

## Dynamics of Concentration Fluctuations for a Micellar Solution

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The decay rate  $\Gamma$  for a micellar solution pentaethylene glycol mono *n*-dodecyl ether + water has been examined near the critical mixing point by light scattering. We find that the dynamic scaling behavior of  $\Gamma^* = [6\pi\eta(T)/k_B T](\Gamma/k^3)$  as a function of  $k\xi$  over the range of  $0.14 \leq k\xi \leq 6.2$  has an obvious kinship with that for a fluid mixture near the critical mixing point, where  $\eta(T)$  is the shear viscosity and  $\xi$  the correlation length. It is also found that the shear viscosity exhibits a critical-like power-law singularity and depends explicitly on shear gradients.

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The importance of micellar systems has been recognized in numerous technical and biological processes, and also in their use as model systems for membranes, lipids, or enzymes. The fundamental feature of micellar systems is a consequence of the dual nature of the surface-active molecule, a hydrophobic alkyl chain and a hydrophilic head group. The amphiphilic molecules have a tendency to collect at any interface where the hydrophobic groups can be partially or completely removed from contact with water and the hydrophilic groups can remain wetted. These processes create aggregates of surfactant molecules — micelles — so that the total contact area of the hydrophobic groups in water is reduced. The same processes create micelles for most nonionic surface-active agents in water.

A homogeneous single phase involving micelles separates into two distinct water-rich isotropic phases when the temperature is raised above the minimal point of the phase diagram. This point has been regarded as the critical mixing point in a micellar solution. In recent years Corti *et al.* have argued for an analogy between a fluid mixture with a critical mixing point and a micellar solution.<sup>1</sup> They have suggested that the critical concentration fluctuations associated with the phase transition play an important role near the critical mixing point in a micellar solution. The fundamental dynamic phenomena of a fluid mixture near the critical mixing point is that the concentration fluctuations decay very slowly in time. The theory of dynamic critical phenomena shows that the decay rate of the concentration fluctuations is related to the shear viscosity in a fluid mixture, which displays a weak enhancement very close to the critical mixing point.<sup>2</sup> It is therefore of great interest to study the dynamical properties associated with the phase transition in a micellar solution on the basis of the critical dynamics. In this work we try to reveal the dynamical behavior of a nonionic micellar solution by focusing on the relaxation time of the fluctuations and the shear viscosity near the critical mixing point.

Pentaethylene glycol mono *n*-dodecyl ether (PEGDE) in water was used in this work. The coex-

istence curve determined from the concentrations of the two coexisting phases by use of a differential cell of the Brice type was represented by a simple power law,  $c^+ - c^- = B\epsilon^\beta$  with  $B = 115.5 \pm 7.5$  mg/g and  $\beta = 0.249 \pm 0.007$  in the range of  $9.84 \times 10^{-6} \leq \epsilon \leq 2.36 \times 10^{-4}$ , where  $\epsilon = |T - T_c|/T_c$ . The quoted error represents the standard deviation. The results of other fits in terms of volume fraction and mole fraction were essentially the same. The critical mixing point was determined to be  $T_c = 305.06$  K and  $c_c = 12.00 \pm 0.40$  mg/g, which was ascertained by the equal-volume criterion. A detailed analysis and discussion will appear elsewhere. The exponent value  $\beta \approx 0.25$  is significantly smaller than the universal one  $\beta \approx 0.32$  for a fluid mixture.<sup>3,4</sup> We have also analyzed our data with a modified composition variable in terms of the Walker-Vause model,<sup>5</sup> which has been satisfactorily applied to closed-loop coexistence curves. For this choice of the composition variable, we were able to estimate an exponent value of  $\beta = 0.270 \pm 0.013$ , irrespective of concentration units. These findings indicate that the coexistence curve for a micellar solution PEGDE + water tends to be rather abruptly flat at the lower critical mixing point.

The range of the fluctuations can be characterized by the correlation length  $\xi$ . To interpret the observed behavior of the decay rate of the fluctuations, it is desirable that the correlation length  $\xi$  as a function of temperature be measured simultaneously. For this purpose, the angular distribution of the scattered light intensity over the range of  $20^\circ \leq \theta \leq 135^\circ$  and the autocorrelation functions at  $\theta = 35^\circ, 45^\circ, 60^\circ, 90^\circ$ , and  $120^\circ$  were measured at the same temperature by use of a 6-mm-diam cylindrical cell in a weakly opalescent region of  $6.60 \times 10^{-4} \leq \epsilon \leq 1.78 \times 10^{-2}$  and by use of a 4-mm-diam cylindrical cell in a strongly opalescent region of  $6.56 \times 10^{-6} \leq \epsilon \leq 1.66 \times 10^{-3}$ , respectively. The light-scattering photometer, sample preparations, and experimental details have been fully described elsewhere.<sup>4,6</sup>

For viscosity measurements, we used a low-shear rotational viscometer of the Zimm-Crothers type.<sup>7</sup> The

viscosity for a critical mixture PEGDE + water between two vertical coaxial cylinders, the inner one of which is driven by an electrically induced magnetic field, was measured over the range of velocity gradients from  $9.4 \times 10^{-2}$  to  $6.8 \times 10^{-1} \text{ sec}^{-1}$  in the range of  $1.64 \times 10^{-5} \leq \epsilon \leq 2.58 \times 10^{-2}$ .

The Ornstein-Zernike-Debye plots of inverse scattered intensity  $I(k)^{-1}$  versus the square of the (momentum-transfer) wave number  $k^2$  showed a small deviation from a linear behavior at large  $k$  values, which is usually attributed to a critical exponent  $\eta$ .<sup>8</sup> To investigate the behavior of the forward-scattered intensity  $I(0) [= \lim_{k \rightarrow 0} I(k)]$ , which is directly proportional to the isothermal osmotic compressibility  $\chi_T$  and the correlation length  $\xi$ , we have analyzed the intensity data by using the correlation function<sup>6,9</sup>

$$[g(k\xi)]^{-1} = 1 + \Sigma_2 k^2 \xi^2 - \Sigma_4 k^4 \xi^4.$$

The Ornstein-Zernike correlation function corresponds to  $\Sigma_2 = 1$  and  $\Sigma_4 = 0$ . The intensity data were corrected for a small attenuation of light in the medium. Our results for the power-law behavior are  $I(0)^{-1} \propto \epsilon^\gamma$ , with  $\gamma = 1.035 \pm 0.028$ , and  $\xi = \xi_0 \epsilon^{-\nu}$ , with  $\xi_0 = (3.27 \pm 0.23) \times 10^{-7} \text{ cm}$  and  $\nu = 0.514 \pm 0.012$ , in the limited region of  $4.64 \times 10^{-4} \leq \epsilon \leq 1.78 \times 10^{-2}$ . The exponent values  $\gamma$  and  $\nu$  are in good agreement with those predicted by the mean-field theory ( $\gamma = 2\nu = 1$ ). These results are essentially equivalent to those for other nonionic micellar systems, for example, octaethylene glycol mono *n*-dodecyl ether + water, tetraethylene glycol mono *n*-octyl ether + water, and hexaethylene glycol mono *n*-dodecyl ether + water in almost the same temperature range of  $\epsilon \gtrsim 10^{-3}$ .<sup>1</sup> It is generally believed that the asymptotic

power law in a fluid mixture should be valid for temperatures sufficiently close to  $T_c$ , i.e., in the range of  $\epsilon < 10^{-3}$ . In contrast with the asymptotic behavior in a fluid mixture near the critical mixing point, the simple power law for both quantities  $\chi_T$  and  $\xi$  in PEGDE + water became invalid, and these quantities approximately leveled off to constant values at temperatures corresponding to  $\epsilon \leq 4.64 \times 10^{-4}$ . It should be noted that  $\epsilon$  is not small, but large, as  $\epsilon \geq 10^{-3}$  in order for the simple power law for  $\chi_T$  and  $\xi$  to be valid. Though we still lack information on the behavior of aggregated micelles near  $T_c$ , it is suggested that the asymptotic critical behavior may be affected significantly by a nonsingular behavior of the aggregated micelles. It is important to consider these effects in order to interpret a fully developed critical region in a micellar solution; however, here we are concerned with a more general investigation of dynamical behavior.

In most measurements for the shear viscosity, the mixtures of small molecules have been treated as Newtonian fluids for which the shear viscosity is independent of velocity gradients. Near the critical mixing point in a fluid mixture the system includes large fluctuations and thus non-Newtonian effects are expected. Onuki and Kawasaki suggest that the shear viscosity  $\eta(S)$  depends very weakly on the velocity gradient  $S$  as  $\eta(S) \propto S^{-\omega}$  with  $\omega \approx 0.013$  for a fluid mixture near the critical mixing point.<sup>10</sup> The dependence of the viscosity on  $S$  has been examined at fixed temperatures in double-logarithmic plots as shown in Fig. 1. The slope of a log-log plot in Fig. 1 is defined as an effective exponent  $\omega_{\text{eff}}$ , as a function of temperature, by  $\eta(S) \propto S^{-\omega_{\text{eff}}}$ . The values obtained for  $\omega_{\text{eff}}$  are shown as a function of  $\epsilon$  in Fig. 2. The data in Fig. 2 exhibit an approximately constant value of  $\omega_{\text{eff}} = 0.131 \pm 0.015$  in the range of  $5.84 \times 10^{-4} \leq \epsilon \leq 2.58 \times 10^{-2}$ . These non-Newtonian effects at tem-

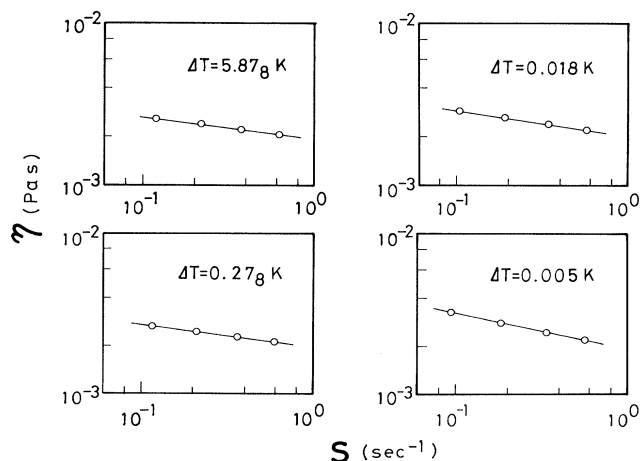


FIG. 1. Dependence of the shear viscosity on velocity gradient  $S$  for a critical mixture of PEGDE + water. The slope of a log-log plot is defined as an effective exponent  $\omega_{\text{eff}}$ , as a function of temperature, by  $\eta(S) \propto S^{-\omega_{\text{eff}}}$ .

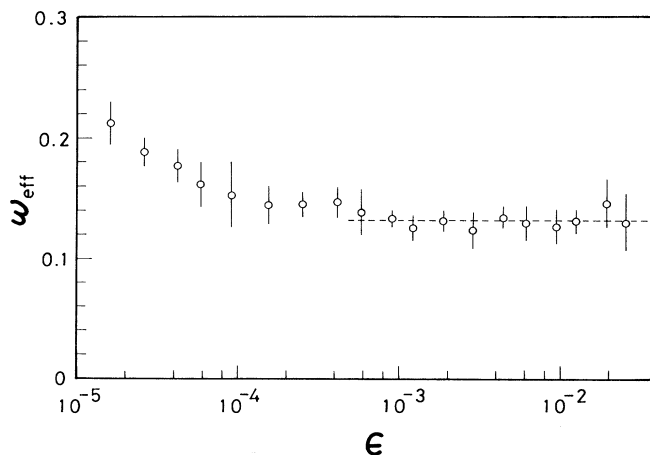


FIG. 2. The effective exponent  $\omega_{\text{eff}}$  as a function of  $\epsilon$  for a critical mixture of PEGDE + water.

peratures away from  $T_c$  may be attributed mainly to the presence of aggregated micelles with a significantly larger size and flexibility in a shear flow.<sup>11</sup> The exponent  $\omega_{\text{eff}}$  should approach  $\omega$  in the limit  $T \rightarrow T_c$ . The extrapolated value  $\omega = \lim_{T \rightarrow T_c} \omega_{\text{eff}}(T)$  has been estimated to be  $0.23 \pm 0.02$ , which is somewhat larger than that predicted for a fluid mixture.<sup>10-12</sup> It should be noted that the shear viscosity for a micellar solution PEGDE + water depends strongly on velocity gradients near the critical mixing point. The power-law behavior has been found to be  $\eta(T)/\eta^B = A\epsilon^{-\phi}$ , with  $A = 0.49 \pm 0.05$  and  $\phi = 0.085 \pm 0.008$  in the range of  $1.64 \times 10^{-5} \leq \epsilon \leq 9.18 \times 10^{-5}$ , for the viscosity data at the lowest shear gradients among the data obtained in this work.<sup>13</sup> The background viscosity  $\eta^B = (2.59 \pm 0.03) \times 10^{-3}$  Pa sec has been evaluated in the range of  $1.24 \times 10^{-3} \leq \epsilon \leq 6.16 \times 10^{-3}$ , in which the viscosities yield an approximately constant value. It should be noted that the shear viscosity for PEGDE in water exhibits a critical-like power-law behavior with an exponent  $\phi$ , whose value is significantly larger than the universal one  $\phi \simeq 0.04$  predicted for a fluid mixture.<sup>3,6,14</sup> These data for the viscosity are used in the analysis for the decay rate of the fluctuations near  $T_c$ .

The experimental autocorrelation data have been well represented by an exponential decay law. At temperatures well away from  $T_c$  the diffusion coefficient  $D = \Gamma/k^2$  was observed to be independent of wave number  $k$ , i.e., scattering angle  $\theta$ . We obtained  $D = (9.62 \pm 0.44) \times 10^{-8}$  cm<sup>2</sup>/sec at  $\epsilon = 3.84 \times 10^{-2}$ , which may be identified with the diffusion coefficient in the hydrodynamic limit  $k \rightarrow 0$ . For a fluid mixture, the hydrodynamic diffusion coefficient decreases upon approach to the critical mixing point, indicating the critical slowing down of the fluctuations. At the same time, the diffusion coefficient becomes explicitly dependent on  $k$ . At temperatures closer to  $T_c$ , the behavior of the diffusion coefficient for PEGDE + water was found to be quite similar to that for a fluid mixture near  $T_c$ .<sup>14</sup> In order to examine the experimental data in terms of dynamic scaling,<sup>2,15</sup> we show the scaled decay rate  $\Gamma^* = [6\pi\eta(T)/k_B T](\Gamma/k^3)$  as a function of the scaling variable  $k\xi$  in Fig. 3. The data obtained at the five different wave numbers collapse well onto a single curve, thus confirming the applicability of the dynamic scaling for a micellar solution PEGDE + water in the range of  $0.14 \leq k\xi \leq 6.22$ , corresponding to the range of  $3.08 \times 10^{-5} \leq \epsilon \leq 3.84 \times 10^{-2}$ . It is concluded that the decay rate for a large  $k\xi$  region varies as  $\Gamma \propto k^z$  with a dynamical exponent  $z \approx 3$ , corresponding to the dynamical behavior in a fluid mixture near  $T_c$ .<sup>3,6,14-16</sup> A similar conclusion has been reported by Abillon *et al.*<sup>17</sup> and by Appell and Porte<sup>18</sup> for ionic-surfactant solutions, which exhibit three-dimensional Ising values for  $\gamma$  and  $\nu$ . The solid curve in Fig. 3 represents a universal function

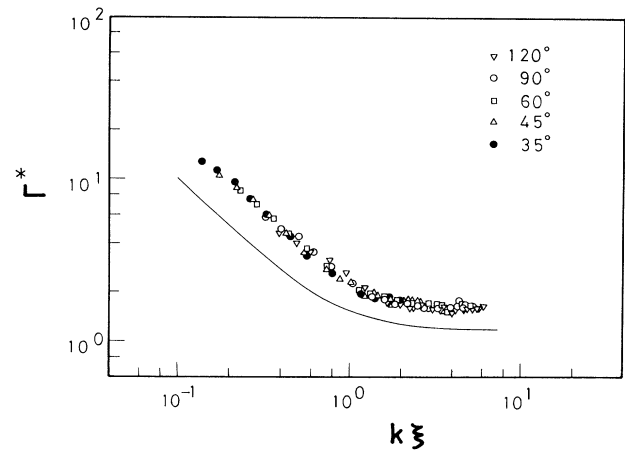


FIG. 3. Scaled decay rate  $\Gamma^* = [6\pi\eta(T)/k_B T](\Gamma/k^3)$  as a function of  $k\xi$  for a critical mixture of PEGDE + water. The solid curve represents a universal function  $K(k\xi)/(k\xi)^3$  independent of the system, where  $K(k\xi)$  is the Kawasaki function.

$K(k\xi)/(k\xi)^3$  independent of the system, where  $K(x)$  is the original Kawasaki function defined by<sup>16</sup>

$$K(x) = \frac{3}{4} [1 + x^2 + (x^3 - x^{-1}) \tan^{-1} x].$$

We present a few arguments for the apparent disagreement in Fig. 3 between the theoretical prediction and the experiment. In the treatment of dynamical critical phenomena it is customary to separate the  $\Gamma$  into a nonsingular background contribution  $\Gamma^B$  and additional contributions  $\Gamma^c$  due to the critical fluctuations as  $\Gamma = \Gamma^c + \Gamma^B$ .<sup>3,6,14,15</sup> We need to estimate the  $\Gamma^B$  in the present system for further analysis. However, no independent experimental information or theoretical expression is available for the background estimation associated with the aggregated micelles with a substantial growth with  $T$ .<sup>19</sup> If we assume these discrepancies in Fig. 3 to be attributed to the  $\Gamma^B$ , the contribution of  $\Gamma^B$  to the measured  $\Gamma$  would amount to about 50% in the hydrodynamic region of  $k\xi \simeq 0.2$  and to about 30% even in the critical region of  $k\xi \simeq 5$ . We note that the background contribution estimated with this procedure is very large for PEGDE in water even in the critical region, which contrasts with the nearly negligibly small one in the critical region of fluid mixtures<sup>3,6,14,15</sup> and also in some ionic micellar solutions.<sup>18</sup>

Thus we have examined the dynamical behavior near the critical mixing point of a nonionic micellar solution PEGDE + water on the basis of the critical dynamics. We have found that the shear viscosity depends on velocity gradients approximately as  $\eta(S) \propto S^{-\omega}$ , with  $\omega \simeq 0.23$  in the limit  $T \rightarrow T_c$ , and the viscosity data at very low shear gradients can be represented with a critical-like power law of the form

$\eta(T)/\eta^B \propto \epsilon^{-\phi}$ , with  $\phi \approx 0.085$ . The dynamic scaling behavior of the decay rate for PEGDE in water is concluded to have an obvious kinship with that for a fluid mixture near the critical mixing point.

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