

Application of the dynamical droplet model to critical nonionic amphiphile-water micellar solutions

E. Ducros, S. Haouache, and J. Rouch

Centre de Physique Moléculaire Optique et Hertzienne, Université Bordeaux I, 351 Cours de la Libération, 3405 Talence, France

K. Hamano and K. Fukuhara

Department of Biological and Chemical Engineering, Faculty of Technology, Gunma University, Kiryu, Japan

P. Tartaglia

Dipartimento di Fisica, Università di Roma La Sapienza, Piazzale Aldo Moro 2, Roma, Italy

(Received 30 November 1993)

A modified version of the dynamical droplet model, originally derived by Sorensen *et al.* [Phys. Rev. A **13**, 1593 (1976)], is used to explain experimental results on alkyl-oxyethylene-glycol monoether (C_iE_j)-water critical micellar solutions. The model assumes that the physical clusters formed close to the critical point can be treated much like percolating clusters with a fractal dimension $d_f=2.49$ and a polydispersity exponent $\tau=2.21$. For C_6E_3 -H₂O and $C_{10}E_4$ -H₂O critical mixtures, the modified version of the dynamical droplet model provides results in very good agreement with the experimental determinations of the scattered intensity, the turbidity, and the order parameter relaxation rate, when using as input parameters the three-dimensional universal Ising values of the critical exponents and the proper sizes of the individual scattering micelles. Static and dynamical background effects can be explained by the finite size of the monomers, which is explicitly taken into account by the model.

PACS number(s): 82.70.-y, 64.70.-p, 78.20.-e

I. INTRODUCTION

Critical phenomena have been the subject, for several years now, of various extensive studies, both theoretical [1,2] and experimental [3], spanning a wide range of systems, including single fluids as well as binary solutions, which are the topic of the present work. Those studies have brought to light one of the manifold features of the critical phenomena, namely, universality in the divergence of some quantities. Among the physical parameters behaving in that way, one finds the correlation length [2] ξ , which measures the mean extent over which fluctuations of the order parameter are correlated. The static phenomena's scaling hypothesis states that ξ is the only relevant length close to the critical point. Its divergence at that point implies the lack of a length for the characterization of what happens. Such an absence is to be likened to the same one that occurs in fractal objects [4]. On observing a phase separation in binary fluid mixtures at some temperatures and concentrations, the analogy was made between critical phenomena in simple fluids and that separation. At first, the same model could apply in both cases, with the same universal exponents, since binary and single fluids belong to the same universality class [three-dimensional (3D) Ising].

The study of nonionic amphiphile alkyl-oxyethylene-glycol monoether (C_iE_j)-water critical micellar solutions is of the greatest interest in the scope of critical phenomena since some of these systems seem to break the law of universality. Indeed, recently, extensive experiments [5] have revealed large discrepancies between the universal values of the critical exponents and the measured ones. For instance in $C_{12}E_5$ -water micellar solu-

tions, the measured value of the exponent ν characterizing the divergence of the long-range correlation length $\nu=0.514\pm 0.012$ is found to be much smaller than the theoretical one, $\nu=0.63$ for a 3D Ising system, and close to its mean field value $\nu=0.50$. To explain those disparities, it has been argued that for supramolecular systems, growth of the scattering particles should be taken into account as the temperature and the concentration are modified [6]. Another approach [7] was to consider the effect on the critical dynamics of the background terms of the transport coefficients, in this case the shear viscosity, and to account for possible deviations from the ideal critical state. Indeed due to polydispersity effects, the coexistence curve of nonionic amphiphile-water micellar systems is extremely flat and thus the critical point is practically difficult to locate very precisely. This way of analyzing the experimental data produces results in favor of universality for nonionic amphiphile-water micellar solutions, in agreement with the experimental findings of Strey and Pakusch [8] and of Dietler and Cannell [9] whose data are in fact very close to those published in Ref. [5].

Some very important points, however, remain unclear as far as the dynamical critical phenomena are concerned and we would like to address these questions in the present paper. Indeed, the analyses of experimental results performed using mode coupling theory involve a large dynamical background contribution Γ_B to the linewidth. In binary mixtures, this background is connected to the background term of the shear viscosity. When the dynamical background is small, as is the case for simple fluids or molecular binary critical mixtures, it can be calculated by using the Oxtoby and Gelbart pro-

cedure [10]. When it is not very small, Γ_B can be evaluated by using the procedure proposed by Burstyn *et al.* [11] or by the model given in Ref. [7]. Up to now, however, no completely satisfactory theory has been given to treat the case of supramolecular critical systems where Γ_B can account for more than 30% of the total linewidth.

It is noteworthy that in percolation as well as in critical phenomena, a characteristic length diverges on approaching a threshold. From a very extensive set of low frequency electrical conductivity measurements performed in an AOT [sodium bis(2-ethylhexyl) sulfosuccinate]-water-decane microemulsion system, it has already been shown [12] that the well-defined percolation locus corresponding to a very steep increase of the conductivity starts very close from the critical point. Thus if we consider solutions where the solute forms percolating droplets, there will be, at the same time, divergence of the correlation length and divergence of the clusters' size, so one can apply the percolation model at the critical point. By using an extended version of the so-called dynamical droplet model originally proposed by Sorensen *et al.* [13] and Martin *et al.* [14], Tartaglia, Rouch, and Chen [15] and Rouch, Tartaglia, and Chen [16] have been able to account for both the percolation phenomenon and the critical behavior of water-in-oil critical microemulsion systems, including the scattered intensity $I(q)$, the decay rate Γ of the order parameter, and also the shape of the order parameter time correlation function $S(q,t)$ which slightly departs from a single exponential decay. In the droplet model, the microemulsion system is considered to be made of polydispersed fractal clusters having a fractal dimension d_f of 2.5 and a polydispersity index τ of 2.2 as given by percolation theory [17]. The main advantage of the approach of critical phenomena in supramolecular fluid systems in terms of the extended version of the dynamical droplet model is that static and dynamical background which are physically connected to the quasimacroscopic size of a single microemulsion droplet are treated in a very natural way. Therefore, experimental data can be analyzed without subtracting any background.

The remaining problem is whether the analogy between percolation and critical phenomena, at the critical point, is also valid for solutions in which a percolation line has not been observed experimentally. This analogy has indeed been proved to be valid theoretically by Coniglio and Klein [18], who showed that, when properly defined, the physical clusters at the critical point are identical with the percolating clusters, having the same fractal dimension and the same polydispersity index. Moreover, the fractal nature of the correlated regions close to the critical point has been experimentally verified by Guenoun, Perrot, and Beysens [19] and Beysens, Guenoun, and Perrot [20] by performing direct observations of the clusters using a video camera. They arrive at the conclusion that these domains are self-similar in shape (fractal), with a fractal dimension d_f close to 2.8, a value slightly higher than the theoretical estimate, but reasonable when accounting for experimental errors.

Therefore, we will use in what follows the extended

version of the dynamical droplet model [15,16] to analyze a new extensive set of experimental data on water-alkyloxyethylene-glycol monoether (C_iE_j) critical micellar solutions, including the scattered intensity, the turbidity, the order parameter relaxation rate, and the shear viscosity. We shall also reanalyze experimental results obtained by some of us and previously published [21–23]. We shall focus in this paper on the case of nonionic amphiphiles C_6E_3 and $C_{10}E_4$ -water solutions which have been previously analyzed in terms of mode coupling theory including backgrounds, by using the 3D Ising values of the critical indices. We shall show in particular that when the finite size of the critical micelles is properly taken into account via the use of the modified dynamical droplet model, it is not necessary to introduce static or dynamical backgrounds to fit the experimental data, much as in the case of microemulsion systems [16].

II. THEORETICAL BACKGROUND

When the experimental conditions of the system are altered, the interparticular interactions change accordingly. Indeed, one can go from regions where the interactions are predominantly attractive to regions where repulsive ones dominate. For mixtures, not only are the interactions among the solute's molecules of importance but so are the interactions between the solute's and the solvent's molecules. Those interactions are notably responsible for the shape, concave or convex, of the coexistence curve. They are obviously at the heart of the aggregation process widely observed in supramolecular multicomponent systems such as micelles, microemulsions, and gels. To characterize the aggregation process, numerous models have appeared, all of which acknowledge the fractal character and the polydispersity of the aggregates formed.

As far as percolation is concerned, numerical simulations [17] led to the following universal values of the fractal dimension d_f and of the polydispersity index τ :

$$d_f = 2.5, \quad \tau = 2.2.$$

These indices are connected through a hyperscaling relation [17] involving the dimension d of the space:

$$d = d_f(\tau - 1). \quad (1)$$

By defining new clusters (called physical clusters) which obey new percolation rules, Coniglio and Klein [18] were able to reproduce the usual Ising behavior at the critical point. Thus concentration fluctuations can be considered as clusters having a fractal dimension d_f given by

$$d_f = d - \frac{\beta}{\nu}, \quad (2)$$

where $\beta = 0.33$ and $\nu = 0.63$ are, respectively, the universal exponents of the coexistence curve and of the long-range correlation length, and $d = 3$ is the dimensionality of space. From formula (2) we infer $d_f = 2.5$, which, when introduced in the hyperscaling relation (1), leads to $\tau = 2.2$. These two values are, respectively, equal to the

fractal dimension and the polydispersity index of percolating clusters.

In fact, when accounting for corrections to the static pair correlation function by introducing the Fisher's exponent η , the fractal dimension d_f is

$$d_f = \frac{5-\eta}{2}, \quad (3)$$

and the polydispersity index τ deduced from the hyper-scaling relation is

$$\tau = \frac{11-\eta}{5-\eta}. \quad (4)$$

With η close to 0.03, we infer $d_f=2.49$ and $\tau=2.21$, values which are extremely close to those relevant for percolation. When comparing the experimental results to the modified version of the Martin and Ackerson [13,14] dynamical droplet model, which we shall develop briefly in what follows, we will use those values of the indices d_f and τ as input parameters.

For fractal objects, the density's correlation function has the interesting characteristic of being homogeneous [17]. From that, Chen and Teixeira [24] were able to deduce the structure factor of a fractal aggregate. Their result, valid in the limit of small scattering wave vector q relevant for quasielastic light scattering, can be written as

$$S_k(q) = k \frac{\sin[(d_f-1)\arctan(q\xi_k)]}{(d_f-1)q\xi_k(1+q^2\xi_k^2)^{(d_f-1)/2}}. \quad (5)$$

In the above formula, the wave vector q is given in a quasielastic light scattering experiment by $q=(4\pi/\lambda)\sin(\theta/2)$ where λ is the wavelength in the medium of the incoming laser radiation and θ is the scattering angle. As was shown by Sorensen, Cai, and Lu [25], the radius of gyration R_k of the k cluster containing k droplets is connected to ξ_k by

$$R_k = \xi_k \left[\frac{d_f(d_f+1)}{2} \right]^{1/2}.$$

A direct relation links k , R_k , and R_1 , the radius of a single droplet:

$$R_k = R_1 k^{1/d_f}. \quad (6)$$

We shall use the following approximate Gaussian expression for the q -dependent static structure factor of a k cluster, shown to be valid for critical phenomena [16]:

$$S_k(q) = k \exp[-\frac{1}{3}q^2 R_k^2]. \quad (7)$$

When performing experiments on a polydispersed sample, the measured quantities are averaged over a size distribution. So we need to postulate a cluster size distribution. In his extensive study on percolation, Stauffer [17] introduced the following distribution $N(k)$, which is a scaling function of the variable k :

$$N(k) = k^{-\tau} f \left[\left[\frac{k}{s} \right]^\sigma \right]. \quad (8)$$

In Eq. (8), s is the average cluster size, $f[y]$ is a smooth

cutoff function of k/s decaying more rapidly than any power, τ is the polydispersity index, and σ is a universal exponent equal to about 0.5. The value of σ entices us to take the cutoff function as a Gaussian. Assuming that the total mass of the system is unity, the normalized cluster size distribution for percolating clusters reads

$$kN(k) = \frac{s^{\tau-2}}{\Gamma \left[2-\tau, \frac{1}{s} \right]} k^{1-\tau} \exp \left[-\frac{k}{s} \right], \quad (9)$$

where $\Gamma(x,y)$ is the incomplete Euler's Γ function. In what follows we shall assume that the size distribution of the critical clusters is identical to that given by Eq. (9) and pertinent for percolation.

A. Scattered intensity

As we shall see below, the critical composition of the sample in an amphiphilic molecule is very small (in any case, less than 15%). Furthermore, close to the critical point, the density of clusters goes to zero. Thus we can assume, at least as a first approximation, that the fractal clusters are dilute and not interacting. With these hypotheses, the scattered intensity $I(q)$ is given by the sum of the intensities scattered by each aggregate weighted by the normalized size distribution $kN(k)$. Hence,

$$I(q) = \int_1^\infty dk kN(k) S_k(q). \quad (10)$$

To calculate this integral, we define the correlation length ξ by

$$\xi = \frac{R_1}{\sqrt{3}} s^{1/d_f}. \quad (11)$$

With those definitions, by combining Eqs. (9), (10), and (11), one can show [16] that the scattered intensity $I(x)$ is given by

$$I(q) = I_0 \left[\frac{x}{x_1} \right]^{d_f} (1+x^2)^{d_f(\tau-3)/2} \times \frac{\Gamma \left[3-\tau, \left[\frac{x_1}{x} \right]^{d_f} (1+x^2)^{d_f/2} \right]}{\Gamma \left[2-\tau, \left[\frac{x_1}{x} \right]^{d_f} \right]}, \quad (12)$$

where I_0 is a term depending upon the geometry of the experiment and almost independent of temperature, $x=q\xi$ is the scaling variable, and $x_1=(1/\sqrt{3})qR_1$ can be considered as the effective reduced size of the monomer and enters explicitly into play in Eq. (12).

When plotted as a function of x , and for realistic values of the parameters, the scattered intensity given by Eq. (12) reduces to the usual form

$$I(q) = I'_0 \chi_T \mathcal{C}_{OZ}(q\xi), \quad (13)$$

where $\chi_T = \chi_0 \varepsilon^{-\gamma}$ is the osmotic compressibility, $\varepsilon = (T_c - T)/T_c$, γ is a universal exponent equal to 1.23, I'_0 is a constant, and $\mathcal{C}_{OZ}(x)$ is the Ornstein-Zernike static correlation function. The correlation length ξ diverges

when the temperature nears its critical value T_c according to $\xi = \xi_0 \varepsilon^{-\nu}$, with ξ_0 the short-range correlation length and $\nu = 0.63$.

The situation is different when the intensity is plotted as a function of the reduced temperature. In the so-called hydrodynamic regime, $x \ll 1$, the radius R_1 of the monomer plays a very important part. When R_1 is very small, as is typically the case for simple fluids or molecular binary mixtures, the plot of the intensity versus ε shows the usual $\varepsilon^{-\gamma}$ behavior. However, when the size R_1 of the monomer is not very small compared to ξ , which is typically the case for solutions made of supramolecular aggregates, significant departures from the $\varepsilon^{-\gamma}$ law are observed. In particular, in this regime, it is no longer possible to fit the scattered intensity to a power law in a large temperature range since an upward curvature of the plot is observed. Moreover, fitting intensity data to a power law in a restricted temperature domain would give an apparent value of the critical exponent γ smaller than the Ising's value used as input parameter. Besides, this value would depend upon the temperature domain in which the data have been fitted.

B. Turbidity

The turbidity Θ is the whole intensity scattered. Its computation entails not only a summation over the cluster size distribution but also a summation over the solid angle [26]:

$$\begin{aligned} \Theta(\xi) = \Theta_0 \int_0^{2\pi} d\phi \int_0^\pi d\theta \sin\theta \int_1^\infty dk k N(k) \\ \times (1 - \cos^2\phi \sin^2\theta) \\ \times S_k(q), \end{aligned} \quad (14)$$

where Θ_0 is a constant.

The integration over the solid angle can be easily performed and gives

$$\Theta(\xi) \approx \Theta_0 \int_1^\infty dk k^2 N(k) H(q_m^2 R_k^2), \quad (15)$$

where q_m is the wave vector corresponding to back-scattering and the function $H(y)$ is given by

$$H(y) = y^{-3} [y^2 - 2y + 4 - (y^2 + 2y + 4)\exp(-y)]. \quad (16)$$

As for the remaining integration, the analytical computation is not possible so the turbidity will be obtained numerically for each value of the reduced temperature or of the correlation length. When the size of the monomer is not negligible compared to ξ , the expression of the turbidity Θ as given by Eqs. (15) differs from the Puglielli and Ford result [26] calculated from Ornstein-Zernike formula. Indeed, in this case the turbidity Θ calculated from Eqs. (15) shows an upward curvature when plotted as a function of the reduced temperature, much like the scattered intensity. However, the Puglielli and Ford result [26] and the present calculation are very close numerically when R_1 is much smaller than ξ .

C. Dynamical critical phenomena

The order parameter relaxation rate $\Gamma(x)$ corresponds to the initial decay rate (first cumulant) of the cluster density-density time-dependent correlation function $S(q, t)$. It is given by

$$\Gamma(x, x_1) \equiv \lim_{t \rightarrow 0} \left[\frac{d}{dt} \ln[S(q, t)] \right]. \quad (17)$$

We shall assume that the physical clusters are rigid, spherical, and noninteracting. Thus the only diffusive process that has to be accounted for is the translational diffusion. The expression for Γ is then given by

$$\Gamma(x, x_1) = \frac{q^2}{I(x)} \int_1^\infty dk k N(k) S_k(q) D_k, \quad (18)$$

where D_k , the diffusion coefficient of the k cluster, is given by

$$D_k = R \frac{k_B T}{6\pi\mu R_k} = D_1 k^{-1/d_f}. \quad (19)$$

In formula (19), μ is the shear viscosity of the solution, and D_1 , the renormalized diffusion coefficient of a single droplet, reads

$$D_1 = R \frac{k_B T}{6\pi\mu R_1}, \quad (20)$$

R being a fitting parameter.

From the above equations, it is easy to calculate the reduced first cumulant $\Gamma^*(x, x_1)$, which reads

$$\Gamma^*(x, x_1) = \frac{\Gamma(x, x_1)}{D_1 R_1 q^3}. \quad (21)$$

Integrating Eq. (18), we obtain

$$\begin{aligned} \Gamma^*(x, x_1) = \frac{3\pi}{8} \frac{\Gamma[3 - \tau, x_1^{d_f}]}{\Gamma\left[3 - \tau - \frac{1}{d_f}, x_1^{d_f}\right]} \frac{\Gamma\left[3 - \tau - \frac{1}{d_f}, u\right]}{\Gamma[3 - \tau, u]} \\ \times \left[1 + \frac{1}{x^2}\right]^{1/2}, \end{aligned} \quad (22)$$

where $u = (x_1/x)^{d_f} (1 + x^2)^{d_f/2}$.

Much like intensity and turbidity calculated from the droplet model, the reduced first cumulant Γ^* explicitly depends on the reduced size x_1 of the monomer. It is then impossible to cast the relaxation rate of the order parameter into the product of a universal function of $x = q\xi$ by a system-dependent function as is the case for mode coupling or model decoupling original theories. However, very close to the critical point where the long-range correlation length ξ is much larger than R_1 , or when R_1 is of microscopic size as is the case, for instance, for molecular binary mixtures, the reduced first cumulant becomes a quasiuniversal function of $x = q\xi$. It reduces exactly to the Perl and Ferrel [27] mode decoupling result when $R_1 \rightarrow 0$ and in this case, it is numerically very close

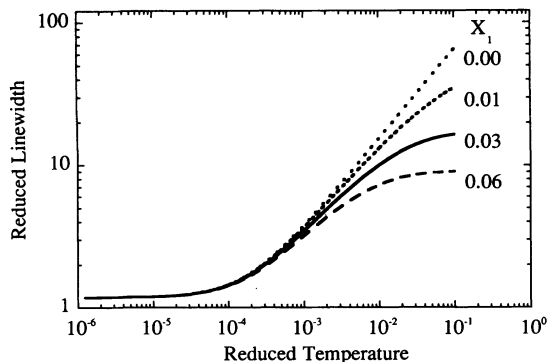


FIG. 1. Plot of the reduced linewidth calculated from formula (22) as a function of the reduced temperature for various values of the parameter x_1 . The dotted curve corresponding to $x_1=0$ reduces to Perl and Ferrel's expression [27] and is nearly identical with Kawasaki's universal function [1].

to the Kawasaki formula [1]. This is shown in Fig. 1 where we have plotted the reduced linewidth Γ^* as a function of the reduced temperature ε at a wave vector $1.025 \times 10^7 \text{ m}^{-1}$ (scattering angle $\theta=45^\circ$) for different values of x_1 . The numbers used to draw the different curves are those relevant for the mixture C_6E_3 -H₂O and will be given below. It can be seen in Fig. 1 that the curves drawn for nonzero values of x_1 significantly deviate in the hydrodynamic regime from Kawasaki's universal plot corresponding to $x_1=0$.

At that point it has to be stressed that the modified dynamical version of the droplet model given above can be applied only if the monomer units are quasispherical, and have a size nearly independent of temperature at least near the critical point. In what follows we shall assume that the micellar systems that have been experimentally studied obey the above requirements. However, these points are debated experimentally as well as theoretically and will be discussed in the Conclusion.

III. EXPERIMENTAL RESULTS AND DISCUSSION

For some of the surfactant-water binary mixtures forming micelles, as for simple fluids, one can observe a phase separation leading to two homogeneous domains, of different concentrations, and only kept apart by a meniscus. In the temperature-vs-concentration plane, one plots all the points for which such a transition occurs and thus determines the mixture's coexistence curve which divides the phase diagram in monophasic and diphasic regions. It can have a concave or convex curvature. The mixtures considered here are aqueous solutions of nonionic amphiphile alkyl-oxyethylene-glycol monoether



also called C_iE_j . The two nonionic amphiphiles we studied are C_6E_3 and $C_{10}E_4$. For these systems one observes a lower critical point. So we will define the critical temperature T_c as the nethermost point of the coexistence curve. To that temperature corresponds a critical concentration C_c . The monophasic region being beneath the di-

phasic one, we shall increase the temperature in order to reach T_c , keeping constant the concentration in amphiphile. In the case of C_iE_j -water critical micellar solutions, the coexistence curve is extremely flat, which may lead to some uncertainties in the critical composition. The flatness as well as the skewness of the coexistence curve toward the higher concentrations have been explained by Blankstein, Thurston, and Benedeck [28] by introducing polydispersity effects. However, at least for the two mixtures studied in this paper, when reduced to a small concentration range close to the critical composition, the coexistence curve can be fitted to a power law with an exponent β very close to its Ising value which is equal to 0.33.

A. C_6E_3 -H₂O solution

A complete presentation of the properties of this solution can be found in Ref. [21]. We give here only the main results of importance for the actual study. The determination of the coexistence curve gives a critical temperature $T_c=317.4 \text{ K}$ and a critical mass fraction of amphiphilic molecule $C_c=0.146$. Intensive measurements of the scattered intensity, of the turbidity, of the shear viscosity, and of the order parameter relaxation rate have been performed. So we can consider this solution to be an excellent case to test the model.

The scattered intensity's measurements were performed at $\theta=90^\circ$, corresponding to a wave vector q equal to $1.894 \times 10^7 \text{ m}^{-1}$. The order parameter relaxation rate has been measured at four different scattering angles: $\theta=45^\circ, 60^\circ, 90^\circ$, and 120° . The shear viscosity $\mu(T)$ of the micellar solution at the critical composition was also measured in a large temperature range corresponding to

$$3.15 \times 10^{-5} \leq \varepsilon \leq 1.88 \times 10^{-2}.$$

The experimental data fit very well a law of the type $\mu(T)=\mu^B\mu^C$. The multiplicative background viscosity μ^B is given by an Arrhenius law: $\mu^B=\mu_0\exp(-U/T)$, with $\mu_0=2.6 \text{ Pa s}$ and $U=2.27 \times 10^3 \text{ K}$, whereas the critical viscosity μ^C is given by $\mu^C=0.795\varepsilon^{-\phi}$, with an exponent $\phi=0.04$, in very good agreement with the renormalization group theoretical estimate [29].

In Figs. 2, 3, and 4 are plotted the scattered intensity,

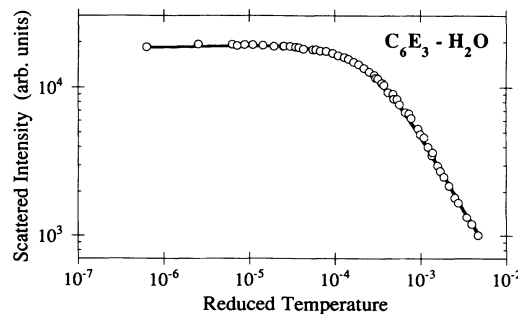


FIG. 2. C_6E_3 -H₂O critical micellar solution. The scattered intensity is plotted as a function of the reduced temperature. The symbols refer to experiment, whereas the solid line is the theoretical estimate deduced from formula (12).

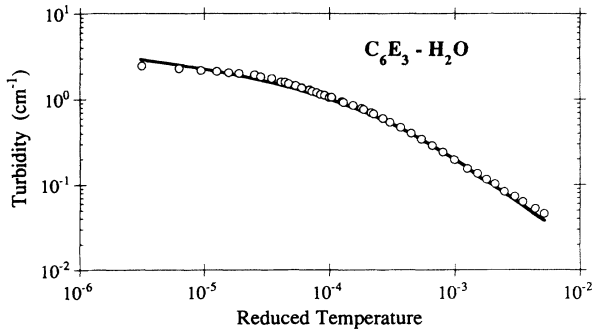


FIG. 3. C_6E_3 - H_2O critical micellar solution. The turbidity is plotted as a function of the reduced temperature. The symbols refer to experiment, whereas the solid line is the theoretical estimate deduced from formula (15).

the turbidity, and the linewidth, respectively, as a function of the reduced temperature. The solid lines are the theoretical results we obtained by using the modified version of the dynamical droplet model, whereas the symbols are the experimental determinations. As indicated in Sec. II, the correlation length's exponent ν was kept constant throughout this work and taken equal to its theoretical value 0.63 or, if one prefers, the fractal dimension and the polydispersity index are fixed, respectively, to 2.49 and 2.21. We can see on the graphs that a very good agreement is achieved between the experimental determination of the parameters and the theoretical estimates, always within the limit of the experimental errors.

The three adjustable parameters used to fit the data to the modified version of the dynamical droplet model are the short-range correlation length ξ_0 , the radius of the monomer R_1 and the amplitude R . The values we get for these parameters are

$$\xi_0 = (3.9 \pm 0.3) \text{ \AA} ,$$

$$R_1 = (22.0 \pm 1.0) \text{ \AA} ,$$

and

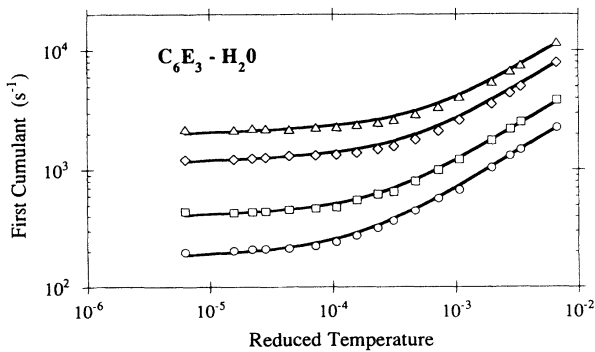


FIG. 4. C_6E_3 - H_2O critical micellar solution. The relaxation rate of the order parameter is plotted as a function of the reduced temperature for different values of the scattering angle. The symbols refer to experiments: circles, $\theta=45^\circ$; squares, $\theta=60^\circ$; diamonds, $\theta=90^\circ$; triangles, $\theta=120^\circ$. The solid lines are the theoretical estimates deduced from formula (22).

$$R = 1.15 \pm 0.05 .$$

We can compare these values to those previously published for this mixture. The analysis of the experimental data by means of the mode coupling theory of critical phenomena, including background effects implying fitting of ξ_0 and ν , leads to the following results:

$$\xi_0 = (3.560 \pm 0.012) \text{ \AA} , \quad \nu = 0.627 \pm 0.006 .$$

Within the experimental errors, the exponent ν is found equal to its theoretical value 0.63. As for ξ_0 , its value is confirmed by Corti *et al.* [5] whose measurements yield $\xi_0 = (3.40 \pm 0.03) \text{ \AA}$. So the value we obtained for ξ_0 using the droplet model is in good agreement with the previous determinations. As far as the amplitude R is concerned, the value we get is 1.15. In classical mode coupling theory, this amplitude should be equal to 1.027 [1]. On the other hand, the theoretical values inferred from the renormalization group range from 0.9 to 1.1 [29]. So the numerical result we obtain is slightly greater than the mode coupling theoretical estimate but it is close to the renormalization group predictions. It is, however, difficult to draw some conclusion from this last result since in the frame of the dynamical droplet model, it seems not to be possible presently to calculate this amplitude and even to show if the amplitude is universal or not.

The radius of C_6E_3 -water micelles has been estimated from a static light scattering experiment performed by Corti *et al.* [25] to be 12 \AA . The value we infer for the parameter R_1 from fitting our experimental data to the droplet model, namely, $(22 \pm 1) \text{ \AA}$, is nearly equal to the diameter of the micelles which represents the closest approach of the center of mass of the two monomers.

B. $C_{10}E_4$ - H_2O solution

For $C_{10}E_4$ - H_2O solution, linewidth and turbidity have been very carefully measured [22]. As in the former case, we only state here the indispensable quantities.

The critical point was estimated to be located at $T_c = 292.4 \text{ K}$ and $C_c = 22 \text{ mg/g}$. The linewidth was determined at the following angles: $\theta = 30^\circ, 60^\circ, 90^\circ$, and 120° . In the case of this mixture, the shear viscosity can be represented by the law

$$\mu(T) = \mu^B (Q_0 \xi_0)^{x_\mu} \varepsilon^{-\phi} .$$

The values of the critical exponents are $x_\mu = 0.065$ and $\phi = 0.041$, in perfect agreement with the predictions of the renormalization group theory. The system-dependent wave vector cutoff is equal to $Q_0 = 9.1 \times 10^6 \text{ m}^{-1}$. As for the background term μ^B , it was fitted accurately to an Arrhenius law, $\mu^B = \mu_0 \exp(-U/T)$, with

$$\mu_0 = (85.6 \pm 2.1) \text{ mPa s}$$

and

$$U = (1.01 \pm 0.02) \times 10^3 \text{ K} .$$

Figures 5 and 6 represent the data points obtained experimentally (symbols) together with the best fits (solid

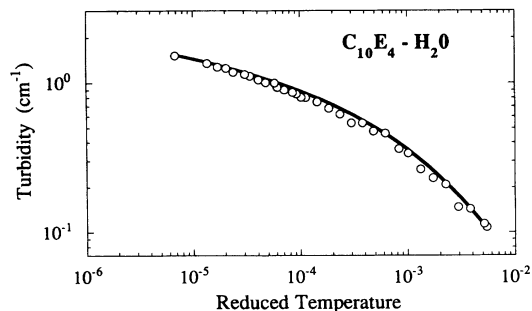


FIG. 5. $C_{10}E_4$ - H_2O critical micellar solution. The turbidity is plotted as a function of the reduced temperature. The symbols refer to experiment, whereas the solid line is the theoretical estimate deduced from formula (15).

line) to the dynamical droplet model. The parameters used for the fits are $\xi_0 = (12.2 \pm 0.5) \text{ \AA}$, $R_1 = (30 \pm 1) \text{ \AA}$, and $R = 1.05 \pm 0.03$. We can compare our findings to those deduced from fitting the experimental data to Kawasaki's theory, i.e., $\xi_0 = (10.7 \pm 0.5) \text{ \AA}$, $\nu = 0.63 \pm 0.01$.

The values inferred for ξ_0 by the two theoretical models are very similar. As to R_1 , no experimental value could be obtained, so we cannot judge of its accuracy. However, the C_{10} chain is longer than the C_6 one and so getting a micellar radius slightly larger than in the case of C_6E_3 - H_2O solutions seems to be very reasonable. Moreover, the value we infer for the amplitude R is about 1.05, and is in good agreement with the mode coupling theoretical estimates, 1.03.

IV. CONCLUSION

The analogies between critical fluctuations and percolation clusters established theoretically by Coniglio and Klein [18] and experimentally by Guenoun, Perrot, and Beysens [19] and Beysens, Guenoun, and Perrot [20] have allowed us to apply a modified version of the dynamical droplet model proposed by Tartaglia, Rouch, and Chen [15] to explain our experimental data on nonionic

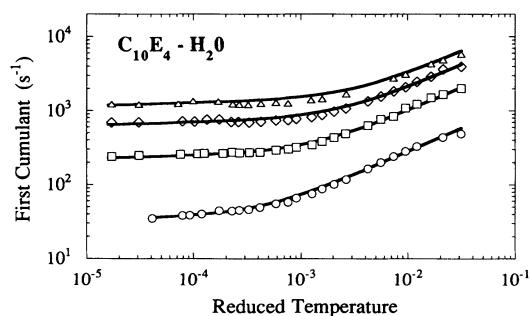


FIG. 6. $C_{10}E_4$ - H_2O critical micellar solution. The relaxation rate of the order parameter is plotted as a function of the reduced temperature for different values of the scattering angle. The symbols refer to experiments: dots, $\theta = 30^\circ$; squares, $\theta = 60^\circ$; diamonds, $\theta = 90^\circ$; triangles, $\theta = 120^\circ$. The solid lines are the theoretical estimates deduced from formula (22).

amphiphile-water micellar solutions near their critical point. These results have been obtained making the assumption of spherical micelles of constant size, the phase transition occurring by cluster growth. Thus they seem an indication against micellar growth with temperature and concentration. In this regard, Kato and Seimiya [30] and Corti [5] have performed extensive researches based on measurements of micelles' hydrodynamic radius by means of quasielastic light scattering, and on measurements of the mutual diffusion and the self-diffusion coefficients using NMR. Kato and Seimiya [30] draw the conclusion that micelles' growth combined with the structural transition from sphere to rod is rather likely. On the other hand, the conclusions of Corti *et al.* [5] weaken Kato's. Furthermore, small-angle neutron scattering (SANS) experiment performed by Hayter [31] shows that C_8E_5 - D_2O micelles remain constant in size, the diameter being equal to 47 \AA , and develop a short-ranged attractive potential with increasing temperature towards the critical point. A similar conclusion was drawn by Di Meglio *et al.* [32] for $C_{12}E_5$ - H_2O micelles. So, close to the critical point, it seems that the model of spherical micelles of approximately constant radius is sensible in the case of not-too-long molecular chains (C_6 , for example), whereas the longer chains' behavior may not agree with that representation. Therefore, at least for the case of nonionic surfactant molecules studied in the present paper, we can then conclude that our hypothesis of spherical micelles of constant size is not unrealistic.

The results obtained in this analysis, while different from those yielded by the theory of classical critical phenomena including backgrounds [21–23], are confirmed by other studies either performed directly on the same solutions as those used here [21–23] or indirectly on solutions similar to them [5]. The important conclusion is that to fit the experimental results to the modified version of the dynamical droplet model, the exponent ν always keeps its universal value 0.63. This was also the case when data obtained on the mixtures studied in the present paper are fitted to conventional theories of critical phenomena. However, to get this result, static as well as dynamical background effects have to be accounted for. On the other hand, when using the modified version of the dynamical droplet model of Tartaglia *et al.* [15,16], no background effects either on the static (intensity and turbidity) or on the dynamical critical phenomenon (order parameter relaxation rate) have to be introduced. The size of monomer R_1 , which is a parameter of the theory, comes into play in a natural way and accounts for the observed deviations of the relaxation rate of the order parameter when compared to mode coupling or mode decoupling theories. The finite size effect of the monomer introduces what could be called nonuniversality. This sort of nonuniversality is only sizable rather far away from the critical point, in the cross-over regime. However, close to the critical point, the normalized scattered intensity and the reduced relaxation rate of the order parameter are scaling functions of the scaling variable x . Furthermore, the critical indices are always set to their universal values. So in the frame of the modified version of the dynamical droplet model, the

critical phenomena are universal.

As a final comment, we do not observe deviations from exponentiality of the scattered intensity correlation function, as was very recently reported for an AOT-water-decane critical microemulsion system [16]. In this latter case the measurements of the intensity correlation function have been performed using a log correlator, and small deviations from exponentiality have been observed at long delay time, i.e. for large values of the production Γt . We believe that these deviations from exponentiality, which are also connected to finite size effects, cannot be observed for the nonionic amphiphile-water micellar solutions discussed in this paper for two main reasons. First, the intensity correlator used in the actual experi-

ments is a linear one. With this type of correlator it is extremely difficult to achieve a great accuracy for values of the reduced decay time Γt greater than 2, which is the lower bound for detectability of nonexponential effects. Second, the radius of the nonionic micelles studied in the present paper, being roughly five times smaller than those of the microemulsion droplets, are not large enough to lead to sizable effects.

ACKNOWLEDGMENT

The Centre de Physique Moléculaire Optique et Hertzienne is "Unité Associée No. 283 au CNRS."

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