International Journal of Thermophysics, Vol. 10, No. 2, 1989

Critical Behavior of Nonionic Micellar Solutions[1]

K. Hamano,[2] T. Kaneko,[2] K. Fukuhara,[2] and N. Kuwahara[2]

The critical behavior of micellar solutions of triethylene glycol mono *n*-hexylether in water has been investigated in view of the issue of critical-point universality for such systems close to their critical mixing point. The values of the critical exponents obtained in this work are in excellent agreement with the theoretical ones for three-dimensional Ising-like systems. The dynamical critical behavior is also discussed.

KEY WORDS: critical phenomena; coexistence curve; light scattering; diffusion; micelles; viscosity.

1. INTRODUCTION

Great attention has been directed to critical phenomena in fluid systems that contain aggregates of surfactant molecules, known as micelles. Corti and co-workers [1] have found critical-like anomalies in a series of aqueous micellar solutions near their critical mixing points, which have been analyzed in terms of the analogy with the liquid–vapor transition and the phase separation of a binary fluid mixture. In contrast with the hypothesis of critical-point universality [2], their work suggested a nonuniversal dependence of the critical exponents on the system studied [3]. Theoretical attempts have been made for understanding this possible nonuniversal behavior of micellar systems [4].

Recently, Dietler and Cannell [5] reexamined the exponent γ for the osmotic susceptibility and the exponent ν for the long-range correlation length for the system octaethylene glycol mono *n*-dodecylether ($C_{12}E_8$) with water and heavy water from the light-scattering measurement. Including multiple-scattering corrections to the light-scattering data [6],

---

[1] Paper presented at the Tenth Symposium on Thermophysical Properties, June 20–23, 1988, Gaithersburg, Maryland, U.S.A.

[2] Department of Polymer Science, Gunma University, Kiryu, Japan.

they found Ising-like universal values for γ and ν for this system, independent of whether water or heavy water was the solvent. Their result is in contrast with that of Corti and Degiorgio [7]. In this work we report extensive measurements by focusing on the decay rate of fluctuations, including the coexistence curve, the viscosity, and the static and the dynamical light scattering, in nonionic micellar solutions of triethylene glycol mono *n*-hexylether (C_6E_3) in water close to its critical mixing point.

The theory of dynamic critical phenomena [8] has suggested that the decay rate of the concentration fluctuations is related to the viscosity of a fluid mixture, which displays a weak enhancement very close to the critical mixing point. The asymptotic equation for the viscosity can be represented by

$$\eta(T) = \eta^{\mathrm{B}}(Q_0\xi)^{x_\eta} = \eta^{\mathrm{B}}(Q_0\xi_0)^{x_{\eta_\varepsilon}-\phi} \tag{1}$$

where η^{B} is the background viscosity, Q_0 a system-dependent wave number, $\xi = \xi_0\varepsilon^{-\nu}$ the correlation length, ε the reduced temperature difference $(T - T_{\mathrm{c}})/T_{\mathrm{c}}$, and $\phi = x_\eta \nu$ the critical viscosity exponent. The values reported for x_η cover a range from 0.05 to 0.065, in reasonable agreement with the theoretical estimations [9].

On the other hand, it is customary to separate the diffusion coefficient D into a nonsingular background contribution D^{B} and an additional contribution D^{c} due to the critical fluctuations as $D = D^{\mathrm{c}} + D^{\mathrm{B}}$. The asymptotic diffusion coefficient can be represented by

$$D^{\mathrm{c}} = \frac{R k_{\mathrm{B}} T}{6\pi\eta(T)\xi} \tag{2}$$

where R is a universal amplitude ratio associated with the dynamic scaling relation, which has a value slightly larger than unity [10].

2. EXPERIMENTAL

Triethylene glycol mono *n*-hexylether synthesized and purified by Nikko Chemical Co. Ltd. and water were used in this work. The coexistence curve was determined by a specially designed differential refractometer. The critical mixing point has been estimated to be $T_{\mathrm{c}} = 317.4$ K and $c_{\mathrm{c}} = 0.146_5$ in the weight fraction of C_6E_3 in water.

The static and dynamic light-scattering measurements were performed for the critical mixture by the use of a cell with an optical path length of 0.096 ± 0.002 cm in order to reduce multiple-scattering effects [11]. The measurements were carried out at a scattering angle of 90°, which corresponds to a transfer wave number of $k = 1.89_4 \times 10^5\ \mathrm{cm}^{-1}$. The static light-scattering measurements were obtained in the temperature range $2.54 \times 10^{-6} \leqslant \varepsilon \leqslant 4.73 \times 10^{-3}$, and the dynamic light-scattering measurements in the temperature range $6.30 \times 10^{-6} \leqslant \varepsilon \leqslant 4.73 \times 10^{-3}$. The turbidity measurement was also carried out by the use of a 1.0-cm quartz cell in the range $3.15 \times 10^{-6} \leqslant \varepsilon \leqslant 5.20 \times 10^{-3}$. The differential refractometer, the light-scattering photometer, the viscometer, sample preparations, and experimental details have been described fully elsewhere [12].

3. RESULTS

The coexistence curve was examined for the concentration difference of $c'' - c'$ as a function of ε, where c' and c'' refer to the dilute and the concentrated phases in terms of the weight fraction. The results gave the simple power law of $c'' - c' = B\varepsilon^{\beta}$, with $B = 1.56 \pm 0.06$ and $\beta = 0.327 \pm 0.004$ in the range of $1.32 \times 10^{-4} \leqslant \varepsilon \leqslant 1.51 \times 10^{-2}$. In the data analysis no systematic deviations from the simple power law were found over the entire temperature range. The quoted error represents the standard deviation. The deviation from the rectlinear diameter was also examined for the relation $(c' + c'')/2 - c_c = A\varepsilon^{\mu}$, where the exponent μ is related to the specific heat exponent α by $\mu = 1 - \alpha$. We have estimated $\mu = 0.89_2 \pm 0.044$, i.e., $\alpha = 0.11 \pm 0.04$, and $A = 3.1 \pm 1.3$. The estimated exponent values concerned with the coexistence curve are in good agreement with the theoretical value for three dimensional Ising-like systems [13].

The scattered light intensities are shown as a function of ε in Fig. 1.

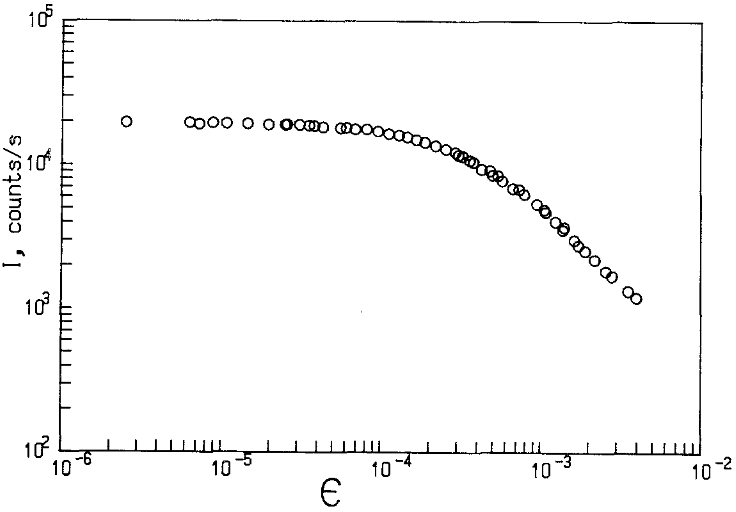

Fig. 1. The scattered light intensity as a function of ε.

The measured scattered light intensity including corrections for turbidity and double-scattering may be represented by [14]

$$I_m = I_0[e^{-\tau L} + \bar{R}(1 - e^{-\tau L})]\, A\chi_T\, g(k\xi) + I_B \tag{3}$$

where $\chi_T = \Gamma_0 \varepsilon^{-\gamma}$ is the osmotic susceptibility, A a nearly temperature-independent constant, L the light-path length, I_B the background scattering, $\bar{R}$ the double-scattering correction parameter, and $g(y)$ the correlation scaling function. Using the Ornstein–Zernike correlation function, the turbidity can be represented by

$$\tau_m = A\pi\chi_T \left[\frac{2\alpha^2 + 2\alpha + 1}{\alpha^3} \ln(1 + 2\alpha) - \frac{2(1+\alpha)}{\alpha^2}\right] + \tau_B \tag{4}$$

where $\alpha = 2(k_0\xi)^2$ with the wave number k_0 of the incident light. We analyzed our intensity data using the Ornstein–Zernike correlation function, in conjunction with the turbidity data in the range of $1.93 \times 10^{-1} \leqslant k\xi \leqslant 3.68$. In this range the double-scattering corrections were estimated to be within 1% and we obtained, by setting $\bar{R} = 0$ in Eq. (3),

$$\gamma = 1.24_0 \pm 0.010, \qquad \nu = 0.627 \pm 0.006$$

$$\xi_0 = (3.56_4 \pm 0.012) \times 10^{-8}\ \text{cm}, \qquad I_0 A\Gamma_0 = 1.5_1 \pm 0.10$$

$$I_B = (1.4_7 \pm 0.25) \times 10^2$$

$$A\Gamma_0 = (5.185 \pm 0.004) \times 10^{-6}\ \text{cm}^{-1}, \qquad \tau_B = (1.6_2 \pm 0.52) \times 10^{-6}\ \text{cm}^{-1}$$

We repeated our data analysis with the approximate correlation function of $1/g(y) = 1 + \Sigma_2 y^2 - \Sigma_4 y^4$ in the range of $1.93 \times 10^{-1} \leqslant k\xi \leqslant 6.02$ in Eq. (3) [15]. In this analysis the parameters of γ, ν, ξ_0, I_0, $A\Gamma_0$, and I_B were fixed. The turbidity data were fitted to the equation $\ln \tau = \sum_{i=0}^{8} a_i\ (\ln \varepsilon)^i$ and used for the turbidity correction. The double-scattering correction was calculated using the asymptotic function $1 - \bar{R} = C(\gamma_0)/\ln(k_0\xi)$ with $C(\gamma_0) \simeq 1$ for $\gamma_0 = 2r/h \simeq 9.6$, for example, 6% at $k\xi = 6.02$ and 1.3% at $k\xi = 4.18$. We fitted our data to Eq. (3) with the parameters Σ_4 and T_c as free parameters, which yielded $\Sigma_4 = (2.37 \pm 0.08) \times 10^{-4}$. The critical temperature deduced from this fit was the same as that determined experimentally within 0.5 mK. We estimated the value of the exponent η to be $\eta = 0.016 \pm 0.005$. The intensity data for $k\xi > 6.02$ were discarded in the present analysis because of large corrections for turbidity and also for multiple scattering. Our values of the exponents γ, ν, and η are in excellent agreement with the theoretical ones for the universality class of a fluid, in agreement with the result for C_6E_3 + water of Corti and co-workers [1].

The experimental viscosity data were examined as a function of the velocity gradient S by $\eta(S) \propto S^{-\omega_{\mathrm{eff}}}$ at each temperature in the entire range $1.42 \times 10^{-1} \leqslant S \leqslant 1.19\ \mathrm{s}^{-1}$. A noticeable small dependence with $\omega_{\mathrm{eff}} = 0.020 \pm 0.005$ was observed at $\varepsilon \leqslant 1.54 \times 10^{-3}$, but in the remaining range no dependence was detected within experimental error. The value of $\omega = \lim_{S \to 0} \omega_{\mathrm{eff}} \simeq 0.02$ is close to the theoretical prediction made by Onuki [8]. The viscosity extrapolated to $S = 0$ with a linear function of S is shown in Fig. 2. The background viscosity evaluated in the range $4.60 \times 10^{-3} \leqslant \varepsilon \leqslant 1.88 \times 10^{-2}$ was represented by $\eta^{\mathrm{B}} = U \exp(V/T)$ Pa · s with $U = 2.6_1 \pm 0.05$ and $V = -(2.3_2 \pm 0.24) \times 10^3$. The critical viscosity was represented by $\eta(T)/\eta^{\mathrm{B}} = (0.79_5 \pm 0.010)\, \varepsilon^{-\phi}$ with $\phi = 0.040 \pm 0.003$ in the range $3.15 \times 10^{-5} \leqslant \varepsilon \leqslant 3.05 \times 10^{-3}$. This result yields $x_\eta = 0.064 \pm 0.005$. The values of ϕ and x_η are in good agreement with the theoretical predictions and the experimental results of Berg et al. [16].

The diffusion coefficient $D(k) = \Gamma(k)/k^2$ at $k = 1.89_4 \times 10^5\ \mathrm{cm}^{-1}$ was deduced from the experimental autocorrelation data by fitting to an exponential decay law. The diffusion data were corrected for double-scattering effect [12, 17], which were less than 5% over the entire temperature range, and examined in terms of the dynamic scaling function. The diffusion coefficient D may be given by [9]

$$D = \frac{k_{\mathrm{B}} T}{6\pi\eta(T)\xi}\, \Omega(k\xi) + D^{\mathrm{B}} \tag{5}$$

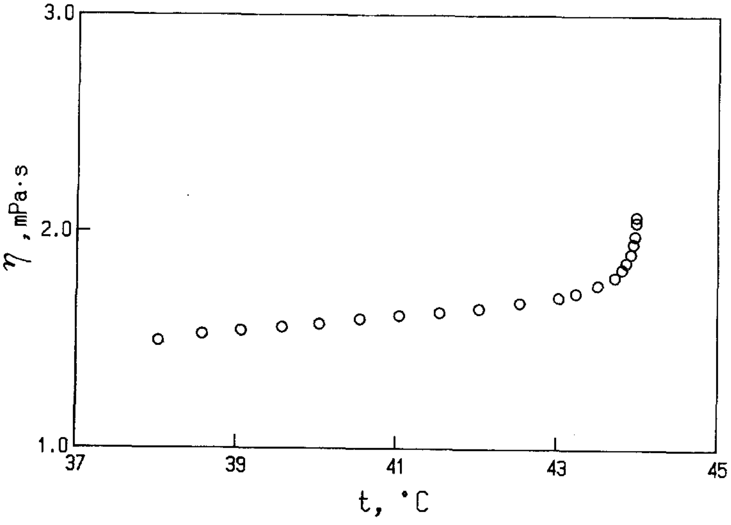

Fig. 2. The viscosity at the velocity gradient $S = 0$ as a function of temperature.

with the recently proposed dynamic scaling function $\Omega(y)$, which is given by

$$\Omega(y) = \Omega_K(y)\, S(y)^{x_\eta}$$

with the correction $S(y) = a_0(1 + b^2 y^2)^{1/2}$. Here $\Omega_K(y)$ is the original Kawasaki function. The coefficient a_0 is related to the universal amplitude ratio R by $R = a_0^{x_\eta}$. The background diffusion coefficient D^B can be evaluated from the expression

$$D^B = \frac{k_B T}{16\eta^B \xi}\left(\frac{1 + k^2\xi^2}{q_c \xi}\right) \tag{6}$$

where q_c is a system-dependent wave number. The data were fitted to Eq. (5) using a_0, b, and q_c as adjustable parameters. We obtained the values of $a_0 = 55._5 \pm 6.0$, i.e., $R = 1.29 \pm 0.03$, $b = 0.26 \pm 0.07$, and $q_c = (9.2 \pm 0.7) \times 10^8\ \mathrm{cm}^{-1}$. In Fig. 3 we show the difference between the experimental diffusion coefficient D and the calculated one with the values estimated for the parameters a_0, b, and q_c. The estimated value for the amplitude R is fairly larger than the values from 1.01 to 1.06 reported for a binary fluid mixture [18]. In this analysis the background contribution estimated from Eq. (6) with q_c seems to be too small in comparison with

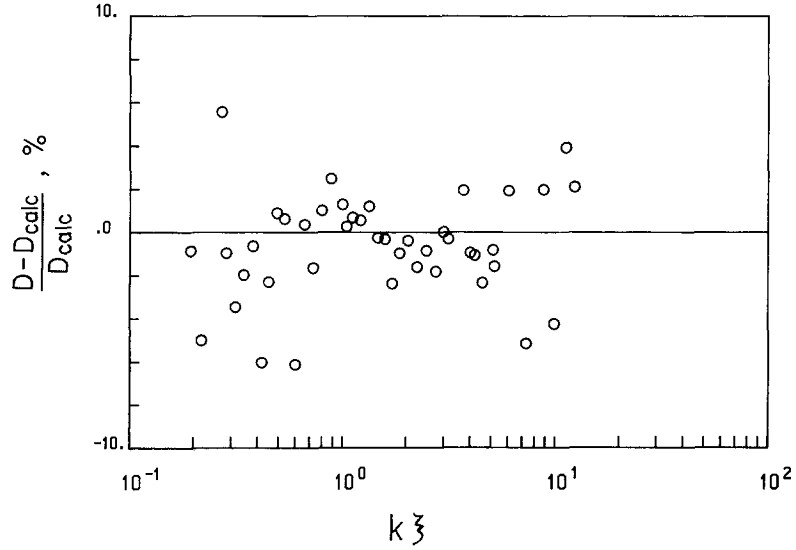

Fig. 3. Comparison between the experimental diffusion coefficient D and the calculated one by Eq. (5) with $a_0 = 55.5$, $b = 0.26$, and $q_c = 9.2 \times 10^8\ \mathrm{cm}^{-1}$ as a function of $k\xi$.

other systems of a fluid. In order to confirm this we have tried to analyze our data using two parameters, a_0 and b, by setting $D^B = 0$ in Eq. (5). This procedure yields $a_0 = 48._6 \pm 4.0$, i.e., $R = 1.28 \pm 0.03$ and $b = 0.29 \pm 0.06$. Both analyses are compatible with each other within estimated errors. It is noted that our value for R may include the background contributions.

4. CONCLUSIONS

In this work we have examined the critical behavior in nonionic micellar solutions of C_6E_3 in water close to the critical point of mixing. The values obtained for the critical exponents are in excellent agreement with those predicted for the three dimensional Ising-like model. The dynamical amplitude R estimated from the present analysis is about 25% larger than the expected universal value.

ACKNOWLEDGMENTS

The authors acknowledge many stimulating discussions with Professor J. V. Sengers. This work was motivated by the research in the laboratory of Professor J. V. Sengers at the University of Maryland. It is a genuine pleasure also to acknowledge the help of Dr. H. C. Burstyn through many valuable discussions.

REFERENCES

1. M. Corti, V. Degiorgio, and M. Zulauf, *Phys. Rev. Lett.* **23**:1617 (1982); M. Corti, C. Minero, and V. Degiorgio, *J. Phys. Chem.* **88**:309 (1984).
2. For a review, see P. C. Hohenberg, and B. I. Halperin, *Rev. Mod. Phys.* **49**:435 (1977).
3. K. Hamano, N. Kuwahara, and T. Koyama, *Phys. Rev. A* **32**:3168 (1985).
4. M. E. Fisher, *Phys. Rev. Lett.* **57**:1911 (1986); C. Bagnuls and C. Berviller, *Phys. Rev. Lett.* **58**:435 (1987); L. Reatto, *Nuovo Cimento* **8D**:497 (1986).
5. G. Dietler and D. S. Cannell, *Phys. Rev. Lett.* **60**:1852 (1988).
6. J. G. Shanks and J. V. Sengers, *Phys. Rev. A* **38**:885 (1988).
7. M. Corti and V. Degiorgio, *Phys. Rev. Lett.* **55**:2005 (1985).
8. T. Ohta, *Prog. Theor. Phys.* **54**:1566 (1975); T. Ohta and K. Kawasaki, *Prog. Theor. Phys.* **55**:1384 (1976); B. J. Halperin, P. C. Hohenberg, and E. G. Siggia, *Phys. Rev. Lett.* **22**:1289 (1974); E. G. Siggia, B. I. Halperin, and P. C. Hohenberg, *Phys. Rev. B* **13**:2110 (1976).
9. J. V. Sengers, *Int. J. Thermophys.* **5**:803 (1985).
10. H. C. Burstyn and J. V. Sengers, *Phys. Rev. Lett.* **45**:259 (1980); H. C. Burstyn, J. V. Sengers, and P. Esfandiari, *Phys. Rev. A* **22**:282 (1980).
11. K. Hamano, N. Kuwahara, and M. Kaneko, *Phys. Rev. A* **21**:1312 (1980).
12. K. Hamano, T. Kawazura, T. Koyama, and N. Kuwahara, *J. Chem. Phys.* **82**:2718 (1985); K. Hamano, T. Sato, T. Koyama, and N. Kuwahara, *Phys. Rev. Lett.* **55**:1472 (1985).

13. C. Le Guillou and J. Zinn-Justin, *Phys. Rev. Lett.* **39**:95 (1974).
14. A. J. Bray and R. F. Chang, *Phys. Rev. A* **12**:2594 (1975).
15. C. A. Tracy and B. M. McCoy, *Phys. Rev. B* **12**:368 (1975).
16. R. F. Berg, R. Moldover, and J. S. Huang, *J. Chem. Phys.* **87**:3687 (1987).
17. R. A. Ferrell and J. K. Bhattacharjee, *Phys. Rev. A* **19**:348 (1979).
18. K. Hamano, S. Teshigawara, T. Koyama, and N. Kuwahara, *Phys. Rev. A* **33**:485 (1986), and references therein.