Experimental Evidence for an Apparent Field Variable in a Critical Microemulsion System

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Composition and light scattering results in a three-phase equilibrium of a microemulsion system provide evidence for the existence of an apparent field variable related to composition. This variable, the water-over-surfactant ratio (X), takes the same value in the three coexisting phases. This three-phase equilibrium disappears by a critical end point which is approached by varying X. The dependences of the scattered intensity and the correlation length as a function of X are described by power laws with Ising exponents.

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Recent experimental interest has been focused on the critical behavior of micellar solutions and microemulsions. Two-, three-, four-, and even five-component systems were investigated.[1-6] In all these studies critical exponents were measured along a constant-composition (except Ref. 2) path in the single-phase region as a function of temperature.

In 1970 Griffiths and Wheeler[7] pointed out the importance of the field variables in multicomponent systems. In contrast to densities, the fields have the property that they take an identical value in all the phases which are in thermodynamic equilibrium. Temperature, pressure, and chemical potential are fields, whereas concentration or refractive index are densities. These authors also indicate that the direction parallel to the coexisting surface in the space of fields is singled out by the phase transition itself. Theoretical predictions also state that along such a path the critical behavior is described by the same exponents whatever the field considered. Up to now, in multicomponent systems, there is no experimental evidence for the possibility of approaching a critical point by varying a field variable at constant temperature and pressure. The main difficulty is to find an appropriate field variable, different from temperature or pressure, which may be experimentally controlled.

In this Letter we analyze the critical behavior of a microemulsion system near a critical end point. The mixtures studied are made of water, dodecane, sodium dodecyl sulfate, and pentanol. They are located along an isothermal path inside a three-phase region. At constant pressure and temperature, the three-phase equilibrium of a quaternary system has only one degree of freedom. Consequently, in the field space, the path followed is a coexistence line ended by a critical point. This path is, from a geometrical point of view, similar to the approach in the two-phase region of a liquid-gas critical point of a pure fluid. We show from phase composition analysis that the water-over-surfactant ratio (defined in the following as X) behaves as a field variable. The field character of this variable is also evidenced by light scattering studies in one of the three phases in equilibrium. Divergences of the scattered intensity and of the correlation length have been measured as a function of X. The universality of the obtained critical exponents confirms the existence of the field X.

We have recently reported[8] preliminary results on the phase diagram of the quaternary system mentioned above. This phase diagram is very complex; a three-phase domain where two isotropic phases are in equilibrium with a liquid crystalline phase was evident. We have entirely explored, in the composition space, the boundaries of this three-phase volume. This volume extends from a four-phase region (at $X=1.05$) to a critical end point (at $X=2.98$). The global percentage of alcohol is within 10% and 16% in weight and the global percentage of oil varies between 80% and 50%. All the phases in equilibrium are situated in the oil-rich part of the phase diagram (the water content never exceeds 25% in weight). Between $X=1.05$ and $X=2.80$ the two isotropic phases are the upper and the lower phases. The middle phase is a liquid crystalline phase: Observation of its texture under a polarizing microscope indicates a smectic symmetry. For the low values of X, the isotropic upper phase exhibits flow birefringence. Above $X=2.80$, due to the increasing proximity of the two isotropic phase densities, the liquid crystalline phase becomes the lower phase and the two isotropic phases are adjacent. At $X=2.98$ these two phases merge at a critical end point. Twenty-one three-phase samples were prepared from $X=1.10$ to 2.90, by fixing the overall water-over-surfactant ratio (X)

and by adjusting the oil and the alcohol quantities. Prior to phase analysis or light scattering experiments, the samples were sealed and equilibrated for several weeks in a constant temperature chamber (controlled to 0.1 K). Analysis of the four components in each phase has been performed. Oil, water, and alcohol concentrations have been measured by gas chromatography. The separation was effected on a 1-m-long Porapack P column at $T = 190\,°\mathrm{C}$. The surfactant is weighed after evaporation of all the liquids. The value of X measured in each phase (X^*) is compared in Fig. 1 with the value of the overall mixture (X). The conservation of X in each phase is better than 1%, which is within the experimental accuracy. This remarkable result is the indication of the important role played by X in the oil-rich region of the phase diagram. Consequently, this result strongly supports the idea that X is an apparent field variable because its value is the same in each of the three phases in equilibrium.

The total intensity of the scattered light has been measured in the two isotropic phases by varying the position of the cell in the laser beam. The angular dissymmetry of the total scattered intensity was obtained over the range 40–140 degrees of scattering angle. Temperature in the cell is controlled within 0.01 K. The plot of the inverse of the total intensity as a function of q^2 [$q = 4\pi n \sin(\theta/2)/\lambda$ is the scattering vector] indicates the the Ornstein-Zernike law is very well verified: $I(q) = I(0)/(1+q^2\xi^2)$ where ξ is the correlation length of the refractive index fluctuations. In the lower microemulsion phase, both $I(0)$ and ξ show a large variation as X is varied. As the critical end point is approached, the large increase of these two measured quantities is characteristic of a critical behavior. ξ varies from 140 Å for $X = 1.7$ to 700 Å for $X = 2.90$. An increase of the intensity and of the correlation length is also observed in the proximity of the four-phase equilibrium (towards small values of X). This "critical-like" behavior observed in the vicinity of the four-phase equilibrium is consistent with the very close values of the compositions of the phases in equilibrium. This result suggests the proximity of a critical point that one expects to reach by changing temperature. In order to test our assumption of the field variable character of X, we have investigated, in a log-log plot, the behavior of the intensity $I(0)$ and of the correlation length ξ as a function the reduced field variable ϵ. ϵ indicates the distance from the critical point and is defined as $\epsilon = (X - X_c)/X_c$, where X_c is the value of X at the critical point where the three-phase region disappears. The results given in Fig. 2 show that $I(0)$ and ξ follow power laws

$$I(0) = I_0 \epsilon^{-\gamma^*}, \quad \xi = \xi_0 \epsilon^{-\nu^*} ;$$

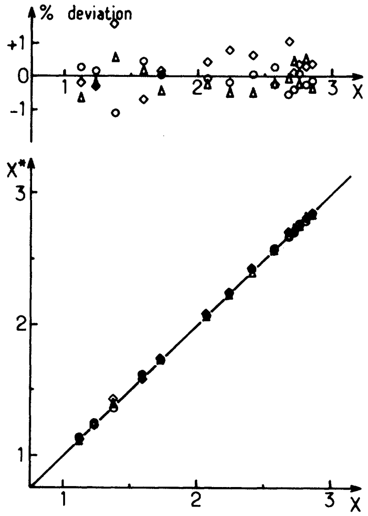

FIG. 1. Plots of X measured in each phase (X^*) as a function of the global value of X. The standard deviation is also reported. Lozenges, circles, and triangles, respectively, represent the values of the X^* in the lower, the middle, and the upper phases.

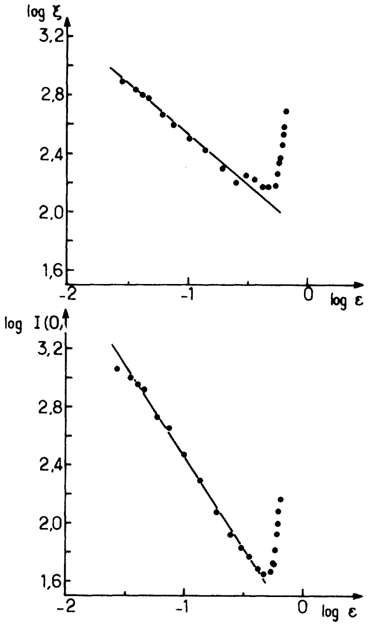

FIG. 2. Log-log plots of total intensity $I(0)$ and correlation length ξ measured in the lower phase as a function of the reduced variable ϵ. ϵ indicates the proximity of the critical end point. $\epsilon = (X - X_c)/X_c$ where X_c is the value of X at the critical end point ($X_c = 2.98$).

the asterisks indicate that the path we have chosen is not the classical isochore path. A least-squares fitting to the data gives $\nu^* = 0.65 \pm 0.05$, $\gamma^* = 1.20 \pm 0.08$, $X_c = 2.98 \pm 0.02$. These exponents are very close to the universal exponents found in binary[9] and ternary fluids including microemulsion systems.[3] The power-law dependence of the thermodynamic behavior clearly confirms that X can be considered as a field variable. The values of γ^* and ν^* are the "liquid-gas" values predicted by an Ising model; this result was not obvious in view of the existence of a liquid crystalline phase in the equilibrium.

Measurements in the upper phase, which is flow birefringent, give different results. In this phase, the critical behavior is only observed very close to the critical end point (for X values larger than 2.8). The particular behavior observed in this phase is most likely related to the existence of anisotropic particles.

In order to test the generality of this field variable in oil-rich microemulsion systems, we have undertaken[10] the study of the critical point evidenced by Huang and Kim[3] in the ternary system: AOT, water, and decane. We have investigated the critical behavior along two different paths; the first path is similar to that followed by Huang and Kim. In this case the critical point is approached by raising temperature at fixed composition. In the second approach, temperature is held constant and the water-over-surfactant (X) ratio is varied. Figure 3 shows the intensity and correlation length data measured along these two paths. In both cases data are fitted by power laws. The exponents ν and γ are, respectively, equal to 0.76 ± 0.05 and 1.30 ± 0.08 for the temperature-variable path and 0.61 ± 0.06 and 1.26 ± 0.10 for the X-variable path. The indices obtained from the temperature dependence are very close to those previously deduced by Huang and Kim.[3] With consideration of the experimental accuracy the critical exponents obtained along the two routes are very close. The slightly higher value of ν (0.76) obtained along the first path could be in agreement with the renormalized Ising value $[\nu/(1-\alpha)$ with $\nu = 0.63$ and $\alpha = 0.1]$ found near an ordinary plait point of a ternary liquid mixture.[11] Furthermore, our results obtained in the X scan are more in accordance with the Ising value; this is probably due to the fact that we do not follow, in the second approach, a path with constant composition.

In summary, we have found the existence of a field variable, different from temperature or pressure, which is directly related to the composition as the chemical potential. The fact that this field variable is the water-over-surfactant ratio seems very important. Although the exact structure of the different phases involved in the equilibrium studied is still unknown, one common structural feature of the three phases is the occurrence of an interface, filled with the surfactant, between water and oil.[12] Due to the location of these phases in the oil-rich region, the microscopic structure of the medium can most probably be described as a dispersion of water particles in oil. This is known to be true for the classical microemulsion phase. In this description, the water-over-surfactant ratio fixes the size of the particles. Besides, the interactions between inverted micelles which are most likely the driving force of the critical point[7,13,14] are strongly dependent upon the size.[15,16] Consequently the relation between X and the droplet size is perhaps the key to the field variable nature of X.

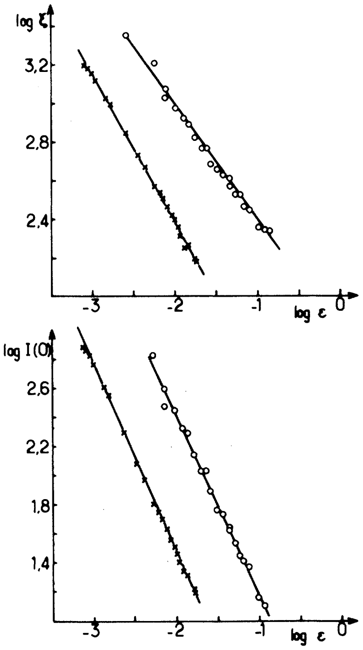

FIG. 3. Log-log plots of total intensity $I(0)$ and correlation length ξ measured by approaching the critical point of the ternary system (AOT, water, decane) along two paths. The crosses correspond to a constant-composition path in changing temperature $[\epsilon = (T - T_c)/T_c]$ and the circles correspond to an isothermal path in changing X $[\epsilon = (X - X_c)/X_c]$.

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