

not be described in the nonadiabatic limit, in agreement with Ref. 7. In any case (3) shows that  $t_0 W_2(t) \sim 10n_2/n_{2T}$  at  $E(t)=0$ . At about room temperature the effective density of states  $n_{2T}$  is  $4 \times 10^{17} - 3 \times 10^{18} \text{ cm}^{-3}$  for  $m_2$  of 0.1–0.4 times the true electron mass. Therefore, in this example, if the majority-carrier density  $n_2$  is at least  $10^{17} - 10^{18} \text{ cm}^{-3}$ , we get  $\int_0^{t_0} W_2(t) dt \gtrsim 1$ , and multiphonon nonradiative recombination is completed in a very short time, of the order of  $t_0$  ( $\sim 10^{-13}$  sec), after a minority carrier is first captured by a defect. In this case a trapped carrier cannot be detected by the usual techniques such as deep-level transient spectroscopy since it exists only for a very short time. Even if  $n_2$  is not so large, multiphonon nonradiative recombination occurs dominantly by this successive capture mechanism when the lifetime of a trapped carrier is much shorter than  $10^8 t_0$  in this example limited by other mechanisms such as radiative decay.

In operating semiconductor-laser devices we usually inject (both minority and majority) carriers with concentrations of the order of  $10^{18} \text{ cm}^{-3}$ . Then an electron and a hole are captured successively in a very short time, during which a large amount of energy of about  $E_G$  is emitted in the form of phonons around a defect. This causes a recombination-enhanced defect reaction active only in the operating condition.

When the phonon dispersion  $2\omega_B$  is small, or when the trapped electron interacts dominantly

with localized phonons, oscillations of  $\bar{Q}(t)$  along  $V_2(Q)$  do not dampen so rapidly. In this case  $E(t) \approx 0$  can be reached when the crossing point between  $V_2(Q)$  and  $V_0(Q)$  is lower than that between  $V_2(Q)$  and  $V_1(Q)$  in Fig. 1. This condition is written as  $(E_d - S)^2 / (4S) < E_G - E_d + (E_G - E_d - S)^2 / (4S)$ , which gives  $E_d < E_G / 2 + S$ . Since  $S$  is of the order of several tenths of an electron volt<sup>4,11</sup> and  $E_G \lesssim 2 \text{ eV}$ , this condition can be satisfied for deep levels distributed widely in the forbidden gap.

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## Critical-Like Behavior Observed for a Five-Component Microemulsion

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The light-scattering techniques of intensity angular dissymmetry and photon correlation spectroscopy are used to determine the static correlation length, osmotic compressibility, and diffusivity of an oil-in-water microemulsion. The observed temperature dependence of these quantities near a phase separation point qualitatively resembles the critical behavior found for simple fluids and binary mixtures, but with substantially larger values of the critical exponents  $\bar{\nu}$  and  $\bar{\gamma}$ .

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Hydrophobic compounds such as oils can be readily solubilized in water (or, alternatively, water solubilized in oil) by using surfactants.<sup>1</sup> Surfactants contain a hydrophilic (polar) head group attached to a hydrophobic hydrocarbon

group and in water above a critical micelle concentration, they spontaneously self-assemble to form micellar aggregates.<sup>2</sup> With an addition of oil and a cosurfactant (usually an alcohol), transparent solutions may also result, generated by a

similar aggregation process. In water these microemulsions are generally believed to be dispersions of submicroscopic oil droplets surrounded by cosurfactant and surfactant.<sup>1,3</sup> The head groups of cosurfactant and surfactant are probably in contact with the solvent (water), with the hydrocarbon groups tails immersed to some degree in the oil core.

Interest in the properties of microemulsions stems from their scientific, industrial, and commercial applications.<sup>1</sup> Previous studies using dynamic light scattering<sup>4-6</sup> have concentrated on determination of the droplet particle size by measuring the diffusion coefficient, corrected for interparticle interactions. However, many microemulsions exhibit phase separation; consequently it is compelling to consider their resemblance to critical systems, i.e., both pure fluids and binary fluids whose universal critical behavior has been well established.<sup>7,8</sup> Critical exponents have already been measured for ternary liquid mixtures<sup>9</sup> and a three-component microemulsion.<sup>10</sup> Nicoli *et al.*<sup>11</sup> recently reported qualitative evidence of critical-type behavior in a five-component oil-in-water microemulsion. In this Letter we report measurements of the correlation length, osmotic compressibility, and diffusion coefficient of the above system using both classical and dynamic light scattering.

Our system contains (by wt.%): 2.30% cetyltrimethylammonium bromide (CTAB), a 16-carbon cationic surfactant; 2.30% *n*-octane (oil); 4.60% *n*-butanol; 1.77% sodium bromide; 89.03% water. The complicated phase diagram of this system would require four axes for compositional variables plus one for temperature. However, a simple coexistence curve describes the phase boundary in the plane of sodium bromide concentration versus temperature,<sup>11</sup> with constant octane and butanol concentrations (Fig. 1). This coexistence curve differs from those normally encountered in critical systems, in that it possesses an extremum with respect to chemical composition (i.e., salt concentration) rather than temperature, at approximately 1.77% NaBr and 38°C. We prepared a microemulsion having essentially the critical NaBr concentration by starting at 1.75% NaBr and carefully adding salt, monitoring the closure of the lower and upper phase separation temperatures. We performed our experiments as a function of temperature, from 5°C to 32°C, as shown by the dashed line in Fig. 1. We stress that this path does *not* correspond to the critical isochore normally followed in other critical

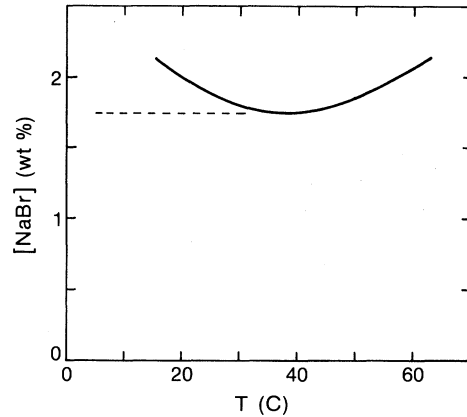


FIG. 1. Coexistence curve for the microemulsion investigated, in the plane of NaBr concentration (wt.%) vs temperature (C). The dashed line indicates the temperature range studied (at 1.77% NaBr).

systems (e.g., binary fluids). Furthermore, while our path intersects the coexistence curve at approximately the critical NaBr concentration, it is by no means clear that it is the preferred path with respect to the remaining compositional variables of the system.

The angular dissymmetry of the scattered intensity,  $d(\theta) = I(\theta)/I(\pi - \theta)$ , is related to the (static) correlation length  $\xi$  by the expression

$$d(\theta) = (1 + K_{\pi-\theta}^2 \xi^2) / (1 + K_{\theta}^2 \xi^2) \quad (1)$$

if one assumes an Ornstein-Zernike form<sup>7,8</sup> for the density correlation function. Here  $K_{\theta}$  is the scattering wave vector at angle  $\theta$ ,  $K_{\theta} = (4\pi n / \lambda) \sin(\theta/2)$ , where  $n$  is the solvent index of refraction and  $\lambda$  the exciting wavelength. We measured  $d(\theta)$  rather than the intensity  $I(\theta)$  to avoid the need for solid angle and first-order turbidity corrections to the data.

The scattering cell was a rectangular cuvette ( $1 \times 2$  cm<sup>2</sup>). Values of  $d(\theta)$  were obtained over the range 67.9°–118.9° with use of a 5-mW He-Ne laser and a microprocessor-controlled angular dissymmetry apparatus (photon counting). The data were corrected for reflection and second-order turbidity effects and fitted by least squares to Eq. (1). The resulting correlation range  $\xi$  increased smoothly from 76 Å at 5°C to 523 Å at 32°C.

In obtaining the  $T$  dependence of  $\xi$ , we assume that  $I(\theta)$  couples directly to the order parameter<sup>12</sup>  $\psi$  of the microemulsion via the dielectric constant  $\epsilon$ . We do not know the precise nature of  $\psi$  for this system, but assume that  $\partial\psi/\partial\epsilon$  is non-

singular. However, the coexistence curve (Fig. 1) obeys the power-law  $(C - C^*)/C^* \propto (|T - T^*|/T^*)^\beta$ ,  $\beta \cong 2.4$ , where  $C$  and  $T$  are the NaBr concentration and temperature, respectively ( $C^* \sim 1.77\%$  and  $T^* \sim 38^\circ\text{C}$  at the extremum). This is analogous to the power-law relation obeyed by the order parameter in fluids.

We model the  $T$  dependence of  $\xi$  using the power-law behavior found for pure fluids and binary mixtures,

$$\xi(t) = \xi_0 t^{-\tilde{\nu}}, \quad (2)$$

where  $t = (|T - T_c|/T_c)$  is the reduced temperature and  $T_c$  the critical temperature. We use the symbol  $\tilde{\nu}$ , rather than the usual  $\nu$ , for the critical exponent to emphasize that our measurements of  $\xi$  have not been made on the critical isochore. Least-squares fitting of the data to Eq. (2) gives  $T_c = 310.7 \pm 0.5$  K,  $\xi_0 = 6 \pm 0.6$  Å, and  $\tilde{\nu} = 1.13 \pm 0.07$ . The data points and best-fit curve are shown in Fig. 2(a).

We emphasize that our system differs markedly from simpler critical systems in that  $\xi$  changes significantly at temperatures normally considered to be far from  $T_c$ . Fully  $10^\circ\text{C}$  below  $T_c$  the solution exhibits strong scattering and substantial turbidity, presumably caused by the increasing spatial correlation of relatively large aggregates. Because of the turbidity and multiple-scattering effects, we were unable to make reliable measurements of  $d(\theta)$  above  $32^\circ\text{C}$ . Thus, our smallest values for  $t$  are more than an order of magnitude larger than those usually reported for critical systems and the relatively large uncertainties in  $T_c$ ,  $\xi_0$ , and  $\tilde{\nu}$  merely reflect this limitation. The exponent  $\tilde{\nu}$  is roughly twice the value of 0.63 typically found for fluid critical systems,<sup>7,8</sup> and our prefactor  $\xi_0$  is substantially larger than that found for those systems. This may be a reflection of the basic structural unit in our microemulsion, a 50–100-Å droplet, being much larger than the individual molecules which compose the critical fluid systems.

From the scattered intensity at  $90^\circ$  (corrected for turbidity) and the previously determined  $\xi$  values, we compute the osmotic compressibility  $\kappa_T$ ,

$$\kappa_T \propto I(90^\circ)(1 + K_\pi^2 \xi^2)/T. \quad (3)$$

A least-squares fit of the  $\kappa_T$  values (normalization arbitrary) to the power law

$$\kappa_T(t) \propto t^{-\tilde{\gamma}} \quad (4)$$

yields  $T_c = 310.5 \pm 0.5$  K and  $\tilde{\gamma} = 2.24 \pm 0.10$ . The

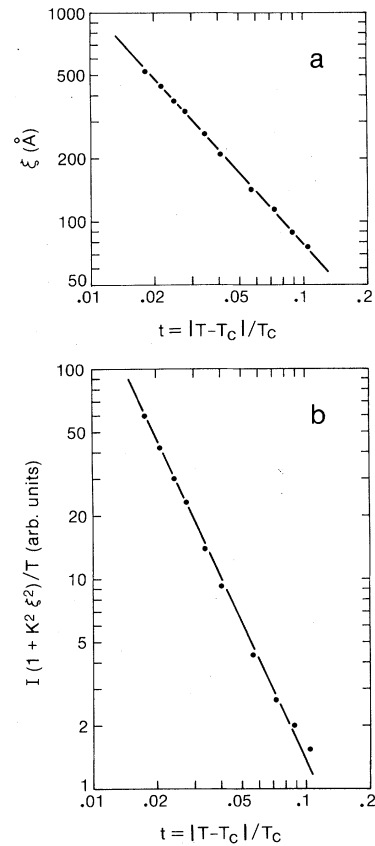


FIG. 2. (a) Correlation range  $\xi$  (Å) vs reduced temperature  $t$ ; (b) osmotic compressibility (arbitrary units) vs reduced temperature  $t$ . The straight lines are the best power-law fits to the data (dots).

data points and best-fit curve are shown in Fig. 2(b).

Two results are important. First, the power-law behavior of  $\kappa_T$  yields the same  $T_c$  value as the  $\xi$  data, within the experimental error. Second, the important scaling law  $\tilde{\gamma} = 2\tilde{\nu}$  is satisfied to within the least-squares fitting uncertainties. Again, our values for  $\tilde{\nu}$  and  $\tilde{\gamma}$  are markedly higher than those for many simpler systems, as well as for the three-component water-in-oil microemulsion investigated by Huang and Kim<sup>10</sup> ( $\nu = 0.75$  and  $\gamma = 1.22$ ).

Finally, using photon correlation spectroscopy we measured the diffusion coefficient  $D_K$  (at scattering wave vector  $K$ ) for the microemulsion as a function of angle for temperatures below  $T_c$ . Below approximately  $27^\circ\text{C}$ ,  $D_K$  exhibited no appreciable angular dependence. We confined our measurements to the temperature range below  $33^\circ\text{C}$  due to the onset of significant multiple scattering closer to  $T_c$ . We analyzed our data using

Kawasaki's theory,<sup>13</sup> in which the diffusivity  $D_K$  can be written as<sup>14</sup>

$$D_K = D_0 [H(x)/x^2], \quad (5)$$

where  $H(x) = \frac{3}{4} [1 + x^2 + (x^3 - x^{-1}) \tan^{-1} x]$  with  $x = K\xi$ . We assumed the validity of Eq. (5) for our system, even though as noted earlier it may not be isomorphic to a simple fluid or binary mixture. We note that corrections to Eq. (5) previously employed for other multicomponent systems<sup>15</sup> are significant only for  $K\xi > 1$ , while our values lie in the range  $0.4 < K\xi < 1.2$ .

Using the previously determined values of  $\xi$ , we made a least-squares fit to the diffusivity data to determine  $D_0$  at each temperature. The experimental scatter resulted in larger uncertainties for the  $D_0$  values than for the previously determined  $\xi$  and  $\kappa_T$ . The resulting  $D_0$  values can be described by the power-law expression

$$D_0 = D_0' t^{\tilde{\nu}'} \quad (6)$$

consistent with  $T_c = 310.5 \pm 1$  K and  $\tilde{\nu}' = 1.10 \pm 0.1$ . Hence, the "dynamic" critical exponent  $\tilde{\nu}'$  is in approximate agreement with its "static" counterpart,  $\tilde{\nu}$ , given the larger experimental uncertainties associated with the diffusivity results [a consequence of the relatively smaller changes in  $D_K$  compared to  $d(\theta)$  and  $I(\theta)$  over the measured temperature range].

In an earlier series of experiments we measured  $\xi$  and  $\kappa_T$  for a microemulsion whose NaBr concentration, 1.80%, was slightly higher than the critical concentration, 1.77% (with all other components but the water held constant). Figure 1 shows that the phase separation temperature is extremely sensitive to the NaBr concentration near the critical composition; at 1.80% NaBr, the lower phase separation point occurs at approximately 29°C, rather than at 37.5°–38°C at the extremum concentration of 1.77%. Interestingly, a significantly smaller value of  $\tilde{\nu}$  was obtained at this higher NaBr concentration:  $0.9 \pm 0.1$ .

In summary, we reemphasize that our five-component microemulsion is much more complex than other critical systems, hence there is no *a priori* reason to believe that the critical behavior of the microemulsion should resemble that of simpler systems. Also, the critical-like behavior is consistent with a constant microemulsion droplet particle size such that as  $T$  approaches  $T_c$  the measured quantities reflect the correlative motion of many individual particles. This differs from interpretations of particle-size growth as a function of temperature. In our previous qualita-

tive investigation of a family of related microemulsions, we observed a smooth transition in the dependence of diffusivity on temperature as the oil content was reduced to zero. By studying the critical-type behavior of these systems as a function of oil and cosurfactant content, we hope to relate the behavior of microemulsions near a phase transition to the apparent aggregate *growth* claimed for simple micellar systems. Indeed, Corti and Degiorgio<sup>16</sup> have recently observed critical behavior in a micellar solution using a non-ionic surfactant.

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