

Criticality in aqueous solutions of 3-methylpyridine and sodium bromideA. F. Kostko,^{1,*} M. A. Anisimov,^{1,2,†} and J. V. Sengers^{1,2}¹*Institute for Physical Science and Technology, University of Maryland, College Park, Maryland 20742, USA*²*Department of Chemical Engineering, University of Maryland, College Park, Maryland 20742, USA*

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We address a controversial issue regarding the nature of critical behavior in ternary electrolyte solutions of water, 3-methylpyridine, and sodium bromide. Earlier light-scattering studies showed an anomalous critical behavior in this system that was attributed to the formation of a microheterogeneous phase associated with ion-molecule clustering [M. A. Anisimov, J. Jacob, A. Kumar, V. A. Agayan, and J. V. Sengers, *Phys. Rev. Lett.* **85**, 2336 (2000)], while some other investigators subsequently found this system to exhibit ordinary Ising-like critical behavior. This contradiction forced us to revisit the problem and perform an accurate and comprehensive study of light scattering in this system paying attention to the achievement of thermodynamic equilibrium, hysteresis effects, aging, and prehistory of the samples, and a possible role of impurities. We show that properly aged, equilibrium samples of aqueous solutions of 3-methylpyridine with NaBr exhibit universal Ising-like critical behavior, typical for other aqueous solutions. No evidence for an equilibrium microheterogeneous phase was found. We have been able to reproduce anomalous behavior (similar to that reported initially) in a fast run on a freshly prepared sample. We attribute the observed anomalies to mesoscopic nonequilibrium aggregates, possibly associated with supramolecular restructuring in aqueous solutions. To support this conclusion we performed a study of aqueous solutions of 3-methylpyridine without NaBr and have found long-living nonequilibrium states in aqueous solutions of 3-methylpyridine.

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I. INTRODUCTION

Fluids and fluid mixtures with short-range intermolecular forces exhibit fluctuation-induced universal critical behavior that belongs to the three-dimensional Ising-like universality class [1]. Sufficiently close to the critical point, the correlation length of critical fluctuations becomes so large that microscopic details of short-range intermolecular interactions become unimportant. However, the nature of criticality in fluids containing ions has remained a challenging problem. Such systems can be roughly divided in two classes: “Coulombic” and “solvophobic” [2–8]. Phase separation driven by Coulombic forces is expected in solvents of low dielectric constant with large-size ions. Phase separation in aqueous solutions containing ions is usually driven by non-Coulombic forces. It does not mean that ions play no role in the phenomenon, but it means that the phase separation can occur even in the absence of ions. Examples are vapor-liquid separation of salty water or liquid-liquid separation of solutions of weakly dissociated organic solutes (such as isobutyric acid) in water.

To interpret experimental data one needs to account for possible nonasymptotic corrections to the observed critical behavior [9]. An analysis of existing experimental data for Coulombic and solvophobic fluids has shown that the asymptotic critical behavior is Ising-like for both classes

[10]. In systems with low dielectric constant the Coulombic interactions are exponentially screened (a short Debye screening length). In solvophobic systems with high dielectric constant long-range Coulombic forces are too weak to play an essential role in the nature of criticality.

It has also been noticed that at least some aqueous electrolyte solutions exhibit a pronounced crossover from asymptotic Ising behavior to mean-field critical behavior. Gutkowski *et al.* [10] have suggested that this phenomenon can possibly be interpreted as a crossover to mean-field tricriticality. It has indeed been demonstrated in the case of polymer solutions that a coupling between two different order parameters may cause crossover from asymptotic Ising-like critical behavior very close to the critical point to mean-field tricritical-point behavior further away from the critical point [11]. However, the physical conditions, that determine the temperature difference from the critical point (also referred to as the Ginzburg number) where the crossover takes place, has remained unclear [6–8,10,12–16].

To investigate the dependence of any crossover behavior in aqueous ionic solutions as a function of the salt concentration, Jacob *et al.* performed a set of light-scattering experiments in ternary mixtures of water+3-methylpyridine+sodium bromide in the vicinity of their lower consolute critical points. The actual experiments were performed at the Indian Institute of Science in Bangalore [17] and the data were interpreted by our research group at the University of Maryland [18–20]. Light-scattering measurements of the osmotic susceptibility in this system indicated that the range of Ising critical behavior shrank with increasing salt concentration so that at the NaBr mass fraction of 0.17 the behavior became completely mean-field-like. Moreover, a pronounced background scattering was observed in the same range of salt concentrations and was explained by formation of a micro-

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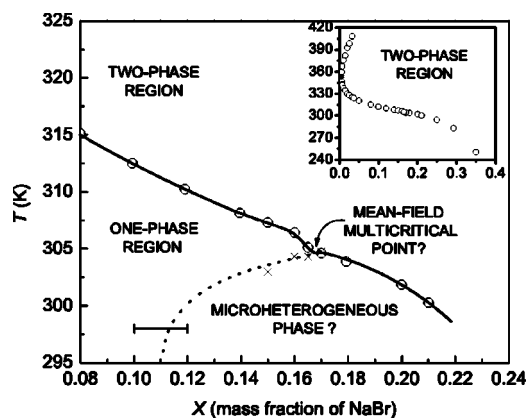


FIG. 1. Proposed phase diagram of aqueous solutions of 3-methylpyridine and sodium bromide inferred from the experimental data observed by Jacob *et al.* [17,21,29] and reported in Ref. [20]. The circles represent the experimental values of T_c for various mass fractions of NaBr; the solid curve represents the critical locus implied by these values. The dashed curve indicates the boundary of the temperatures and salt concentrations where the presence of a possible microheterogeneous phase was assumed. The crosses indicate the observed appearance of a large background scattering and the horizontal bar the appearance of clustering inferred from SAXS measurements [21]. The critical locus over a wide range of salt concentrations is shown as an inset.

heterogeneous phase. The existence of clusters in the system was also supported by small-angle x-ray scattering (SAXS) experiments [21] and the phase diagram inferred from the experiments is reproduced in Fig. 1 [20]. It was suggested that the crossover to mean-field behavior provided evidence of a possible multicritical point at about 17 mass % NaBr emerging as a result of ion-molecule clustering and a coupling between fluid phase separation and fluid structural transformation. Huge equilibrium times at NaBr concentrations above 0.16 were also reported [17,20] but were not investigated in detail. Furthermore, another interesting feature of the phase separation was detected in many electrolyte and nonelectrolyte aqueous solutions, namely, the appearance of a soap-like “phase” at the liquid-liquid interface [22]. In the water+3-methylpyridine+sodium bromide solutions this third phase was observed at various salt concentrations and it 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 3-methylpyridine and D_2O without any salt.

The observations described earlier have stimulated experimental studies of ternary mixtures of water+3-methylpyridine+sodium bromide in several laboratories. The shape of the coexistence curve and the turbidity in the one-phase region of the mixture of water+3-methylpyridine+sodium bromide with 17% mass fraction of NaBr were measured by Gutkowski *et al.* [23]. These measurements did not reveal any pronounced crossover to mean-field behavior. Shear-viscosity measurements [24] and refractive-index measurements [25] reported by Wagner *et al.* gave also no evidence for multicriticality or pronounced crossover to mean-field behavior, and these investigators

found the critical behavior to be rather insensitive to the salt concentration. In their most recent publication, Wagner *et al.* [26] further confirmed this conclusion by carefully analyzing their light-scattering data for this system. Moreover, Wagner *et al.* observed microheterogeneities causing a background scattering, which “required waiting times up to 8 days to decay.” Van Roie *et al.* [27] used adiabatic scanning calorimetry to search for a tricritical point in this system and found no specific-heat anomaly to be associated with the possible formation of a new phase. On the other hand, a light-scattering study, recently reported by Hernández *et al.* [28], confirmed the pronounced crossover to mean-field behavior at concentrations near 16% of NaBr and the authors concluded that the data could be described with the same set of crossover parameters earlier reported in Ref. [20]. Additional arguments for the presence of crossover behavior at concentrations near 17% NaBr have recently been reported by Jacob *et al.* [29].

Motivated by these contradictions we have revisited the problem and performed more accurate and more comprehensive light-scattering experiments in ternary aqueous solutions of 3-methylpyridine and sodium bromide. In this study we emphasize the achievement of thermodynamic equilibrium, possible hysteresis effects, aging and prehistory of the samples, as well as a possible role of impurities. We have found that properly aged equilibrium samples exhibit universal Ising-like critical behavior, as is typical for other fluids and fluid mixtures. We have confirmed a nonmonotonic crossover of the effective susceptibility critical exponent from the Ising value 1.24 towards its mean-field value unity. The parameters of the asymptotic critical behavior, such as the amplitude of the correlation length have been found to be in agreement with those reported recently by Wagner *et al.* [26]. However, the characteristic crossover temperature lies at the edge of the critical domain (about 10% below the critical temperature) and thus the crossover is not completed in the critical region. The observed nonmonotonic shape of the crossover behavior is characteristic for aqueous solutions [9,10] (electrolyte and nonelectrolyte) and does not show a significant dependence on the salt concentration. Therefore, we have not confirmed the existence of a multicritical point at 17 mass % NaBr. We believe that the anomalies previously reported for this system are associated with nonequilibrium phenomena. We have been able to reproduce anomalous behavior (similar to that reported in Refs. [18–20]) in a fast run on a freshly prepared sample. We attribute the observed anomalies to mesoscopic long-living nonequilibrium aggregates, possibly associated with slow supramolecular restructuring in aqueous solutions. To support this conclusion we performed a study of aqueous solutions of 3-methylpyridine without NaBr and have found long-living (at least of the order of days) nonequilibrium states.

II. SAMPLE PREPARATION AND EXPERIMENTAL PROCEDURE

For the purpose of the present study a set of samples of aqueous solutions of 3-methylpyridine and sodium bromide was prepared at the University of Maryland. For the prepa-

ration of our samples we purchased 3-methylpyridine (99.5+ %) and NaBr (99.99+ %) from Aldrich Chemical Company. The chemicals for the prepared samples were used without further purification except for a dust-removing procedure with 0.2 μ filters. Water for the solutions was purified with a standard Millipore Alpha-Q setup. The mass concentrations of NaBr in our samples are 16.0%, 16.7%, 17.0%, and 24.0%. The concentration of 24.0% is interesting because mixtures of aqueous solutions of 3-methylpyridine at salt concentrations larger than 17.0% have not been investigated in any laboratory before. The corresponding critical concentrations of 3-methylpyridine are: 24.0₃%, 23.4₇%, 23.0₈%, and 19.8₀%. Bulk solutions were prepared by first adding an appropriate amount of H₂O (with a syringe) to the 3-methylpyridine and then adding NaBr. To monitor the concentration of the solution during preparation, the flask for the bulk sample was placed on a balance while the H₂O and NaBr were added to the 3-methylpyridine. After the bulk solution had been gently stirred and aged during a period of several hours or overnight, part of the bulk sample was filtered under a laminar dust-free air flow into the optical cell. Each optical cell is a glass cylinder of 6 mm inner diameter rounded at one end with an additional sphere of about 15 mm diameter. This sphere was used to freeze solutions before we flame sealed the cell. For the light-scattering measurements the cell was overturned so that the solution filled the cylinder, while the sphere at the top was empty.

Since the light-scattering measurements that we obtained from the samples prepared at the University of Maryland turned out to be quite different from the data obtained earlier by Jacob in Bangalore [17] and by Hernández *et al.* in Madrid [28], the samples used in these laboratories were shipped to the University of Maryland for further investigation. The samples prepared in Bangalore consist of 3-methylpyridine with a stated purity of 99%, triply distilled water and dried analytical grade NaBr with a purity of 99%. The purities of the samples prepared in Madrid are 99.9% for 3-methylpyridine and 99.99+ % for NaBr. Hence, among all samples studied, the samples prepared in Madrid seem to have the highest purity. In practice we performed the light-scattering experiments with two samples from the collection prepared in Bangalore, namely the ones with 14.0% and 17.0% mole fraction of NaBr. From the collection of samples prepared in Madrid we investigated the sample with a NaBr mass fraction of 16.0%.

The light-scattering experiments were performed with the same instrument previously used for a study of critical fluctuations in polymer solutions [11,30,31]. For a detailed description of the light-scattering instrument we refer to an earlier publication [30]. We measured the magnitude I , as well as the dynamic correlation function $g_2(\tau)$, of the scattered-light intensity with a photon-counting system using both a PhotoCor and an ALV-5000/E correlator (for consistency checks) [30]. All light-scattering measurements were performed at a scattering angle of 90°. As soon as the scattered intensity became large on the approach to the critical temperature, we reduced the intensity of the incident beam of the He-Ne laser (10 mW) with the aid of two calibrated neutral density filters so as to keep the measured intensities in the linear dynamic range of the photon-counting system.

This procedure also prevented possible local heating of the sample. The signal proportional to the intensity of the incident beam was periodically directed by a shutter and optical guide to the photon-counting system alternatively with the scattered intensity. This procedure was used to correct for any drift of the laser-light intensity. The intensity of the transmitted beam was measured with a photodiode. This provided us with turbidity data that were used for evaluating multiple-scattering corrections and turbidity losses to the observed scattering intensities. The temperature T of the sample was maintained by a three-shell thermostat with an accuracy of ± 1 mK. The external shell was cooled with a water-bath loop down to 14 °C for measurements at lower-than-room temperatures. To verify that the samples were at the critical concentration, we checked that the meniscus in the two-phase region above the critical temperature appeared at the center of the sample. The light-scattering measuring procedure is controlled by a computer and can run automatically for several days. Before each measurement, the samples were stirred at room temperature and then kept in the thermostat of the light-scattering instrument at 18 °C for several hours. We also tried to subject the samples to ultrasonic stirring with an ultrasonic Brandon-2000 agitator before starting the experimental runs as had been recommended by Jacob *et al.* [18,19]. However, we did not find any significant effect on the experimental results, so this procedure was abandoned.

In a typical experimental run at a fixed temperature the successive measurements (5 min) of the light-scattering intensity and measurements (90 s) of the intensity of the incident laser beam were performed for a period of about 50 min. Before each intensity measurement the photomultiplier was exposed to light during a minute for better accommodation. The accuracy of the intensity measurements is about 1%–2%. We started at a temperature well below the critical temperature and then increased the temperature with decreasing temperature steps. After each (small) temperature change a delay of about 40 min turned out to be enough for the samples to reach an equilibrium state. Equilibrium was verified by observing the stability of the scattered-light intensity and of a photodiode signal that registered the intensity of the transmitted beam. The critical temperature T_c was determined by approaching and passing it with temperature steps as small as 4 mK. Passage through T_c was registered by the appearance of a distinct instability of the photodiode signal. Thus the error in the evaluation of the critical temperature T_c was less than 4 mK. The values obtained for T_c are shown in Fig. 2 as a function of the salt concentration together with values previously reported by several other investigators [18,25,28]. Within the experimental accuracy we do not find evidence for the presence of a dip in the critical locus at a mass fraction of NaBr between 16.5% and 17.0% previously inferred from the data collected in Bangalore [17,18] and indicated in Fig. 1.

At temperatures substantially below the critical temperature T_c , where light scattered from concentration fluctuations becomes much less intense, we observed some random splashes while monitoring the scattering intensity as a function of time. As an example we show in Fig. 3 the light-scattering intensity as a function of time for the aqueous solution of 3-methylpyridine with 16.7% NaBr at two differ-

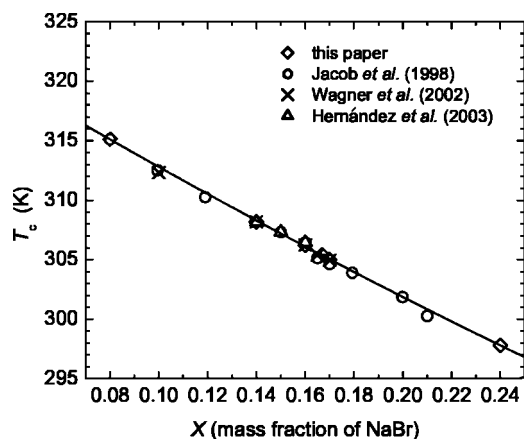


FIG. 2. Locus of lower critical temperatures of aqueous solutions of 3-methylpyridine and sodium bromide: (\diamond): this study; (\circ): Ref. [18]; (\times): Ref. [25]; and (\triangle): Ref. [28].

ent temperatures, namely at $T=21.83$ °C and $T=26.88$ °C corresponding to a reduced temperature distance $\varepsilon=(T_c - T)/T$ of 0.035 and 0.018, respectively. The presence of splashes in the time dependence of the light-scattering intensity curiously disappears at temperatures above approximately 25 °C. Our first guess was that such intensity splashes might be attributed to dust particles. However, all attempts to filter the solution more carefully did not help. Moreover, we met the same problem with the samples from Bangalore that had been filtered carefully and sealed several years ago. In some cases we noticed that in the second and the following runs the average amplitude and frequency of the splashes appeared to be smaller than in freshly prepared samples. We concluded that this phenomenon is not a true equilibrium phenomenon and obviously not related to the critical fluctuations and, hence, to the osmotic susceptibility. Since we did not find any way to avoid this nonequilibrium background scattering, we eliminated the effect in processing the experimental data. Specifically, from every sequence of 5 min measurements that were made at a given temperature we selected the measured scattering intensities that were not

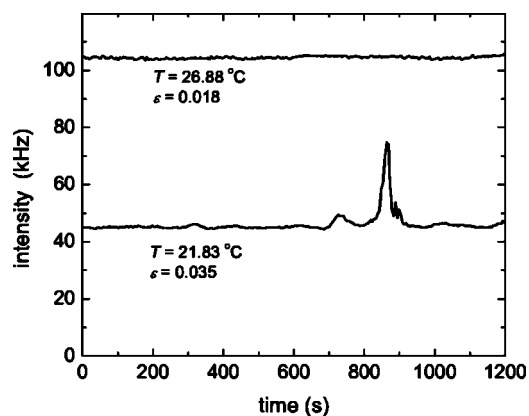


FIG. 3. Observed light-scattering intensity as a function of time at 21.83 °C (lower curve) and at 26.88 °C (upper curve) for an aqueous solution of 3-methylpyridine and sodium bromide with 16.7% mass fraction of NaBr.

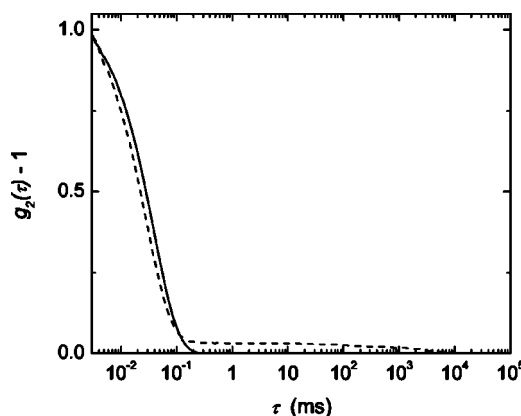


FIG. 4. Dynamic correlation function at 21.83 °C (dashed curve) and at 26.88 °C (solid curve) for an aqueous solution of 3-methylpyridine and sodium bromide with 16.7% mass fraction of NaBr.

affected by the background contribution and used only those data for further analysis. After the data had been corrected by eliminating the intensity splashes, the temperature dependence of scattered intensity became smooth and suitable for analysis. We should note that this correction was only needed for three to five of the lowest temperatures more than 5° below the critical temperature.

The effect of these spurious intensity splashes on the dynamic correlation function is shown by the tailed dashed curve in Fig. 4. The length of the tail is related to the average time of the appearance of rare large-size scatterers in the scattering volume. The correlation function at the temperatures above 25° can be represented by a single exponential as is to be expected for the decay of critical fluctuations. We have not made a detailed study of the dynamics of critical fluctuations in the aqueous solutions of 3-methylpyridine and sodium bromide (except for the long-tail effect shown in Fig. 4 and observed only at the lower temperatures), since it appears to be similar to that observed in molecular liquid mixtures. However, we shall comment on the dynamics of fluctuations in binary aqueous solutions of 3-methylpyridine without salt in Sec. IV as it appears to be relevant to some of the anomalous critical behavior reported for the ternary solutions with salt present.

The observed light-scattering intensities need to be corrected for multiple scattering and turbidity losses. For the implementation of these corrections we used a Monte-Carlo simulation program developed by Kleemeier [32]. This program is based on the procedure presented by Bailey and Cannell [33] and has been used by Wiegand and coworkers in the analysis of light-scattering measurements of critical fluctuations in some liquid solutions [34–36]. With the turbidity values that we measured independently and the geometric parameters of the samples as input, the program provides the ratio of the singly scattered light intensity to the total scattered light intensity. We did not analyze the intensity data measured within 0.03 K from the critical temperature, since at these temperatures the multiple scattering and turbidity corrections exceeded 30%–50%.

The values needed for the refractive index of the solutions as a function of temperature and concentration were mea-

sured with an Abbé refractometer. In the range 14.0%–24.0% of mass fraction X of NaBr and in the temperature range 18–35 °C, where we determined the refractive index n of our samples in the one-phase region, the data could be represented by

$$n = 1.395 + 0.85 \times 10^{-3}X - 2.53 \times 10^{-4}t, \quad (1)$$

where t is the temperature in degrees Celsius and X is the mass fraction of NaBr in %. Equation (1) agrees with a deviation of 0.003 with refractive-index data recently reported for the same system by other investigators [23,25].

III. ANALYSIS OF LIGHT-SCATTERING DATA

The experimental light-scattering data, corrected for multiple scattering and turbidity losses have been analyzed in terms of a theory that accounts for a crossover from Ising-like critical behavior asymptotically close to the critical temperature to mean-field critical behavior further away from the critical temperature [37]. The procedure for applying the theory to the light-scattering measurements of critical fluctuations has been described in some previous publications [9,10,18].

In fluids, like in other Ising-like systems, the physical properties such as the susceptibility and the order parameter generally exhibit crossover from Ising behavior asymptotically close to the critical point towards mean-field behavior further away from the critical point. The crossover is controlled by two independent parameters: \bar{u} , a coupling constant that reflects the range of interactions, and Λ , a dimensionless cutoff wave number. Numerical simulations of the three-dimensional Ising model ($\Lambda=1$) demonstrate a complete crossover to mean-field critical behavior when the coupling constant \bar{u} vanishes with the divergence of the interaction range [38]. An alternative kind of crossover to mean-field behavior is observed in near-critical polymer solutions with the divergence the degree of polymerization at the *theta* point [11]. In the polymer case, the coupling constant \bar{u} remains of order unity independent of the degree of polarization, while the cutoff Λ vanishes inversely proportional to the radius of gyration of the polymer molecule. The radius of gyration serves as an additional correlation length associated with an additional order parameter in polymer solutions. Thus, the crossover towards mean-field behavior in polymer solutions appears to be crossover to *theta*-point tricriticality [11,39].

Experimentally, crossover to mean-field behavior can be studied by analyzing the temperature dependence of the susceptibility. The intensity I_s of the scattered light is proportional to a generalized susceptibility χ and may be written as

$$I_s = I_0 \chi G(q\xi) + I_b, \quad (2)$$

where I_0 is an instrumental constant, I_b is a regular background scattering intensity, and $G(q\xi)$ is the order-parameter correlation function, that depends on the correlation length ξ and the wave number $q=4\pi n\lambda_0^{-1} \sin(\theta/2)$ of the critical fluctuations (λ_0 is the wavelength of the incident light and θ the scattering angle). In practice, we adopted for $G(q\xi)$ an ap-

proximation proposed by Fisher and Burford [40]

$$G(q\xi) = \frac{[1 + 0.084^2(q\xi)^2]^{\eta/2}}{1 + (q\xi)^2 \left(1 + \frac{\eta}{2} 0.084^2\right)} \quad (3)$$

with $\eta=0.033$, a universal critical exponent.

The crossover equations for the susceptibility χ and correlation length ξ are [9,10,18]:

$$\chi = [c_\rho^2 c_t \varepsilon Y^{(\gamma-1)/\Delta_s} (1+y)]^{-1}, \quad (4)$$

$$\xi = q_0^{-1} \kappa^{-1} = q_0^{-1} [c_t \varepsilon Y^{(2\nu-1)/\Delta_s}]^{-1/2}, \quad (5)$$

with

$$y = \frac{u^* \nu}{2\Delta_s} \left\{ 2 \left(\frac{\kappa}{\Lambda} \right)^2 \left[1 + \left(\frac{\Lambda}{\kappa} \right)^2 \right] \left[\frac{\nu}{\Delta_s} + \frac{(1-\bar{u})Y}{1-(1-\bar{u})Y} \right] - \frac{2\nu-1}{\Delta_s} \right\}^{-1}, \quad (6)$$

while the variable ε represents the reduced temperature proximity to the critical temperature

$$\varepsilon = (T_c - T)/T. \quad (7)$$

In these equations, \bar{u} and Λ are the crossover parameters, $u^*=0.472$ the universal renormalization-group fixed point value of the coupling constant, c_ρ and c_t are scaling amplitudes, Y is a crossover function, $\gamma \cong 1.239$, $\nu \cong 0.630$, and $\Delta_s \cong 0.51$ are the Ising critical exponents. In Eq. (5) $q_0 = \pi/v_0^{1/3}$ is a wave number, where v_0 is a microscopic volume of the order of the molecular volume. The parameter κ is a normalized inverse correlation length. In some earlier publications [10,18] we have used $\xi = v_0^{1/3} \kappa^{-1}$ for the relationship between ξ and κ^{-1} , thus effectively incorporating a factor π^{-1} into the definition of $v_0^{1/3}$. However, we have concluded subsequently that the relation $\xi = q_0^{-1} \kappa^{-1} = (v_0^{1/3}/\pi) \kappa^{-1}$ leads to a more physical meaning of the volume v_0 for the Ising lattice [38] as well as for fluids [41]. The crossover function Y in the earlier equation is to be determined from

$$1 - [1 - \bar{u}]Y = \bar{u} \left[1 + \left(\frac{\Lambda}{\kappa} \right)^2 \right]^{1/2} Y^{\nu/\Delta_s}. \quad (8)$$

It is convenient to represent the crossover behavior of the susceptibility in terms of an effective susceptibility exponent defined as [42]

$$\gamma_{\text{eff}} = - \frac{\partial \log \chi}{\partial \log \varepsilon}. \quad (9)$$

Such an effective exponent may exhibit crossover from the Ising value $\gamma_{\text{eff}} \cong 1.239$ to the mean-field value $\gamma_{\text{eff}} \cong 1.00$ as ε increases. The crossover between these two limits can be characterized by a crossover temperature T_\times or by a reduced crossover temperature $\varepsilon_\times = (T_\times - T)/T$. A natural definition of ε_\times is the value of ε that corresponds to the inflection point of γ_{eff} as a function of $\log \varepsilon$.

In ordinary fluids with short-range interactions, crossover to mean-field behavior is never completed in the critical do-

TABLE I. Crossover parameters and correlation-length amplitudes as a function of the NaBr mass fraction X .

X	\bar{u}	c_t	Λ	ξ_0 (Å)	$\bar{\xi}_0$ (Å)	ε_\times
0.14 ^a	1.3	0.13	0.11	3.0	3.7	0.06 ₃
0.16	1.3	0.12	0.09	2.9	3.8	0.04 ₄
0.16 ^b	1.2	0.15	0.20	3.0	3.4	0.09 ₁
0.167	1.1	0.11	0.11	3.2	4.1	0.06 ₄
0.17	1.1	0.13	0.14	3.0	3.7	0.10
0.17*	1.5	0.14	0.12	2.9	3.6	0.07
0.24	1.0	0.10	0.09	3.2	4.5	0.04 ₇

^aBangalore sample.

^bMadrid sample.

main (roughly $\varepsilon \lesssim 0.1$) and γ_{eff} never drops to a value lower than about 1.10–1.15 [9]. An analysis of osmotic-susceptibility data and of data for the order parameter [10] shows that in aqueous solutions (electrolyte and nonelectrolyte) the coupling constant \bar{u} is larger than unity, in which case the crossover towards mean-field behavior is controlled by the ratio $\Lambda/\kappa < 1$ [43]. If $\bar{u} > 1$, the effective exponent approaches its asymptotic Ising value $\gamma_{\text{eff}} \cong 1.239$ from above so that the crossover towards the mean-field value $\gamma_{\text{eff}} \cong 1$ is nonmonotonic. This feature can imply the existence of a structural-length scale $\xi_D \sim \Lambda^{-1}$ that exceeds the molecular size but which usually does not become large enough to complete the crossover. This is why, the apparent mean-field behavior in the solution of 3-methylpyridine + water + 17% NaBr was met with such an interest and was attributed to the divergence of the structural length ξ_D at a multicritical point [20].

Asymptotically close to the critical temperature, the correlation length ξ satisfies a power law $\xi = \xi_0 \varepsilon^{-\nu}$, while in the mean-field limit ξ varies as $\xi = \bar{\xi}_0 \varepsilon^{-\nu}$. The amplitudes ξ_0 and $\bar{\xi}_0$ are given by [41]

$$\xi_0 = q_0^{-1} c_t^{-1/2} \left(\frac{\bar{u}\Lambda}{c_t^{1/2}} \right)^{2\nu-1}, \quad (10)$$

and

$$\bar{\xi}_0 = q_0^{-1} c_t^{-1/2}. \quad (11)$$

Apart from the coefficient $c_\rho^2 c_t$ in Eq. (4), which we shall incorporate in the instrumental coefficient I_0 in Eq. (2), the crossover equations for the susceptibility χ and for the correlation length ξ depend on \bar{u} and on $\Lambda/c_t^{1/2}$, while Eq. (5) for ξ also contains $q_0^{-1} c_t^{-1/2}$ as a prefactor. We fitted the experimental light-scattering intensities to Eqs. (2)–(5) using I_0 , \bar{u} , $\Lambda/c_t^{1/2}$ and $q_0^{-1} c_t^{-1/2}$ as adjustable parameters. For most samples the background scattering I_b was insignificant and could be omitted in the fits. The experimental data do not yield values for c_t and Λ directly, but only for $q_0^{-1} c_t^{-1/2}$ and $\Lambda/c_t^{1/2}$. We estimated c_t from $q_0^{-1} c_t^{-1/2} = v_0^{1/3} \pi^{-1} c_t^{1/2}$ with $v_0^{1/3} = 3.5$ Å for our samples [18]. The values thus obtained for \bar{u} , c_t , and Λ , as well as the corresponding values for ξ_0 , $\bar{\xi}_0$, and ε_\times , are presented in Table I.

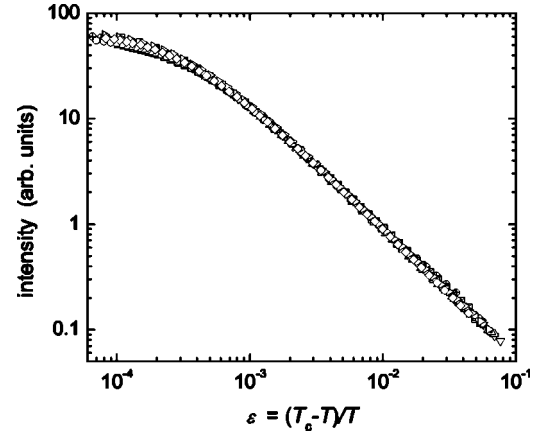


FIG. 5. Experimental light-scattering intensities, measured at $\theta = 90^\circ$ and corrected for multiple scattering and turbidity losses, as a function of ε for all samples of aqueous solutions of 3-methylpyridine and NaBr investigated in the present study. Data symbols: \triangleright 14% NaBr (Bangalore sample), \triangle 16% NaBr, \diamond 16% NaBr (Madrid sample), \oplus 16.7% NaBr run 1, \circ 16.7% NaBr run 2, ∇ 17% NaBr, \square 17% NaBr (Bangalore sample), and \boxtimes 24% NaBr.

In the mean-field limit the order-parameter correlation function $G(q\xi)$ is given by the Ornstein-Zernike expression [44]:

$$G_{\text{OZ}}(q\xi) = \frac{1}{1 + q^2 \xi^2}. \quad (12)$$

Our experimental data cover a range of $q\xi$ values from 0.025 far away from the critical temperature to a maximum value of 2 at $\varepsilon \approx 10^{-4}$. Equation (3) accounts for deviations from the Ornstein-Zernike expression when $q\xi > 1$. Away from the critical temperature $q\xi$ becomes smaller than unity and the difference between Eqs. (3) and (12) becomes negligibly small.

The experimental light-scattering intensities, corrected for multiple scattering and turbidity losses, obtained for all samples of aqueous solutions of 3-methylpyridine and sodium bromide, including samples earlier prepared in Bangalore and in Madrid, are shown in Fig. 5 as a function of the reduced temperature ε . It turns out that these light-scattering data for mass fraction of NaBr ranging from 14% to 24% virtually collapse onto a single curve and we do not find any significant differences in the temperature dependence of the intensity either for the samples with different NaBr concentration or for the samples prepared in different laboratories. Some small deviations in the close vicinity of the critical temperature are within the errors of the corrections for multiple scattering and turbidity losses. The region far away from the critical temperature is more important for searching any crossover to mean-field critical behavior. Here we also do not find any significant differences for the samples prepared in different labs and for different concentrations. A first run in our sample of 16.7% NaBr seemed to exhibit some systematic deviations from other runs at $\varepsilon > 10^{-2}$. However, a second run on the same sample did not show such deviations.

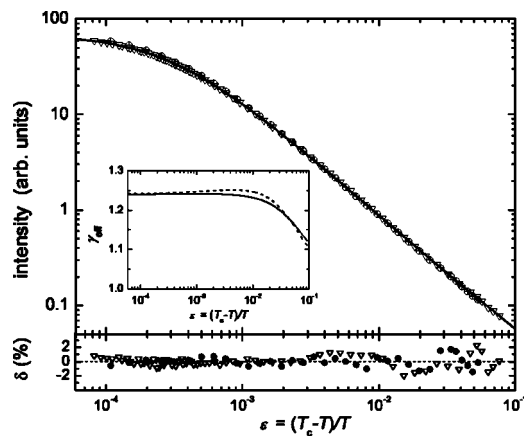


FIG. 6. Experimental light-scattering intensities, corrected for multiple scattering and turbidity losses, obtained for the aqueous solution of 3-methylpyridine with 17% mass fraction of NaBr from our sample (∇) and from the old sample prepared in Bangalore (\oplus). The solid curve represents a fit to the crossover theory. The differences, δ , between experimental and calculated intensities are shown at the bottom. The temperature dependence of the effective susceptibility exponent γ_{eff} deduced from the fit to the data for our sample (solid curve) and for the fit to the data for the old Bangalore sample is shown in the inset.

A detailed comparison between the experimental data that we observed from a sample of an aqueous solution of 3-methylpyridine and NaBr prepared in our laboratory with data obtained with the sample prepared previously in Bangalore with the same NaBr concentration is presented in Fig. 6. A similar comparison between the experimental data obtained from the sample prepared in our laboratory and one with the same NaBr concentration prepared in Madrid is presented in Fig. 7. Our results obtained from the samples prepared at these different laboratories agree with each other within the experimental accuracy of our measurements. The temperature dependence of the effective susceptibility exponent $\gamma_{\text{eff}}(\varepsilon)$ implied by the measurements is shown in the insets in Figs. 6 and 7. We note that for small ε , $\gamma_{\text{eff}}(\varepsilon)$ increases with increasing ε consistent with the nonmonotonic crossover behavior of γ_{eff} associated with $\bar{u} > 1$, which is typical for other aqueous solutions that are characterized by intermolecular interaction with very short ranges. The crossover to a mean-field value of unity is not completed in the critical domain ($\varepsilon \lesssim 1$) as is also the case for nonionic fluids [9]. The so-called Fisher renormalization of the critical exponents [45], generally expected in ternary mixtures, is negligible for the one-phase samples with around 16%–17% mass fraction of NaBr [18,28].

The earlier results are consistent with the behavior inferred from turbidity measurements reported by Gutkowski *et al.* [23], from refractive-index measurements reported by Wagner *et al.* [25], and from measurements of the specific heat capacity measured by Van Roie *et al.* [27]. Moreover, our results are in full agreement with the most recent studies of light-scattering reported by Wagner *et al.* [26]. Although Wagner *et al.* did not analyze the crossover behavior, the parameters of the Ising asymptotic critical behavior, in particular, the amplitude of the correlation length, ξ_0 , presented

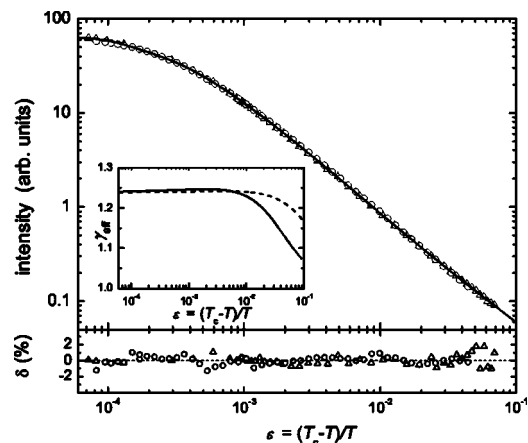


FIG. 7. Experimental light-scattering intensities, corrected for multiple scattering and turbidity losses, obtained for the aqueous solution of 3-methylpyridine with 16% mass fraction of NaBr from our sample (Δ) and from the sample prepared in Madrid (\circ). The solid curve represents a fit to the crossover theory. The differences, δ , between experimental and calculated intensities are shown at the bottom. The temperature dependence of the effective susceptibility exponent γ_{eff} deduced from the fit to the data for our sample (solid curve) and for the fit to the data for the Madrid sample is shown in the inset.

in Table I, have been found to be in excellent agreement with the values $\xi_0 = 2.84\text{--}3.09 \text{ \AA}$ reported in Ref. [26].

However, our results differ fundamentally from those reported in earlier publications [18–20] based on experiments performed at Bangalore [17] and at Madrid [28]. The previous measurements indicated that the crossover temperature ε_{\times} decreased with increased NaBr and becoming vanishingly small at a concentration of about 17% mass fraction of NaBr, a feature confirmed by Hernández *et al.* [28]. These results were interpreted as indicating the presence of a multicritical point at a concentration of about 17% mass fraction of NaBr [20]. However, the values obtained for ε_{\times} from our experimental data do not significantly depend on the salt concentration in contrast to those reported previously, as shown in Fig. 8. The values of the reduced crossover temperature obtained in this study are close to the value of 0.1 that is approximately at the edge of the critical domain. The first run for the sample with $X=0.167$ yielded a somewhat smaller value of ε_{\times} (closed circle), but the second run brought ε_{\times} up to the average value. We note that ε_{\times} even has the same average value for a solution with $X=0.24$, a NaBr concentration significantly above the maximum value $X=0.17$ investigated previously. We do not find any enhanced background scattering (if we do not take into account intensity splashes observed at the lowest temperatures) reported previously at the higher salt concentrations [20]. In conclusion, our measurements do not provide evidence for the existence of a multicritical point in aqueous solution of 3-methylpyridine and NaBr.

IV. EQUILIBRIUM OR NONEQUILIBRIUM?

While our light-scattering data do not provide evidence for the presence of a multicritical point in aqueous

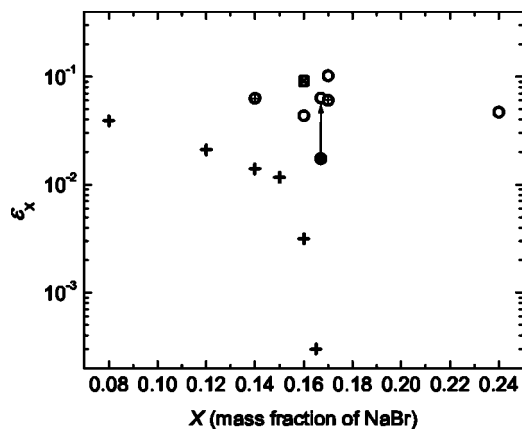


FIG. 8. Reduced crossover temperature ε_x for different salt concentrations in the aqueous solutions of 3-methylpyridine and sodium bromide obtained in this study as compared with ε_x from Ref. [18]. ○ from our samples, ⊕ from our measurements for samples prepared in Bangalore, ⊠ from our measurements for a sample prepared in Madrid [28], + Ref. [18].

3-methylpyridine solutions with NaBr, the question remains why previous studies have yielded experimental data indicating a quantitative different kind of critical behavior, even for the same samples. Wagner *et al.* [26] have observed nonequilibrium microheterogeneities with the size of about $3 \mu\text{m}$ in this system, which required waiting times up to 8 days to vanish. Wagner *et al.* attributed the apparent mean-field behavior in aqueous 3-methylpyridine solutions with NaBr to nonequilibrium heterogeneities and stated that “the origin of these, however, remains unexplained.” Another mysterious and probably related phenomenon, namely the appearance of soap-like “particles” at the liquid-liquid interface in a broad range of salt solutions, appeared to be a general phenomenon encountered in aqueous solutions of organic solutes without salt [22]. Hence, we decided to investigate the possibility that the anomalous behavior reported in Refs. [18–20,28] including the enhanced backscattering, could be associated with some kind of supramolecular restructuring in aqueous solutions of 3-methylpyridine even in the absence of salt. We therefore prepared same aqueous solutions of 3-methylpyridine without salt, keeping the 3-methylpyridine/water ratio the same as in the critical ternary mixture with 17% mass fraction of NaBr, namely 28.6% mass fraction (6.85 mol %) of 3-methylpyridine. The 3-methylpyridine for the same samples was taken from different bottles all with a nominal purity of 99.5+%. We noticed that the solutions from different sources of 3-methylpyridine would exhibit different levels of turbidity. One of the samples became very turbid immediately after the sample preparation and remained turbid for months. Our first guess was that enhanced background light scattering observed in solutions with salt could be due to small impurities in 3-methylpyridine that lead to the formation of precipitants. While we still believe that to be true, we were not able to find any differences in the composition of the different samples of 3-methylpyridine with gas chromatography and nuclear magnetic resonance spectroscopy at the level of accuracy to our disposal.

As a next step we performed some dynamic light-scattering studies of the aqueous mixtures of

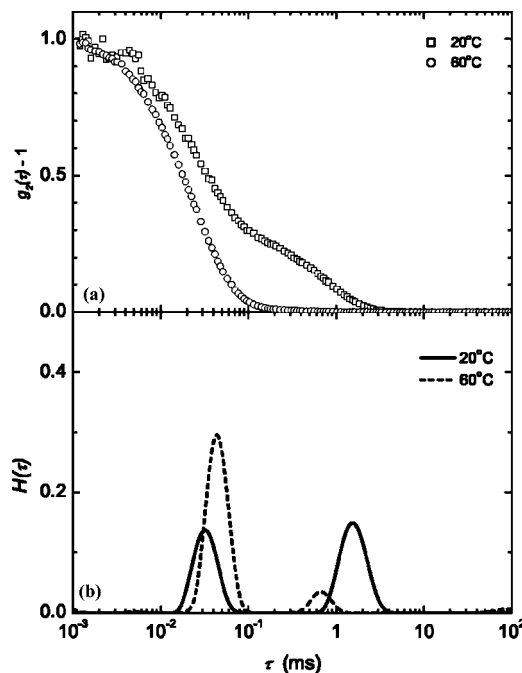


FIG. 9. (a) Dynamic correlation functions $g_2(\tau)$ for an aqueous solution of 3-methylpyridine at 20°C (circles) and at 60°C (squares); (b) corresponding probability distributions $H(\tau)$ of the decay time τ at 20°C (solid curve) and at 60°C (dashed curve).

3-methylpyridine without salt. In Fig. 9 the dynamic correlation function for an aqueous solution of 3-methylpyridine (sample No. 1) is shown. The shape of this correlation function is obviously not a single exponential. Along with the usual diffusion mode (with a relaxation time from 30 to $50 \mu\text{s}$) associated with concentration fluctuations, it has an additional very slow mode, which appears to be also diffusive (q^2 dependent), corresponding to a characteristic time scale of about $1000\text{--}2000 \mu\text{s}$. After the temperature was raised from 20 up to 60°C , the relative contribution of this mode decreased considerably. Results obtained for sample No. 2 with the same composition but with 3-methylpyridine from a different bottle showed a very different picture. At room temperature the slow mode dominates and becomes even slower than in sample No. 1 as is shown in Fig. 10. This sample looked very turbid even with a naked eye.

These strange results stimulated us to further investigate aqueous solutions of 3-methylpyridine without salt. Specifically, we prepared a slightly more concentrated aqueous solution of 3-methylpyridine with a concentration of 32 mass % (8.2% mol fraction). This composition corresponds to the so-called double critical point in the phase diagram (Fig. 1), where a small amount of NaBr induces a critical-point phase separation. This sample also exhibited some strange light-scattering effects. The temperature dependence of the light-scattering intensity was measured at four scattering angles 30° , 45° , 90° , and 140° . In Fig. 11 we show that, after we heated the sample up to 85°C and then cooled it back down to the starting temperature of 25°C , the intensity of scattering did not return to its initial value. Moreover, a huge asymmetry in the angular distribution of the intensity gave evi-

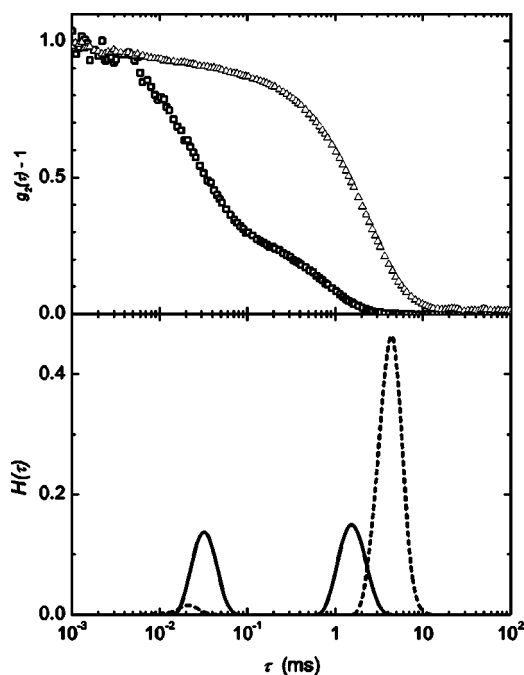


FIG. 10. Dynamic correlation functions $g_2(\tau)$ and corresponding probability distributions $H(\tau)$ of the decay time τ for two aqueous solutions of 3-methylpyridine at 20 °C. The circles and the solid curve are for the same transparent sample (sample No. 1) shown in Fig. 9; the triangles and dashed curve are for a turbid sample (sample No. 2).

dence of large-size scatterers that persist in the solution for a long time. It is not surprising that around 80 °C the intensity is large: the system has almost reached the double critical point of phase separation. What is surprising is that the non-equilibrium opalescence remained unchanged for a long time after the sample was cooled down to 25 °C.

We conclude that the energy landscape in aqueous solutions of 3-methylpyridine is such that states with nonequilibrium supramolecular structure can exist during time periods longer than the ordinary times for conducting light-scattering experiments. Addition of salt not only can induce a phase separation but also may make these apparent states less stable. We noticed that addition of NaBr to a turbid aqueous solution of 3-methylpyridine eventually made it transparent, unless the sample was brought to the critical point of phase separation. In Fig. 12 we show several runs on an initially turbid sample after the addition of NaBr. One can see that we virtually reproduced the anomalous behavior of the light-scattering intensity reported in Ref. [20] for 17% NaBr. After the sample was cooled back to 20 °C the scattering intensity dropped and continued to drop at this temperature in succeeding runs.

We now tend to believe that some unexpected and unconfirmed phenomena previously observed in near-critical non-aqueous ionic solutions, such as in mixtures of triethyl *n*-hexyl ammonium triethyl *n*-hexyl borate ($N_{2226}B_{2226}$) in diphenyl ether, that looked like absolutely different substances in experiments performed by different research groups (see Ref. [10], and citations therein), may be similar to what we have observed in this study. Moreover, the

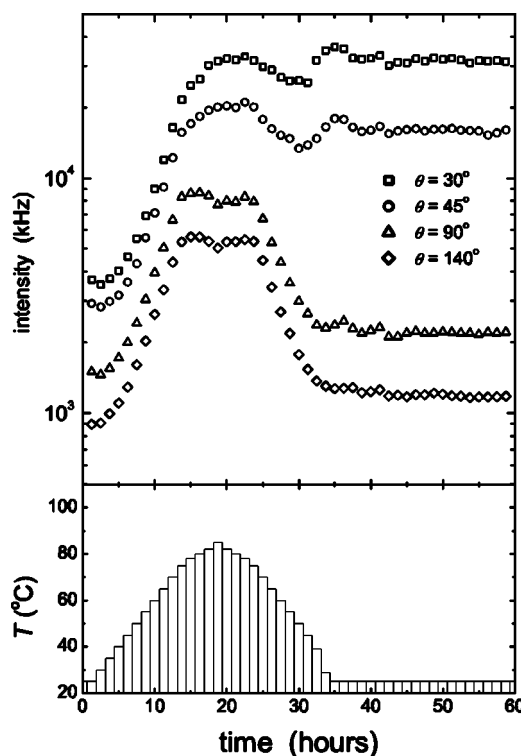


FIG. 11. Result of an experimental study of long-living nonequilibrium states in aqueous solutions of 3-methylpyridine. We show the scattering intensity for four scattering angles as a function of time while the temperature is cycled between 25 and 80 °C.

anomalies that we encounter in the mixtures of 3-methylpyridine and water are remarkably similar to those observed many years ago in aqueous solutions of alcohols. Actually, anomalous light-scattering behavior of aqueous alcohol solutions was discovered by Vuks and Shurupova [46,47]. Later it was found in dynamic light-scattering ex-

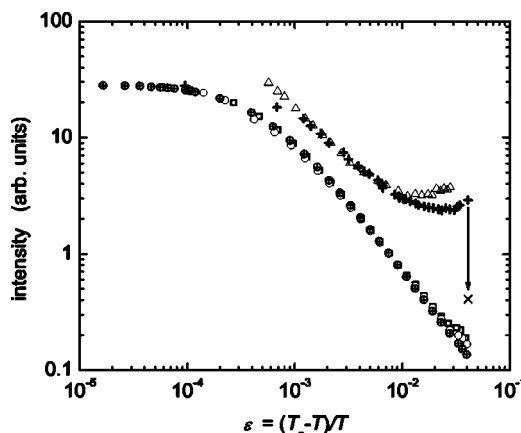


FIG. 12. Experimental light-scattering intensities for an initially turbid aqueous solution of 3-methylpyridine with 17% mass fraction of NaBr after the addition of salt. Data obtained with the freshly prepared sample are indicated by +; data from Ref. [20] for a sample with the same concentration are indicated by Δ . Data obtained the next day at room temperature are indicated by \times , and subsequent runs by, \square , \circ , and \oplus .

periments that the average size of scatterers in this system was about hundred nanometers and decreased upon heating [48]. An anomaly of the specific heat was also found in such systems [49,50] and was attributed to a structural transformation, while the anomalous light scattering was interpreted as a side effect associated with precipitation of impurities [50]. The phenomenon has still not been studied sufficiently, because it has characteristic equilibration times of over a week. Euliss and Sorensen observed a strange precipitate in aqueous solutions of tertiary butyl alcohol (tBA) [51], which strikingly resembles our experience with aqueous solutions of 3-methylpyridine. In Ref. [51] they say: “The precipitate disappeared upon heating to room temperature. We tried double distilling the tBA and redistilling the water in a quartz still, but the precipitate persisted. This problem is very similar to that discussed by Beer and Jolly [52] and is, “*if other desires were not more pressing, rather interesting.*” Iwasaki and Fujiyama [53] interpreted the appearance of such “precipitate” as a result of clathrate hydrate formation. We believe that such clusters may grow up to submicron sizes and may be responsible for the scattering intensity splashes in aqueous solutions of 3-methylpyridine with NaBr as well as for nonequilibrium character of light scattering in aqueous solutions of 3-methylpyridine without NaBr. After demixing in the presence of salt such clusters are often trapped by a meniscus where they may appear as a third phase [22]. Small impurities produce nucleation centers that initiate hydrogen-bonds structuring in water. The effect of impurities on water structuring was recently discussed by Southall *et al.* [54]: they clearly demonstrated this effect in computer simulations. The characteristic times of cluster formation and melting may be very long as we deal with ice-like structures formed by hydrogen bonds. This can explain the observed hysteresis of the light-scattering intensity in our relatively quick experiments with aqueous solutions of 3-methylpyridine without NaBr.

Another hint that could help in understanding the nature of observed anomalies in aqueous solution of 3-methylpyridine comes also from a study of aqueous alcohol solutions, as Dixit *et al.* wrote recently in *Nature (London)* [55]: “The anomalous thermodynamics of water-alcohol systems arises from incomplete mixing at the molecular level

and from retention of remnants of the three-dimensional hydrogen-bounded network structure of bulk water.”

V. CONCLUSION

We conclude that properly aged, equilibrium samples of the aqueous solutions of 3-methylpyridine and NaBr exhibit Ising-like critical behavior with a nonmonotonic crossover to mean-field behavior similar to that observed in other aqueous solutions. No evidence for an equilibrium microheterogeneous phase and multicriticality was found. However, we have also observed mesoscopic nonequilibrium aggregates that are even more persistent in aqueous solutions without salt. This phenomenon appears to be reminiscent of anomalous behavior in aqueous solutions observed by other investigators. It is plausible that the energy landscape in aqueous solutions of 3-methylpyridine is such that states with nonequilibrium supramolecular structure can exist during time periods longer than the ordinary times for conducting light-scattering experiments. Further studies of the physical and chemical variables that govern the appearance of long-living nonequilibrium structures would be highly desirable, also in view of their possible importance in the study of aqueous biofluids.

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