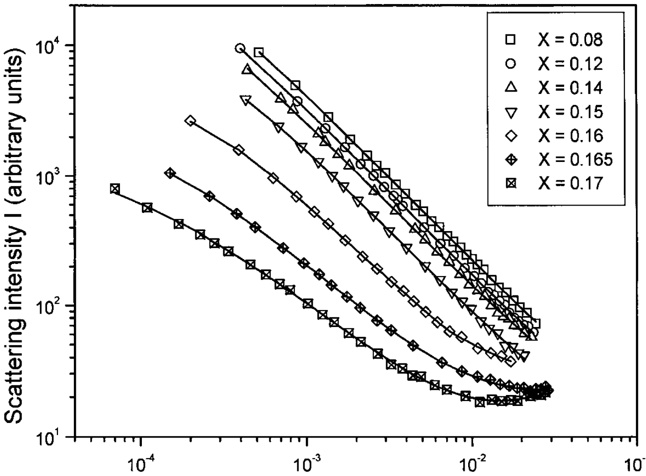

FIG. 2. Scattering intensity as a function of $\tau = (T_c - T)/T$ for seven different mass fractions of NaBr. The symbols designate the experimental data and the curves represent values calculated from the crossover model with a correction for enhanced background scattering due to cluster formation for $X \geq 0.16$.

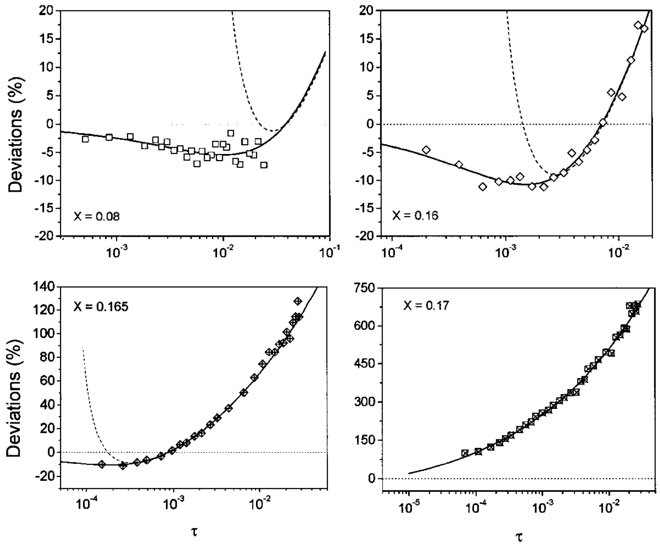

FIG. 3. Deviations of the scattering intensity from asymptotic Ising critical behavior as a function of $\tau = (T_c - T)/T$ for four different salt concentrations. The symbols designate experimental data. The dashed curves represent mean-field behavior and the solid curves represent the actual behavior as calculated from the crossover model with a correction for enhanced background scattering for $X \geq 0.16$. The solid curve for $X = 0.17$ corresponds to the insignificant crossover temperature $\tau_\times = 3 \times 10^{-6}$ and coincides with the dashed curve.

follow the mean-field curve except for the two data points closest to T_c, and at $X = 0.17$ the parameter Λ becomes insignificantly small and the crossover temperature becomes undetectable. Thus within our experimental resolution, complete mean-field critical behavior is observed at $X = 0.17$. In Fig. 4 we show the crossover temperature $\tau_\times$ and the crossover length scale ξ_D as a function of the salt concentration. As follows from the theory of crossover from Ising critical behavior to mean-field tricritical behavior, at $\tau = \tau_\times$ the correlation length ξ of the critical fluctuations is equal to the competing correlation length ξ_D associated with an additional order parameter [9]. It is seen that the crossover temperature $\tau_\times$ vanishes and the crossover length ξ_D diverges at a salt concentration between 16.5% and 17%. Thus both ξ and ξ_D diverge at this point, giving strong evidence for tricriticality.

The light-scattering measurements at the lower salt concentrations have been presented in a previous publication [6], where we found a tendency for $\tau_\times$ to rapidly decrease with increasing salt concentration. First, our new measurements confirm that the crossover temperature $\tau_\times$ indeed vanishes and the crossover length scale ξ_D indeed diverges at a high salt concentration. Even more importantly and unexpectedly, we found a concomitant simultaneous increase of the background scattering not observed in the measurements previously obtained at the lower salt concentrations. We attribute the enhanced background scattering starting at the lower temperatures as arising from some type of ion/molecular clustering. The possibility of ionic cluster formation in electrolyte solutions has been discussed in the literature [12]. The presence of clustering in the MP + H_2O + NaBr system at $X \geq 0.12$ has been found by Jacob *et al.* [13] from small-angle x-ray scattering (SAXS) measurements. The SAXS data for samples with $X < 0.1$ do not indicate any clustering. Equation (2) implies that clustering appears at $\tau = \tau_0$ corresponding to the temperatures indicated by crosses in the phase diagram shown in Fig. 1. The horizontal bar in Fig. 1 indicates the concentration range at $T = 298$ K, where clustering appears according to the SAXS measurements [13]. We conclude that the crossover length scale ξ_D is a new correlation length of fluctuations that ultimately lead to the formation of a microheterogeneous phase. This length competes with the correlation length ξ of the concentration fluctuations and leads to a tricritical point at which both ξ_D and ξ become infinite. At this point the (assumed) second-order transition to a microheterogeneous phase becomes first order as it is accompanied by macroscopic phase separation. We should record that for the samples with $X > 0.16$ we obtained reproducible light-scattering data only after allowing the samples to equilibrate for periods of about 24 h. We believe that these long equilibration times are related to formation of a microheterogeneous phase. We have also performed light-scattering measurements at $X = 18\%$ and $X = 21\%$. At these concentrations we find weak critical opalescence only very close to the phase separation, huge equilibration times, and the enhancement of the background scattering due to proposed clustering is present in the entire temperature range studied.

The crossover behavior shown in Fig. 3 turns out to be very similar to the crossover behavior of the scattering intensities observed near the critical point of polymer solutions [10]. In polymer solutions the crossover length scale ξ_D can be identified with the radius of gyration

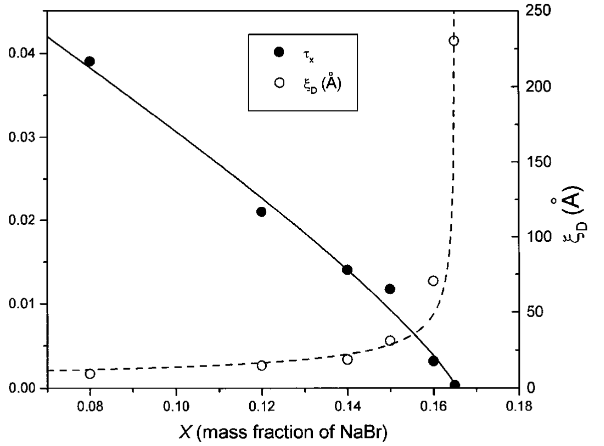

FIG. 4. The crossover temperature $\tau_\times$ and the crossover length-scale ξ_D as a function of the salt concentration. The solid curve represents an empirical power law $\tau_\times \propto (X_0 - X)^{0.8}$ with $X_0 = 0.1652$. The dashed curve represents a power law $\xi_D \propto (X_0 - X)^{-1/2}$.

R_g and the susceptibility exhibits crossover to tricritical behavior at the *theta* point where both R_g and ξ diverge. The critical exponent of the susceptibility near a tricritical point has the same value $\gamma = 1.00$ as that associated with usual mean-field critical behavior. However, the critical exponent β of the concentration difference along the liquid-liquid phase-separation boundary would be very different from mean-field critical behavior, namely, $\beta = 1$ as opposed to $\beta = 1/2$ [7,14]. Hence, it would be very interesting to also measure the coexistence curves of the 3MP + H_2O + NaBr for various salt concentrations.

We note that a ternary liquid mixture at constant pressure does not have enough thermodynamic degrees of freedom to form an ordinary asymmetric tricritical point [15]. However, if a new phase is formed, which is characterized by an additional order parameter (associated with a structural transformation and different from density or concentration), the system has enough degrees of freedom to exhibit various kinds of multicritical points. The coupling between formation of a microheterogeneous (micellarlike) phase and liquid-liquid phase separation can lead to tricritical behavior [11]. The possibility of a multicritical Lifshitz point in which two fluid phases in an electrolyte solution coexist with a microheterogeneous charge-density wave phase was suggested by Nabutovskii *et al.* [16] and discussed by Høye and Stell [17] and Fisher [5]. Evidence for tricritical behavior in restricted primitive models for ionic fluids has been reported by Dickman and Stell [18] and by Panagiotopoulos and Kumar [19]. In our system at higher salt concentration the 3-methylpyridine molecules are assumed to be shielded from the ions by water molecules. In turn, the ions may form a double layer over the water molecules forming a charge layering or microemulsionlike domains.

There are still a number of issues that require further investigation. The physical nature of the branch (Fig. 1) of the phase-separation line at $X > 0.17$ needs further investigation. Also, we encountered another intriguing feature of the phase separation in some electrolyte solutions, namely, the appearance of a solidlike phase at the liquid-liquid interface. In the 3MP + H_2O + NaBr system this third phase was observed at concentrations both smaller and larger than the concentration at the multicritical point and appeared even in samples prepared with chemicals of high purity. The third phase appeared also when NaBr was replaced with NaCl and traces of the third phase were observed even in samples with 3MP and D_2O without any salt. To our surprise the third phase was also found in samples of isobutyric acid + water used earlier by Greer for measuring the coexistence curve of this system [20], as well as in some other aqueous ionic solutions. It is not clear yet whether this effect is associated with the crossover phenomenon observed in our system.

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[1] G. Stell, Phys. Rev. A **45**, 7628 (1992).
[2] S. Wiegand, M. E. Briggs, J. M. H. Levelt Sengers, M. Kleemeier, and W. Schröer, J. Chem. Phys. **109**, 9038 (1998).
[3] R. R. Singh and K. S. Pitzer, J. Am. Chem. Soc. **110**, 8723 (1988); K. J. Zhang, M. E. Briggs, R. W. Gammon, and J. M. H. Levelt Sengers, J. Chem. Phys. **97**, 8692 (1992).
[4] T. Narayanan and K. S. Pitzer, J. Chem. Phys. **102**, 8118 (1995).
[5] M. E. Fisher, J. Stat. Phys. **75**, 1 (1994); *New Approaches to Problems in Liquid State Theory,* edited by C. Caccamo *et al.,* NATO Advanced Study Institutes, Ser. C, Vol. 529 (Kluwer, Dordrecht, 1999), p. 3.
[6] J. Jacob, A. Kumar, M. A. Anisimov, A. A. Povodyrev, and J. V. Sengers, Phys. Rev. E **58**, 2188 (1998).
[7] I. D. Lawrie and S. Sarbach, in *Phase Transitions and Critical Phenomena,* edited by C. Domb and J. L. Lebowitz (Academic Press, New York, 1984), Vol. 9, p. 2.
[8] M. A. Anisimov, A. A. Povodyrev, V. D. Kulikov, and J. V. Sengers, Phys. Rev. Lett. **75**, 3146 (1995); **76**, 4095 (1996).
[9] M. A. Anisimov, A. A. Povodyrev, and J. V. Sengers, Fluid Phase Equilib. **158–160**, 537 (1999).
[10] Y. B. Melnichenko, M. A. Anisimov, A. A. Povodyrev, G. D. Wignall, J. V. Sengers, and W. A. van Hook, Phys. Rev. Lett. **79**, 5266 (1997).
[11] M. A. Anisimov, A. S. Kurlandsky, and N. F. Kazakova, Mol. Cryst. Liq. Cryst. **159**, 87 (1988).
[12] J. A. Given and G. Stell, J. Chem. Phys. **96**, 9233 (1992).
[13] J. Jacob, A. Kumar, S. Asokan, D. Sen, R. Chitra, and S. Mazumder, Chem. Phys. Lett. **304**, 180 (1999).
[14] A. A. Povodyrev, M. A. Anisimov, and J. V. Sengers, Physica (Amsterdam) **264A**, 345 (1999).
[15] C. M. Knobler and R. L. Scott, in *Phase Transitions and Critical Phenomena* (Ref. [7]), Vol. 9, p. 164.
[16] V. M. Nabutovskii, N. A. Nemov, and Yu. G. Peisakhovich, Zh. Eksp. Teor. Fiz. **79**, 2196 (1980); [Sov. Phys. JETP **52**, 1111 (1980)]; Phys. Lett. **79A**, 98 (1980); Mol. Phys. **54**, 979 (1985).
[17] J. S. Høye and G. Stell, J. Phys. Chem. **94**, 7899 (1990); G. Stell, J. Stat. Phys. **78**, 197 (1995).
[18] R. Dickman and G. Stell, in *Simulation and Theory of Electrostatic Interactions in Solution,* edited by L. R. Pratt and G. Hummer (American Institute of Physics, New York, 1999), p. 225; G. Stell, in *New Approaches to Problems in Liquid State Theory* (Ref. [3]), p. 71.
[19] A. Z. Panagiotopoulos and S. K. Kumar, Phys. Rev. Lett. **83**, 2981 (1999).
[20] S. C. Greer, Phys. Rev. A **14**, 1770 (1976).