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Influence of Ions on the Critical Behavior of a Binary Mixture Near the Consolute Point[1]

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The lower critical point of stratification of a 3-methylpyridine (MP) + heavy water (D_2O) mixture in the presence of Na^+ and Cl^- ions has been studied by the Toepler shadow method. Addition of 0.3% ions lowered the critical temperature and reduced the equilibration time and the gradient of the refractive index (compressibillity). The analysis of the form of the near-critical isotherm demonstrated the ionic mixture to be described by the index $\delta = 3.05 \pm 0.15$, which corresponds to the classical mean-field theory. The results obtained provide evidence that even small admixtures of charged particles result in a substantial suppression of fluctuations near the critical point by the long-range Coulomb interaction.

KEY WORDS: critical consolute point; critical exponents; ionic mixtures; isotherm; long-range interaction.

1. INTRODUCTION

The fluctuation theory of second-order phase transitions and critical phenomena [1] relies on the fundamental assumption that the determining role in these processes is played by fluctuations and their interaction. Microscopic features of substances, including the intermolecular interaction, become insignificant. In the thermodynamic fluctuation region, where the laws of the fluctuations or scaling theory shoud operate, the values of the critical exponents differ from the classical values of the Landau mean-field theory [2]. Experimental studies of dielectric liquids with short-range

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interactions, and of their mixtures, show these to be described by nonclassical critical exponents; despite some numerical discrepancies, it can be asserted that they belong to the same universality class as the Ising model.

Of particular interest is the problem of critical phenomena in liquids with long-range interactions [3, 4]. Long-range Coulomb potentials are present in electrolytes and other charge-containing liquids. In such systems there arises in principle the possibility for suppression of fluctuations associated with the short-range interaction, so that the system might belong to the universality class of the classical mean-field theory where fluctuations are neglected.

Based on experimental studies it has been demonstrated that most ionic fluids belong to the Ising model universality class, but in a few publications [5–7] mean-field critical behavior has been reported for ionic binary mixtures with low dielectric constant. Weingärtner et al. [8], having analyzed results of systematic experimental studies of a great number of ionic binary mixtures, came to the conclusion that two mechanisms of phase separation exist. The first type of phase separation, the so-called Coulomb immiscibility, is determined by long-range electrostatic forces. The second stratification type, so-called solvophobic immiscibility, is due to the prevalence of short-range forces, like hydrophobic interaction, in aqueous solutions. The systems of this type should be exhibit an Ising-type critical behavior, characteristics of short-range interactions, and as a rule, have a high permittivity.

Stell [9], however, concludes that the restricted primitive model (RPM) of ionic mixtures and the Ising model have to belong to the same universality class. Besides, according to the Ginzburg criterion [10], a fluctuation region should exist also in an ionic system, but it is closer to the critical point than in nonionic mixtures. So the existing picture of the critical behavior of ionic fluids is incomplete and discrepant.

2. MEASUREMENTS

The goal of our study was to explore critical phenomena in an ionic system, which was formed by the addition of ions to a dielectric binary mixture exhibiting a consolute point. The present state of the theory of electrolytes does not yet allow prediction of the type of critical behavior to be exhibited by such an ionic system. It can be expected that the critical behavior will depend on the amount of the ionic admixture and its quality (electric charge, sizes, etc.). Investigation of such ionic systems should result in a deeper insight into the behavior of physical properties of electrolytes near critical points.

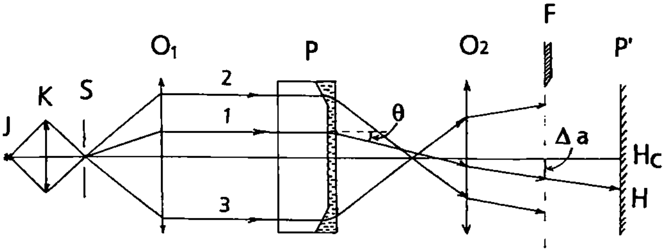

Fig. 1. Schematic diagram of the optical arrangement.

This paper reports results of an experimental study of the lower consolute point of a $MP + D_2O$ binary mixture with a small number of Na^+ and Cl^- ions. Earlier studies of the initial $MP + D_2O$ binary mixture [11, 12] had ascertained that the critical value of the mass concentration of MP at both the lower and the upper critical point of demixing is $x_c = 0.30 \pm 0.02$ and that the temperature of the lower critical point of demixing is 38.3°C [11, 12]. The sample studied in this work was prepared with a MP mass concentration $x_c = 0.2825 \pm 0.0005$ and was contained in a hermetically sealed chamber with plane-parallel glass windows.

The experiment was conducted using a Toepler shadow method setup (Fig. 1), which had been applied earlier to investigate the critical state of both pure fluids [13] and of binary mixtures, and which provides for measurements of absolute values of the refractive index n and of its vertical gradient dn/dH, induced by the gravitational field due to increasing compressibility or osmotic compressibility of the fluid. The light beam of wavelength $\lambda = 576$ nm of a 125-W mercury lamp (J) is used. Passing through the lens K and horizontal slit S a plane wave is formed by a convex lens O_1 with a diameter of 100 nm, which then propagates through chamber P. The refractive angle θ of light beam 1 due to the refractive index gradient dn/dH is obtained by measurements of Δa with the help of knife F, or a wire, in the focal plane of lens O_2:

$$dn/dH = \Delta a / f W \tag{1}$$

where $f = 500 \pm 1$ mm is the focal length of lens O_2, and $W = 3.11$ mm is the thickness of fluid layer. The Δa value is measured with an accurancy of ± 0.01 mm, which corresponds to a relative uncertainty of less than 0.5% of the refractive index gradient. In the image plane P' the height H, which corresponds to value Δa, is measured with an uncertainty of ± 0.05 nm. Measurements of the absolute values of n with uncertainty ± 0.0001 near the top and the bottom of the chamber is possible due to two quartz prisms (beams 2 and 3 pass through them).

The temperature T is measured using a calibrated platinium resistance thermometer coupled with a potentiometer. The resolution of the temperature measurement is ± 0.3 mK. The test cell is placed in a double-stage thermostat, whose temperature stability is better than ± 5 mK over 50–80 h for the whole temperature range investigated. The critical temperature was determined visually from the disappearance and appearance of the meniscus between two liquid phases. A restriction on the height L of the column of the mixture under study was imposed by the equilibration time in the system, which was proportional to L^2, and made it possible to determine the height dependence dn/dH along $L = 26$ mm with a relaxation time that never exceeded 3 to 4 days. The corresponding volume of sample was 3 cm^3.

The first stage involved exploration of the initial $MP + D_2O$ binary mixture near the lower consolute point. The process of a slow heating of the system with a step of 0.1 to 0.005 K, at which appearance of the liquid–

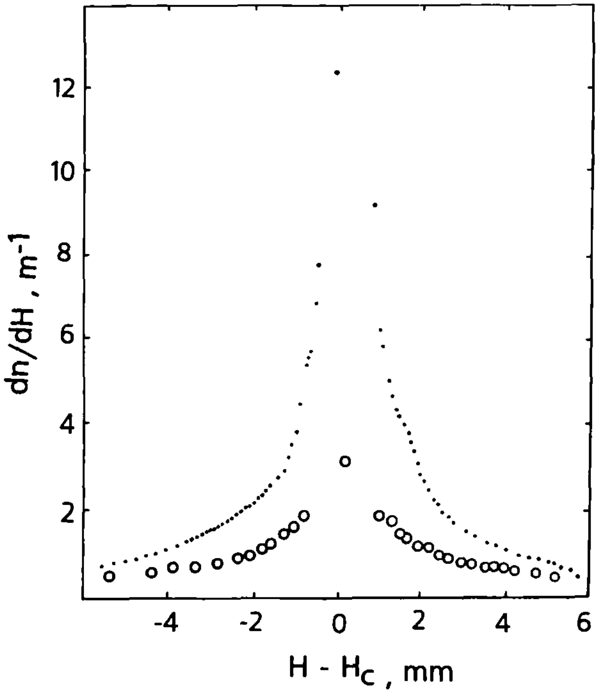

Fig. 2. Height dependencies of the refractive index gradient for a nonionic mixture (●) at $\tau = 7.7 \times 10^{-4}$ and an ionic mixture (○) at $\tau = 6.3 \times 10^{-4}$.

liquid meniscus was observed, and its cooling, at which the meniscus disappeared, repeated six times, yielded a value of the lower consolute temperature $T_{c,0} = (38.75 \pm 0.10)°C$. The equilibration time of the refractive index gradient depends on the distance both from the critical temperature T_c and from the critical level H_c, where the critical value of concentration is realized. At the reduced temperature $\tau = 7 \times 10^{-4}$ [where $\tau = (T_c - T)$ T_c^{-1}], the average equilibration time was 78 ± 15 h. The variation of the refractive index gradient with height for an isotherm with $\tau = 7.7 \times 10^{-4}$ below T_c after 4 days of equilibration is shown in Fig. 2.

At the second stage, about 0.01 g of the salt NaCl was added to the prepared binary mixture; the salt dissolved instantaneously and formed a ternary system with an NaCl concentration of 0.265 wt%. The resulting ionic system was heated in the same manner as the parent binary and both the temperature and the refractive index gradient were measured during 2 weeks. The lower consolute temperature was found to decrease to $T_{c,1} = (34.65 \pm 0.10)°C$. This strong shift was anticipated because it is known that even small mixtures cause a substantial shift of the critical temperature in liquids [12]. Another essential feature of this ionic mixture compared with the parent binary was a considerable (severalfold) decrease in the equilibration time at a corresponding distance from the critical temperature. The processing of the measurement results indicated that at nearly the same (within 30%, given the uncertainty in T_c) reduced temperature, the distance from the critical point the refractive index gradient in the ionic mixture is several times less than dn/dH in the initial mixture. This is illustrated in Fig. 2, showing the height profile of dn/dH along an isotherm of the ionic mixture at $\tau = 6.3 \times 10^{-4}$, which is at nearly the same (slightly smaller) distance from the critical temperatures is the isotherm of the initial system shown in the same Fig. 2. The dn/dH values at the maximum for the ionic and nonionic systems for these isotherms equal 31.96×10^{-4} and 123.60×10^{-4} mm^{-1}, respectively, that is, the addition of Na^+ and Cl^- ions reduces the dn/dH gradient approximately fourfold.

Analyzing the shape of the near-critical isotherm and determining the critical exponent of the ionic mixture are of the greatest interest. The weighted non-linear least-squares fit program FUMILI was applied to fit the data of both isotherms for the parent binary and the ionic fluid. The direct fitting of the experimental data by the scaling formula

$$dn/dH = D_0 \, |\Delta H|^{y} \qquad (2)$$

(where $y = 1/\delta - 1$, and $\Delta H = H - H_c$) shows great sensitivity of the quality of approximation and its parameters to the form of fitting function. The best goodness-of-fit χ^2 was obtained when the data were processed by the formula

$$\Delta n = D_n \, |\Delta H|^x \tag{3}$$

where the exponent $x = 1/\delta$; the values of $\Delta n = |n - n_c|$ (n_c is the refractive index value at the critical level H_c) were obtained by a numerical integration.

Justification for the use of the power law Eq. (3) is, first, that the refractive index is, asymptotically, as acceptable an order parameter as composition, and, second, that the composition-versus-height profile of a binary near a consolute point is asymptotically isomorph with the critical isotherm of a one-component fluid for which such a power law holds. Strictly speaking, Eq. (3) is valid only at the critical temperature. Since we analyze an isotherm that is not critical, we excluded the data within 1 mm from H_c, which are the data close to the critical isochore. By choosing the distance from the critical point to be the same in the binary and in the ionic ternary, we expect at least partial cancellation of errors due to the finite slope at the critical density.

To prove the first of the above assertions, we carried out the staistical processing of experimental data on the isotherm of the initial nonionic binary mixture, shown in Fig. 2. In the case of a two-component mixture the concentration C was determined using the Lorentz–Lorenz formula. The statistical analysis of derived dependencies $C(H)$ and $n(H)$ for the nonionic binary mixture demonstrated that changeover from $C(H)$ and $n(H)$ changes the value of the exponent by less than 1%. As regards the second assertion, it can be noted only that today there exist no recipes for a more well-reasoned selection of the order parameter in a direction isomorphic to the critical isotherm other than the selection of $C(H)$.

The statistical analysis of the form of the isotherm of both the ionic and the nonionic solutions was conducted separately for the lower ($H < H_c$) and the upper branches, values of the critical parameters H_c and n_c being varied within the error of their experimental determination. The uncertainty of the critical height, H_c, determination was ± 0.05 mm and the influence on the fitting parameters D_n and δ is almost negligible, while the uncertainty of n_c, which may be estimated as $\pm 0.1\%$, influences the values δ and D_n significantly. The goodness-of-fit χ^2 and residual sum of squares S are minimized by varying n_c in small steps of 0.00005 around its empirical estimate. Figure 3 shows the lower and the upper branches of the ionic isotherm on a double scale and, also, the finally refined values of critical parameters as well as two branches of the isotherm of the solution without salt. Experimental points of the lower branch of the ionic isotherm fall ideally on a straight line with $x = 1/\delta = 0.325 \pm 0.009$ ($\delta = 3.07 \pm 0.03$)

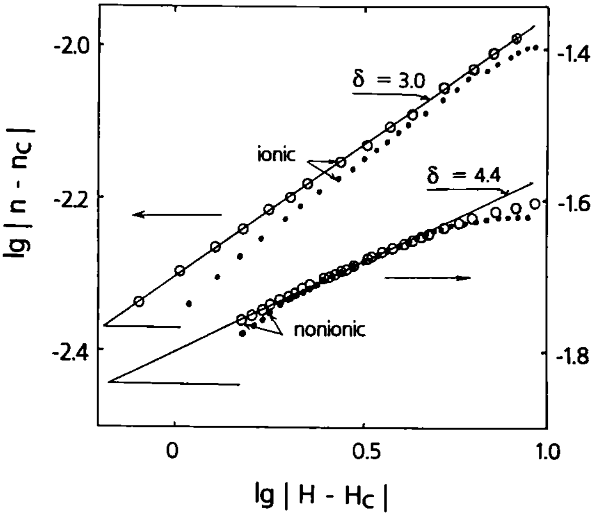

Fig. 3. Logarithmic plots of height dependencies of Δn for upper (●) and lower (○) branches of ionic and nonionic (without salt) isotherms. Height is in millimeters.

and the corresponding residual of squares S equals 1.2×10^{-5}. When the experimental error of determination of n_c and H_c is taken into account, the δ error for the liquid branch increases to ± 0.15.

From Fig. 3 it is seen that the upper branch of the isotherm for the ionic system departs somewhat from a straight line both close to the critical level and near the upper liquid–vapor meniscus. Its computer approximation yielded as an average value for all experimental points $x = 1/\delta = 0.332 \pm 0.015$ and $D_n = 0.0050 \pm 0.001$, which corresponds with $\delta = 3.01 \pm 0.10$ and $S = 1.2 \times 10^{-4}$.

The two branches of the isotherm $\tau = 7.7 \times 10^{-4}$ for the parent binary mixture and fitted with an average value $\delta = 4.4 \pm 0.3$, with $S = 2.7 \times 10^{-4}$. In contrast to the ionic fluid, the experimental points of the lower branch of this isotherm do not fall completely on a straight line. Probably a better fitting of the isotherm for the binary system demands the insertion of additional scaling terms. However, the fits and Fig. 3 evidently indicate an essential difference between the values of the critical exponent δ for the ionic and the parent binary fluid.

Although the system $\mathrm{MP} + \mathrm{D_2O} + \mathrm{Na}^+ + \mathrm{Cl}^-$ is deemed to be quasi-binary in nature, we analyzed the change in the δ due to the Fischer renormalization, based on Ref. 14. In the present case δ will not change by more than 0.3% as a result of the renormalization, which is well within our experimental resolution.

3. CONCLUSIONS

The statistical analysis of the near-critical isotherm of the ionic mixture yields the value $\delta = 3.05 \pm 0.15$ for the two branches, which fully agrees with the classical value given by the mean-field theory. This shows convincingly that the binary mixture with small ($\sim 0.3\%$) ionic admixtures, which was studied, is not described by the fluctuation theory of phase transformations, whereas judging from Refs. (11) and (12), the initial binary mixture corresponded to the Ising model. This unexpected finding is evidence that even a small admixture of Coulomb charges (1 ion per 750 D_2O molecules) can supress fluctuations and shift the near-critical system to another universality class. In our opinion, the inference of suppression of fluctuations by the long-range Coulomb interaction is in full agreement with the above-presented observations of acceleration of equilibration processes (increase in the diffusion coefficient), decrease in the scattering on fluctuations, and decline in the compressibility.

It should be noted that the essential difference between the forms of nonionic and ionic isotherms may be caused partly by possibly different distances from their respective critical temperatures, given the uncertainty in the latter.

Our results contradict the conclusions given in Ref. 8 that hydrophobic mechanisms of the phase stratification should dominate in such high-permittivity solutions, resulting in an Ising-like behavior near the critical point. Therefore further experimental investigation and a special theoretical study of interactions in such a system are needed.

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