Critical phenomenon of nonaqueous microemulsion (AOT/DMA/decane)

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Abstract

The critical phenomenon of nonaqueous microemulsion was studied for the first time. The coexistence curves of (T, n), (T, ϕ), and (T, ψ) (n and ϕ are refractive index and volume fraction, respectively; ψ is defined as $\psi = \phi/[\phi + \phi_c(1 - \phi)/(1 - \phi_c)]$) for a ternary microemulsion [ϕ (AOT–DMA) + $(1 - \phi)$ decane] at constant pressure and a constant molar ratio ($\omega = 2.86$) of DMA to AOT have been determined within about 7 K from the critical temperature T_c by measurements of refractive index. The critical exponent β has been deduced from (T, n), (T, ϕ), and (T, ψ) coexistence curves within 1 K below T_c. They all were 0.329 ± 0.005 and were consistent with the 3D Ising value. The experimental results in a temperature range of $(T_c - T) < 7$ K also have been analyzed to obtain critical amplitudes and the Wegner correction terms, to examine the diameters of the coexistence curves.
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1. Introduction

The majority of studies of microemulsions utilize water as the polar compound. Recently, attempts have been made to prepare and study nonaqueous microemulsions [1–6]. In this effort, polar nonaqueous solvents have replaced water and the preparations are essentially oil-continuous [3,4]. It has been reported that such preparations can be a useful medium for organic reactions such as Diels–Alder and others [7,8]. Although nonaqueous microemulsions may have this and other prospects, the literature on different aspects of this type of microemulsions is so far scanty.

Over the past 20 years, a great deal of progress has been made both experimentally and theoretically in understanding critical phase separation in fluids. The general concepts of scaling and universality are well established. Recently, the study of critical phenomena in fluids has been extended to multicomponent microemulsion and micellar systems [9–15]. A few experimental studies have been carried out to determine the critical exponent β that characterizes the shape of the coexistence curve and have observed an Ising value of the critical exponent β [10–12]. However, the critical behavior of nonaqueous microemulsion systems is lacking. Therefore the critical phenomena of nonaqueous microemulsions are of great interest in relation to whether systems near the critical points belong to the 3D Ising universality class.

Three-component mixtures of dimethylacetamide (DMA), sodium di(2-ethylhexyl) sulfosuccinate (AOT), and decane can form polar compounds in oil microemulsion [3,4]. The experimental results of dynamic light scattering indicate that the shape of the droplets detected is relatively spherical and the size of droplets is dependent upon the molar ration of polar solvent to AOT (ω) and the volume fractions of polar solvent and surfactant in the continuous phase for the nonaqueous microemulsion systems [4]. For the mixture with $\omega = 2.86$ and $\phi = 0.390$, a higher consolute critical point was observed. Below the critical temperature T_c the sample separates into two microemulsion phases of different

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compositions but with the same ratio ω [10–13]. Therefore such a microemulsion system can be regarded as a pseudobinary mixture [10,11]. The phase behavior can be depicted in a two-dimensional diagram with concentration of droplets along the abscissa and temperature along the ordinate [10]. A coexistence curve of temperature against a concentration variable can be drawn in the same way as it was done for binary mixtures.

In this work, we present precise coexistence curve measurements of a ternary microemulsion, consisting of DMA, AOT, and decane, at the critical volume fraction (ϕ_c) and a constant molar ratio (ω) within about 7 K below the critical temperature. The experimental results are analyzed to determine the critical exponent β and the critical amplitude B and to examine the size of asymptotical range and the anomalies of the diameters for different choices of order parameters.

2. Materials and methods

2.1. Materials

The AOT (purity >98%) obtained from Fluka Co. was purified according to the standard procedure [14]. The n-decane (purity >99.9%) supplied from Merck Chemical Co. was used without further treatment. The DMA obtained from Tianjin Chemical Regent Co. Ltd. (purity >99%) was shaken over barium oxide and distilled under reduced pressure from fresh barium oxide, and the middle fraction was collected and redistilled under reduced pressure in the presence of calcium hydride [15]. The was distillate was analyzed by gas chromatography, and showed no evidence of appreciable impurities.

2.2. Determination of critical composition and critical temperature

The critical composition ϕ_c of the mixture was approached by fixing the molar ratio ω of DMA to AOT at 2.86 and by adjusting the amounts of n-decane to achieve

equal volumes of the two phases at the phase-separation temperature [10]. The phase-separation temperature of the mixture with the critical composition was carefully measured and taken as the critical temperature. It is noticed that the critical temperature is sensitive to even a minute amount of impurities. The difference of the critical temperature might be explained from many aspects, such as the uncontrollable impurities introduced into the preparation of the sample, the hydrolysis of AOT, and the inevitable infiltration of high-temperature water vapor into the crucial sample tube. However, it did not affect the final results, because only one sample was used throughout the measurements of the whole coexistence curve and only the temperature difference ($T_c - T$) was important in data reduction to obtain the critical parameters. Therefore the phase diagram of ($T_c - T$) against a density variable is well reproducible.

2.3. Measurements of refractive indices

The refractive indices were measured by the method of minimum deviation [10,11]. An apparatus used in this work was described previously [10]. During measurements the temperature was constant to ± 0.001 K. The accuracy of measurement was about ± 0.01 K for temperature and ± 0.0001 for refractive index. The accuracy in measurement of the temperature difference ($T_c - T$) was about ± 0.002 K. A sample with the critical composition was prepared in a rectangular fluorometer cell provided with a Teflon plug.

3. Results and discussion

The critical volume fraction of the microemulsion system was determined to be $\phi_c = 0.390 \pm 0.001$. The critical temperature T_c was 322.4 K. The refractive indices n of coexisting phases in the cell were measured at various temperatures and the results are shown in Fig. 1a.

To obtain the (T, ϕ) coexistence curve, a series of ternary mixtures of (DMA–AOT–decane) with known volume fractions were prepared and their refractive indices in the one-
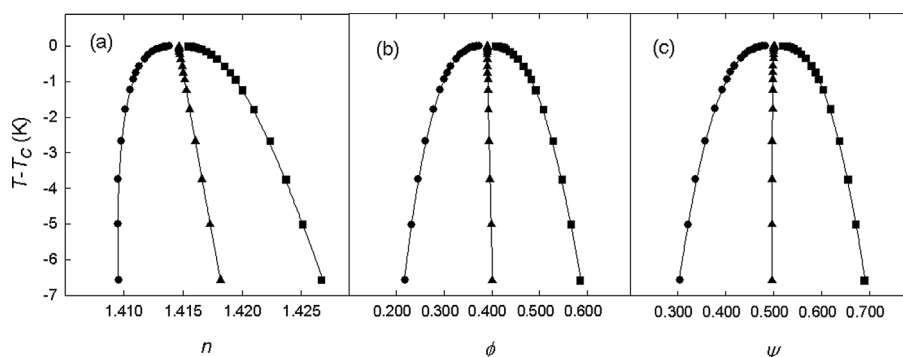

Fig. 1. Coexistence curves of (T,n), (T,ϕ), and (T,ψ) for the [ϕ (AOT–DMA) + (1 − ϕ) n-decane] microemulsion system: (a) ($T - T_c$) versus refractive index n, (b) ($T - T_c$) versus volume fraction ϕ, and (c) ($T - T_c$) versus effective volume fraction ψ. (●) Experimental values of concentration variables (ρ) of the coexisting phases; (▲) experimental values of diameter (ρ_d) of the coexisting phases; (—) concentration variables (ρ_{cal}) and diameter ($\rho_{d,cal}$) of coexisting phases from calculation.