Critical Exponents near the Lower Consolute Point of Nonionic Micellar Solutions

Mario Corti
Centro Informazioni Studi Esperienze S.p.A., Segrate, Milano, Italy

and

Vittorio Degiorgio
Dipartimento di Elettronica, Sezione di Fisica Applicata, Università di Pavia, 27100 Pavia, Italy

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New and accurate light-scattering measurements near the critical point of the nonionic micellar solution *n*-dodecyl octaoxyethylene glycol monoether in H_2O in the reduced temperature range $6\times10^{-5} < \epsilon < 2\times10^{-2}$ confirm that this binary system presents anomalous critical exponents γ and ν. The values obtained are $\gamma = 0.88 \pm 0.03$ and $\nu = 0.43 \pm 0.03$. The substitution of D_2O for H_2O changes the exponents to $\gamma = 1.20 \pm 0.03$ and $\nu = 0.59 \pm 0.03$. Intermediate exponents are obtained by use of a mixture of H_2O and D_2O as the solvent. Both the osmotic compressibility and the correlation range closely follow a power-law behavior as function of ϵ without showing any crossover effect or correction-to-scaling contribution.

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Laser-light–scattering studies of the critical behavior of the binary liquid mixture water plus the nonionic amphiphile *n*-alkyl polyoxyethylene glycol monoether (called earlier[1] C_iEt_j, where i is the number of carbons in the alkyl chain and j the number of oxyethylene groups in the hydrophilic portion of the molecule) have shown that the critical exponents γ and ν are markedly influenced by the choice of the amphiphile[1,2] and are also dependent on the nature of the solvent.[3] We recall in particular the results obtained for the system *n*-dodecyl octaoxyethylene glycol monoether (OOEDGE) in H_2O, $\gamma = 0.92 \pm 0.03$ and $\nu = 0.44 \pm 0.04$, which are in strong disagreement with the predictions of the renormalization-group theory of critical points. Such results are striking because it is generally believed that the asymptotic critical behavior of any binary mixture should belong to the same universality class as ferromagnets and pure fluids, irrespective of the self-association properties of the amphiphile or of the specific solute-solvent interactions.

Because of the large turbidity of this class of solutions, previous light-scattering studies were limited to the region $T_c - T > 0.3\,°C$ in order to avoid multiple-scattering problems. Since it is possible that the observed departure from universality is due to the fact that the investigated range of temperatures is not sufficiently close to T_c, we have repeated the measurements on OOEDGE solutions with a considerably improved apparatus. Although the lowest reduced temperature in the present experiment is 15 times smaller than in the previous one, the observed exponents γ and ν are the same as found before. The exponents observed with OOEDGE-D_2O are different from those found with OOEDGE-H_2O, namely, $\gamma = 1.20 \pm 0.03$ and $\nu = 0.59 \pm 0.03$. Intermediate exponents are obtained by use as the solvent of a mixture of H_2O and D_2O.

The high-purity compound OOEDGE was obtained from Nikko Chemicals, Tokyo, and used without further purification. The coexistence curves were determined by a turbidimetric technique which allows a sufficiently accurate evaluation of the critical concentration c_c, but gives the critical temperature T_c only within 0.01 °C. A more accurate evaluation of T_c is performed by visual observation of the phase separation in the light-scattering cell. The critical point of OOEDGE-H_2O is found at $T_c = 74.205\,°C$, and $c_c = 3.0\%$ by weight. The substitution of D_2O for H_2O shifts the critical point to $T_c = 71.415\,°C$ and $c_c = 2.5\%$. We recall that mixtures of this class involving H_2O present a lower consolution point.[1,2,4] All our measurements were performed in the single-phase region below T_c.

The light-scattering apparatus, similar to the one used in previous works,[1-3] has been modified to give better performance with measurements close to the critical point. The temperature stability has been improved to 0.5 mdeg long term (over 24 h) and 0.1 mdeg short term (over 1 h). The square scattering cell (length 0.4 cm, width 0.4 cm, and height 0.5 cm) is made of fused silica and can be filled via small Teflon tubings through a microporous filter. It is suspended from the top at the center of a second cell made of an optically polished fused-silica circular ring (diameter 3 cm, width 0.5 cm, and height 0.8 cm) kept between two black-anodized aluminum blocks. The inner space is filled with glycerol which provides index matching and proper thermal contact. The apparatus is equipped with an He-Ne laser operating on the 6328-Å line. Adjustable attenuation is also provided to avoid self-heating problems when measurements are taken close to the critical temperature. The scattered light is collected at three fixed angles (20°, 40°, and 90°) with three photomultipliers. Incident and transmitted light are also accurately monitored.

The total intensity of light scattered from a binary mixtures is $I_s + I_0$, where I_s is the contribution of concentration fluctuations and I_0 the contribution of density fluctuations. In our case, I_0 practically coincides with the contribution of the solvent. Near a critical consolution point the intensity I_s depends on the scattering angle θ according to the Ornstein-Zernike relation, $I_s = I_{s0}/(1+k^2\xi^2)$, where $k = (4\pi n/\lambda)\sin\theta/2$ is the modulus of the scattering vector, θ is the scattering angle, λ is the wavelength of incident light, and n is the index of refraction of the medium; ξ is the correlation length of concentration fluctuations. The extrapolated scattered intensity at zero scattering angle I_{s0} is related to the derivative of the osmotic pressure with respect to the concentration, $(\partial\Pi/\partial c)_{T,p}$, as follows:

$$I_{s0} = Ac(dn/dc)^2 RT(\partial\Pi/\partial c)_{T,p}^{-1}, \tag{1}$$

where A is an instrumental constant, dn/dc is the refractive index increment, R is the universal gas constant, and T is the absolute temperature. When the system approaches the critical point in the single-phase region at the critical concentration, both $(\partial\Pi/\partial c)_{T,p}^{-1}$ and ξ are predicted to diverge according to the simple power-law behavior[5]

$$(\partial\Pi/\partial c)_{T,p}^{-1} = C\epsilon^{-\gamma}, \quad \xi = \xi_0\epsilon^{-\nu}, \tag{2}$$

where $\epsilon = (T_c - T)/T_c$ and the two critical exponents γ and ν are related by $\gamma = \nu(2-\eta)$, where $\eta << 1$ is the exponent introduced by Fisher.[5]

The experiment was performed by our preparing the solutions at the critical concentration, and measuring, as a function of $T_c - T$, $I_s(k)$ and the ratio between the transmitted and the incident power of the laser beam, P_T/P_0. The measured $I_s(k)$ was found to follow with very good accuracy the Ornstein-Zernike relation. The behavior of $(\partial\Pi/\partial c)_{T,p}^{-1}$ and of ξ as functions of ϵ is reported in Fig. 1 for both OOEDGE-H_2O and OOEDGE-D_2O solutions. The absolute calibration for the osmotic compressibility was obtained according to the same method described in previous papers.[1-3] The results are very well described by Eqs. (2), with $\gamma = 0.88 \pm 0.03$, $C = 6.8\times10^{-7}$ cm^{-2} s^2, $\nu = 0.43 \pm 0.03$, and $\xi_0 = 2.3 \pm 0.3$ nm for OOEDGE-H_2O, and $\gamma = 1.20 \pm 0.03$, $C = 1.7\times10^{-7}$ cm^{-2} s^2, $\nu = 0.59 \pm 0.03$, and $\xi_0 = 0.9 \pm 0.2$ nm for OOEDGE-D_2O.

The values of γ and ν reported here are in very good agreement with previous data.[1-3] Note that present results cover the range $6\times10^{-5} < \epsilon < 2\times10^{-2}$ for OOEDGE-H_2O, whereas previous data were confined to $\epsilon > 10^{-3}$. For both systems the ratio γ/ν is very close to 2. The critical exponents of OOEDGE-H_2O are even smaller than the mean-field-theory values, $\gamma = 1$ and $\nu = 0.5$, whereas those of OOEDGE-D_2O are slightly lower than the predicted universal values.

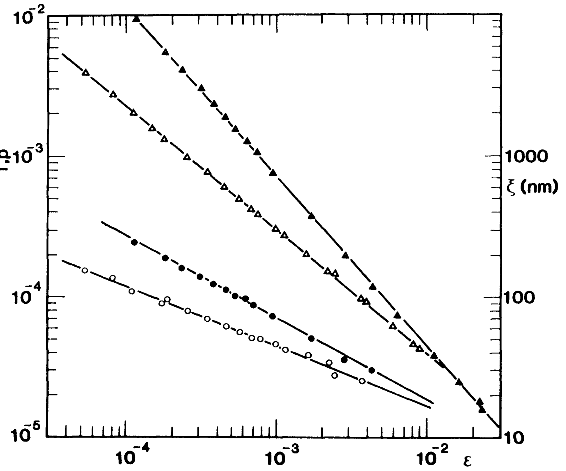

FIG. 1. The osmotic isothermal compressibility $(\partial c/\partial\Pi)_{T,p}$ (circles) and the correlation range ξ (triangles) of OOEDGE solutions as functions of the reduced temperature $\epsilon = (T_c - T)/T_c$ along the critical isoconcentration line. Open circles and triangles refer to the OOEDGE-H_2O system; full circles and triangles, to the OOEDGE-D_2O system.

In order to verify whether the observed exponents change continuously with the H_2O-to-D_2O ratio, we have prepared a OOEDGE solution containing 50% H_2O and 50% D_2O by simply mixing equal amounts of OOEDGE-H_2O and OOEDGE-D_2O solutions at the critical concentration. The critical temperature of such solution is $T_c = 73.115$ °C. The light-scattering results are shown in Fig. 2. Both the osmotic compressibility and the correlation range diverge according to power laws, with best-fit parameters $\gamma = 1.03 \pm 0.03$, $C = 3.20\times10^{-7}$ cm^{-2} s^2, $\nu = 0.52 \pm 0.03$, and $\xi_0 = 1.50 \pm 0.2$ nm. We find that all the parameters take intermediate values with respect to the pure H_2O and pure D_2O cases.

We have reported in Fig. 3 the turbidity α, derived as $\alpha = (1/L)\ln P_0/P_T$, where L is the path length of the laser beam in the scattering cell. The full lines represent the values calculated from the experimental I_s and ξ. The fact that the agreement is very good represents a check of the internal consistency of the data. Note that, for OOEDGE-H_2O at $\epsilon = 6\times10^{-5}$, α is 0.62 cm^{-1}, which means that the transmittance of the sample is 0.75. This represents the limit below which multiple scattering may appreciably influence the results.

We first note that the observed nonuniversality is not influenced by the uncertainty in the determination of T_c and c_c, as discussed in detail in Ref. 3. Another point to consider is that the coexistence curve is asymmetric,[4] and therefore the critical-concentration path followed in our measurements does not coincide with the maximum compressibility path. This latter path is

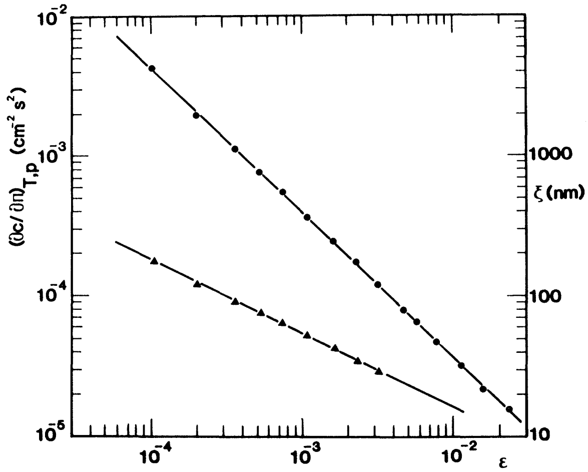

FIG. 2. The osmotic isothermal compressibility $(\partial c/\partial\Pi)_{T,p}$ (triangles) and the correlation range ξ (circles) of OOEDGE in a mixed solvent (50% H_2O and 50% D_2O) as functions of ϵ along the critical isoconcentration line.

probably the ideal path along which power-law divergences should be measured. We found, however, that the difference between the two paths is very small when $T_c - T < 15\,°C$, so that we can assume that the exponents taken along the critical-concentration path (much easier to follow experimentally) can be meaningfully discussed as critical exponents. It should also be noted that exponents measured along the critical-concentration path cannot, in any case, be smaller than those found along the maximum-compressibility path.

A possible explanation for our results is that the investigated temperature range is not sufficiently close to T_c, so that the measured exponents are not true asymptotic exponents. Our data do not show any trend toward a crossover from nonuniversal to universal behavior. Of course, it cannot be excluded that such a crossover exists closer to T_c.

Note that our range of ϵ values is comparable to that explored with usual critical mixtures or critical fluids,[6] and furthermore, over all the investigated range of ϵ, ξ is much larger than the micelle size and the range of interactions.

Neutron-scattering,[7] NMR,[8] and fluorescent-probe[9] experiments seem all to indicate that OOEDGE micelles grow only moderately as T is raised from room temperature to T_c. This suggests that it may be reasonable to treat the micellar solution, as far as the static properties are concerned, as a one-component fluid of spherical particles which are interacting through a potential which is prevalently repulsive at low T, where water is a good solvent for the hydrophilic chains of the amphiphile molecule (H-bond formation), but may become attractive at high T because of the combined effect of van der Waals forces among the hydrocarbon cores and the less complete hydration of the hydrophilic chains. Such a model can describe qualitatively many properties of the phase transition,[10] but it is not known whether it can be appropriate for the critical region.

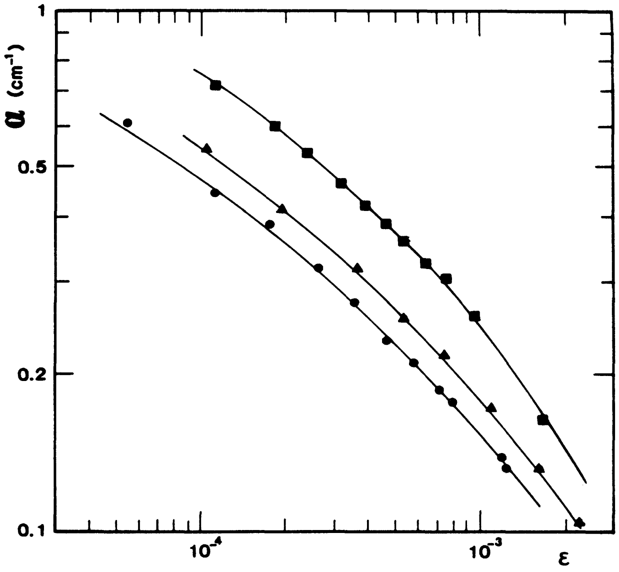

FIG. 3. The turbidity α of OOEDGE solutions as function of ϵ. The three curves refer to three distinct solvents: H_2O (dots), D_2O (squares), 50% H_2O + 50% D_2O (triangles).

Whereas the measurements performed with different homologs of OOEDGE in H_2O have shown that the departure of γ and ν from the universal values is larger when the micelle size is larger,[1] the data obtained with OOEDGE in different solvents indicate that the micelle size is not the only significant parameter, but the solvent-micelle interaction is equally important. Although it is known that hydrogen bonding is weaker in D_2O than in H_2O, it is surprising to see how large the effect of isotopic substitution is on the experimental critical exponents.

As a concluding remark, we recall that experimental evidence of nonuniversal critical exponents was recently obtained for a four-component microemulsion.[11]. The exponents γ and ν were found to vary continuously from the Ising values to mostly smaller ones as the water over surfactant ratio is changed. It is possible that these and our results have a similar explanation.

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