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Critical Behavior of a Micellar Solution

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The static and dynamic critical properties of a nonionic amphiphile aqueous solution showing a lower consolution point are investigated by laser-light scattering. The osmotic isothermal compressibility and the correlation length of the concentration fluctuations diverge with mean-field–theory critical exponents. The behavior of the mass diffusion constant in the hydrodynamic region is in good agreement with the predictions of the mode-mode–coupling theory.

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We present in this Letter a light-scattering investigation of the static and dynamic critical behavior of a binary liquid mixture of water and a nonionic amphiphilic compound, *n*-dodecyl hexaoxyethilene glycol monoether ($C_{12}Et_6$). It is known that $C_{12}Et_6$ molecules spontaneously associate in aqueous solution to form micelles,[1] and that the micellar solution shows a lower consolution point at a temperature of about 50 °C.[2] Several papers in the chemical literature have reported measurements of the temperature dependence of the scattered-light intensity for aqueous solutions of $C_{12}Et_6$ and other nonionic amphiphiles.[1-3] In most cases an increase of the scattering cross section with temperature was observed, and was attributed to an increase in the micelle aggregation number without paying attention to the effects due to the existence of a critical consolution point. A few years ago we suggested that critical concentration fluctutions are indeed responsible for the enhancement of the turbidity of the micellar solution,[4] but so far no micellar solution has been investigated as a critical binary mixture.

Besides its intrinsic interest, the study of phase transitions in nonionic micellar solutions may also be relevant for such biochemical applications[1,5] as the enhancement of the enzymatic hydrolysis and oxidation of water-insoluble lipids by forming mixed micelles of lipid and detergent, the solubilization of biological membranes, and the isolation of membrane proteins.

Our measurements (in the single-phase region) of the osmotic isothermal compressibility κ_T and of the long-range correlation length ξ indicate that both these static quantities follow, in the investigated range of temperatures and along the critical isochore, a power-law dependence on the normalized temperature difference $\epsilon = (T_c - T)/T_c$, and that the corresponding critical exponents γ and ν are consistent with the predictions of the mean-field theory.[6] The decay time of concentration fluctuations is found to diverge in quantitative agreement with the predictions of the mode-mode–coupling theory.[7]

High-purity $C_{12}Et_6$ was obtained from Nikko Chemicals, Tokyo, in crystalline form, and was dissolved without further purification in doubly distilled and degassed water at a temperature of about 40 °C. It is absolutely important to avoid contact with oxygen because $C_{12}Et_6$ may undergo an oxidation process which changes its physicochemical properties. The rectangular scattering cell (length 1 cm, width 2 cm, height 0.5 cm) is made of fused silica, and is temperature controlled within one millidegree over 24 h. The cell is filled with the micellar solution through a microporous filter (pore size 0.2 μm) having a Teflon holder. We have found that prolonged contact of the $C_{12}Et_6$ solution with metals (Al, Fe) should be avoided because the critical temperature may be changed by some degrees by metal ions. The critical temperature was determined by visual observation of the meniscus in sealed cells in a temperature-controlled water bath, and found to be 50.35 °C, with an absolute accuracy of 0.01 °C.

The average scattered intensity I_s and the intensity correlation function of the scattered light are measured at two distinct scattering angles, $\theta = 22.6°$ and 90°, by two International Telephone & Telegraph Co. FW-130 photomultiplier tubes. The apparatus is equipped with an argon-ion laser operating on the 5145-Å green line, and with a 108-channel digital correlator. We have also monitored with separate photodetectors the power of the incident laser beam before and after the scattering cell in order to obtain a rough evaluation of the turbidity. This evaluation is useful for several reasons: (i) it indicates the range of ϵ in which multiple scattering is not negligible, (ii) it allows correction of the measured I_s for the attenuation of the laser beam when the attenuation is not negligible and multiple scattering is not yet relevant, and (iii) it allows an absolute calibration to the osmotic compressibility.[8]

An appreciable asymmetry is found for I_s already at a distance of 5 °C from the critical temperature. By using the Ornstein-Zernike relation, $I_s = I_{s0}/(1+k^2\xi^2)$, where $k=(4\pi n/\lambda)\sin\frac{1}{2}\theta$ is the modulus of the scattering vector, λ being the wavelength of the laser light and n the index of refraction of the solution, we have derived from the measurement of I_s at two scattering angles the extrapolated scattered intensity at zero scattering angle I_{s0} and the correlation length ξ. The quantity I_{s0} is proportional to κ_T according to the relation[9]

$$I_{s0} = Ac^2(dn/dc)^2 k_B T \kappa_T, \tag{1}$$

where A is an instrumental constant and dn/dc is the refractive index increment which is weakly dependent on T. Figure 1 shows κ_T and ξ measured along the critical isochore ($c = 12.5$ mg/cm^3). The attenuation suffered by the laser beam over the 1-cm path in the scattering cell is about 13% for the closest point to T_c ($\epsilon = 9.5\times10^{-4}$). The results are well described by the power laws

$$\kappa_T = \kappa_0 \epsilon^{-\gamma}, \tag{2}$$

$$\xi = \xi_0 \epsilon^{-\nu}, \tag{3}$$

with $\kappa_0 = (1.5 \pm 0.03)\times10^{-7}$ cm s^2/g, $\gamma = 0.97 \pm 0.05$, $\xi_0 = 20 \pm 5$ Å, $\nu = 0.53 \pm 0.05$. Note that ξ_0 is of the order of the micelle radius and that κ_0 is very large notwithstanding that the solution is dilute. We have verified that the values of γ and ν are not critically dependent on the choice of the isochore. Measurements performed as a function of T at $c = 10$ mg/cm^3 have shown that κ_T and ξ diverge also along this isochore with the mean-field exponents, the only difference being that the apparent critical temperature T_c^+ is higher, $T_c^+ = 50.700$ °C. Since the coexistence curve is strongly asymmetric,[2] it is interesting to check if the critical isochore coincides with the line of maximum $(\partial c/\partial\mu)_{T,p}$, where μ is the chemical potential. We have measured I_{s0} along two isotherms at $T = 37.715$ and 49.615 °C, and we have found indeed that the quantity $I_{s0}/c \propto (\partial c/\partial\mu)_{T,p}$ peaks at $c = 12.5$ mg/cm^3 for both temperatures.

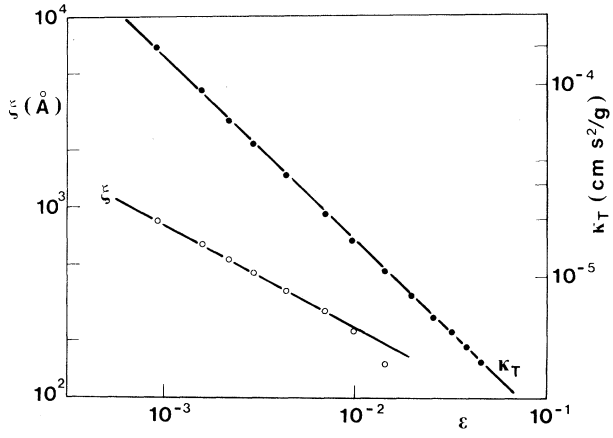

FIG. 1. The osmotic isothermal compressibility κ_T (solid circles) and the correlation length ξ (open circles) as function of reduced temperature $\epsilon = (T_c - T)/T_c$ along the critical isochore.

The obtained values of the static critical exponents γ and ν do not agree with the predictions of the renormalization-group theory[10] ($\gamma = 1.23$, $\nu = 0.63$), contrarily to all previously reported experiments on critical fluids and binary mixtures,[9] with the exception of the mean-field exponents found by Ishimoto and Tanaka in their investigation of the critical mixing point of a globular protein, lyzozyme, in a 0.5M NaCl aqueous solution.[11] Similarly to the case of the lysozyme solution, the micellar solution shows a value of κ_0 two orders of magnitude larger and a value of ξ_0 one order of magnitude larger than the values determined for critical binary mixture of nonmacromolecular components.

The time-dependent part of the measured correlation function was approximately exponential. The hydrodynamic mass-diffusion coefficient D is derived from the decay time τ_c of the correlation function as the limit of $(2k^2\tau_c)^{-1}$ as κ goes to zero. We have calculated D from the measurements performed at two scattering angles by assuming a linear dependence of $(2k^2\tau_c)^{-1}$ on k^2. Such a procedure may introduce some error very near to T_c where the Kawasaki function[7,9] should be used to describe the k dependence of the relaxation rate of concentration fluctuations. In our case the error is small because one of the two scattering angles is already small. Figure 2 shows the temperature dependence of D. Only the value corresponding to the smallest ϵ is slightly overestimated by our extrapolation procedure. In the hydrodynamic regime the prediction of the mode-mode-coupling theory is that[7]

$$D = hk_BT/6\pi\eta\xi, \tag{4}$$

where η is the macroscopic shear viscosity and h is a numerical constant very close to one. We have measured η with an Ubbelhode flow viscometer. As shown in Fig. 2, η changes very little in the interval 30–50 °C. The solid line which follows the D points in Fig. 2 represents a fit of Eq. (4) to the experimental results by use of the values of ξ reported in Fig. 1 and the values of η reported in the Fig. 2. The only free parameter is the constant h which has a best-fit value of $h = 1.1$ in good agreement with the prediction of the mode-mode-coupling theory. In contrast, Ishimoto and Tanaka found for the lysozyme solution a discrepancy of several orders of magnitude between the measured D and Eq. (4), due to an extremely large viscosity anomaly in the critical region.

The micelle is a statistical aggregate, formed when c exceeds a critical value (about 0.04 mg/cm^3 for $C_{12}Et_6$ aqueous solutions), which is in dynamic association-dissociation equilibrium with the amphiphile monomers which are present at a concentration coincident with the critical value.[1] In our discussion of measurements performed on a commercial nonionic amphiphile we suggested that the average micelle size may change very little with T,[4] so that the micellar solution could be considered from the point of view of critical properties as a macromolecular solution. Recent measurements of NMR spectra of $C_{12}Et_6$ solutions indicate indeed that there is no appreciable change of micelle size in the region 30–50 °C.[12]

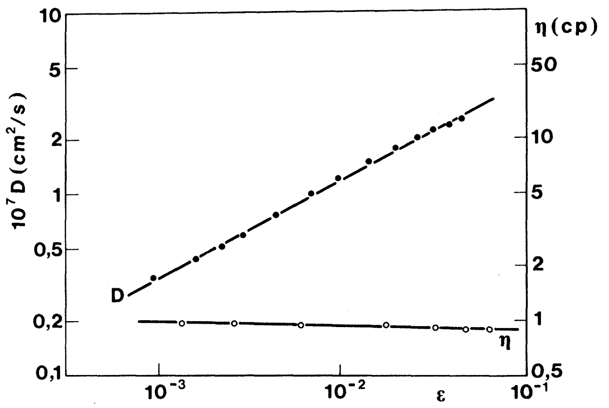

FIG. 2. The mass diffusion coefficient D (solid circles) and the macroscopic shear viscosity η (open circles) as function of ϵ along the critical isochore. The line relative to D is calculated from Eq. (4) with $h = 1.1$. The line relative to η is an interpolating curve.

We are not aware of any theoretical treatment of critical binary mixtures having components with molecules of unequal size as it is the case for micellar or macromolecular solutions. It is possible that we obtain mean-field critical exponents because the values of ϵ involved in our measurements are too large for the normalization-group theory to apply, as pointed out also by Ishimoto and Tanaka for their experiment.[11] In fact the mean-field theory is expected to break down for critical fluids and binary mixtures at some distance from the critical point. Such a distance may be roughly evaluated by using the Ginzburg criterion[13] which states that the mean-field theory applies only in the region where fluctuations of the order parameter are small compared to the order parameter itself.[14] As shown, for instance, by Eq. (2.39) of Ref. 13, the reduced temperature ϵ_c at which the mean-field theory breaks down is proportional, according to the Ginzburg criterion, to $(\xi_0/a)^{-6}$ where a is the intermolecular spacing in the critical fluid. In usual systems $\xi_0/a \simeq 1$, and $\epsilon_c \simeq 1$. However, if $\xi_0/a \simeq 10$, ϵ_c may be several orders of magnitude smaller than 1. In our case and in the case of the lysozyme solution the ratio ξ_0/a is of the order of 10 if a is the intermolecular distance for water molecules. Another qualitatively similar argument is that the number of nearest-neighbor water molecules is much larger for the macromolecule than for a small molecule.

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[14] This formulation refers clearly to the two-phase region. It is, however, reasonable to assume that the range of validity is the same above and below T_c.