Pressure-Induced Critical Phenomena of a Microemulsion System

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(Received 29 August 1984)

The critical phenomena of a microemulsion system were studied by applied external pressure for the first time. The divergence of the scattering intensity and the static correlation length as functions of $\Delta P \equiv |P - P_c|$ are described by the critical exponents γ and ν, respectively. The critical exponents ν and γ associated with ΔP are the same as those obtained with other thermodynamic variables such as temperature and oil alkane carbon number.

PACS numbers: 64.70.Ja, 64.60.Fr, 82.70.Dd

Two immiscible liquids and one or more surface-active agents (surfactants) can form a thermodynamically stable and homogeneous fluid called a microemulsion.[1] If a small amount of liquid is added to another immiscible liquid containing a low concentration of surfactant, the minor-component liquid may form dispersed droplets stabilized by the surfactant molecules on the interface. Once the droplets of minor-component liquid are formed, then the system can be considered as a binary system consisting of droplets in a continuous fluid phase. These droplets are thought to be of spherical shape with radii from 30 to 1000 Å.[1] The microemulsion system that we have studied contains 3 wt.% of surfactant, sodium-di-2-ethyl-hexyl sulfosuccinate (AOT), in 5 vol% of distilled water and 95 vol% of decane. In this system, water is the minor component which forms small spherical droplets in the continuous oil (i.e., decane) phase. The detailed structure of this system has been studied extensively by small-angle neutron scattering.[2]

The homogeneous single-phase microemulsion becomes unstable and phase separates into two coexisting microemulsion phases when the system is heated above a certain temperature called the upper cloud point temperature. The properties of the microemulsion system with 8% dispersed volume near the cloud point temperature are very similar to those of a binary fluid system near its critical temperature. As in many binary systems, the underlying structure of the microemulsion is not changed even near the critical point and beyond where the fluid splits into two microemulsion phases. This critical phenomenon was studied by dynamic light scattering[3] and small-angle neutron scattering.[4] These studies demonstrated a dramatic increase in the scattering intensity and a narrowing of the scattered linewidth in the immediate neighborhood of the cloud point of the microemulsion. These phenomena are commonly known as critical opalescence and critical slowing down of the fluctuations in the system.

Critical phenomena were observed by changing not only temperature, but also the alkane chain number of the external oil phase,[5] the composition molar ratio of decane and cyclohexane,[6] and recently the molar ratio of the water and surfactant.[7] The critical exponents, ν and γ, describing the critical slowing down and critical opalescence, respectively, are reasonably consistent for the different paths of thermodynamic variables.[7]

In this Letter, we describe a study of externally applied pressure as the thermodynamic variable to drive the microemulsion to its cloud point. Very limited work has been done to define the effect of pressure on the behavior and properties of surfactant solutions. Included are a critical micellar concentration study[8] and a study of micellar size.[9] We conjecture that the reason for this lack of pressure studies is the complexity of designing and operating a high-pressure cell, and the difficulty in measuring the small value of the thermal pressure coefficient of liquids.[10] Also, the pressure usually has a very small effect compared with temperature on the phase behavior of fluids, unless the system is near the cloud point or some other phase boundary. However, pressure is a very important thermodynamic variable for understanding phase diagrams (P-V-T diagram) of fluids and for many practical applications.

The sample cell,[11] a sapphire cylindrical column (i.d., 2.02 cm; o.d., 4.20 cm; and height, 16.33 cm), is supported with a stainless-steel housing with an O-ring seal at each end. This sample cell provides full angular vision with the exception of the housing posts. This capability allows us to make light scattering intensity $I(q)$ measurements as a function of scattering angle. Pressures up to 5000 psi were generated by hydraulic compression with a piston-type pump. The cell was thermostated in a constant temperature bath. The microemulsion system was isolated by a mercury trap from the hydraulic compression liquid. The spectrometer was calibrated with a dilute solution of monodispersed spheres (diameter, 0.087 ± 0.0046 μm). Our measured values of the radius of gyration and hydrodynamic radius agreed with the manufacturer's (Duke Scientific Corporation) specification to within 5%.

We have measured the intensity at angles of 60° and 120° as a function of pressure P for three different temperatures. The experimental data were fitted by the Ornstein-Zernike-Debye[12] expression:

$$I(q) \sim I_0(1+\xi_I^2 q^2)^{-1},$$

where I_0 is a quantity proportional to the osmotic compressibility (χ) of the droplets, but independent of the scattering vector $q = (4\pi/\lambda)\sin(\theta/2)$ (λ and θ represent the wavelength of laser light in the medium and the scattering angle, respectively), and ξ_l is the static correlation length of the medium. I_0 is obtained by extrapolation of the intensity measurements to zero scattering angle, and ξ_l^2 is obtained from the slope of the inverse of the scattering intensity as a function of q^2. A large increase of the correlation length (ξ_l) and zero-angle scattering intensity (I_0) is observed as pressure is increased. This result suggests that the system is reaching a critical region by changing pressure. We have studied ξ_l and I_0 as a function of the relative thermodynamic field variable, ΔP, defined as $\Delta P = |P - P_c|$, where P_c is the value of P at which ξ_l and I_0 diverge. The ξ_l and I_0 for different temperatures diverge at different pressures. The divergence of the static correlation length as a function of relative pressure, ΔP, for three different temperatures is shown in Fig. 1. P_c was determined by extrapolating $1/\xi_l$ and $1/I_0$ to zero simultaneously. The values of P_c for 26.306 °C, 28.201 °C, and 29.996 °C are 15.2 MPa, 10.8 MPa, and 6.5 MPa, respectively. The best straight-line fit on this log-log plot gives a slope of -0.7, i.e., $\xi_l \sim |P - P_c|^{-\nu_P}$, where $\nu_P = 0.7 \pm 0.03$. This value of ν is very close to the critical exponent values obtained from the study of other thermodynamic variables (i.e., $\nu_T \simeq 0.75$, where T represents temperature).[3] The estimated error in the exponent is mainly due to the uncertainty in the value of P_c, which is determined only to ± 0.15 MPa.

Figure 2 shows the divergence of I_0 as pressure approaches the previously determined critical values of P_c. The straight-line fit on this log-log plot gives a slope of -1.5, i.e., $I_0 \sim \chi \sim |P - P_c|^{-\gamma_P}$, where $\gamma_P = 1.5 \pm 0.05$. This value is a little bit larger than the value observed in the temperature dependence by laser light scattering ($\gamma_T \simeq 1.3$),[3] but essentially identical to the temperature dependence found with small-angle neutron scattering ($\gamma_T \simeq 1.5$).[4] With consideration of experimental accuracy, the critical exponents from the pressure dependence are very close to those from the other thermodynamic field variables including temperature, carbon chain length of external oil phase, molar ratio of surfactant and internal water phase, and the composition of the hydrocarbon oil.

However, the values of critical exponents are expected to be dependent on the route by which the critical point was approached.[13] For instance, the divergence of the compressibility, χ, for a single-component system along the critical isochore ($\rho = \rho_c$) is of the form $\chi \sim |T - T_c|^{-\gamma_T} \sim |P - P_c|^{-\gamma_P}$ with $\gamma_T \simeq \gamma_p \simeq 1.2\text{–}1.3$. On the other hand, if the critical point is approached along the critical isotherm, then $\chi \sim |P - P_c|^{-\epsilon}$ with $\epsilon \simeq 0.7\text{–}0.8$, which is very different from $\gamma \simeq 1.2\text{–}1.3$. For multicomponent systems, such as microemulsions, the situation is more complicated. Thus, it is of great interest that at constant overall composition the divergence of both the correlation length and the isothermal compressibility with respect to $|T - T_c|$ and $|P - P_c|$ are similar. This implies that the constant overall composition is roughly equivalent to the critical-isochore concentration if the number density of microemulsion droplets does not vary as the major thermodynamic variables such as temperature or pressure approach the critical point. This finding is consistent with the result shown in the small-angle neutron scattering,[2] in which the droplet size remains constant and the number density is conserved as the critical point is approached. That is to say, to the first approximation, controlling the pressure at constant overall composition and temperature has the same effect as controlling the temperature at

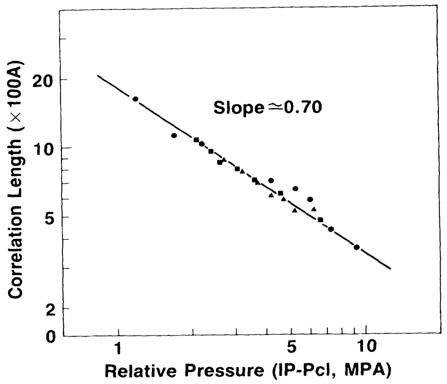

FIG. 1. The power-law dependence of the static correlation length on the relative pressure $|P - P_c|$. Circles, squares, and triangles are for 26.306 °C, 28.201 °C, and 29.995 °C, respectively.

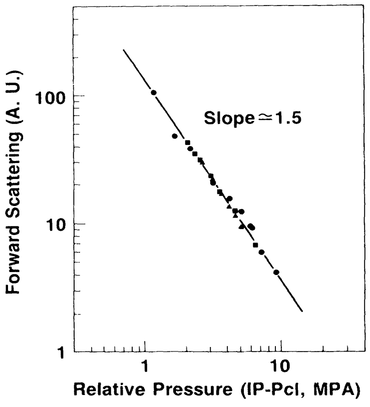

FIG. 2. The power-law dependence of the relative isothermal osmotic compressibility (I_0) on the relative pressure $|P - P_c|$. Circles, squares, and triangles are for 26.306 °C, 28.201 °C, and 29.995 °C, respectively.

constant pressure near the phase boundary.

In summary, we have measured the scattering intensity of a three-component oil external microemulsion near the phase transition as a function of applied external pressure. The scattering intensity and the static correlation length were found to diverge with the critical exponents $\gamma_P = 1.5$ and $\nu_P = 0.7$. These critical indices are close to those found with other thermodynamic variables such as temperature, oil composition, etc. Since the attractive potential between droplets is most likely the driving force for the critical point behavior observed in microemulsions,[14] the pressure in a sense contributes to this attractive force by increasing the density of the oil. It is known that higher-alkane-number oils have higher density. Consequently, increasing the pressure increases the effective alkane number of the oil which in turn brings the microemulsion system closer to its critical boundary.

The authors are grateful for the experimental help of Mr. W. Gallagher.

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