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Dynamical universality in a critical mixture of a nonionic micellar solution

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The decay rate of critical fluctuations in a nonionic micellar solution of tetraethylene glycol *n*-decylether ($C_{10}E_4$) in water has been investigated very close to its critical point of mixing from the time-dependent correlation function of scattered light. We find the scaled decay rate Γ_c^* $(=[6\pi\eta(T)/k_BT](\Gamma-\Gamma_B)/k^3)$ for $C_{10}E_4$ in water obeys a universal function over the range from a scaled variable of $k\xi\simeq0.3-26$, where Γ_B is the noncritical background contribution. Our experimental findings suggest that the micellar solution of $C_{10}E_4$ in water should belong to the static and the dynamical universality class as a fluid, in conjunction with our previous works [K. Hamano *et al.*, Phys. Lett. A **150**, 405 (1990); J. Chem. Phys. **94**, 2172 (1991).

I. INTRODUCTION

In view of the involvement of micelles in numerous technical and biological processes, as also their use as model systems for diverse colloidal, interfacial, and membrane systems, it is worthwhile to elaborate on the study of dynamics in a micellar solution close to a critical mixing point. Surfactant solutions including amphiphilic detergentlike monomers have the dual tendencies as the surface-active molecule, which consists of a soluble hydrophilic region and an insoluble hydrophobic alkyl chain in water. These dual natures cause them to undergo self-association in solution leading to the formation of micelles, in which the surfactant molecules are put together in close packing so that the total contact area of the hydrophobic groups of the amphiphilic molecules with water is reduced. It is suggested that there is a certain range of concentrations separating the limit below which virtually no micelles are detected and the limit above which virtually all additional surfactant forms micelles. The existence of a critical mixing point above this limit has been suggested from the investigation of phase diagrams and cloud points in solutions of many nonionic amphiphiles in water. Phase diagrams in nonionic micellar solutions of pure synthesized ethylene oxide amphiphiles were established clearly that, above a critical temperature, solutions which contain as little as about a few percent of the amphiphiles separate into two isotropic micelle-poor and micelle-rich phases. A common family of surfactant molecules with the type C_iH_{2i+1}—O—$(CH_2CH_2O)_jH$ is often referred to as C_iE_j. As the critical point of mixing is approached, the concentrations at the two branches of the phase diagram should be more nearly equal. There is no doubt that the first micelles formed in such a dilute solution are globular rather than other different intrinsic shapes, for example, lamella.[1] This suggests phase separation in a micellar solution may be attributed to interactions among micelles, which has expanded the range of interest in critical phenomena greatly. Hence, the investigation of micellar solutions close to a critical mixing point is a special and very fruitful branch in the view point of critical-point universality.[2]

The first approach to examine critical behaviors in a nonionic micellar solution was made in a series of works by Corti, Degiorgio, and co-workers.[3] They found criticallike anomalies of the osmotic susceptibility χ_T and of the long-range correlation length ξ for several nonionic micellar solutions from light-scattering measurements close to their critical points. In a critical micellar solution most workers would probably agree that the critical-point universality could be tested from a fundamental picture of phase separation in a nonionic micellar solution. Indeed, the recently observed values[4-6] of γ for $\chi_T\propto\epsilon^{-\gamma}$ and ν for $\xi\propto\epsilon^{-\nu}$ were in excellent agreement with the universal ones of $\gamma\simeq1.24$ and $\nu\simeq0.63$ for a fluid mixture.

On the other hand, the dynamical behavior in a critical micellar solution is in itself a very interesting problem with respect to the applicability of the critical dynamic theory on the properties of the solution which arise from the presence of micelles due to the dual nature of the amphiphilic molecule. This procedure would be a fundamental step necessary for an understanding of the critical dynamics in a micellar solution from the hypothesis of dynamical universality. This hypothesis has been established clearly in recent works, for example, by Guttinger and Cannell[7] and by Chang and Doiron[8] for a simple liquid, by Burstyn *et al.*[9] for a binary mixture, and by the present authors[10] for a macromolecular solution. The prediction of critical dynamics has been developed by two theoretical treatments of mode-coupling theory and of renormalization-group theory.[11] These two approaches provide a similar profile for many different systems within the same universality class in terms of having an identical critical exponent and an identical dynamic scaling function. The decay rate Γ associated with the diffusive decay of concentration fluctuations can be determined by measuring the time-dependent correlation function of scattered light. The asymptotic behavior in Γ may be represented by $\Gamma\propto k^z$ in the limit $\lim_{T\to T_c}\xi^{-1}=0$, in which the exponent z is the dynamic scaling exponent for the relaxation rate of concentration fluctuations. The asymptotic behavior of the diffusion coefficient $D_c = \lim_{k\to 0}(\Gamma - \Gamma_B)/k^2$ can be represented by

$$D_c = Rk_B T/[6\pi\eta(T)\xi] , \tag{1}$$

where $\eta(T)$ is the shear viscosity and R a universal amplitude ratio associated with the dynamic scaling relation, and $k = 2k_0 \sin(\theta/2)$ the transfer wave number with k_0 and θ being the incident-light wave number and scattering angle, respectively. The universal value of R has been examined theoretically and experimentally from the viewpoint of critical universality. Recently most experimental values for R were in good agreement with that predicted by the mode-coupling equation, whose numerical value is a few percent larger than unity.[12]

The dynamical behavior in a micellar solution close to a critical mixing point has been examined by Wilcoxon and Kaler for $C_{12}E_6$ in water[4] and by the present authors for C_6E_3 in water[6] and $C_{12}E_5$ in water,[13] in terms of the dynamic scaling. These experimental results suggest that the dynamical behavior in a nonionic micellar solution has an obvious kinship with that for a fluid mixture near a critical point. In critical decay-rate measurements the deviations from the theory at higher temperature ranges could be attributed to noncritical background terms.[7–10] As reported in earlier works[4,6,13] the background terms in the measured decay rate might be not as easily estimable for micellar solutions as it was for binary mixtures, if it can depend on an effective molecular weight and/or a shape in aggregate micelles which might depend on temperature and concentration. However, the earlier works for $C_{12}E_6$ in water, C_6E_3 in water, and $C_{12}E_5$ in water indicated that a possibly large discrepancy was reduced even further if the data measured in the region very close to the critical mixing point were compared with the theory. In this work we try to examine the validity of the dynamic scaling for a nonionic micellar solution of tetraethylene glycol *n*-decylether ($C_{10}E_4$) in water in the region very close to its critical mixing point from dynamic light-scattering measurements. For this system we have found three-dimensional Ising values of $\gamma = 1.25 \pm 0.02$ for the osmotic susceptibility and $\nu = 0.63 \pm 0.01$ for the long-range correlation length,[14] including double-scattering corrections proposed recently by Shanks and Sengers.[15]

II. EXPERIMENT

Tetraethylene glycol *n*-decylether ($C_{10}E_4$) synthesized and purified by Nikko Chemical Co. Ltd. (lot no. 7003) and water were employed in this work. The critical mixing point was determined to be $T_c = 19.25\,^\circ\mathrm{C}$ and $C_c = 22 \pm 1$ mg/g from phase equilibrium measurements.[16] Detailed phase diagram for this system has been extensively examined by Lang and Morgan over a wide range of temperature and surfactant concentration, in which a universal-like value of $\beta \simeq 0.36$ has been found for the coexistence curve close to its critical point of mixing.[17] Our value in the critical concentration was in good agreement with their value, but the critical temperature was about 1.2 °C lower than their value. Little noticeable effects were observed in the location of the critical concentration from a significantly large difference in T_c for the present system.

The time-dependent correlation function of scattered light from a critical mixture of $C_{10}E_4$ in water was measured at four different angles of $\theta = 30°$, 60°, 90° and 120° in the temperature range of $1.71 \times 10^{-5} \le \epsilon \le 3.16 \times 10^{-2}$. The sample used here was the same as employed in our previous work for the measurement of the angular distribution of scattered intensity using of a 6-mm-diam cylindrical cell flame sealed under mild vacuum.[14]

The phototube signal was analyzed by a 48-channel, single-clipped correlator (Malvern K7023). The time-dependent correlation function measured in the region very close to the critical mixing point for $C_{10}E_4$ in water showed a systematic deviation from the exponential decay law as will be seen later. Hence, we analyzed our experimental data with the quadratic polynomial by[18]

$$\ln g(t) = K_0 - K_1 t + \tfrac{1}{2} K_2 t^2 . \tag{2}$$

The first term K_0 should be attributed to an arbitrary factor in $g(t)$ normalized at the first channel. The normalized second moment $k_2 = K_2/K_1^2$ is used to characterize the magnitude of the deviations from the exponential decay. If $g(t)$ has the exponential decay, then $K_1 = \Gamma$ and $K_2 = 0$, i.e., $k_2 = 0$. A presence of small deviations from exponential decay law with the size of approximately 3%, which should be attributed to the effect of a frequency-dependent critical viscosity as predicted by Ferrell and co-workers,[19] has been confirmed in the very careful work by Burstyn and Sengers[20] for an approximately isorefractive mixture of 3-methylpentane in nitroethane in the region very close to the critical mixing point. Besides, light scattering measurements in fluid mixtures very close to the critical mixing point are significantly affected by multiple-scattering contributions, which cause apparent deviations from exponential decay in the time-dependent correlation function.[21] Thus, the observed deviations from the exponential decay law could be attributed to two causes, i.e., a small deviation due to a frequency-dependent critical viscosity and multiple-scattering contributions. In light-scattering measurements, possible stray effects, such as the scattered light from dust particles in the sample and from the reflected beam at the glass surface would also cause additional deviations from the exponential decay. To examine these possible effects roughly, we tried to estimate the k_2 value for the polystyrene latex (Dow Chemical Co., lot no. 1A82) following Eq. (2) by measuring the time-dependent correlation function over the experimental angular range. The averaged value over the entire angular range was estimated to be $k_2 = 0.017 \pm 0.009$, which was in reasonable agreement with that expected for our sample of the latex.[22] The quoted error represents a standard deviation. In this case we detected no contributions due to the stray effects such as the reflected light. Phase diagram, sample preparations, light-scattering photometer, the thermometer, and experimental details have been fully described elsewhere.[10,16,23]

III. RESULTS AND DISCUSSION

The correlation function $g(t)$ normalized at the first channel is shown as a function of the channel number for $T_c - T \simeq 5$ mK in Fig. 1, where the symbols of square, triangle, and diamond denote the data measured with sampling times of 25 μs at $\theta=60°$, 11 μs at $\theta=90°$, and 12 μs at $\theta=120°$, respectively. The analysis of the fit in $g(t)$ to the exponential decay law gives systematic deviations as shown in Fig. 2. Hence, the data were fitted to Eq. (2) using K_0, K_1, and K_2 as adjustable parameters. The residuals from this fit are quite random as shown in Fig. 3. This result suggests that our experimental autocorrelation data could be described by a quadratic in t following Eq. (2). This yields $k_2=0.14\pm0.02$ at $\theta=60°$, $k_2=0.26\pm0.04$ at $\theta=90°$, and $k_2=0.12\pm0.02$ at $\theta=120°$ for the normalized second moment, which could be attributed mainly to multiple-scattering contributions. In fact, we observed a significant contribution of multiple scattering in the temperature range of $\epsilon \lesssim 3.4\times10^{-4}$ in the previous work for $C_{10}E_4$ in water.[14] Clearly, these sizes of deviations observed in the present analysis could easily mask a small deviation due to a frequency-dependent critical viscosity. Though it would be desirable to investigate this effect for a nonionic micellar solution through a more careful experiment, here, we will treat this subtle effect as to be included in multiple-scattering contributions. In principle, it is considered that higher-order contributions in multiple scattering should be relatively small when compared with doubly scattered contributions, which allows us to infer the observed deviations in $g(t)$ from the exponential decay to be attributed mainly to the effect of double scattering. It would be worthwhile to confirm the above consideration from a comparison of the observed deviations in $g(t)$ with the theoretical estimation of double scattering. In the double-scattering theory,[21] the time-dependent correlation function $g(t)$ can be given in terms of $\tau=\Gamma t$,

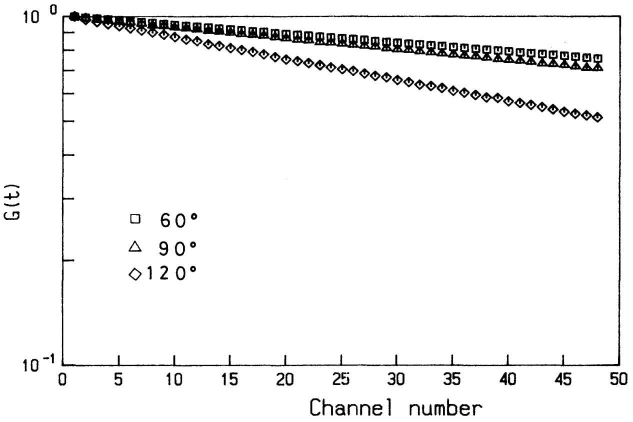

FIG. 1. Experimental autocorrelation data $g(t)$ normalized at the first channel as a function of channel number at $T_c - T \simeq 5$ mK for $C_{10}E_4$ in water. The data correspond to $\theta=60°$ with a sampling time of 25 μs (symbol □), $\theta=90°$ with 11 μs (△), and $\theta=120°$ with 12 μs (◇).

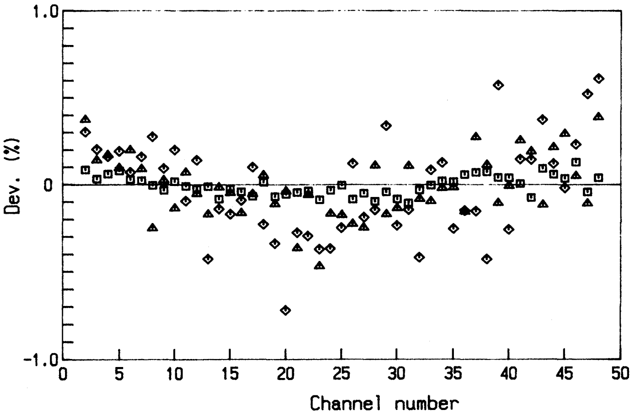

FIG. 2. The deviation from the exponential decay law as a function of channel number, in which each symbol denotes the same data appearing in Fig. 1.

$$\ln g(t) = -(1+\bar{\epsilon}C_1)\tau + \bar{\epsilon}C_2\tau^2F(\tau) , \tag{3}$$

where $\bar{\epsilon}$ is a parameter proportional to the scattering strength of the medium. In the extreme critical region by setting $T-T_c=0$, the coefficients C_1 and C_2 are given by

$$C_1(0) = -0.17\gamma_0^{-1}(\ln\gamma_0 - 2.2) , \tag{4a}$$

$$C_2(0) = 1.12\gamma_0^{-1}(\ln\gamma_0 + 0.13) , \tag{4b}$$

in terms of a parameter $\gamma_0 = 2r/h$, where r is the radius of the sample cell and h the height of the detector. The first moment (4a) represents a correction to the slope, i.e., the decay rate and the second term (4b) represents effects on a curvature. $F(\tau)$ indicates a possible correction factor, which has been evaluated theoretically by the parabolar function in the interval $0 \le \tau \le 2.5$. This term yielded at most a 10% correction in C_2 over the experimental range of $\tau \lesssim 0.37$, whose sizes were within errors estimat-

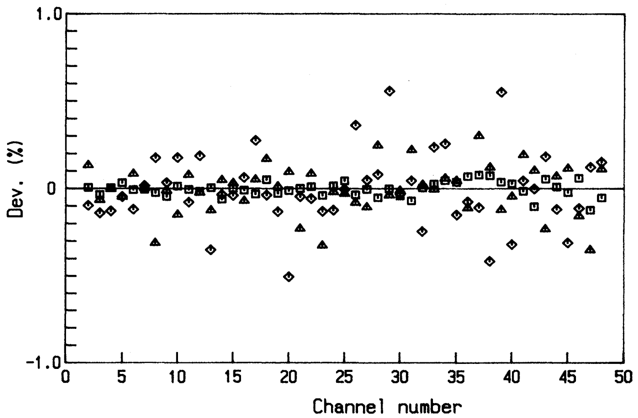

FIG. 3. The deviation from the fit to the quadratic polynomial of Eq. (2) as a function of channel number for the same data as shown in Fig. 1.

ed in k_2. The temperature dependence in C_2 may be estimated in the form

$$C_2(\alpha)=C_2(0)/(1+\alpha+\tfrac{9}{8}\alpha^2) \tag{4c}$$

with $\alpha=(k_0\xi)^{-1}$. If the measured deviations from the exponential decay can be attributed to a double-scattering contribution, then $K_1=(1+\bar{\epsilon}C_1)\Gamma$ and $K_2=2\bar{\epsilon}C_2(\alpha)\Gamma^2$ by setting $F(\tau)=1$. Taking into account the parameter values of $\bar{\epsilon}\simeq0.27$ and $\gamma_0\simeq12$ for $T_c-T\simeq5$ mK we estimated $\bar{\epsilon}C_1(0)\simeq1\times10^{-3}$. This correction to the decay rate is negligibly small, which allows us to set $K_1=\Gamma$. Thus, we obtained $\bar{\epsilon}C_2(\alpha)\simeq6.2\times10^{-2}$, which yields $k_2\simeq0.12$. The numerical values used for the estimation of C_1 and C_2 have been presented in our previous work.[16] The estimated values in k_2 are almost consistent with the measured ones, suggesting that double-scattering contributions may be mainly responsible for the observed deviations from the exponential decay.

The decay rate data for $C_{10}E_4$ in water are plotted on double logarithmic scales against the reduced temperature ϵ in Fig. 4. For $C_{10}E_4$ in water, the decay rate decreases upon approach to the critical mixing point, suggesting the critical slowing down of local fluctuations. According to the original Kawasaki theory[24] the decay rate may become explicitly dependent on k^3 in the critical region. This behavior in the decay rate is shown in Fig. 5 for Γ/k^3 as a function of the scaled variable $k\xi$. The data measured at four different angles collapse well onto a single curve, which has been confirmed experimentally for many fluid mixtures near the critical point. Our experimental autocorrelation data for $C_{10}E_4$ in water suggests that Γ/k^3 should be nearly proportional to a constant value, i.e., $\Gamma\propto k^3$.

On the other hand, the theory of dynamic critical phenomena shows that the decay rate of the fluctuations is related to the shear viscosity in a fluid mixture, which displays a weak enhancement very close to a critical point of mixing. The shear viscosity $\eta(T)$ can be represented by[25]

$$\eta(T)=\eta^B(Q_0\xi)^{x_\eta}=\eta^B(Q_0\xi_0)^{x_\eta}\epsilon^{-\phi}\ , \tag{5}$$

where η^B is the background viscosity, Q_0 the system-dependent wave number, and $\phi=x_\eta\nu$ the critical viscosity exponent. The exponent x_η is related to the dynamic scaling exponent z by the relation $z=3+x_\eta$. The viscosity exponent has been determined for $C_{10}E_4$ in water using a low-shear rotational viscometer in our previous work.[18] The obtained value of $\phi=0.041\pm0.005$ for $C_{10}E_4$ in water yields $x_\eta=0.065\pm0.008$, which is in excellent agreement with recently experimental and theoretical estimations covering a range from 0.05 to 0.065 for a fluid system.[12] In view of the consistency of measured quantities it is of great interest to examine the dynamic behaviors of the present system in terms of the dynamic scaling for a fluid. The scaled decay rates for the measured Γ defined as Γ^* $(=[6\pi\eta(T)/k_BT](\Gamma/k^3))$ are shown in Fig. 6 as a function of $k\xi$. The solid curve in Fig. 6 represents the theoretical prediction expressed as $K(k\xi)/(k\xi)^3$ using

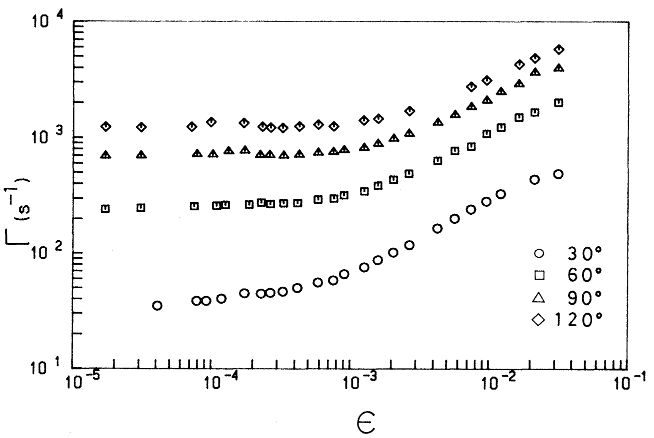

FIG. 4. The measured decay rate data Γ as a function of ϵ at the scattering angles of $\theta=30°$ (symbols ○), $\theta=60°$ (□), $\theta=90°$ (△), and $\theta=120°$ (◇).

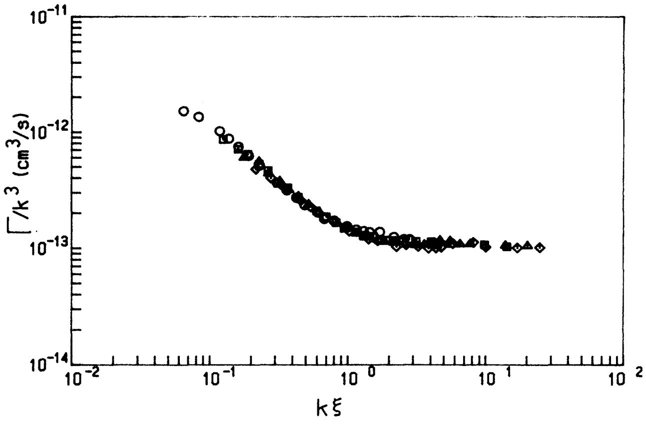

FIG. 5. The plot of Γ/k^3 as a function of $k\xi$.

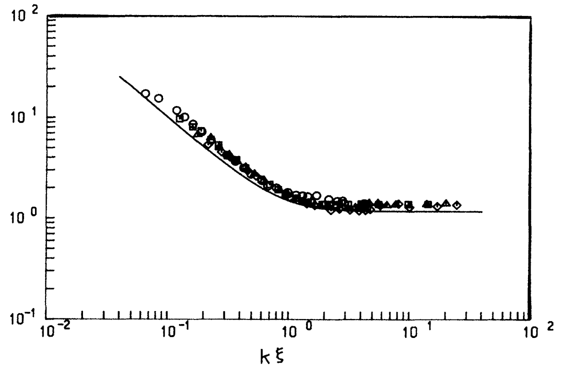

FIG. 6. The scaled decay rate for the measured Γ as a function of $k\xi$, in which the solid curve represents $K(k\xi)/(k\xi)^3$.

the original Kawasaki function defined by

$$K(y)=\tfrac{3}{4}[1+y^2+(y^3-y^{-1})\tan^{-1}y] \;. \qquad (6)$$

The observed deviation from the theory at a small $k\xi$, i.e., a high-temperature region as shown in Fig. 6, could be attributed usually to the noncritical background contribution. In most fluid mixtures the background contribution to the measured decay rates should be negligibly small in the region very close to the critical point of mixing. Besides, a small deviation from the solid curve is observed even further if the data at large $k\xi$ values were compared with the theory as shown in Fig. 6, suggesting a critical enhancement in the viscosity. The relevant formulas associated with the dynamic universal function can all be obtained by modifying slightly the deviation of the original Kawasaki function. In the analysis of dynamic critical phenomena it is customary to subtract a nonsingular background contribution Γ_B from the measured decay rate Γ. Thus, the scaled decay rate may be expressed with the aid of the recently proposed dynamic scaling function by

$$[6\pi\eta(t)/k_B T](\Gamma-\Gamma_B)/k^3=(1/y^3)K(y)S(y)^{x_\eta} \qquad (7)$$

with the correction $S(y)=a_0(1+b^2y^2)^{1/2}$. The coefficient a_0 is related to the universal amplitude ratio R by $R=a_0^{x_\eta}$. The background decay rate Γ_B was evaluated from the expression redefined by Burstyn *et al.*, which includes a system-dependent parameter q_c.[11] This expression for the background contribution was confirmed to be quite reasonable for the critically binary mixtures of 3-methylpentane in nitroethane,[11] isobutyric acid in water, and butylcellosolve in water.[23]. In the present analysis we roughly estimated $q_c \simeq 2.5\times10^6$ cm^{-1}. The scaled decay rate Γ_c^* for the critical contribution Γ_c ($\equiv \Gamma-\Gamma_B$) is shown in Fig. 7 as a function of $k\xi$, in which the solid curve represents the original Kawasaki function. The dotted curve denotes the universal function defined in Eq. (7) with $R\simeq1.03$ and $b\simeq0.1$. It is observed that the systematic deviations from the theoretical prediction appears in our data at each k value in the range of $k\xi \lesssim 0.3$. It would be followed by an estimation in the background term dependent on wave number and temperature. Considerable theoretical efforts have been devoted to describe the thermodynamic and transport properties of fluids in terms of a crossover from the singular behavior at the critical point to the regular behavior far away from the critical point.[26] Unfortunately, the background term would not be as theoretically estimable for micellar solutions as it is for a fluid because of the properties of self-association in solution, which might depend on temperature and concentration. Hence, our discussion has been concerned mainly with a critically dynamic behavior of a nonionic micellar solution in the restricted region very close to the critical mixing point. It should be noted that our decay rate data for $C_{10}E_4$ in water are well represented by the universal scaling function of a fluid in the range of $0.3 \lesssim k\xi \lesssim 26$.

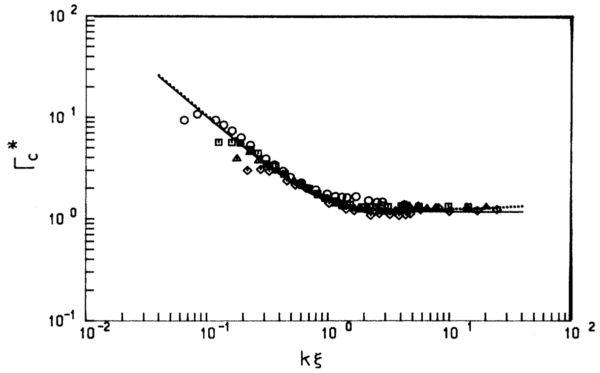

FIG. 7. The scaled decay rate for the critical part, with the background contribution Γ_B subtracted from the measured Γ, as a function of $k\xi$, in which Γ_B has been evaluated from a system-dependent parameter of $q_c \simeq 2.5\times10^6$ cm^{-1}. The solid curve represents the same one as shown in Fig. 6 and the dotted one denotes Eq. (7) with $R\simeq1.03$ and $b\simeq0.1$.

In this work we have examined the dynamical behavior for a critical nonionic micellar solution of $C_{10}E_4$ in water in terms of the dynamic scaling function, which should be independent of the system used. The scaled decay data for $C_{10}E_4$ in water have been found to obey a universal function having a universal amplitude ratio of $R\simeq1.03$ with a correction associated with a small enhancement in the viscosity very close to the critical mixing point. Our experimental findings suggest that critical behaviors in a nonionic micellar solution of $C_{10}E_4$ in water should be principally assigned to the universal class as a fluid in terms of having an identical critical exponent and an associated scaling function, in conjunction with our earlier experimental results for this system, except for the problem in the estimation of noncritical-background contributions.

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