

Critical behaviors in the two-phase region of a micellar solution

K. Hamano, N. Kuwahara, and T. Koyama

*Faculty of Technology, Department of Polymer Science,
Gunma University, Kiryu, Japan*

S. Harada

*Chemical Laboratory, Shizuoka Women's College,
Nunohashi, Hamamatsu, Japan*

(Received 24 June 1985)

This work investigates the critical behavior of a micellar solution pentaethylene glycol-mono-*n*-dodecyl ether ($C_{12}E_5$) + water when the critical mixing point is approached within the two-phase region. The coexistence curve with exponent $\beta \approx \frac{1}{4}$ and light scattering measurements in the two coexisting phases are reported. The temperature dependence of the isothermal osmotic compressibility and the correlation length in the two coexisting phases have been found to obey power laws which disagree with those expected for the mean-field theory and also for the three-dimensional Ising-like model.

INTRODUCTION

Aqueous micellar solutions show complex phase behavior at ambient temperatures. In very dilute solution, the amphiphilic molecules exist as molecules distributed in water. Above a critical micellar concentration, extensive association takes place to form aggregated micelles due to the presence of both polar and nonpolar portions in the same amphiphilic molecule, the distribution of which is random in the system. At higher concentrations, liquid crystalline phases consist of aggregates of different intrinsic shapes packed with a characteristic symmetry. As the temperature is raised above the minimal point in certain water-rich areas of the phase diagram, the system may undergo a phase separation into two coexistent isotropic phases. This point has been regarded as the critical mixing point in a micellar solution. Below the critical temperature there exists only a single phase including micelles.

Recently reported light scattering measurements^{1,2} have suggested that micellar solutions exhibit a critical-like power-law behavior as the temperature approaches the critical mixing point in a micellar solution. A common feature of systems near critical points is that the power-law behaviors of corresponding physical properties exhibit quantitative as well as qualitative similarities and have identical critical exponents within the same universality class.³

In contrast with the hypotheses of critical-point universality, the exponents γ for the isothermal osmotic compressibility χ_T and ν for the correlation length ξ deduced from light scattering experiments for several micellar systems appear to depend on the system studied and to be inconsistent with the corresponding ones predicted from the three dimensional Ising-like model⁴ for the universality class of a fluid ($\beta \approx \frac{1}{3}$, $\gamma \approx 1.25$, and $\nu \approx 0.63$), except for the system triethylene glycol hexylether (C_6E_3) + water.² To interpret the behavior of a micellar solution near the critical mixing point, it is important to examine the asymptotic behavior of a number of physical properties along the specific thermodynamic paths associated with the critical mixing point. Little experimental work has been reported on the two coexisting phases of a micellar solution, although it would be interesting. The homogeneity and the scaling hypotheses in

critical phenomena predict the symmetry relations that the critical exponents for corresponding physical properties are identical both above and below T_c .⁵ In this work we report measurements of the coexistence curve and scattered-light intensities in the two coexisting phases for a micellar solution pentaethylene glycol-mono-*n*-dodecyl ether ($C_{12}E_5$) + water near the critical mixing point. To compare the results in the two-phase region ($T > T_c$) with those in the one-phase region ($T < T_c$), we also report the results obtained from light scattering measurements in the one-phase region along the critical isochore.

EXPERIMENT

A differential refractometer has been used to determine the concentrations of two coexisting phases at various temperatures. The concentration dependence of the refractive index for the system $C_{12}E_5$ + water was evaluated to be $n = (1.3325 \pm 0.0009) + [(1.240 \pm 0.016) \times 10^{-1}]c$ at 22°C for a He-Ne laser ($\lambda_0 = 633$ nm), in which the concentration c is expressed in the weight fraction of $C_{12}E_5$. The quoted error represents the standard deviations. The differential refractometer was also calibrated with solutions of known composition for $C_{12}E_5$ + water. The coexistence curve of the system $C_{12}E_5$ + water is shown in Fig. 1, where the closed symbols represent the diameter associated with the symmetry of the coexistence curve. The critical mixing point was determined to be $T_c = 305.06$ K and $c_c = (1.200 \pm 0.040) \times 10^{-2}$, which was ascertained by the equal-volume criterion. The density measurement was carried out in the range of $2.44 \times 10^{-5} \leq \epsilon \leq 9.62 \times 10^{-3}$ by using an Anton Paar densimeter. The density data showed a small systematic deviation at temperatures very close to T_c , which can be attributed to a critical anomaly in the density, i.e., $1.8 \times 10^{-3}\%$ at $\epsilon = 8.11 \times 10^{-4}$ and $2.5 \times 10^{-3}\%$ at $\epsilon = 2.44 \times 10^{-5}$. This negligibly small deviation was ignored in the present analysis.

Light scattering measurements for the angular distribution over the angular range of $25^\circ \leq \theta \leq 130^\circ$ were carried out at five temperatures in the range of $5.57 \times 10^{-5} \leq \epsilon \leq 1.24 \times 10^{-3}$ along the coexistence curve. The light scattering measurements were performed in a thermostat having a

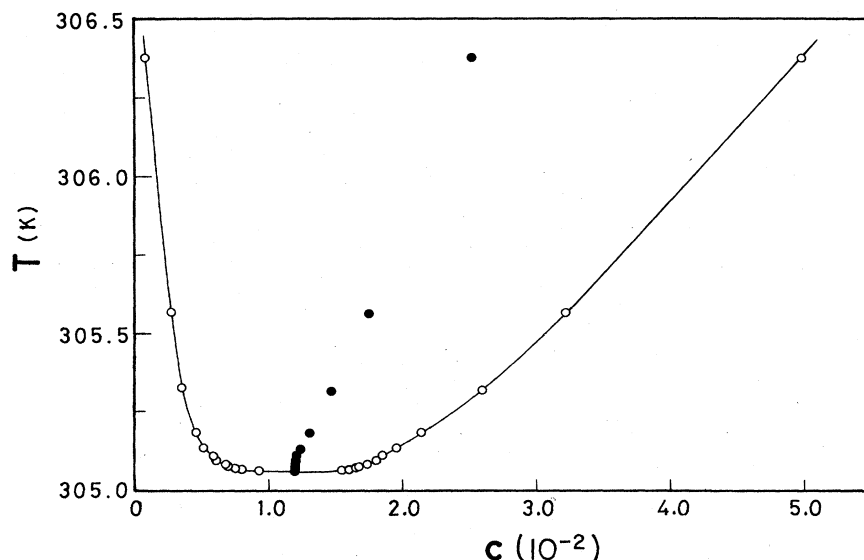


FIG. 1. The coexistence curve and the diameter of the system $C_{12}E_5$ + water. Open symbols stand for the coexistence curve and closed ones for the diameter, in which the concentration c is expressed in the weight fraction of $C_{12}E_5$.

temperature stability within ± 1 mK over 24 h. In order to reduce the effect of multiple scattering⁶ we used a 4.0-mm cylindrical cell in the light scattering measurements. The differential refractometer, the light scattering photometer, sample preparations, and experimental details have been fully described elsewhere.⁷

RESULTS AND DISCUSSION

In order to consider the choice of the proper order parameter for a micellar solution, we have analyzed the coexistence-curve data in terms of weight, volume, and

mole fraction for $C_{12}E_5$ in water. The volume fraction was evaluated from the density measurements for pure $C_{12}E_5$ and for the critical mixture $C_{12}E_5$ + water. We might expect that another possible choice of the order parameter would be the composition associated with the finite-size micelles randomly distributed in the system. However, it is not practical to choose the composition in terms of micelles as the order parameter because of the temperature- and the concentration-dependence of a degree of aggregation in the form of micelles. Log-log plots of the concentration difference $c'' - c'$ (symbol \circ) and the diameter $(c' + c'')/2$ (symbol \bullet) are shown as a function of ϵ in Fig. 2, where c' and c'' refer to the concentrations of the dilute and the concen-

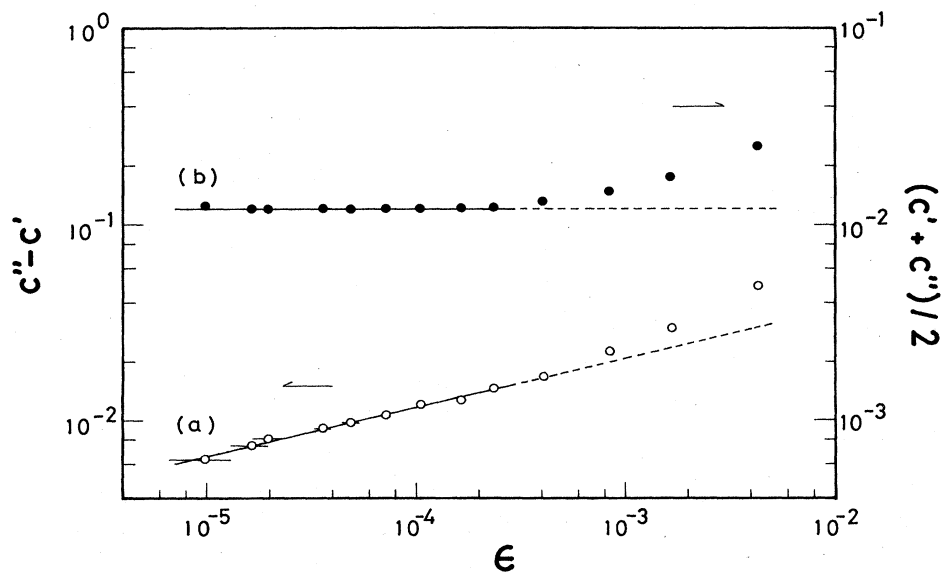


FIG. 2. The log-log plots of the concentration difference $c'' - c'$ (symbol \circ) and the diameter $(c' + c'')/2$ (symbol \bullet) vs the reduced temperature ϵ , where c' and c'' refer to the concentrations of the dilute and the concentrated phases in terms of the weight fraction.

trated phases in terms of the weight fraction. The plot $c'' - c'$ for ϵ is seen to give a good straight line over the range of $9.83 \times 10^{-6} \leq \epsilon \leq 2.36 \times 10^{-4}$ and a marked curvature at large ϵ in Fig. 2. The result of the fit $c'' - c'$ for ϵ gives a simple power law $c'' - c' = B\epsilon^\beta$ with $B = (1.155 \pm 0.075) \times 10^{-1}$ and $\beta = 0.249 \pm 0.007$ in the range of $9.83 \times 10^{-6} \leq \epsilon \leq 2.36 \times 10^{-4}$ as shown in the solid line (a) of Fig. 2. The results of the other fits were essentially the same. We have also analyzed these data on the asymptotic coexistence curve by the fit $c' - c_c = -B'\epsilon^\beta$ for the dilute phase and by the $c'' - c_c = B''\epsilon^\beta$ for the concentrated one, respectively, where the values β and T_c are kept fixed. The asymptotic behavior of the coexistence curve has been confirmed to be symmetric, with $B' = B'' = B/2$ within a 5% error and $c_c = (1.200 \pm 0.040) \times 10^{-2}$. To investigate the coexistence curve over the entire range of $9.83 \times 10^{-6} \leq \epsilon \leq 4.32 \times 10^{-3}$ we have tried to apply the Wegner expansion with a higher-order correction to a simple power law by⁸

$$c'' - c' = \epsilon^\beta (B + B_1 \epsilon^\Delta), \quad (1)$$

where Δ is a correction exponent which has been calculated to be 0.50 for the universality class of a fluid. We have estimated $\Delta = 1.01 \pm 0.05$ and the ratio $B_1/B = (1.9 \pm 0.1) \times 10^2$ by means of a three-parameter least-squares fit for the fixed β . The residuals from the fit to Eq. (1) were almost random. The result for the ratio B_1/B is considerably larger than the value $B_1/B \approx 0.31$ for xenon,⁹ $B_1/B \approx 0.47$ for carbon disulfide + nitromethane,¹⁰ and $B_1/B = 0.4 - 3.1$ for macromolecular solutions.^{11,12} The correction to the simple power law in Eq. (1) is small at small ϵ and very large at large ϵ , i.e., approximately 4% at $\epsilon = 2.36 \times 10^{-4}$ and 79% at $\epsilon = 4.32 \times 10^{-3}$. It should be noted that the asymptotic exponent β and the correction exponent Δ for the system $C_{12}E_5$ + water significantly differ from those predicted for the universality class of a fluid.^{9-12,13}

Theoretical and experimental suggestions^{9-13,14} have been made that the diameter of the coexistence curve for a fluid near the critical point exhibits a weak anomaly as $\epsilon^{1-\alpha}$ with the specific-heat exponent $\alpha \approx 0.12$ different from that of the law of the rectilinear diameter. This means that the diameter would become tangent to the coexistence curve at a critical point. The diameter of the coexistence curve for the present system has been described by

$$(c' + c'')/2 = c_c + A\epsilon^{1-\alpha} \quad (2)$$

over the entire range of $9.83 \times 10^{-6} \leq \epsilon \leq 4.32 \times 10^{-3}$. We have estimated $1 - \alpha = 0.97 \pm 0.04$ and $A/c_c = (2.2 \pm 0.5) \times 10^2$. Our result gives no indication of the anomaly in the diameter of the coexistence curve. The reduced coefficient A/c_c associated with the second term in Eq. (2) is somewhat larger than those for macromolecular solutions.¹² In the asymptotic range of $\epsilon < 2.36 \times 10^{-4}$, the second term in Eq. (2) gives little contribution at the level of the experimental error. Thus, the diameter for the present micellar solution, $(c' + c'')/2$, gives a constant value with the critical concentration c_c , independent of temperature over the range of $9.83 \times 10^{-6} \leq \epsilon \leq 2.36 \times 10^{-4}$ as shown in the solid line (b) of Fig. 2.

For the light scattering data of the dilute and the concentrated phases on the coexistence curve at temperature T , the plots of inverse scattered-light intensity $[I(k)]^{-1}$ versus the square of the (momentum-transfer) wave number k^2 were found to obey an approximate linear behavior predicted by

the Ornstein-Zernike-Debye theory.¹⁵ The zero-momentum-transfer-scattered-light intensity $I(0) [= \lim_{k \rightarrow 0} I(k)]$, which is directly proportional to the isothermal osmotic compressibility χ_T , and the correlation length ξ are shown in Fig. 3, where the values for the dilute and the concentrated phases are denoted by open and closed symbols, respectively. The symbols of triangles and circles are used to stand for $[I(0)]^{-1}$, i.e., χ_T^{-1} and ξ . Figure 3 shows that the data plotted as a function of ϵ obey power laws with the exponents $\gamma' = 1.66 \pm 0.03$ (Δ) and $\nu' = 0.676 \pm 0.012$ (\circ), and $\gamma'' = 0.740 \pm 0.011$ (\blacktriangle) and $\nu'' = 0.464 \pm 0.010$ (\bullet) over the range of $5.57 \times 10^{-5} \leq \epsilon \leq 1.24 \times 10^{-3}$, where the prime and double prime refer, respectively, to the dilute and the concentrated phases. We find that $\gamma'/\gamma'' = 2.24 \pm 0.05$ and $\nu'/\nu'' = 1.64 \pm 0.04$. It should be noted that along the coexistence curve the temperature dependence of χ_T and ξ has a great asymmetry between the dilute and the concentrated phases.

On the other hand, it is of particular interest to compare the results above and below T_c for the present system. The power-law behaviors of $\chi_T \propto \epsilon^{-\gamma}$ with $\gamma = 1.035 \pm 0.028$ and $\xi = \xi_0 \epsilon^{-\nu}$ with $\xi_0 = (3.27 \pm 0.23) \times 10^{-7}$ cm and $\nu = 0.514 \pm 0.012$ have been confirmed to be valid over the range of $4.64 \times 10^{-4} \leq \epsilon \leq 1.78 \times 10^{-2}$ along the critical isochore in the one-phase region of the system $C_{12}E_5$ + water. Experimental details will appear elsewhere. The values for γ and ν in the one-phase region are in good agreement with those predicted by the mean-field theory ($\gamma = 2\nu = 1$). We find the inequalities $\gamma' > \gamma > \gamma''$ and $\nu' > \nu > \nu''$ for the system $C_{12}E_5$ + water. Specifically, the scaling relations between the corresponding exponents for χ_T and ξ above T_c , i.e., $\gamma'/\nu' = 2.46 \pm 0.06$ and $\gamma''/\nu'' = 1.59 \pm 0.04$, are found not to agree with $\gamma/\nu = 2$ for the mean-field theory or with $\gamma/\nu = 2 - \eta$ at a small positive value of the critical exponent $\eta \approx 0.03$ for the three-dimensional Ising-like model within the universality class of a fluid.^{4,5}

We have also examined the nature of the critical behavior

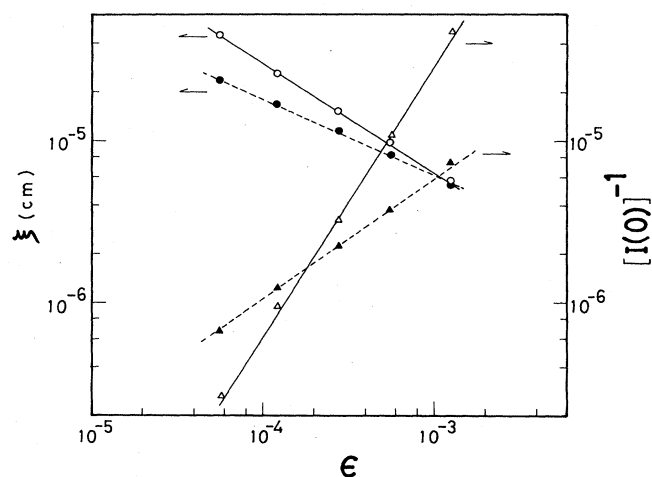


FIG. 3. The log-log plots of $[I(0)]^{-1}$, i.e., the isothermal osmotic compressibility χ_T , and the correlation length ξ vs ϵ in the two coexisting phases. The values for the dilute and the concentrated phases are denoted by open symbols (\circ and Δ) and closed ones (\bullet and \blacktriangle), respectively, where the symbols of circles and triangles are used to stand for ξ and for $[I(0)]^{-1}$, i.e., χ_T^{-1} , respectively.

in the two-phase region of the micellar solution $C_{12}E_5$ + water. It is found that the asymptotic coexistence curve is quartic, flatter than cubic. The present analysis provides no indication of the anomaly in the diameter of the coexistence curve. The quartic coexistence curve has been predicted by the analytical classical equation of state in the fifth degree, i.e., the five-point contact in the terminology of Baehr.¹⁶ This is suggestive, not only of the results associated with the coexistence curve and the diameter, but also for the mean-field values of the exponents γ and ν in the one-phase region. A similar coexistence curve has been also predicted by Keyes for the model of the nematic-isotropic tricritical transition,¹⁷ although we are unable to present a reasonable explanation for regarding the present work as demonstrating this kind of transition. The temperature dependence of the isothermal osmotic compressibility χ_T and the correlation length ξ along the two branches of the coexistence curve obey a power law, but there is a great asymmetry between the dilute and the concentrated phases. We find then the inequalities $\gamma' > \gamma > \gamma''$ and $\nu' > \nu > \nu''$ among the exponents for χ_T and ξ both above and below T_c . One might ask whether the values of the exponents for χ_T and ξ are the true asymptotic ones. In fact, we have al-

ready observed an apparent deviation from the power-law behaviors of χ_T and ξ very close to T_c , i.e., within the range $\epsilon \leq 1.97 \times 10^{-5}$ above T_c and the range $\epsilon \leq 4.64 \times 10^{-4}$ below T_c . We feel further work is still necessary for a fully developed interpretation of the region of a micellar solution. In spite of these problems, it is worth noting that the power-law behaviors of χ_T and ξ should be valid over the intermediate range of $5.57 \times 10^{-5} \leq \epsilon \leq 1.24 \times 10^{-3}$ above T_c . Thus, we conclude that the behavior of the physical properties investigated in this work resembles in some important aspects that of a fluid near the critical point, while the set of the exponent values differs significantly from those predicted by the mean-field theory and also by the three-dimensional Ising-like model for the universality class of a fluid.

ACKNOWLEDGMENTS

The authors are indebted to Mr. Y. Yamamoto for help in the light scattering measurements. We would like to thank Professor S. Saeki and Dr. T. Dobashi for very useful discussions. We also wish to thank the Ministry of Education in Japan for supporting this work with a grant-in-aid.

- ¹M. Corti and V. Degiorgio, Phys. Rev. Lett. **45**, 1045 (1980); M. Corti, V. Degiorgio, and M. Zulauf, *ibid.* **23**, 1617 (1982).
- ²M. Corti, C. Minero, and V. Degiorgio, J. Phys. Chem. **88**, 309 (1984).
- ³For a review, see P. C. Hohenberg and B. I. Halperin, Rev. Mod. Phys. **49**, 435 (1977).
- ⁴J. C. Le Guillon and J. Zinn-Justin, Phys. Rev. Lett. **39**, 95 (1974); Phys. Rev. B **21**, 3976 (1980).
- ⁵H. B. Tarko and M. E. Fisher, Phys. Rev. Lett. **31**, 926 (1973); Phys. Rev. B **11**, 1217 (1975); D. Stauffer and C. S. Kiang, Phys. Rev. Lett. **27**, 1783 (1971).
- ⁶K. Hamano, N. Kuwahara, and M. Kaneko, Phys. Rev. A **21**, 1312 (1980), and references therein.
- ⁷K. Hamano, T. Nomura, T. Kawazura, and N. Kuwahara, Phys. Rev. A **26**, 1153 (1982); K. Hamano, T. Kawazura, T. Koyama, and N. Kuwahara, J. Chem. Phys. **82**, 2718 (1985).
- ⁸F. J. Wegner, Phys. Rev. B **5**, 4529 (1972).
- ⁹W. T. Estler, R. Hocken, T. Charlton, and L. R. Wilcox, Phys.

- Rev. A **12**, 2118 (1975).
- ¹⁰S. C. Greer, Phys. Rev. A **14**, 1770 (1976).
- ¹¹M. Nakata, T. Dobashi, N. Kuwahara, M. Kaneko, and B. Chu, Phys. Rev. A **18**, 2683 (1978).
- ¹²T. Dobashi, M. Nakata, and M. Kaneko, J. Chem. Phys. **72**, 6685 (1980).
- ¹³G. A. Baker, Jr., B. N. Nickel, M. S. Green, and D. I. Meiron, Phys. Rev. Lett. **36**, 1351 (1976).
- ¹⁴M. S. Green, M. J. Cooper, and J. M. H. L. Sengers, Phys. Rev. Lett. **26**, 492 (1971); N. D. Mermin, *ibid.* **26**, 169 (1971); **26**, 957 (1971); M. Ley-Koo and M. S. Green, Phys. Rev. A **16**, 2483 (1977).
- ¹⁵L. S. Ornstein, and F. Zernike, Proc. K. Ned. Akad. Wet. **17**, 793 (1914); P. J. W. Debye, J. Chem. Phys. **31**, 380 (1959).
- ¹⁶H. D. Baehr, Forsch. Geb. Ingenieurwes. **29**, 143 (1963); J. V. Sengers and J. M. H. L. Sengers, in *Progress in Liquid Physics*, edited by C. A. Croxton (Wiley, New York, 1978), Chap. 4.
- ¹⁷P. H. Keyes, Phys. Lett. **67A**, 132 (1978).