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Reexamination of the static and dynamic critical phenomena in water-amphiphile micellar solutions

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A source of the apparent deviation from three-dimensional (3D) Ising model behavior of the static critical phenomenon experimentally observed in several binary mixtures of water–nonionic-amphiphile systems has been identified. Analyses were made, in particular, on two ethylene glycol mono-*n*-dodecyl ether-water systems $C_{12}E_5$-H_2O and $C_{12}E_8$-H_2O (where E represents ether), for which a very extensive set of data has been published. Our analyses show that, in fact, all published experimental data are consistent with the 3D Ising exponents if several isochores, including the most critical one, are simultaneously analyzed using the linear model equations of state. Owing to the flatness of the coexistence curves it is experimentally rather hard to locate very precisely the critical concentration. With added difficulties of obtaining very pure amphiphile samples and correcting data for multiple-scattering contribution near the critical point in a conventional light-scattering experiment, the determination of the critical indices is always subject to large errors. All the sources of errors tend to lower the measured indices. For the dynamic critical phenomena, a combined use of the linear model equations of state and the full mode-coupling theory, including the background effect, allows us to fit all the dynamic light-scattering data along the "critical" and off-critical isochores by assuming a single value of the Debye cutoff wave number q_D which is equal to the inverse of the average hydrodynamic diameter $2R_H$ of the micelles. We point out the strong influence of the background effect on the critical concentration fluctuation dynamics for systems formed from unusually large objects in solution.

I. INTRODUCTION

During the last few years great interest has been aroused by the experimental discovery of the nonuniversality in the critical phenomena of supramolecular systems such as binary mixtures of water and nonionic amphiphile[1,2] or multicomponent water-oil-amphiphile mixtures, namely microemulsions.[3] Subsequently some theoretical works have been published[4–6] giving plausible arguments for the observed nonuniversality. It was, however, difficult to explain theoretically why the universal exponents γ and ν describing, respectively, the divergences of the osmotic compressibility χ_T and of the long-range correlation length ξ could be less than the limiting values $\gamma = 1.0$ and $\nu = 0.50$ given by the mean-field theory[7] in some instances.

The experimental results of Corti and Degiorgio[1] and of Hamano *et al.*[2] have been questioned recently and some new measurements have been performed to check these results. For the static critical phenomena Strey and Pakusch,[8] and Dietler and Cannell[9] have found normal 3D Ising exponents, namely, $\gamma = 1.24$ and $\nu = 0.63$, from doing very careful static and dynamic light scattering experiments on binary mixtures of $C_{12}E_6$-H_2O and $C_{12}E_8$-H_2O (where E represents ether), in sharp contrast with the results of Refs. 1 and 2. On the other hand, for the ternary system water-decane-AOT [AOT denotes sodium di(2-ethylhexyl) sulfosuccinate], Huang and Kim[10] and Kotlarchyk *et al.*[11] also obtain the three-dimensional (3D) Ising results. More recently, we demonstrated that for the latter system, renormalized 3D Ising exponents were in better agreement with both static and dynamic light-scattering experiments when the background effects were properly taken into account.[12]

The aim of this paper is to provide a quantitative calculation of the correlation length ξ, the osmotic compressibility χ_T, and the decay rate of the order parameter Γ in binary critical mixtures of water and nonionic amphiphiles, ethylene glycol mono-*n*-dodecyl ether ($C_{12}E_n$-H_2O), by combining both the linear model equation of state and the complete mode-coupling theory, including the background effect for the transport coefficients. Our theoretical predictions are compared to the experimental results for critical and off-critical samples. The previously observed deviations from normal 3D Ising behavior for the so-called critical sample can be understood if one takes into account the extreme difficulty of locating precisely both the critical composition and the critical temperature in systems for which the amplitude of the coexistence curve is very small and also the nontriviality of correcting data for multiple scattering when close to the critical point. Our calculations provide a very good check of the internal consistency of the results of Corti and Degiorgio for the off-critical samples. We then show how crucial the criticality of the sample is for the determination of the critical indices in a system like a micellar solution where (a) the critical composition C_c of the sample is uncommonly shifted toward the water-rich side of the coexistence domain ($C_c > 90\%$ of H_2O), and (b) the coexistence curve is extremely flat so that the amplitude factor is very small. Furthermore, we show how important the background contribution of the order parameter decay rate is in a supramolecular system, where the diameter of the objects, of the order or greater than 100 Å, is very large compared to the molecular dimensions of the solvent.

II. THEORETICAL BACKGROUND

A. Mode-coupling theory

The complete treatment of the mode-coupling theory has been reported by many authors.[13–15] We want to emphasize here especially the most important point, the effects of the background on the transport coefficients as far as the analysis of light-scattering data is concerned. Since the solution is a binary system, the hydrodynamic slow variables are the local concentration C of the amphiphile, the velocity field transverse to the wave vector $\mathbf{q}$, and the local entropy. The corresponding transport coefficients are the concentration conductivity α and the shear viscosity η. The mass diffusion coefficient D can be expressed in terms of α, the number density of the micelles ρ, and the nonlocal q-dependent osmotic compressibility χ_T as $D=\alpha/\rho\chi_T$. When close to the critical point, the transport coefficients can be written as a sum of a regular (or background) part, α_B and η_B, and a nonlocal frequency-dependent critical part, α_c and η_c, respectively. One can set up the mode-coupling equations taking into account both parts.[14] In order to solve them self-consistently one uses the following simplifying assumptions: (i) neglect the frequency dependence of the transport coefficients; (ii) neglect the higher-order contributions to the transport coefficients; (iii) use the Ornstein-Zernike form for the nonlocal susceptibility $\chi_T(q,T)$, taking Fisher exponent η to be zero. One has

$$\chi_T(q,T)=\frac{\chi_T}{1+q^2\xi^2}=\frac{\chi_0}{\xi_0^2}\frac{\xi^2}{1+q^2\xi^2}\ , \tag{1}$$

where χ_0 is a constant. Since in a light-scattering experiment the frequency change is negligible, the magnitude of the wave vector is $q=(4\pi n/\lambda)\sin(\theta/2)$, where n, λ, and θ are the refractive index of the sample, the wavelength of light in vacuum, and the scattering angle, respectively.

The decay rate of the order parameter fluctuations $\Gamma(q,T)$, the quantity directly measured by photon correlation spectroscopy, is proportional to D and can be written like the transport coefficients as the sum of two terms $\Gamma(q,T)=\Gamma_c(q,T)+\Gamma_B(q,T)$. The background part $\Gamma_B(q,T)$ and the critical part $\Gamma_c(q,T)$, respectively, are given by

$$\begin{aligned}\Gamma_B(q,T)&=q^2\frac{\alpha_B(T)}{\rho\chi(q,T)}\\&=q^2D_B(T)(1+q^2\xi^2),\quad D_B(T)=\frac{\alpha_B(T)\xi_0^2}{\rho\chi_0\xi^2}\end{aligned} \tag{2}$$

and

$$\Gamma_c(q,T)=q^2\frac{\alpha_c(T)}{\rho\chi(q,T)}=q^2D_c\frac{K(q\xi)}{(q\xi)^2},\quad D_c=\frac{k_BT}{6\pi\eta\xi}\ . \tag{3}$$

The $K(x)$ apparent in Eq. (3) is a universal scaling function for the decay rate depending on a scaling variable $x=q\xi$. In an analogous way one can introduce a q-dependent shear viscosity $\eta(q,T)=\eta(T)[1+F(q\xi,T)]$, where $F(x)$ is a scaling function and $\eta(T)$ its macroscopic value $\eta(T)=\lim_{q\to 0}\eta(q,T)=\eta_c(T)+\eta_B(T)$, with

$$\eta_c(T)=\eta(T)\frac{3}{15\pi}\int_0^\infty dy\frac{y^6}{(1+y^2)^2K(y,T)+[D_B(T)/D_c(T)]y^2(1+y^2)}\ , \tag{4}$$

which clearly shows the dependence of the viscosity on the background of the decay rate. In the same long wavelength limit Γ gives

$$\begin{aligned}&\lim_{q\to 0}\frac{\Gamma_c(q,T)}{q^2}=R\frac{k_BT}{6\pi\eta(T)\xi}\ ,\\&R=\frac{2}{\pi}\int_0^\infty dy\frac{1}{(1+y^2)[1-F(y,T)]}\ .\end{aligned} \tag{5}$$

R is the correction factor to the Stokes-Einstein law applied to correlated regions of size ξ in the critical system. A set of coupled integral equations can be written for the two scaling functions $K(x)$ and $F(x)$ and can be solved numerically if the background is included. Otherwise a self-consistent perturbation scheme can be used when D_B/D_c is neglected. This type of calculation is valid only very close to the critical point, when the scaling functions $K(x)$ and $F(x)$ become universal, and in this case one gets a value $R=1.027$. Since the viscosity anomaly is experimentally known to be weak, a simple iterative procedure can be used to evaluate both transport coefficients. To the lowest order one neglects the q dependence of the viscosity, so that $F(x)=0$ and $K(x)$ have a universal expression

$$K(x)=\frac{3}{4}\left[1+x^2+\left[x^3-\frac{1}{x}\right]\tan^{-1}x\right]\ . \tag{6}$$

Substitution of this expression into the equation for $\eta_c(T)$ allows the evaluation of the critical part of the shear viscosity in terms of the background linewidth Γ_B. It must be noted that neglect of the background term would prevent the integral for the critical part of the viscosity from converging. An approximate evaluation of $\eta_c(T)$ has been given by Oxtoby and Gelbart[14] in the form

$$\eta(T)=\eta_B(T)\left[\frac{Ck_BT\rho\chi_0}{6\pi\eta_B\alpha_B\xi_0^2}\xi\right]^{\psi}=\eta_B(T)(q_D\xi)^{\psi}\ , \tag{7}$$

where ψ is a universal exponent equal to $8/15\pi^2=0.054$, and $C=0.9$. The parameter q_D is the Debye upper cutoff wave number for the integral giving the nonlocal shear viscosity. To the same order of approximation the background decay rate $\Gamma_B(q,T)$ is given by[16]

$$\Gamma_B(q,T)=q^2D_c\frac{3}{4}\frac{C}{q_D\xi}(1+x^2)\frac{\eta}{\eta_B}\ . \tag{8}$$

In order to compare more easily the theoretical predictions with the experimental results, it is customary to express Eqs. (2) and (3) in a reduced form involving only universal quantities. We therefore define a reduced relaxation rate which is the sum of the two following contributions:

$$\Gamma_c^*=\Gamma_c\frac{6\pi\eta}{k_BTq^3R}=\frac{K(x)}{x^3};\quad \Gamma_B^*=\Gamma_B\frac{6\pi\eta}{k_BTq^3R}\ . \tag{9}$$

The comparison between the mode-coupling theory and the dynamic light-scattering experiment can be easily done along the line of critical concentration $C=C_c$ where the long-range correlation length ξ has the usual definition

$$\xi=\xi_0\epsilon^{-\nu}\ , \tag{10}$$

and can be deduced from combined total scattered intensity and turbidity measurements.[16]

B. Linear model equations of state

For off-critical mixtures, ξ is no longer given by Eq. (10). In order to derive this quantity we adopt the model used in Ref. 17. In this method one first expresses the correlation length ξ as a function of the compressibility χ_T and then calculates χ_T in terms of a scaling equation of state valid close to the critical point.[18] In order to do that, we first relate it to the spatial integrals G_{ij} $(i,j=1,2)$ of the partial pair-correlation function of the two species $g_{ij}(r)$,

$$\chi_T=\frac{C(1-C)}{N_Ak_BT}\left[1+\frac{C(1-C)}{V}N_A(G_{11}+G_{22}-2G_{12})\right]\ , \tag{11}$$

where C is the mass fraction of the amphiphile, V is the molar volume of the mixture, N_A is the Avogadro number, and k_B is the Boltzmann constant. Using the Ornstein-Zernike form for the pair-correlation functions $g_{ij}(r)=a_{ij}\exp(-r/\xi)/r$, which is a good approximation, one obtains[19]

$$G_{ij}=a_{ij}\int d\mathbf{r}\frac{\exp(-r/\xi)}{r}=4\pi a_{ij}\xi^2\ , \tag{12}$$

where the coefficients a_{ij} are constant. Since the compressibility is directly linked to the order-parameter fluctuations, by putting $a=a_{11}+a_{22}-2a_{12}$, one gets

$$\xi^2=\frac{V}{4\pi aN_AC(1-C)}\left[\frac{k_BTN_A\chi_T}{C(1-C)}-1\right]\ . \tag{13}$$

The linear model equation of states can be used to obtain an explicit temperature and mass fraction dependence of χ_T and then of ξ. In this model,[18] the critical part of the appropriate thermodynamic potential Π, the field conjugate to the order parameter h, and the reduced temperature ϵ are expressed in terms of two parametric variables r and θ, expressing the reduced distance from the critical point. In the case of a two-component system,[19] the linear model equations can be written in the following way:

$$\begin{aligned}&h(r,\theta)=ar^{\beta\delta}\theta(1-\theta^2)\ ,\\ &\epsilon(r,\theta)=r(1-b^2\theta^2)\ ,\\ &C-C_c=\frac{\partial\Pi}{\partial h}=g\theta r^{\beta}\ ,\end{aligned} \tag{14}$$

where the critical indices β and δ have their usual meaning, the parameter g is the nonuniversal amplitude of the coexistence curve, and $b^2=(\delta-3)/(\delta-2\beta\delta+2\beta-1)$. The compressibility is then

$$\chi_T=\frac{1}{N_Ak_BT}\frac{g}{a}\frac{r^{-\gamma}}{1+d_2\theta^2},\quad d_2=\frac{2\beta\delta-3}{(1-2\beta)}\ . \tag{15}$$

Substituting Eq. (15) into Eq. (13) we get, knowing that for $\theta=0$, ξ is given by Eq. (10),

$$\xi=\xi_0\left[\frac{V}{V_c}\right]^{1/2}\frac{C_c(1-C_c)}{C(1-C)}\frac{r^{-\gamma/2}}{(1+d_2\theta^2)^{1/2}}\ , \tag{16}$$

where V_c is the critical molar volume of the system. Two special cases are of particular interest: Along the critical isochore $\theta=0$, $r=\epsilon/(1-b^2)$, the correlation length reduces to the correct expression of Eq. (10); along the coexistence curve $\theta=\pm1$ the correlation length $\xi_{\rm CC}$ is given by

$$\xi_{\rm CC}=\xi_0\left[\frac{V}{V_c(1+d_2)}\right]^{1/2}\frac{C_c(1-C_c)}{C(1-C)}\left[\frac{C-C_c}{g}\right]^{-\gamma/2\beta}\ . \tag{17}$$

Equation (17) clearly shows that $\xi_{\rm CC}$ does not diverge along the coexistence curve (CC), except at the critical point C_c. This latter result is very important from a practical point of view. It is the source of a number of misinterpretations of experimental data on off-critical isochores.

By inverting the linear model equations (14), we can deduce the parametric variables r and θ in terms of the experimentally accessible variables, the temperature and concentration. It is important to observe from Eq. (14) that for a given reduced distance from the critical point, defined by the coordinates (r,θ), the amplitude factor g controls the variation of the concentration scale, corresponding to this distance. Small g means that for a given reduced distance, the actual concentration deviation from its critical value is amplified by a factor $1/g > 1$.

Knowing the correlation length ξ as a function of temperature and concentration, and using the mode-coupling equations and the viscosity data, we are able to describe completely both the static and the dynamic properties of the surfactant-water mixture over the whole critical regime.

III. THEORETICAL ANALYSIS OF THE EXPERIMENTAL RESULTS

We shall now apply the above described theoretical results to the study of the critical behavior of some water–nonionic-amphiphile binary solutions along critical and off-critical isochores. We shall mainly focus our attention to $C_{12}E_5$-H_2O and $C_{12}E_8$-H_2O since all the system-dependent parameters can be derived from the data independently measured by many different authors.

A. Coexistence curve

Extensive studies of phase separations in several nonionic surfactant-water mixtures near the lower consolute point, have been made by Lang and Morgan.[20] In particular, in a system $C_{10}E_4$-H_2O they determined the coexistence curve carefully near the critical temperature of 20.55 °C, and from this they concluded that the critical exponent $\beta = 0.36 \pm 0.02$. The asymptotic region where the power law is valid is within about 0.1 °C above the critical temperature. However, more recently, a study of Hamano *et al.*[2] on the system $C_{12}E_5$-H_2O concluded that β is approximately equal to 0.25 by fitting the coexistence curve to the power law within about 0.18 °C. The coexistence curve near the lower consolute point is, in this case, extremely flat and is not inconsistent with the universal 3D Ising value $\beta = 0.325$ if the temperature range is limited to 0.02 °C above the critical temperature.

The coexistence curve for the mixture $C_{12}E_8$-H_2O is given in Ref. 21 and exhibits a lower critical point. In the absence of a firm evidence otherwise, we can safely assume that the exponents β and γ are equal to their theoretical values $\beta = 0.325$ and $\gamma = 1.24$ (leading to $b^2 = 1.3594$). The coexistence curve can be quite accurately fitted to a power law with the choice of the critical parameters $T_c = 71.02 \pm 0.01$ °C, $C_c = (3.27 \pm 0.20)\%$ leading to the important critical amplitude factor $g = 0.134 \pm 0.008$ (Fig. 1). The same analysis performed on the data obtained by Hamano *et al.*[2] for the mixture $C_{12}E_5$-H_2O leads to $g = 0.19 \pm 0.01$. These two values for g are fairly smaller than that $g = 0.69$ reported for a molecular critical binary mixture of nitrobenzene and *n*-hexane.[17]

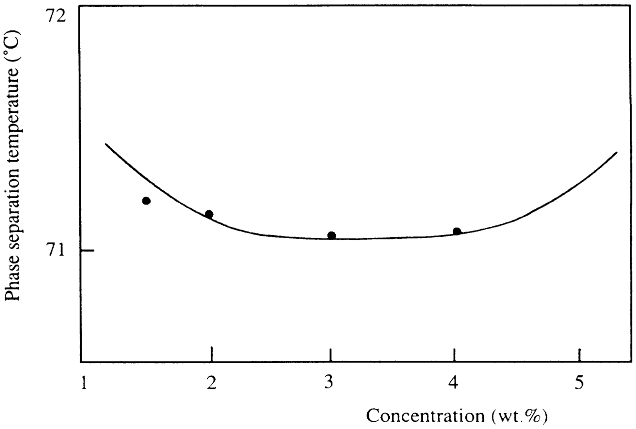

FIG. 1. Coexistence curve for the system $C_{12}E_8$-H_2O. The dots refer to data of Corti and Degiorgio (Refs. 21 and 22); the solid line corresponds to the theoretical calculation with $T_c = 71.02 \pm 0.01$ °C, $C_c = (3.27 \pm 0.20)\%$, and $g = 0.134 \pm 0.008$.

B. Correlation length and compressibility

Using the above values of g, T_c, and C_c, it is easy to invert numerically the linear model equations in order to obtain, for the actual values of the concentration and of the temperature, the two linear model coordinates r and θ, which enter in the expression of ξ. The constraints corresponding to the single-phase domain are $-1 \leq \theta \leq +1$ and $r \geq 0$. The two limits $\theta = \pm 1$ correspond to the coexistence curve, whereas $r = 0$ is the coordinate of the critical point. Putting the numerical values of r and θ in Eq. (16) allows the calculation of ξ once the short-range correlation length ξ_0 is known. Since at present time no satisfactory molecular model exists for the explicit calculation of ξ_0, we shall assume this quantity to be equal to $\xi_0 = 7.5 \pm 0.2$ Å, the value recently deduced experimentally by Dietler and Cannell.[9] Note that Corti *et al.*[22] reported $\xi_0 = 17.5 \pm 1.5$ Å by using a different exponent ν in Eq. (10) in order to fit the values of the correlation length. However, the measured values of ξ along the so-called critical isochore are similar in the two experiments. Besides, since the percentage of surfactant is low (in every case it is not greater than 5% in weight), we will assume that the molar volume V of the off-critical samples is equal to V_c, the critical molar volume, at least as a first approximation. The numerical values of ξ, inferred from the above procedure, have been plotted versus $T_p - T$ in a log-log scale in Fig. 2 for different compositions, whereas the variations of ξ_{CC} versus $|C - C_c|$ are plotted in a log-log scale in Fig. 3. In this latter case, it can be seen that the divergence of ξ_{CC} predicted by the linear model shows the correct critical exponent $\nu/\beta = 1.91$.

The calculated values of the static compressibility $\chi_T \sim \xi^2$ are plotted in Fig. 4 as a function of $T_p - T$ in a log-log scale in the same temperature domain as in Ref. 22. It is apparent that, apart from the critical composition, the plots of the compressibility versus $T_p - T$ are not straight lines in double logarithmic units, since ξ is finite along the coexistence curve (except at the critical point). However, in a restricted range of temperature, spanning one or two decades, these curves can be well assimilated to straight lines. On the same figure [Fig. 4(a)] experimental data obtained by Corti and Degiorgio[22] for off-critical compositions are also reported. Owing to the fact that the linear model equations of state is, in principle, valid only very close to the critical point $r = 0$, whereas it has been effectively applied quite far from it both in tem-

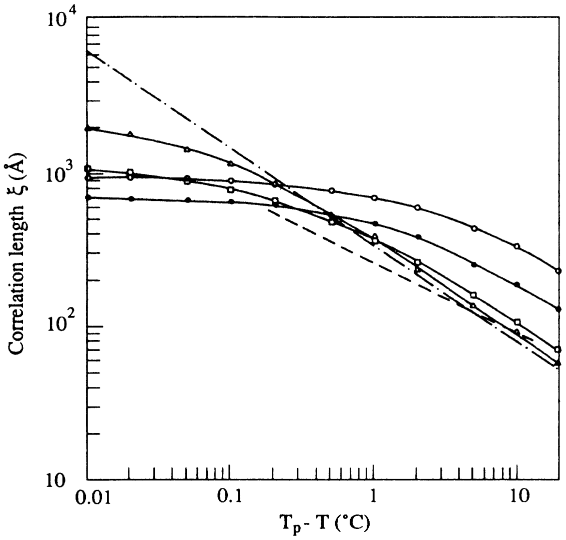

FIG. 2. Correlation length of $C_{12}E_8$-H_2O as a function of the distance in temperature from the coexistence curve $T_p - T$. The dash-dotted line corresponds to a theoretical calculation at $C = C_c$, and to Dietler and Cannell data (Ref. 9). The dashed line refers to the data of Corti *et al.* (Refs. 21 and 22). The solid lines with circles, solid dots, squares, and triangles are theoretical calculations corresponding, respectively, to concentrations of 0.5%, 1.0%, 2.0%, and 2.5%. The values of the parameters are given in Fig. 1 and $\xi_0 = 7.5$ Å.

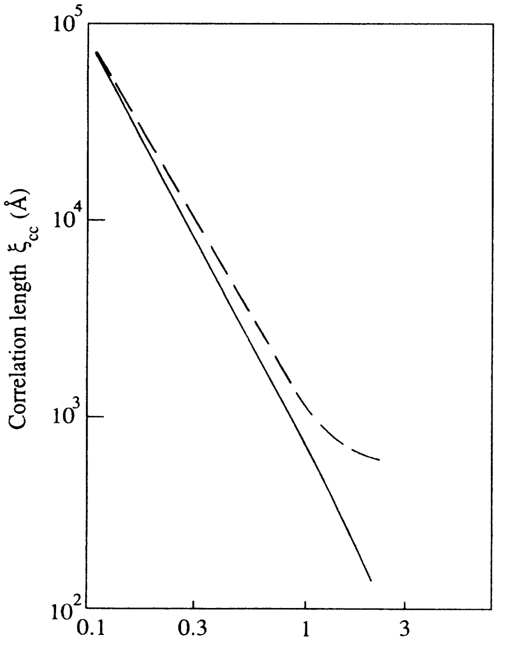

FIG. 3. Calculated values of the correlation length ξ along the coexistence curve for the same system and the same parameters as in Fig. 2. The dashed curve is for $C < C_c$, whereas the solid line is for $C > C_c$.

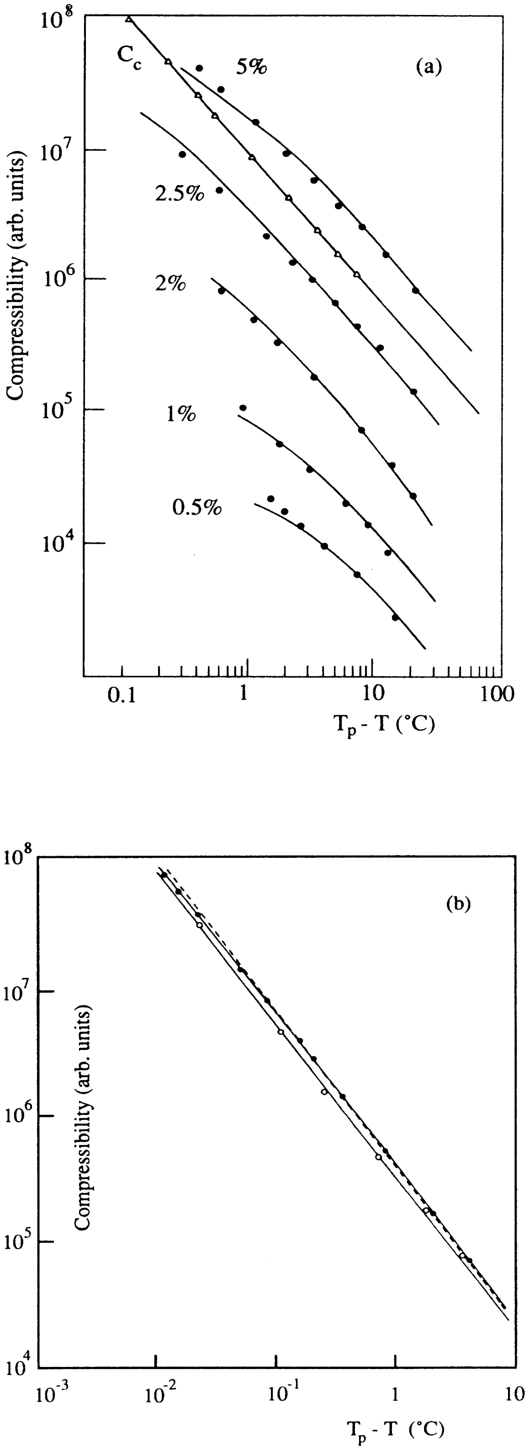

FIG. 4. Compressibility χ_T of $C_{12}E_8$-H_2O as a function of the distance in temperature from the coexistence curve $T_p - T$. The solid lines correspond to the theoretical calculations with the values of the parameters given in Fig. 1. In (a) the dots refer to the data of Corti and Degiorgio (Refs. 21 and 22) and the triangles to the data of Dietler and Cannel. In (b) the solid lines with circles and solid dots correspond, respectively, to theoretical calculations at $C = 3.7\%$ and $C = 4.1\%$, whereas the dashed line is the theoretical result at $C = C_c$.

perature and composition, the overall agreement between the experiments and the theory is good. The value of the apparent critical exponent $\gamma^* = 0.92$ given by Corti *et al.*[21,22] is close to the one that is obtained by fitting ξ^2 versus $T_p - T$ to a power law in a restricted temperature domain, i.e., $\gamma^* = 0.9$. One has to remember, however, that this pseudoexponent γ^* has no physical meaning in the frame of the linear model equation of state, since the compressibility diverges only along paths passing through the critical point, which is not the case for off-critical isochores.

The same calculation has been performed on Dietler and Cannell[9] data using the same value of g. Indeed these authors gave an estimate of the absolute error which can be expected on the determination of the critical composition. In the case of the mixture $C_{12}E_8$-H_2O they obtain $C_c = (3.9 \pm 0.2)$ wt. %; therefore, we have calculated ξ and χ_T for three compositions, 3.9, 4.1, and 3.7%. The corresponding numerical results for χ_T versus $T_p - T$ are plotted in log-log units in Fig. 4(b). In a large temperature domain, the behavior of χ_T versus $T_p - T$ can be well approximated by a power law with an apparent exponent $\gamma^* = 1.2$ for the two off-critical samples. This value is close to 1.24, but definitely lower and outside the experimental error of γ, which is usually of the order of 1 or 2%. These results show that the value of the index γ is extremely sensitive to the criticality of the sample.

The question that arises now is why the correct result, i.e., $\gamma = 1.24$ has always been obtained in regular critical binary mixtures where the critical composition is close to that of the symmetrical model, i.e., 50%. One can assume as a good approximation that the experimental absolute accuracy on the critical composition cannot be significantly better than 0.2%; in this case, if we take the amplitude $g = 0.134$, corresponding to a flat coexistence curve, we obtain, in a large temperature domain, an apparent exponent $\gamma^* = 1.23$. On the other hand, if we use the value of the amplitude $g = 0.60$, which corresponds to the usual shape of the coexistence curve for this type of mixture,[9] the apparent value $\gamma^* = 1.23$ is obtained even for an absolute error on the critical composition of 1%, a value significantly larger than the usual experimental error of 0.2%. This gives a plausible reason why correct values of the indices γ and ν have always been obtained in regular critical binary mixtures. This fact is illustrated in Fig. 5 for the correlation length and the compressibility.

C. Order-parameter relaxation rate

Once the long-range correlation length is known, it is possible to calculate the order-parameter relaxation rate $\Gamma = \Gamma_B + \Gamma_c$ from Eqs. (2) and (3). These equations involve both the shear viscosity of the mixture and Debye cutoff wave number q_D. The kinematic viscosity relative to that of water of $C_{12}E_8$-H_2O solutions is given in Ref. 21. Using the viscosity data for pure water as a function of temperature,[23] and assuming as a first approximation that the density of the mixture is that of water at the same temperature, and since the concentration of the amphiphile in the solution is always small, we can deduce the shear viscosity for the critical and off-critical mixtures as a function of temperature and composition. We can then easily calculate the critical part Γ_c of the relaxation rate Γ from Eq. (3).

On the other hand, the background part Γ_B of the relaxation rate depends not only on the viscosity but also on the Debye cutoff q_D. As in the case of the short-range correlation length ξ_0, no satisfactory theoretical expression in terms of molecular quantities is known at the present time for q_D. Therefore, we shall use the same physical argument as in our previous work on critical ternary microemulsions.[12] We assume as a crude estimate that the amphiphile micelles behave like hard spheres, the Debye cutoff wave number q_D being equal to the inverse of the minimal distance between the centers of mass of the particles. Assuming that the micelles behave as quasimonodispersed spherical droplets, interacting via a hard-sphere intermolecular potential, we may put $q_D = 1/2R_H$, R_H being the hydrodynamic radius of the particles. The numerical value of R_H has been deduced by many authors from various techniques. Nilsson *et al.*[24] reported that $R_H = 31$ Å, Brown *et al.*[25] gave 29 Å, whereas Corti and Degiorgio[21,22] obtain 34 Å. We shall use this last value since it seems to be slightly dependent of the physical nature of the sample which has

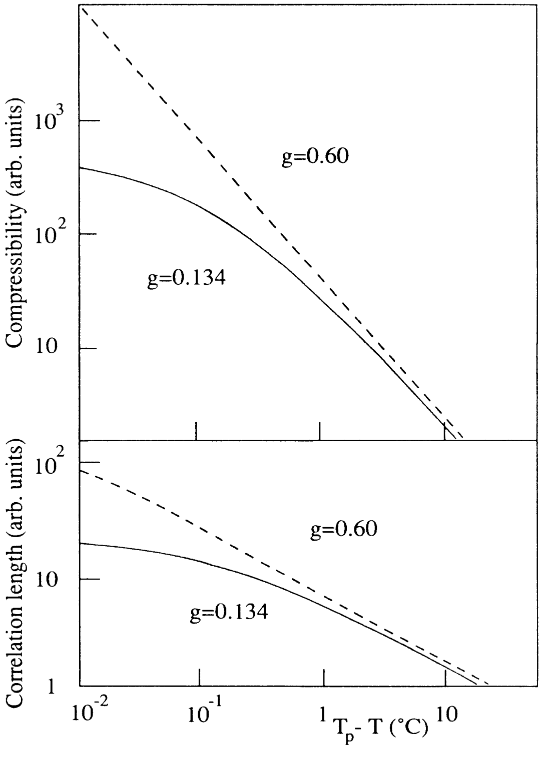

FIG. 5. Calculated correlation length ξ, (a) and the compressibility χ_T, (b) as a function of the distance from the coexistence curve $T_p - T$ for an hypothetical symmetrical mixture ($C_c = 0.50$) at a concentration of 0.51. The solid lines refer to $g = 0.134$, the dashed one to $g = 0.6$.

been studied. Then, using Eq. (2), the calculation of the background part Γ_B of the relaxation rate is straightforward. The total relaxation rate $\Gamma = \Gamma_B + \Gamma_c$ is plotted as a function of $T_p - T$ on a log-log scale and for different compositions in Fig. 6. The most interesting feature of this simulation performed at a q value of 2×10^5 cm^{-1} corresponding to a 90° light-beating spectroscopy experiment or to a small-angle neutron-scattering (SANS) experiment, is that in the critical regime $x > 1$, the calculated value of the ratio Γ/Γ_c is approximately a constant, independent of the temperature and of the concentration of the sample, and is equal to 1.10 ± 0.02. This result very well explains why Corti and Degiorgio[21,22] have been compelled to introduce a multiplicative *ad hoc* coefficient $h = 1.1$ in the definition of the diffusion coefficient D. Indeed, this phenomenological constant h accounts effectively for the background effects of the transport coefficients which have been neglected in the solution of the mode-coupling equations used in Refs. 21 and 22.

In order to show even more vividly the very strong influence of the dynamical background in supramolecular systems, let us consider now the experimental results of Hamano *et al.*[2] on the critical binary mixtures of $C_{12}E_5$ and water. These authors have compared the experimental value of the reduced relaxation rate Γ^* and the theoretical prediction of the mode-coupling theory Γ_c^*. The difference between these two quantities is large, ranging from 30% in the critical regime $x > 1$, up to 50% in the near hydrodynamic regime $x < 1$. We can account quantitatively for this difference by introducing background effects. Since the relaxation rate is $\Gamma = \Gamma_B + \Gamma_c$, when passing to reduced quantities it is easy to obtain $\Gamma^*/\Gamma_c^* = 1 + \Gamma_B^*/\Gamma_c^*$. From the numerical values of the ratio Γ^*/Γ_c^* deduced from Ref. 2, we get an experimental determination of the ratio Γ_B^*/Γ_c^*, which in turn can be evaluated theoretically by combining Eqs. (3) and (8), leading to

$$\frac{\Gamma_B^*}{\Gamma_c^*} = 0.675\frac{q}{q_D}\frac{x(1+x^2)}{K(x)}\,, \tag{18}$$

where the multiplicative term $(q_D\xi)\psi$ has been neglected since it is always of the order of unity in the practical domain of interest. For a given value of the momentum transfer q, and provided that q_D is a smooth function of the temperature, Eq. (18) shows that Γ_B^*/Γ_c^* is a constant in the critical regime since here $K(x)$ varies as x^3, in agreement with the experimental data. Furthermore, a double-log plot of Γ_B^*/Γ_c^* versus $x(1+x^2)/K(x)$ should be straight line of slope 1.0 both in the critical and in the hydrodynamic regime. This is indeed the case for $x > 0.2$, as it can be seen in Fig. 7. Then assuming $q = 2\times 10^5$ cm^{-1}, we calculate $q_D = 4.10^5$ cm^{-1}. This value is very low compared to those of the order of 10^7 cm^{-1}, which have been obtained in molecular critical binary mixtures.[16] If we calculate the corresponding hydrodynamic radius of the micelles using $1/q_D = 2R_H$, we get $2R_H = 250$ Å. This theoretical determination of the diameter of the $C_{12}E_5$-water micelles leads to a numerical result which is fairly larger than the one $2R_H = 68$ Å obtained for the system $C_{12}E_8$-H_2O. However, this numerical value of the diameter of $C_{12}E_5$-water micelles is in excellent quantitative agreement with an experimental determination by Nilsson *et al.*[24] using NMR spectroscopy, namely $2R_H = 200$ Å at low amphiphile concentration.

Let us now discuss the results that can be obtained from the linear model equations of state in an extreme case. We have indeed calculated the reduced diffusion coefficient $D^* = D\eta/T$ for $C_{12}E_8$-H_2O off-critical solutions corresponding to Brown *et al.*[25] experiments reported recently. Although the definition of the shear viscosity entering in D^* is the one of the solvent in the usual Stokes-Einstein formula for the diffusion coefficient, whereas it is that of the solution divided by $R = 1.027$ in

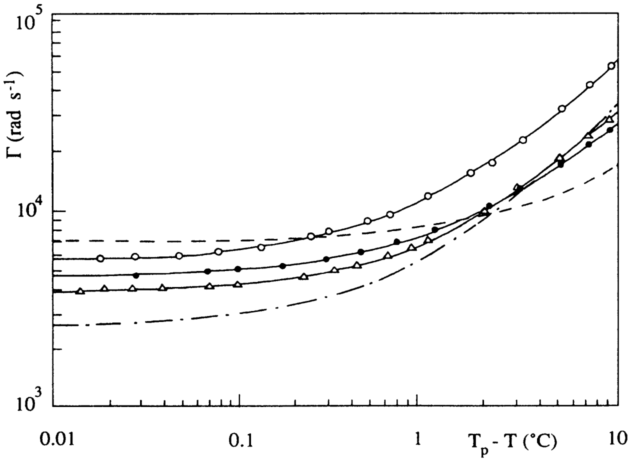

FIG. 6. Calculated total relaxation rate Γ as a function of $T_p - T$ for $C = C_c$ and various off-critical concentrations. The dash-dotted line corresponds to $C = C_c$, the dashed line to $C = 1.0\%$, the solid dots to $C = 2.0\%$, the triangles to 2.5%, and the circles to 5.0%.

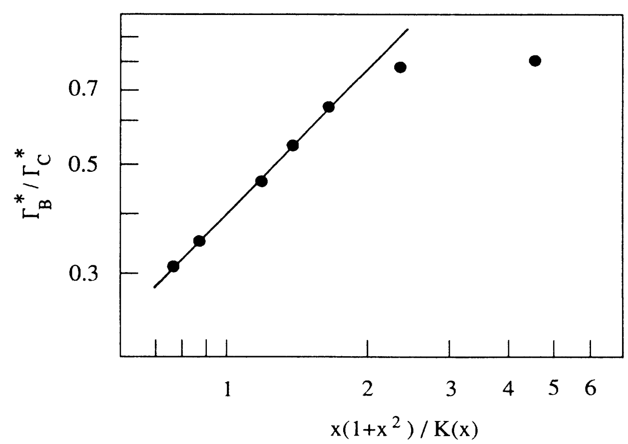

FIG. 7. The ratio Γ_B^*/Γ_c^* as a function of the variable $x(1+x^2)/K(x)$ in the range starting from $8/3\pi$, for the system $C_{12}E_5$-H_2O. The solid lines are the theoretical result, whereas the dots refer to the data of Hamano *et al.* (Ref. 2).

the mode-coupling theory, an estimate of D^* is $D^*=k_B/(6\pi\xi)$, depending only on the correlation length. The simulations that have been performed correspond to points in the phase diagram which are extremely far from the critical one in the sense of the coordinate r of the linear model equation of state. To give an idea, $r=3\times10^{-5}$ for a solution at the critical composition $C_c=3\%$, 10 mK far from T_c, whereas it is equal to 0.1 for a sample of concentration 5% and at room temperature $T_c-T=50$ K. Our numerical results are plotted in Fig. 8 where they are compared to the experimental ones. We obtain a good quantitative agreement for the sample at a concentration of 2%, whereas the agreement is qualitative in the case of a concentration of 5%. Therefore, we can assert that the linear model equations of state provide approximate but still meaningful values for the diffusion coefficient even very far from the critical point.

IV. CONCLUSION

The main conclusions of our analysis based on the data published in the literature are the following.

(a) As far as static critical phenomena are concerned, the determination of the critical indices are subject to large errors coming from the following sources. Owing to the flatness of the coexistence curve and consequently the smallness of the critical amplitude g, the tolerance for determining the critical concentration C_c is much smaller than for the ordinary critical mixtures of molecular liquids. Take, for example, the case of $C_{12}E_8$-H_2O. Because of the skewness of the coexistence curve the critical concentration is at a very low value of the amphiphile concentration (around 3.2%) and the accuracy of C_c has to be better than 0.2% from the actual critical concentration in order that Eq. (10) be valid. Any deviation from the critical isochore leads to the correlation length ξ, which is given by Eq. (16), which when incorrectly analyzed in terms of a power-law behavior, such as Eq. (10), would lead to an apparently lower critical exponent. The added difficulty is that the turbidity of critical nonionic micellar solutions is quite high and the multiple-scattering corrections in the intensity measurements are significant. The analysis of the data without multiple-scattering corrections tends to lead to apparently lower indices γ and ν. The combined effect of the two sources of error tends to reinforce each other. In the case of an AOT-water-decane microemulsion, the problem is less severe because the critical volume fraction of the droplet is higher, around 10%, and then the margin of error can be larger. In this case also, fortunately, the index of refraction matching of the droplets to the oil is good and multiple scattering is very small.[12]

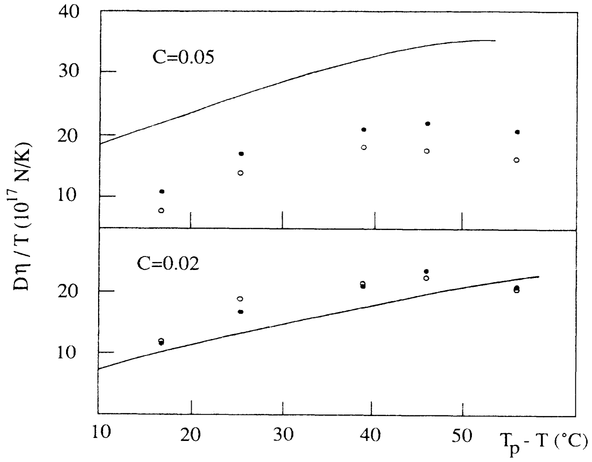

FIG. 8. Reduced diffusion coefficient D^* as a function of temperature for the mixture $C_{12}E_8$-H_2O. (a) refers to $C=0.02$ and (b) to $C=0.05$. The solid lines are theoretical results, whereas the solid dots and the circles are experimental data from Brown *et al.* (Ref. 25), respectively, deduced from a dynamic light-scattering experiment and self-diffusion measurements.

(b) For the dynamic critical phenomena, the discrepancy between the observed order-parameter relaxation rate Γ and the dynamic scaling result of the mode-coupling theory can be traced to the neglect of the background effect in the analysis of the dynamic light-scattering data. The central conclusion of our analysis is that the crucial parameter q_D can be put equal to the inverse of the average hydrodynamic diameter of the micelles. Since in certain cases like $C_{12}E_5$-H_2O the micelles are quite large, the numerical value of q_D turns out to be small. Equation (8) then predicts that the background term is very large (as much as 30% of the decay rate in the critical regime) and that cannot be neglected. When the background effect is properly taken into account, the mode-coupling theory fits quite well the experimental results.

The unusual feature of the critical phenomena in supramolecular systems, such as micellar solutions or microemulsions, is the fact that the constituent particles in the systems, the fluctuations of which we are studying, are much larger compared to the solvent molecules. This leads to two observable phenomena which are absent in the critical phenomena of simple atomic or molecular liquids. First, since the correlation length has a lower bound which is the diameter of the aggregates, the critical phenomena we are describing in terms of power-law behavior would break down once the correlation length falls below the size of the aggregate. Thus there is a rather abrupt crossover phenomenon from critical to noncritical behavior at a certain distance from the critical point. In the microemulsion case, we have found such a crossover phenomenon at a temperature which is roughly 20 °C away from the critical point.[12] The second point concerns the polydispersity of the aggregates, which is a natural consequence of the fact that the surfactant molecules in the micelles are in chemical equilibrium with the free surfactant monomers in the solution.[26] It has been shown by Blankschtein *et al.*[27] that the polydispersity of the aggregates and the asymmetry between molecular sizes of the solute and the solvent are the source of observed skewness of the coexistence curve. This fact has the consequence that the critical concentration is low for the nonionic micellar solution which directly leads to the difficulty we pointed out in (a). Thus it is fair to conclude that with the proper understanding of these unusual features, the study of critical phenomena of supramolecular solutions appears to have added novelty and interest of its own.

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