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Dynamics of phase separation for a micellar solution

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The phase-separation process in a micellar solution has been examined in an unstable region above its lower critical mixing point. We find that phase separation for a critical mixture pentaethylene glycol mono-*n*-dodecyl ether and water is quite analogous to spinodal decomposition observed in critical binary systems near their critical mixing points. A comparison is made of the time dependence of the scattered light intensity between recent theoretical predictions of spinodal decomposition and the experimental results.

INTRODUCTION

The dynamics of phase separation in binary liquid mixtures near their critical mixing points has been investigated with a great interest by light-scattering techniques. When a critical mixture is brought into the unstable region of a phase diagram, phase separation begins with an appearance of a characteristic ring indicating spinodal decomposition.[1] The experimental investigations of spinodal decomposition have been carried out in critically quenched isobutyric acid and water, 2,6-lutidine and water, polydimethylsiloxane and diethylcarbonate, and a few similar systems.[2,3] These critical binary mixtures have been found to decompose into two phases through the spinodal decomposition mechanism[4] rather than the first-order phase separation process, say, nucleation and growth in the metastable region of a phase diagram. Recent theories and experiments suggest that the properly normalized structure factor of a critically quenched binary mixture has a scaling form with a time-independent universal function.[5-7]

A critical mixture of nonionic amphiphiles in water also decomposes into two water-rich phases including micelles when the temperature is raised above its lower critical mixing point; one is dilute and the other moderately concentrated in the amphiphile concentration. In recent years the critical behavior for micellar solutions and microemulsions has attracted increasing attention.[8] An analogy clearly exists between a critical micellar solution and a critical binary liquid mixture. For instance, the isothermal osmotic compressibility χ_T near the critical mixing point in a micellar solution exhibits a critical-like power-law behavior with an exponent γ, whose value depends on the system studied, in apparent violation of universality.[9] It is the purpose of the present work to point out the analogy between phase separation in a critically quenched micellar solution and spinodal decomposition in a critically quenched binary mixture.

EXPERIMENTAL

Water of liquid chromatographic quality and pentaethylene glycol mono-*n*-dodecyl ether ($C_{12}E_5$) obtained from Nikko Chemicals were employed in this work. The coexistence curve for the system $C_{12}E_5$ + water was determined by a differential refractometer[10] in the temperature range of $9.84\times10^{-6}\leq\epsilon\leq2.36\times10^{-4}$ as shown in Fig. 1, where $\epsilon=|T-T_c|/T_c$. The open symbols represent the coexistence curve and the closed symbols the diameter of the coexistence curve. The critical mixing point was determined to be $T_c=305.06$ K and $c_c=12.0_0\pm0.40$ mg/g. The coexistence curve is well represented by the simple power law $c^+-c^-=B\epsilon^\beta$ with $B=115.5_5\pm7.5$ mg/g and $\beta=0.249\pm0.007$ in the range of $9.84\times10^{-6}\leq\epsilon\leq2.36\times10^{-4}$, where c^+ and c^- refer to the concentrations of the concentrated and the dilute phases. The quoted error represents the standard deviation. The β value has been confirmed to be

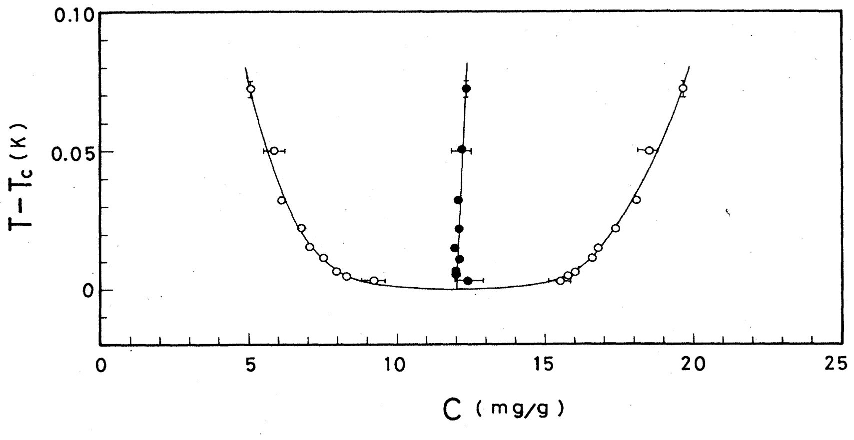

FIG. 1. The coexistence curve and the diameter for $C_{12}E_5$ + water. Open symbols represent the coexistence curve and closed symbols the diameter associated with the shape of the coexistence curve.

the same irrespective of concentration units, i.e., the weight, the volume, and the mole fraction.

The light scattering measurement of phase separation was carried out for a critical mixture of $C_{12}E_5$ + water, flame sealed under vacuum in a rectangular quartz cell with 1.0-mm optical path length. The transmitted and the scattered light intensities as a function of time were measured at eight wave numbers [$k(10^3 \text{ cm}^{-1}) = 0$, 0.9_8, 1.4_7, 1.9_6, 2.4_5, 2.9_4, 3.4_3, and 4.4_1] for six temperature quench depths in the range of $5 \leq T - T_c \leq 14$ mK. Sample preparation, temperature stability of the water bath, and experimental details have been fully described elsewhere.[3,7] We paid close attention to avoid oxidation of the sample.

In order to obtain critical parameters for $C_{12}E_5$ + water, the angular distribution of the scattered light intensity was measured over the angular range of $20° \leq \theta \leq 135°$ in the temperature range of $6.55 \times 10^{-6} \leq \epsilon \leq 1.78 \times 10^{-2}$ along the critical isochore. The autocorrelation function was also measured at five angles of $\theta = 35°$, 45°, 60°, 90°, and 120° in the temperature range of $6.56 \times 10^{-6} \leq \epsilon \leq 3.84 \times 10^{-2}$ along the critical isochore. In order to reduce the effect of multiple scattering we used the cylindrical cell of 4.0-mm i.d. in light scattering experiments[10,11] at temperatures very close to the critical mixing point. The turbidity τ, measured by use of a rectangular cell with 5.0-mm optical path length, varied from $2.9_9 \times 10^{-1}$ cm^{-1} to $1.4_5 \times 10^{-2}$ cm^{-1} over the temperature range of $1.31 \times 10^{-6} \leq \epsilon \leq 2.53 \times 10^{-2}$ along the critical isochore. The attenuation correction for the intensity data in the one-phase region was done within the limit of 11%.

RESULTS AND DISCUSSION

In a relatively small region of $k\xi$, where ξ is the correlation length, the intensity data could be approximately represented by

$$I(k,\xi)^{-1} = I_0^{-1} \epsilon^{\gamma} (1 + k^2 \xi_0^2 \epsilon^{-2\nu}) \quad ,$$

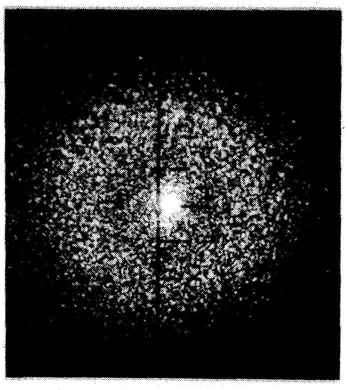

FIG. 2. Scattering pattern with a maximum wave number $k_m \simeq 1.79 \times 10^3$ cm^{-1} following a temperature quench depth of $T = T_c + 10$ mK.

with $\gamma = 1.03_5 \pm 0.028$, $\nu = 0.51_4 \pm 0.012$, and $\xi_0 = (3.2_7 \pm 0.23) \times 10^{-7}$ cm in the temperature range of $4.64 \times 10^{-4} \leq \epsilon \leq 1.78 \times 10^{-2}$. The values γ and ν are in good agreement with those predicted by the mean-field theory and satisfy the relation $\gamma = 2\nu$. When the critical mixture is approached within $\epsilon \lesssim 4.64 \times 10^{-4}$ the isothermal osmotic compressibility χ_T and the correlation length ξ for $C_{12}E_5$ in water asymptotically level off to constants, respectively. This fact clearly exhibits the breakdown of the power-law behaviors for χ_T and ξ in the temperature range very close to T_c. These leveling-off effects for the quantities χ_T and ξ could be caused by their complexity in a micellar system.

In the hydrodynamic region ($k\xi < 1$), the decay rate Γ of concentration fluctuations is given by $\Gamma = Dk^2$, with D being the diffusion coefficient for $C_{12}E_5$ in water. At temperatures close to T_c the diffusion coefficient D for $C_{12}E_5$ in water depends strongly on k. To estimate the dynamic exponent z at $T \rightarrow T_c$, we have examined the k dependence of

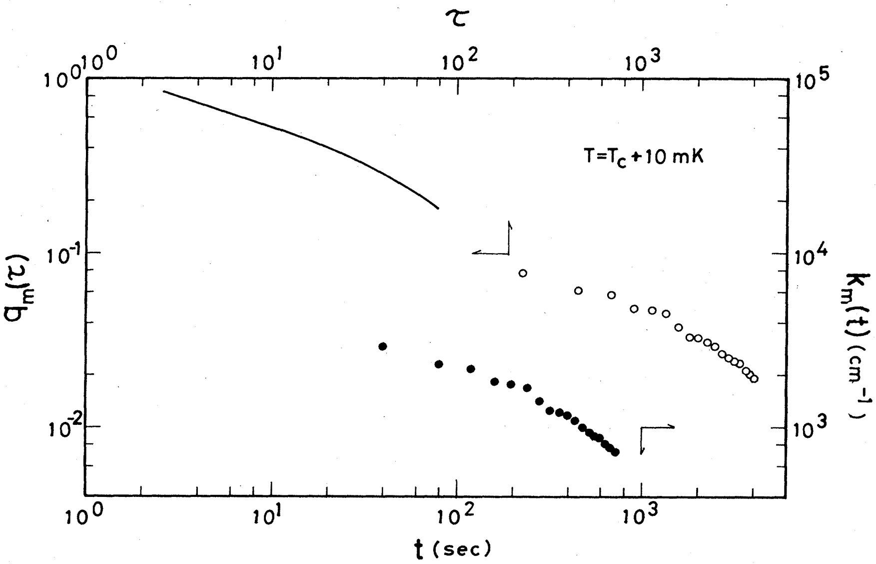

FIG. 3. The scaled location $q_m(\tau)$ (symbol ○) and the wave number $k_m(t)$ (symbol ●) vs the scaled time τ and time t, respectively, following a quench depth $T = T_c + 10$ mK. The solid curve represents the work of Kawasaki and Ohta in Ref. 13.

Γ at each temperature by the relation $\Gamma \propto k^{z_{\text{eff}}(T)}$. The asymptotic value $z = \lim_{T \to T_c} z_{\text{eff}}(T)$ yields 2.90 ± 0.02, which is very close to the universal value $z \simeq 3$. The decay rate Γ has been also examined as a function of the scaling variable $k\xi$ following the Kawasaki theory.[12] The Γ/k^3 vs $k\xi$ is represented by a single curve in the range of $0.14 \lesssim k\xi \lesssim 6.2$. This result suggests that the dynamic scaling expression is applicable even for a micellar solution near the critical mixing point. The numerical value $A = \lim_{k\xi \to \infty}(\Gamma/k^3)$ has been estimated to be $1.2_8 \times 10^{-13}$ cm^3/sec in the region of $k\xi > 1$, whose value is related to the diffusion coefficient by the relation $A = (\frac{3}{8})\pi D\xi$. Further experimental details will appear elsewhere.

When the critical mixture of $C_{12}E_5$ in water is brought into the unstable region above the critical temperature, a ring formed by the forward scattered light is observed on a screen placed in front. A typical scattering pattern indicating phase separation at a quench temperature $T = T_c + 10$ mK is shown in Fig. 2. The wave number $k_m(t)$ at maximum of the forward scattered light and the scaled location $q_m(\tau) = k_m(t)\xi$ in the phase-separation process for $T = T_c + 10$ mK are shown in Fig. 3 as functions of lapse time t and the scaled time τ, where $\tau = Dt/\xi^2$, with D and ξ being the diffusion coefficient and the correlation length in the one-phase region. The scaled location $q_m(\tau)$ has the same time dependence as that of the work of Kawasaki and Ohta,[13] because our data can be superposed on the Kawasaki-Ohta theory by shifting the vertical and the horizontal axes. The necessity of shifting could be partially attributed to the scaling of temperature with D and ξ in the one-phase region. In an early stage of phase separation, the scaled intensity $\epsilon^{-2\beta}\tilde{I}(k,t)$ with $\tilde{I}(k,t)$ being the intensity corrected for the background and the attenuation increases as $\epsilon^{-2\beta}\tilde{I}(k,t) \propto \tau^a$ with a varying from 5.3_3 to 0.5_9 over the range of $0.9_8 \times 10^3 \leqslant k \leqslant 4.4_1 \times 10^3\ \text{cm}^{-1}$ at $T = T_c + 10$ mK, in qualitative agreement with the nonlinear theories of spinodal decomposition.[5] The scaled structure factor $\epsilon^{-2\beta}k_m^3\tilde{I}(k,t)$ is plotted as a function of k/k_m in Fig. 4. Our result suggests the structure factor $F(k/k_m) = \epsilon^{-2\beta}k_m^3\tilde{I}(k,t)$ to be independent of time over the range of $0.7 \lesssim k/k_m \lesssim 2.5$. The solid curve in Fig. 4 represents Eq. (3) in Ref. 7 with a width of $2\delta = 0.32$ at half maximum. The essential behaviors of $q_m(\tau)$, $\epsilon^{-2\beta}\tilde{I}(k,t)$, and $\epsilon^{-2\beta}k_m^3\tilde{I}(k,t)$ on the scaled time τ have been confirmed to be independent of quench depth.

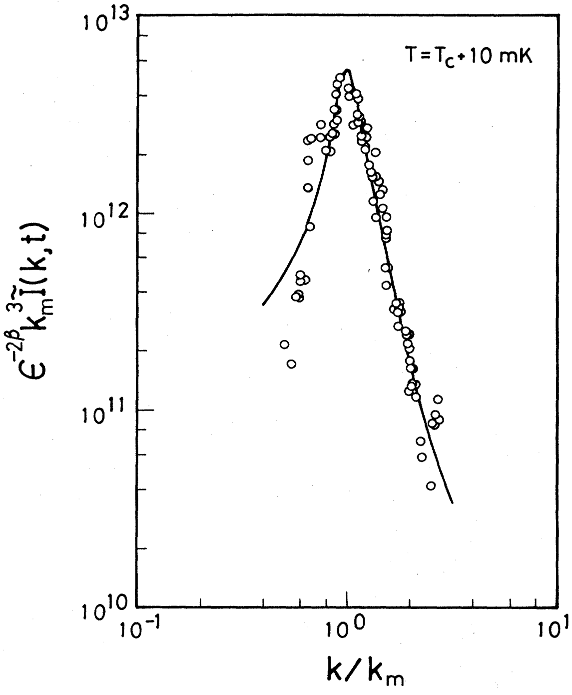

FIG. 4. The scaled structure factor $\epsilon^{-2\beta}k_m^3\tilde{I}(k,t)$ vs k/k_m, following a quench depth $T = T_c + 10$ mK. The solid curve represents a time-independent function with a width of $2\delta = 0.32$ in Ref. 7.

We find the phase separation process in a critically quenched micellar system to bear some resemblance to spinodal decomposition in a critically quenched binary system. Our result also suggests that the scaled location $q_m(\tau)$ and the scaled intensity $\epsilon^{-2\beta}\tilde{I}(k,t)$ have time dependence similar to those of critically quenched binary systems. The scaled structure factor $\epsilon^{-2\beta}k_m^3\tilde{I}(k,t)$ obeys a simple scaling form with a time-independent function in approximate agreement with those of Marro, Lebowitz, and Kalso.[5]

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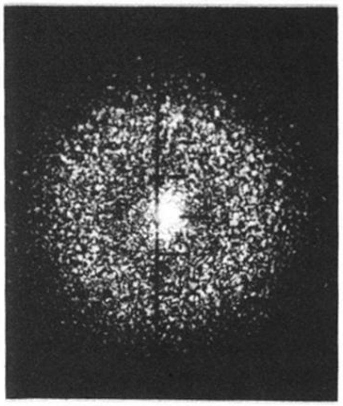

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