

Critical behavior of a three-component microemulsion

R. Aschauer and D. Beysens

Service de Physique de l'Etat Condensé, Centre d'Etudes de Saclay, 91191 Gif-sur-Yvette CEDEX, France

(Received 28 May 1992)

The critical behavior of a ternary microemulsion consisting of water, benzene, and benzyldimethyl-*n*-hexadecylammonium chloride is studied by light-scattering techniques, controlling temperature to approach the critical point. This microemulsion is chosen since it is very stable. Great care was taken to ensure the measurements were performed at the critical concentration, and a wide range of temperature was covered. According to theory, one expects Fisher renormalized Ising critical exponents in a ternary mixture when temperature is the controlled variable. Contrary to this expectation, we find values of the exponents $\gamma = 1.18 \pm 0.03$ and $\nu = 0.60 \pm 0.02$, indicating rather unrenormalized Ising-like behavior of ternary microemulsions.

PACS number(s): 05.70.Jk, 64.60.Fr, 82.70.Kj

I. INTRODUCTION

The critical behavior of microemulsion systems is a topic of considerable interest. It has been shown that the phase transition is driven by increasing interactions between droplets while leaving their size and polydispersity unchanged, and that the two separated phases are again microemulsions with equal droplet size distribution [1,2]. The order parameter is the volume fraction of droplets [1]. Measurements of the values of the critical exponents describing the divergences of the susceptibility and correlation length, γ and ν , have been performed in five- [3,4], four [5–7], and three-component [8–12] microemulsions.

In a three-component system, the critical exponents are expected to be Fisher renormalized with respect to the respective exponents in a binary mixture if one varies temperature to approach the critical point [13,14]. The theoretical renormalized values γ^* and ν^* are $\gamma^* = \gamma/(1-\alpha) = 1.39$ and $\nu^* = \nu/(1-\alpha) = 0.70$ [with the three-dimensional (3D) Ising values of $\gamma = 1.24$, $\nu = 0.63$, and $\alpha = 0.11$, α being the exponent of the specific heat]. Also the exponent of the coexistence curve, β , should be Fisher renormalized, becoming $\beta^* = \beta/(1-\alpha) = 0.365$ (with the 3D Ising value of $\beta = 0.325$). However, it was shown by Fisher and Scesney [15] that full renormalization will be visible experimentally only if the third component causes a large shift in the critical temperature T_c such that the parameter x defined as

$$x = f(T_c - T_c^0)/T_c$$

becomes of the order of unity. Here $f = 0.6$ to 0.9 , T_c^0 is the critical temperature of the binary system, and T_c is the critical temperature of the ternary mixture. Such a renormalization has been shown experimentally in a number of different ordinary ternary mixtures [16–19], although the values for γ^* and ν^* appear to take on rather values of $\gamma^* = 1.50$ and $\nu^* = 0.75$, respectively, that is, different from theoretically expected values. Ternary microemulsions can be seen as good candidates in which to see Fisher renormalized exponents since the binary system of water and oil is practically immiscible, which cor-

responds to a T_c^0 of infinity, and only the addition of a third component, the surfactant, creates a partially miscible system with a finite critical temperature T_c . Hence the parameter x becomes large.

The experimental situation on ternary microemulsions, however, is far from being clear. In a neutron scattering study, Kotlarchyk, Chen, and Huang [9] obtained exponents of $\gamma = 1.61$ and $\nu = 0.72$. A light-scattering study by Huang and Kim [8] gave $\gamma = 1.22$ and $\nu = 0.75$, and Honorat, Roux, and Bellocq [10] measured values of $\gamma = 1.30$, $\gamma = 1.25$ and $\nu = 0.76$, $\nu = 0.71$. All these groups used the water-decane-AOT (sodium di-2-ethylhexylsulfosuccinate) system (which we define as WDA). Jayalakshmi and Beysens [12] determined γ and ν from turbidity measurements in the system water-benzene-BHDC [benzyldimethyl-*n*-hexadecylammonium chloride, $C_6H_5 \cdot CH_2(CH_3)_2(C_{16}H_{33})NCl$] (which we define as WBB), but coupling between γ and ν in this type of experiment is such that they could not discern on purely experimental grounds between Ising and renormalized Ising exponents. In all these cited experiments, temperature was used as the controlled parameter to approach the critical point.

The values of the critical exponents depend on the path that one chooses to reach the critical point [20]. One can vary fields other than temperature as the controlled experimental variable, which should, in general, lead to different apparent values of critical exponents. In microemulsions the water-to-surfactant ratio (W-to-S ratio) X was shown to behave like a field variable [21]. Honorat, Roux, and Bellocq [10] varied X to approach the critical point at constant temperature in a water-decane-AOT microemulsion and obtained values of $\gamma = 1.26$ and $\nu = 0.61$. In the same system, Kim, Bock, and Huang [11] performed a light-scattering experiment where they varied the pressure to approach the critical point while keeping temperature constant. This gave values of $\gamma = 1.50$ and $\nu = 0.70$. The experimental results obtained so far for ternary microemulsions are summarized in Table I.

For the experiments where temperature was the con-

TABLE I. Experimental values of the critical exponents γ and ν and of the amplitude of the correlation length ξ_0 for ternary microemulsions as found in the literature. WDA is the water-decane-AOT system, WBB is water-benzene-BHDC, T indicates temperature, X the water-to-surfactant ratio, and P pressure.

Reference	System	Method	Variable	γ	ν	ξ_0 (Å)
[8]	WDA	light scattering	T	1.22 ± 0.06	0.75 ± 0.05	12.2 ± 2
[9]	WDA	neutron scattering	T	1.61 ± 0.09	0.72 ± 0.04	11 ± 2.1
[10]	WDA	light scattering	T	1.30 ± 0.08	0.76 ± 0.05	7.2 ± 2
			T	1.25 ± 0.05	0.71 ± 0.05	9.3 ± 2
			X	1.26 ± 0.10	0.61 ± 0.06	
[11]	WDA	light scattering	P	1.50 ± 0.05	0.70 ± 0.03	
[12]	WBB	turbidity	T	1.29 ± 0.25	0.70 ± 0.12	23.5 ± 6

trolled variable, the exponent ν for the correlation length appears to be rather close to the Fisher renormalized Ising exponent, whereas the exponent γ for the susceptibility seems to take on the Ising value. This is an unsatisfying situation, since either both or neither of these two experiments should be renormalized. Also, the scaling law $\gamma = (2 - \eta)\nu \approx 2\nu$ [22] (the Fisher exponent $\eta \approx 0.03$ is smaller than experimental errors and therefore negligible, see Table I) is violated if only ν is renormalized.

The present study was motivated by this apparent inconsistency of the results obtained so far. We have performed very careful light-scattering experiments at wide and at small angles with critical samples of a water-benzene-BHDC microemulsion by using temperature as the controlled variable to approach the critical point.

II. SAMPLE SELECTION AND PREPARATION

Most of the experiments concerning critical exponents in ternary microemulsions have been performed with the WDA system (Table I). But it is known that hydrolysis occurs in this system, which leads to a change of the phase diagram with time [23], making this microemulsion a poor candidate to measure critical exponents.

We have chosen the microemulsion water-benzene-BHDC (WBB) for our experiments. This system has been studied by Cazabat *et al.* [24] and Jayalakshmi and Beysens [12]. BHDC is a cationic surfactant with a single hydrocarbon chain. The WBB system appears to be chemically stable as indicated by only a small shift of the critical temperature T_c in our samples (of the order of 10 mk per month).

BHDC was purchased from BDH Chemicals Ltd, and the benzene was a product from Merck (p.A., purity > 99.7%). Milli-Q water was used as the third component. A stock solution with a W-to-S ratio of 1.8989 ± 0.0009 and a benzene concentration of $c_B = 0.9089 \pm 0.0001$ mass fraction was prepared. The criticality was checked using the equal volume criterion. All the cells used in the experiments were filled from this stock solution and sealed with the teflon screwed Rotaflo cap. As a check, the turbidity was measured in the temperature range between $T - T_c = 15.58$ and 0.005 K using the same setup as described in Ref. [12]. The values for the turbidity τ agreed within the experimental uncertainty with the values obtained by Jayalakshmi and Beysens [12].

The coexistence curve was determined by a gradient technique [25–27] in a narrow temperature interval. The results are described elsewhere [28], but we note here that we found a value of β consistent with the 3D Ising value.

III. EXPERIMENTAL PROCEDURE

A. Wide-angle light scattering

The apparatus used for this experiment consisted of a thermostatted cylindrical chamber (temperature stability ± 2 mK) filled with toluene in order to minimize reflections from the interfaces. A photomultiplier served as a light detector. It was mounted on a boom which could be set at scattering angles between 10° and 160° . The incident light came from a He-Ne laser operating at $\lambda = 6328$ Å with a power of 6 mW. Both the incident and the transmitted intensity were recorded using two photodiodes as detectors. A computer controlled the setup.

The turbidity τ of a critical WBB microemulsion close to the critical point is as high as 6 cm^{-1} [12]. Therefore we used a cylindrical cell with a 1-mm diameter in order to minimize multiple scattering effects. However, because of the high cell curvature, the transmission values obtained had a large uncertainty. Therefore, we used the turbidity values measured previously [12] to correct the scattered intensity. Also, due to the small diameter of the cell, we could measure the scattered intensity only at scattering angles between 35° and 140° (in steps of 5°) to avoid stray light from the toluene-glass interface reaching the detector.

Three runs (1, 2, 3) corresponding to slightly different concentrations around the critical concentration were made. After each run, $0.5 \mu\text{l}$ (0.4 mg) of benzene was added to the cell which contained a total sample mass of 420 mg. In this way, we vary concentration around the critical concentration by small amounts. The critical temperature T_c was measured by the drop of the transmitted light after reducing the temperature and a subsequent rise of that quantity at constant temperature. The values of T_c for the three runs were 22.230 ± 0.03 °C, 21.395 ± 0.02 °C, and 19.890 ± 0.02 °C, respectively. The measurements were performed over a wide temperature range, starting at 79.5 °C. This is the highest possible temperature, since benzene boils at 80.1 °C [29] under atmospheric pressure.

B. Small-angle light scattering

In microemulsion systems, the amplitude ξ_0 of the correlation length ξ is several times larger than in ordinary binary mixtures. Therefore, very large fluctuations occur close to the critical point so that most of the incident light is scattered in the forward direction at small scattering angles, and one cannot examine this region using the wide-angle light-scattering apparatus described above.

In order to be able to measure the exponents closer to the critical point, we set up a small-angle light-scattering experiment. The sample was contained in a quartz cell with flat windows and a thickness of 2 mm. It was immersed in a water tank with glass windows. The temperature of the water was kept constant to better than ± 1 mK. A He-Ne laser at $\lambda=6328 \text{ \AA}$ was used as a light source. The light was slightly focused at the position of the sample with a lens ($f=300 \text{ mm}$). A pinhole (diameter 1 mm) was introduced in the water tank in order to block light scattered at small angles from interfaces such as mirrors, lens, and tank walls. The scattered light fell on a screen, while the transmitted beam was blocked with a beamstop of 2 mm diameter. The screen was imaged with a manual gain charge-coupled-device (CCD) video camera, and the images were recorded with a Umatic video recorder. The gain of the camera was kept constant during the experiment, and only the aperture of the objective was changed when the scattered intensity increased such that individual pixels were saturated. Scattering angles between 0.7° and 14° were covered by this setup.

In order to perform the measurements at the critical concentration of the microemulsion we used a gradient technique [25–27]. First, the sample was cooled to 0.07°C below T_c ($T_c=25.501\pm 0.003^\circ\text{C}$) and left overnight until the phase separation was completed and the equilibrium state was reached. Then the temperature was raised slowly, at a rate of about 0.02°C per minute, in order to avoid convection within the sample. After the temperature had reached a value of $T=41^\circ\text{C}$, it was kept constant for about 12 h. By then, a smooth concentration profile over the height z of the cell had developed. Then the sample was cooled down slowly to $T-T_c=0.89^\circ\text{C}$. The resulting concentration profile was measured using the grid shadow technique described by Gurfein *et al.* [30]. The maximum gradient of the refractive index was found to be $\delta n/\delta z=(1.6\pm 0.1)\times 10^{-3} \text{ mm}^{-1}$.

In order to convert $\delta n/\delta z$ into $\delta c/\delta z$, we need to know the variation of the refractive index with concentration $\delta n/\delta c$ for the WBB system. Jayalakshmi and Beysens [12] measured the refractive index at a concentration of 0.909 mass fraction benzene, and the value of pure benzene [29] gives the refractive index at a mass fraction benzene of 1. We estimated $\delta n/\delta c$ therefore by a linear extrapolation through these two points. This leads to a value of $\delta n/\delta c=0.11$. With this value, the maximum concentration gradient is $\delta c_B/\delta z=(1.45\pm 0.15)\times 10^{-2} \text{ mm}^{-1}$.

The diameter of the focal spot of the incident beam in

the sample was 0.1 mm. Therefore we averaged over a concentration range of $c_c\pm 7.5\times 10^{-4}$ benzene mass fraction in this experiment.

The height of the critical concentration was found by measuring the transmission as a function of height, which shows a minimum at the height corresponding to the critical concentration. The experiment was then performed letting the incident beam impinge at this height. The temperature interval covered was from $T-T_c=0.89^\circ\text{C}$ to 0.004°C . The critical temperature T_c was again measured by recording the transmission after each decrease in temperature, as described in Sec. III A.

IV. DATA ANALYSIS

A. Wide-angle light scattering

The scattered intensity as a function of the scattering vector q of a mixture in the critical region is given, if one neglects the very small Fisher exponent η [31], by the well-known Ornstein-Zernike structure factor [32]

$$I(q)=I_{q=0}/(1+q^2\xi^2). \quad (1)$$

q is given by $q=4\pi n/\lambda \sin(\Theta/2)$, where λ is the vacuum wavelength of the incident light, n is the refractive index of the sample (its value and temperature dependence were taken from Ref. [12]), Θ is the scattering angle, $I_{q=0}$ is the intensity at $q=0$, and ξ is the correlation length. The osmotic susceptibility at $q=0$, $\chi_{q=0}$, is proportional to $I_{q=0}$ through the classical relationship, where k_B is the Boltzmann constant,

$$I_{q=0}=k_B T \chi_{q=0}. \quad (2)$$

The temperature dependence of $I_{q=0}$ and ξ is described by

$$I_{q=0}=I_0(1+t)t^{-\gamma}+I_B \quad (3)$$

and ξ is described by

$$\xi=\xi_0 t^{-\nu}. \quad (4)$$

I_B in Eq. (3) is a noncritical background intensity. This background scattering comes from the light scattered by the micelles in the microemulsion, which have a hydrodynamic radius of about 120 \AA [24]. Due to this rather large size, their contribution to the scattering is not negligible, especially far from T_c . We do not know the exact temperature dependence of the radius R of the micelles. However, in the temperature range $T-T_c=35^\circ\text{C}$ to 60°C , the scattered intensity at $q=0$ remains constant, indicating that there is no detectable change of R with temperature within this temperature interval. It is very unlikely that the temperature dependence of R is dramatically different at temperatures closer to T_c . Close to T_c , the noncritical contribution to the scattered intensity should be very small compared to the critical scattering if there is no dramatic change of the size of the micelles. If that is the case, then the background I_B should be negligible in Eq. (1) and plots of $1/I$ versus q^2 at each temperature should yield a straight line. In fact, after correcting the data for turbidity and the variation of the scattering

volume with the scattering angle Θ , plots of $1/I$ versus q^2 at each temperature yield a straight line. This indicates that I_B and therefore R remain in good approximation constant over the whole temperature range of the experiment and that our data can be well described by Eq. (1). $I_{q=0}$ and ξ are found by fitting a straight line to these plots using the nonlinear least-squares fitting program CURFIT by Bevington [33].

For runs 1 and 3, both quantities start to saturate at about $T - T_c = 1.5^\circ\text{C}$. Obviously, sample 1 was below and sample 2 was already above the critical concentration, and therefore $I_{q=0}$ and ξ did not diverge closer to T_c . For run 2, we again see saturation but only for $T - T_c$ smaller than 0.89°C . At this temperature, the correlation length $\xi = 1170 \text{ \AA}$. Since the smallest accessible wave vector is $q_{\min} = 89\,000 \text{ cm}^{-1}$ corresponding to a biggest observable structure of $1/q_{\min} = 1124 \text{ \AA}$, one expects to see saturation closer to the critical temperature, where ξ is still larger. We therefore attribute the observed saturation for run 2 to the limited angular range covered by the experiment, and consider this sample the one closest to the critical concentration. Only the data from this run were used to deduce the critical exponents.

B. Small-angle light scattering

The images of the screen were digitized using an 8-bit digitizer card, and the intensity as a function of the scattering angle was found by azimuthally averaging over the image.

However, the screen is not a perfect isotropic scatterer, and light scattered from the screen has an angular dependence with a maximum at $\Theta = 0^\circ$. Therefore we had to correct our data from this experiment with the response function of the screen.

We measured that response function by placing a white light isotropic point source behind the screen at such a distance that the biggest angle of incidence was 21° . We again recorded the image of the screen with a video system and performed the digitization and azimuthal averaging. Thus one obtains an intensity versus angle of incidence curve. This curve was normalized to $I_{(\Theta=0)} = 1$, and the inverse intensity $I_{(\Theta=0)}/I(\Theta)$ was fitted by a function of the form

$$I_{(\Theta=0)}/I(\Theta) = 1 + A_1\Theta^2 + A_2\Theta^4. \quad (5)$$

The data were then corrected using this analytic function. Other corrections to the scattered intensity have to be made in order to obtain the structure factor. At small angles, one has unavoidably stray light from dust and interfaces. The background scattering was recorded for each aperture of the camera after moving the sample cell out of the beam path and, after digitization and averaging, subtracted from the data. The background was, however, small and decreased rapidly with increasing scattering angle. Another correction is due to the fact that in our setup, the scattered light had to cross flat interfaces between media with different refractive indices (microemulsion-quartz-water-glass-air). At each interface, a small amount of light is reflected. Since the reflectivity depends on the angle of incidence [34], we cal-

culated the loss at each angle and corrected the data accordingly. The camera noise and the transmission of the sample were also taken into account, using again the previously measured transmission values (see Sec. III A) for the latter correction. Finally, since the images at different temperatures were taken with different camera apertures, one has to normalize the intensity to one single aperture.

The data were analyzed as described in Sec. IV A. The values for $I_{q=0}$ and ξ were found to diverge down to $T - T_c = 0.1^\circ\text{C}$, but they saturate at temperatures closer to T_c . At $T - T_c = 0.1^\circ\text{C}$, the turbidity τ of the WBB microemulsion is as large as $\tau = 4.6 \text{ cm}^{-1}$ [12], which corresponds to a transmission for our cell (2 mm thickness) of only 0.4. In such turbid samples, the effect of multiple scattering is no longer negligible and gives rise to a broadening of the measured structure factor. Hence, only the data for $T - T_c \geq 0.1^\circ\text{C}$ were included in the further analysis.

V. RESULTS

A. Exponent γ

The value for the exponent γ was found by fitting Eq. (3) to the experimental values of $I_{q=0}$, using the same fitting program as described in Sec. IV A. I_0 , γ , and I_B of Eq. (3) were the free fit parameters. The critical temperature T_c was fixed at the experimentally determined value. Since the light detectors for the wide-angle light-scattering (WALS), and for the small-angle light-scattering (SALS) experiments were different, one has to fit Eq. (3) to each data set separately. One can, however, try to normalize the SALS data with a constant factor to obtain one single curve for both experiments, and fit the theoretical equation to these data. The results for the fits are shown in Table II and in Fig. 1. The values for the γ exponents from both the WALS ($\gamma = 1.18$) and the SALS ($\gamma = 1.19$) experiments are in excellent agreement. The fit over the whole range gives $\gamma = 1.18$.

For the WALS data set, we tried also to vary certain parameters in order to see their influence and to estimate the total uncertainty of the exponent. Changing T_c by 0.1°C changes the value for the exponent only by $2 \cdot 10^{-6}$. Doubling the errors of $I_{q=0}$ gives $\gamma = 1.16$; making the errors five times larger does not change γ further. When only the data for $T - T_c < 36^\circ\text{C}$ are taken, the fit gives $\gamma = 1.19$. Keeping the background intensity I_B constant at twice the value that the fit gives leads to $\gamma = 1.24$, but

TABLE II. Results for the critical exponents γ and ν and the amplitude ξ_0 from wide-angle light-scattering (WALS) and small-angle light-scattering (SALS) experiments. The errors correspond to one standard deviation in the fit program except for the final results.

Method	γ	ν	ξ_0 (Å)
WALS	1.179 ± 0.008	0.604 ± 0.004	35.0 ± 0.7
SALS	1.19 ± 0.23	0.602 ± 0.008	31.5 ± 1.9
WALS + SALS	1.175 ± 0.006	0.604 ± 0.003	35.1 ± 0.4
Final result	1.18 ± 0.03	0.60 ± 0.02	35 ± 5

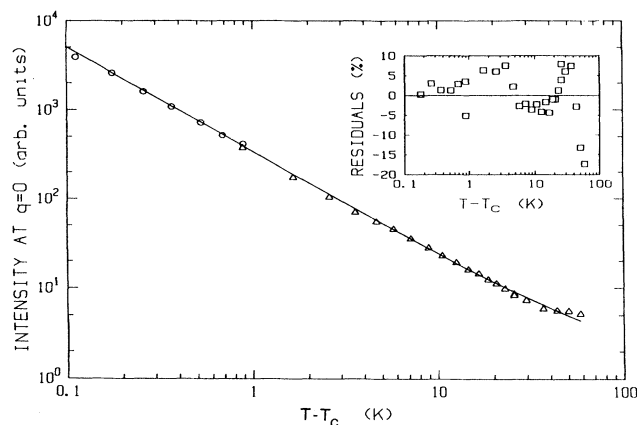


FIG. 1. Scattered intensity extrapolated to $q=0$ from wide-angle light scattering (WALS, Δ) and small-angle light scattering (SALS, \circ). The solid line is the best fit to the data, giving $\gamma=1.18$.

does not fit the data well. Fitting with a temperature-dependent background term of the form $I_B(1+t)$ gives $\gamma=1.17$, the fit with a term $I_B(1-t)$ gives $\gamma=1.18$. We did not try to impose stronger temperature dependence on the background since the variation of I_B with temperature is weak according to the arguments developed above in Sec. IV A. Fitting with a correction-to-scaling term added in Eq. (3) leads to unphysical results.

We therefore conclude that the values for the exponent of the susceptibility is $\gamma=1.18\pm 0.03$.

B. Exponent ν and amplitude ξ_0 of the correlation length

The values for ξ were corrected for the background intensity I_B found by the fits described in the preceding section, and then Eq. (4) was fitted to the data. The free parameters were the amplitude ξ_0 and the exponent ν . Again, T_c was fixed at the experimental value. Since the correlation length ξ is measured in absolute units, the data from both experiments can be included in the fitting procedure without any normalization. The fit gives $\nu=0.60$ and $\xi_0=35$ Å. If each data set is fitted individually, one obtains $\nu=0.60$ and $\xi_0=35$ Å from the WALS data and $\nu=0.60$ and $\xi_0=32$ Å from the SALS data. These results are summarized in Table II and shown in Fig. 2.

Again, changing T_c by 0.1°C does not change the exponent. Not correcting ξ for the background I_B gives $\nu=0.59$ and $\xi_0=37$ Å, correcting with the doubled background leads to $\nu=0.62$ and $\xi_0=32$ Å. Including only the data for $T-T_c < 36^\circ\text{C}$ in the fit gives $\nu=0.59$ and $\xi_0=37$ Å. When the errors for ξ are doubled, we obtain still $\nu=0.60$ and $\xi_0=35$ Å. If a correction-to-scaling term is added to Eq. (4), the fit gives $\nu=0.61$ and $\xi_0=34$ Å.

Therefore the exponent and amplitude of the correlation length given by our experiments are $\nu=0.60\pm 0.02$ and $\xi_0=35\pm 5$ Å, respectively.

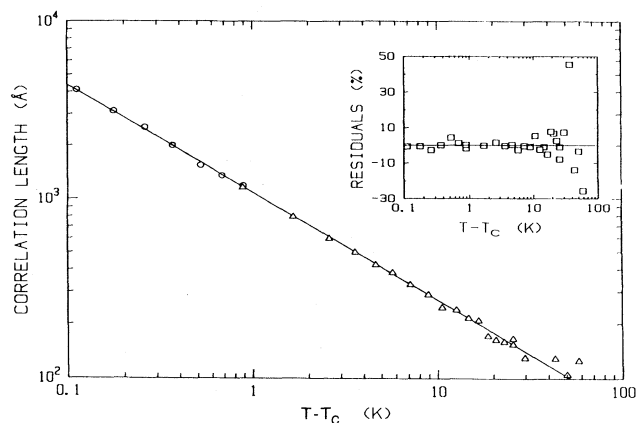


FIG. 2. Correlation length ξ from wide-angle light scattering (WALS, Δ) and small-angle light scattering (SALS, \circ). The solid line is the best fit to the data, giving $\nu=0.60$.

VI. DISCUSSION

Contrary to the theoretical expectation, we did not find renormalized Ising values for γ and ν for a critical ternary microemulsion using temperature as the experimentally controlled variable. Imposing the theoretical Fisher renormalized Ising exponents in the respective equations does not fit the data. Also, setting the exponents to mean field values does not give reasonable fits.

Our measurements indicate normal Ising behavior, as is observed in ordinary binary mixtures, pure fluids, and micellar solutions although the values for both γ and ν are slightly smaller than the theoretical Ising values. The scaling law $\gamma \approx 2\nu$ is well verified, within the experimental uncertainty. This could not be reported in earlier investigations of ternary microemulsions (see Table I).

The amplitude for the correlation length ξ_0 in the WBB microemulsion is found to be very large, $\xi_0=35$ Å. This value is three times as large as in the WDA microemulsion [8–10] and more than ten times larger than in binary mixtures [35]; it is known from the literature that ξ_0 can be large in microemulsion systems [5,6,8–10]. A value of ξ_0 smaller than the microemulsion droplet size can surprise. The meaning of ξ_0 , however, is merely that of a length on which the critical fluctuation correlation function takes the value $1/e$ at $T=2T_c$, and has little to do with a molecular or a droplet size. As a matter of fact, the amplitude ξ_0 in liquid mixtures is generally smaller than the average molecular size of the mixture components. For example, in the triethylamine and water system, ξ_0 is of order 1 Å [35].

Our results compare relatively well with the findings of Jayalakshmi and Beysens [12] for γ , ν , and ξ_0 in the case where a temperature-independent background is assumed for the data analysis (see Tables II and III of Ref. [12]).

At high temperatures, for $T-T_c > 35^\circ\text{C}$, the intensity at $q=0$ does not change appreciably with temperature. The Ornstein-Zernike structure factor [Eq. (1)] describes the angular dependence of the scattered light only in the critical region. Far away from T_c , when the influence of

the critical point becomes negligible, the angular dependence of scattered light is described by the form factor. The rather constant intensity at high $T - T_c$ might indicate the growing influence of the form factor. In general, a water-in-oil microemulsion consists of spherical water droplets covered with a surfactant layer. Therefore the form factor can be written in the Rayleigh-Debye approximation for spherical particles [36] for $qR \leq 1.5$ as

$$F(q) = \exp(-q^2 R^2 / 5), \quad (6)$$

where R denotes the radius of the sphere. Therefore a $\log_{10}(I)$ versus q^2 plot should yield a straight line with slope $R^2/5$. For the high-temperature data, such a plot indeed gives, within the experimental errors, a straight line, and the slope is found to correspond to a radius of $R = 290 \text{ \AA}$ for temperatures $T - T_c > 40^\circ\text{C}$. Cazabat

et al. [24] have measured the radius in a WBB microemulsion only up to W-to-S ratios of 1.5. Extrapolating their data linearly to a W-to-S ratio of 1.9 gives $R = 120 \text{ \AA}$. This discrepancy can be due to the simple extrapolation which might not be correct. Also, their measurement was done by dynamic light scattering and gave therefore the hydrodynamic droplet radius. This technique needs a good theoretical model to infer a droplet size, and also separate viscosity measurements. This adds uncertainties to the results. We note, however, that both values are of the same order of magnitude.

ACKNOWLEDGMENT

We gratefully thank Y. Jayalakshmi, M. L. Broide, and F. Perrot for help with the experiments and very fruitful discussions.

-
- [1] M. Kotlarchyk, S.-H. Chen, J. S. Huang, and M. W. Kim, *Phys. Rev. A* **29**, 2054 (1984).
- [2] A. Jada, J. Lang, and R. Zana (unpublished).
- [3] R. Dorshow, F. de Buzzaccarini, C. A. Bunton, and D. F. Nicolli, *Phys. Rev. Lett.* **47**, 1336 (1981).
- [4] C. M. Sorensen, *Chem. Phys. Lett.* **117**, 606 (1985).
- [5] O. Abillon, D. Chatenay, D. Langevin, and J. Meunier, *J. Phys. (Paris) Lett.* **45**, L-223 (1984).
- [6] A. M. Bellocq, P. Honorat, and D. Roux, *J. Phys. (Paris)* **46**, 743 (1985).
- [7] G. Maisano, F. Mallamace, and N. Micali, *Phys. Rev. A* **39**, 4103 (1989).
- [8] J. S. Huang and M. W. Kim, *Phys. Rev. Lett.* **47**, 1462 (1981).
- [9] M. Kotlarchyk, S.-H. Chen, and J. S. Huang, *Phys. Rev. A* **28**, 508 (1983).
- [10] P. Honorat, D. Roux, and A. M. Bellocq, *J. Phys. (Paris) Lett.* **45**, L-961 (1984).
- [11] M. W. Kim, J. Bock, and J. S. Huang, *Phys. Rev. Lett.* **54**, 46 (1985).
- [12] Y. Jayalakshmi and D. Beysens, *Phys. Rev. A* **35**, 8709 (1992).
- [13] J. C. Wheeler and B. Widom, *J. Am. Chem. Soc.* **90**, 3064 (1968).
- [14] M. E. Fisher, *Phys. Rev.* **176**, 257 (1968).
- [15] M. E. Fisher and P. E. Scesney, *Phys. Rev. A* **2**, 825 (1970).
- [16] C. S. Bak, W. I. Goldberg, and P. N. Pusey, *Phys. Rev. Lett.* **25**, 1420 (1970).
- [17] B. Chu and F. L. Lin, *J. Chem. Phys.* **61**, 5132 (1975).
- [18] K. Ohbayashi and B. Chu, *H. Chem. Phys.* **68**, 5066 (1978).
- [19] J. Rouch, A. Safouane, P. Tartaglia, and S. H. Chen, *Phys. Rev. A* **37**, 4995 (1988).
- [20] R. B. Griffiths and J. C. Wheeler, *Phys. Rev. A* **2**, 1047 (1970).
- [21] D. Roux and A. M. Bellocq, *Phys. Rev. Lett.* **52**, 1895 (1984).
- [22] G. Toulouse and P. Pfeuty, *Introduction au Groupe de Renormalisation et a ses Applications* (Presses Universitaires de Grenoble, Grenoble, 1975).
- [23] P. Delord and F. C. Larche, *J. Colloid Interface Sci.* **98**, 277 (1984).
- [24] A. M. Cazabat, D. Chatenay, P. Guering, W. Urbach, D. Langevin, and J. Meunier, in *Microemulsion Systems*, edited by H. L. Rosano and M. Clause (Dekker, New York, 1987), p. 183.
- [25] R. Aschauer, A. Asenbaum, and W. Schröer (unpublished).
- [26] Y. Jayalakshmi, B. Khalil, and D. Beysens, *Proceedings of the 1st European Symposium on Fluids in Space* (European Space Agency, Paris, 1992), pp. 389-403.
- [27] Y. Jayalakshmi, B. Khalil, and D. Beysens, *Phys. Rev. Lett.* **69**, 3088 (1992).
- [28] R. Aschauer and D. Beysens, *J. Chem. Phys.* (to be published).
- [29] J. Timmermans, *Physico-Chemical Constants of Pure Organic Compounds, Vol. II* (Elsevier, Amsterdam, 1965), p. 96.
- [30] V. Gurfein, D. Beysens, Y. Garrabos, and B. Le Neindre, *Opt. Commun.* **85**, 147 (1991).
- [31] M. E. Fisher, *Rep. Prog. Phys.* **30**, 615 (1967).
- [32] L. S. Ornstein and F. Zernicke, *Proc. K. Ned. Akad. Wet.* **17**, 793 (1914).
- [33] P. R. Bevington, *Data Reduction and Error Analysis for the Physical Sciences* (McGraw-Hill, New York, 1967).
- [34] E. Hecht and A. Zajac, *Optics* (Addison-Wesley, Reading, MA, 1974).
- [35] D. Beysens, in *Phase Transitions (Cargese 1980)*, edited by M. Levy, J.-C. Le Guillou, and J. Zinn-Justin (Plenum, New York, 1982), p. 41.
- [36] M. Kerker, *The Scattering of Light and other Electromagnetic Radiation* (Academic, New York, 1969).