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Dynamical fluctuation of the mesoscopic structure in ternary $C_{12}E_5$–water–n-octane amphiphilic system

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Dynamical fluctuations of the bicontinuous microemulsion and lamellar structures in ternary $C_{12}E_5$–water–n-octane amphiphilic system are studied by means of neutron spin echo (NSE) spectrometry. The decay rates of the time correlation of the concentration were analyzed in terms of three theories: (1) A. G. Zilman and R. Granek, Phys. Rev. Lett. **77**, 4788 (1996), (2) M. Nonomura and T. Ohta, J. Chem. Phys. **110**, 7516 (1999), and (3) R. Granek and M. E. Cates, Phys. Rev. A **46**, 3319 (1992), in the first of which a Langevin equation for membrane plaquettes and in the latter two of which time-dependent Ginzburg-Landau equations for the order parameters are considered. The result shows that the intermediate correlation functions $I(q,t)$ for the ranges of $0<t<15$ ns and $0<q<0.2$ Å^{-1} are well fitted to a stretched exponential function in time, $I(q,t)=\exp[-(\Gamma t)^{2/3}]$, for the bicontinuous microemulsion and the lamellar phases of the same systems with the relaxation rate Γ increasing as q^3 in agreement with theory (1) from which the bending modulus of the membrane κ was estimated. For more restricted ranges of $0<t<5$ ns and $0.05<q<0.15$ Å^{-1} the NSE result can be expressed by an exponential function in time in agreement with theory (2) determined exclusively by hydrodynamic interactions and for extended range of $0<t<10$ ns and $0.03<q<0.15$ Å^{-1} by a nonexponential function in agreement with theory (3), from both of which the effective viscosities η_0 and η_{eff} of the system were estimated. The effective viscosity from the nonexponential η_{eff} is five times greater than that from the simple exponential η_0 that is almost the same as the literature value. The implication of this result is discussed in terms of the effective viscosity η_{eff} that takes into account the renormalization of the bending modulus of the membrane.

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I. INTRODUCTION

Amphiphiles in solution of water and oil self-assemble in a number of basic structures of either disordered or ordered type [1–3]. For example, they form bicontinuous microemulsions in which water and oil are separated from each other by monolayer of amphiphiles, while each domain of water and oil is connected continuously throughout the specimen. In some cases they form a lamellar structure in which water and oil are regularly stacked in two-dimensional layers with a planar monolayer of amphiphiles sandwiched between them. In particular cases where the affinity of the amphiphile toward water and oil is unequal or the amount of water and oil is unbalanced, droplets of oil in continuous water (O/W) or droplets of water in continuous oil (W/O) are formed.

One of such nonionic amphiphilic systems whose phase diagram is well studied is pentaethylene glycol mono-n-dodecyl ether $[=HO(C_2H_4O)_5(CH_2)_{12}H=C_{12}E_5]$/water/$n$-octane ternary system [4,5]. The phase diagram of the same system is shown in Fig. 1. At equal volume fraction of oil and water with more than 15% volume fraction of $C_{12}E_5$ the system exhibits a sequence of structural changes with temperature starting from low-temperature bicontinuous microemulsion phase (LTM), through middle-temperature lamellar phase (MTL) to high-temperature bicontinuous microemulsion phase (HTM). It should be noted that there is a unanimous agreement that HTM phase is bicontinuous in this system, but there is a disagreement whether LTM phase is bicontinuous; Bodet *et al.* believe that LTM becomes O/W droplet phase below 28 °C [5]. However, since the transition from bicontinuous to droplet phase is a very subtle phenomenon, we should be content to interpreting the dynamic behavior of the system irrespective of whether LTM phase is bicontinuous or droplet. Mesoscopic internal structures of the same system were studied by small angle x-ray and neutron scattering (SANS) [6–9].

The structures of such amphiphilic systems are subject to thermal fluctuations and may deform in thermal equilibrium as expressed in the two-point time correlation function of the order parameters $S(q,t)$, such as concentration or volume fraction of the constituents. The decay behavior of the time correlation is observed typically by neutron spin echo (NSE) spectrometry. It probes mesoscopic parameters like the bending modulus κ of the interfacial membrane or the effective viscosity of the system η including the dissipation in the

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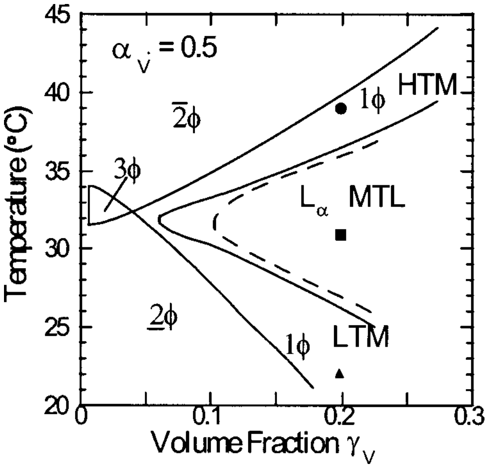

FIG. 1. The phase diagram of the ternary system $C_{12}E_5$–water–*n*-octane in the plane of temperature and volume fraction γ_V of $C_{12}E_5$ at equal volume fraction of *n*-octane and water calculated from Kahlweit *et al.* [4]. Besides lower ($\underline{2\Phi}$) and upper ($\overline{2\Phi}$) two phase and three phase (3Φ), also shown are LTM and HTM isotropic microemulsion phase (1Φ) and lamellar phase MTL sandwiched between them. The samples measured in the present paper are represented by marks of full triangle, square, and circle.

flexible membrane as well as the solvent medium.

Ternary amphiphilic systems of well-defined droplet structures have been studied by means of NSE [10–12], however, very few studies have been reported on ternary amphiphilic systems having bicontinuous microemulsion and lamellar structures so far [13]. Thus the dynamics of such structured systems remain to be clarified. It is the main objective of the present paper to study the dynamics of structured systems of ternary amphiphilic system $C_{12}E_5$–water–*n*-octane by means of NSE spectrometry.

In analyzing the structure and dynamics of microemulsion and lamellar systems three different theories have emerged, (i) microscopic, (ii) Ginzburg-Landau, and (iii) membrane treatments, which are distinguished by different choices of physical quantities of different length scales that characterize the systems [2]. In the present paper we adopt the latter two; in the Ginzburg-Landau theories (ii) order parameters of the system are chosen to describe the behavior of the systems, while in the membrane theories (iii) attention is paid to the monolayer membranes that separate the oil and water regions.

A simple equation was obtained by Zilman and Granek for the dynamic structure factor $S(q,t)$ of membrane phase at large wave numbers q, which reflects the behavior of single membrane disregarding the structure of the system [14,15]. Very recently the decay rate of the correlation of the concentration in ternary systems involving amphiphiles is calculated by Nonomura and Ohta taking into account both van Hove and hydrodynamic interactions [16]. However, their treatment is restricted to the region of small q that enables a simple exponential function in time for the dynamic structure factor.

The dynamical behavior of microemulsion and sponge phase in thermal equilibrium is studied theoretically on a time-dependent Ginzburg-Landau model [17–20]. However, the derived equations for correlation functions $S(q,t)$ are rather complicated to be directly compared with experimental results. Among them Granek and Cates [17] have developed a dynamical theory that is applicable to the sponge phase (L_3 phase) of binary systems and derived analytical equations for dynamic structure. Since the present experiment is performed on a nearly *symmetrical* ternary system, the result may be analyzed in terms of the Granek and Cates theory for *conserved* order parameter ψ [17].

In this paper we therefore analyze the experiment in terms of three theories, (1) Zilman and Granek, (2) Nonomura and Ohta, and (3) Granek and Cates, in the first of which a Langevin equation for membrane plaquettes and in the latter two of which time-dependent Ginzburg-Landau equations for the order parameters are considered. In the theory (2) the range of q is more restricted than the theory (3). The theories (1) and (3) are two alternative approaches for understanding the dynamical behavior of microemulsion and lamellar structures, that are complementary to each other. The theory (2) is a limited case of dynamical theories for rather small range of q, in which a simple exponential decay of the time correlation functions holds.

II. UNDERLYING THEORIES

The dynamical correlation functions $S^{\alpha\beta}(q,t)$ are space Fourier transform of the correlation functions $\langle \delta\phi^{\alpha}(0,0)\delta\phi^{\beta}(r,t)\rangle$ that are calculated for two order parameters represented by α and β, where $\delta\phi^{\alpha}(r,t)$ is the deviation of the volume fraction of αth component from its average value. The superscripts α and β stand for either ψ or ϕ, where $\psi = \phi_w - \phi_o$ represents the difference volume fraction of water ϕ_w from that of oil ϕ_o and $\phi = \phi_s$ represents the volume fraction of amphiphile ϕ_s. For each correlation $S^{\alpha\beta}(q,t)$ a normalized function like $I(q,t) \equiv S(q,t)/S(q,0)$ is defined. Of four correlation functions $S^{\alpha\beta}(q,t)$ with $\alpha\beta = \psi\psi$, $\psi\phi$, $\phi\psi$, or $\phi\phi$, the diagonal correlation $S^{\psi\psi}(q,t)$ corresponds to $I^{b}(q,t)$ that can be obtained from bulk contrast sample and $S^{\phi\phi}(q,t)$ corresponds to $I^{f}(q,t)$ that can be obtained from film contrast sample in experiment.

A. Zilman-Granek theory (single plaquette treatment)

Zilman and Granek [14,15] used the Helfrich-bending free energy to describe membrane undulations in sponge and lamellar phases and derived a Langevin equation. According to their theory, the dynamic structure factor obeys a stretched exponential law in time

$$I(q,t) = \exp[-(\Gamma_Z t)^{\beta}], \tag{1}$$

where Γ_Z is proportional to $q^{2/\beta}$,

$$\Gamma_Z = D_Z q^{2/\beta} \tag{2}$$

and

$$D_Z = \gamma_\alpha \gamma_\kappa (k_B T)^{1/\beta} \kappa^{1-(1/\beta)} \eta_\kappa^{-1}. \tag{3}$$

Here, κ is the bending modulus of the membrane and η_κ the viscosity of the surrounding medium. γ_κ is given by

$$\gamma_\kappa = 1 - 3\ln(q\xi)k_BT/(4\pi\kappa), \tag{4}$$

where ξ is the typical size of the mesoscopic structure of the system. These equations can be applied to two-dimensional membrane cases with an exponent $\beta = 2/3$ and $\gamma_\alpha = 0.025$ and to one-dimensional wormlike micelles cases with $\beta = 3/4$ and $\gamma_\alpha = 0.0056$.

The theory has been confirmed by light scattering experiments for $C_{12}E_5$–water–hexanol ternary system at small q with $\beta = 2/3$ [21,22], but no NSE experiments have been performed at larger q.

B. Nonomura-Ohta theory (microemulsion treatment)

Applying a general theory of Brownian motion, Nonomura and Ohta [16] have shown that the equations of the dynamic structure factor become particularly simple when the amphiphilic systems are nearly *symmetrical*: (i) the volume fractions of water and oil are equal, (ii) the system stays at the hydrophile-lipophile-balance temperature, and (iii) the friction constants for the relative motion of the amphiphile against water and oil are equal. All these symmetrical conditions are satisfied in our present samples $C_{12}E_5$–n-octane–water.

For particular conditions where the system is nearly *symmetrical* and the correlations between the two order parameters ψ and ϕ are almost neglected, the diagonal correlations are given by a single exponential function

$$I^b(q,t) = \exp(-\Gamma_{11}t), \tag{5}$$

$$I^f(q,t) = \exp(-\Gamma_{22}t). \tag{6}$$

Like the decay rate for bulk contrast sample Γ_{11} in their paper, that for film contrast sample Γ_{22} is extended in the present paper heuristically to be given by *hydrodynamic term* mediated by the viscosity η_0 for vanishing *van Hove term* involving Onsager coefficients L_{11} or L_{22}.

$$\Gamma_{11} = k_BTq^2\frac{q_0}{6\pi\eta_0}N(\hat{q},\hat{\kappa}_0), \tag{7}$$

$$\Gamma_{22} = k_BTq^2\frac{\kappa_\phi}{6\pi\eta_0}\Omega(\hat{q}_\phi). \tag{8}$$

The functions $N(\hat{q},\hat{\kappa}_0)$ and $\Omega(\hat{q}_\phi)$ are defined as

$$N(x,y) = \frac{3\sqrt{2}}{8}\,\frac{(x^2-1)^2+y^4}{y^2}\int_0^\pi d\theta\sin^3\theta\left[\frac{\{(x^2\sin^2\theta-1)^2+y^4\}^{1/2}+1-x^2\sin^2\theta}{(x^2\sin^2\theta-1)^2+y^4}\right]^{1/2}, \tag{9}$$

$$\Omega(\xi) = \frac{3}{4\xi^2}\{1+\xi^2+(\xi^3-\xi^{-1})\arctan\xi\}, \tag{10}$$

where x, y, and ξ are arbitrary variables. $\Omega(\xi)$ as given by Eq. (10) is known as Kawasaki function for $\phi\phi$ correlation, while $N(x,y)$ by Eq. (9) is the corresponding counterpart for $\psi\psi$ correlations. The susceptibility for $\psi\psi$ correlation, $\chi_q^{\psi\psi} \equiv S^{\psi\psi}(q,0)$, and that for $\phi\phi$ correlation, $\chi_q^{\phi\phi} \equiv S^{\phi\phi}(q,0)$, are approximated, respectively, in Teubner-Strey and Ornstein-Zernike form,

$$(\chi_q^{\psi\psi})^{-1} = \frac{1}{q_1}[(q^2-q_0^2)^2+\kappa_0^4], \tag{11}$$

$$(\chi_q^{\phi\phi})^{-1} = \kappa_1[q^2+\kappa_\phi^2], \tag{12}$$

where q_0 is the peak position, κ_0^{-1} and κ_ϕ^{-1} the correlation lengths and q_1 and κ_1 numerical factors having the dimension of wave number. The scaled parameters are defined such that $\hat{q} = q/q_0$ and $\hat{\kappa}_0 = \kappa_0/q_0$ in Eq. (7) and $\hat{q}_\phi = q/\kappa_\phi = \hat{q}/\hat{\kappa}_\phi$ where $\hat{\kappa}_\phi = \kappa_\phi/q_0$ in Eq. (8).

This theory has an advantage of allowing an explanation for different behaviors of bulk and film contrast samples particularly at smaller q than q_0, that characterizes the structure of the system.

C. Granek-Cates theory (sponge phase treatment)

Granek and Cates [17] have derived the Ginzburg-Landau equation of *conservative* order parameter ϕ for the sponge phase (L_3 phase) of binary systems. For the high q limit ($2\pi q/\kappa_0 \gg 1$) they obtained a scaling function for the dynamical structure factor for $\phi\phi$ correlation in the form

$$I(q,t) = F(\Gamma_G t), \tag{13}$$

where the decay rate is given by

$$\Gamma_G = \frac{k_BT}{6\pi\eta_{eff}}q^3 \tag{14}$$

and the scaling function by

$$F(z)=\frac{2}{\pi^2}\int_0^\infty dy\int_{-1}^{1}du\frac{\exp\{-(3\pi/8)z[y^3+(1+y^2-2yu)^{3/2}]\}}{1+y^2-2yu}. \quad (15)$$

The effective viscosity η_{eff} in Eq. (14) is used because it is a composite viscosity determined not only by the viscosity of the solvent consisting of oil or water but also by the effect of the dissipation in the membrane composed of the amphiphile in binary system in the original paper of Granek and Cates. The amphiphilic membrane has a bending modulus that is subject to the renormalization corresponding to the size scale of the deformation. The Eqs. (13), (14), and (15) are applied to the dynamical structure factor not only for $\phi\phi$ correlation but also $\psi\psi$ correlation in the present paper, since there is no other suitable candidate available to explain the $\psi\psi$ correlation.

We found that the function $F(z)$ is best approximated by a stretched exponential function

$$F(z)\simeq\exp[-(az)^{\beta'}], \quad (16)$$

with constants $a=2.6213$ and $\beta'=0.517\,06$ for the range of $0<z<1$.

The function $F(z)$ as given by Eqs. (13) and (16) are shown in Fig. 2. In the same figure also shown are an approximate stretched exponential function in a form similar to Eq. (1) with $\beta=2/3$,

$$F(z)\simeq\exp[-(a'z)^{2/3}], \quad (17)$$

with a constant $a'=3.4487$ for the range $0<z<0.2$ and a simple exponential function in a form similar to Eqs. (5) and (6),

$$F(z)\simeq\exp[-(a''z)], \quad (18)$$

with $a''=6.1978$ for the range $0<z<0.1$. These approximate functions Eqs. (16), (17), and (18) to the nonexponential function $F(z)$ in Eq. (13) are used in the later discussion.

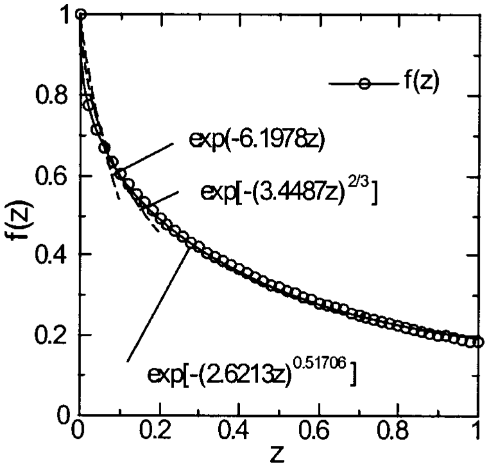

FIG. 2. The nonexponential function $F(z)$ in Eq. (15) by Granek-Cates theory (open circles) that may be approximated by a stretched exponential function Eq. (16) for the range $0<z<1$. The same function may be approximated by a simple exponential function Eq. (18) in the range $0<z<0.1$ and by a stretched exponential function Eq. (17) with a power $\beta=2/3$ in the range $0<z<0.2$.

III. EXPERIMENT

A. Phase behavior

In order to study the dynamics in membrane undulations, NSE experiments were carried out on bulk and film contrast samples in the ternary system $C_{12}E_5$–*n*-octane–water at equal volume fraction of octane and water for volume fraction 0.2 of $C_{12}E_5$, which represents a sequence of low-temperature microemulsion/middle-temperature lamellar/high-temperature microemulsion phase with increasing temperature [4,5] as shown in Fig. 1. The LTM and HTM phases have a bicontinuous structure that divides the volume into two multiply-connected, interpenetrating subvolumes made of oil and water, each of them physically continuous, but separated by surfactant membranes from each other.

B. Sample preparation

For sample preparation, 99.7% pure $C_{12}E_5$ was purchased from Tokyo Chemical Co., 99% *n*-octane from Aldrich Chemical Co., 99 at. % deutrated n-octane from Isotec Inc., and 99.9 at. % D_2O from Isotec Inc. These materials were used without further purification. In the ternary system $C_{12}E_5$–*n*-octane–D_2O at equal volume fractions of octane and D_2O with volume fraction 0.2 of $C_{12}E_5$, we used protonated *n*-octane for the bulk contrast sample and deuterated *n*-octane for the film contrast sample.

C. NSE experiment

The experimental condition is almost same as the one already reported [23,24]. The NSE experiments were carried out using the NSE spectrometer at C2-2 port of JRR-3M, JAERI [25–27] over the range $0.03<q<0.15$ Å^{-1} and also MESS at LLB in C. E. Saclay in order to extend q higher than 0.18 Å^{-1} up to 0.25 Å^{-1} on the same film contrast sample. Silica gel and Grafoil were used to measure the resolution function of the spectrometers. Neutrons with wavelength $\lambda=5.9$ Å (full width at half maximum of its resolution $\Delta\lambda/\lambda=15\%$) and $\lambda=7.14$ Å ($\Delta\lambda/\lambda=18\%$) were used at JRR-3M and neutrons with $\lambda=6.0$ Å ($\Delta\lambda/\lambda=18\%$) at MESS. We have chosen three temperatures; 22 °C corresponding to LTM phase, 31 °C to MTL and 39 °C to HTM for the $C_{12}E_5$–water–*n*-octane system.

D. SANS experiment

The parameters q_1, q_0, κ_0, κ_1, and κ_ϕ of the partial structure functions in Eqs. (11) and (12) were determined from a SANS experiment at the SANS-U spectrometer at

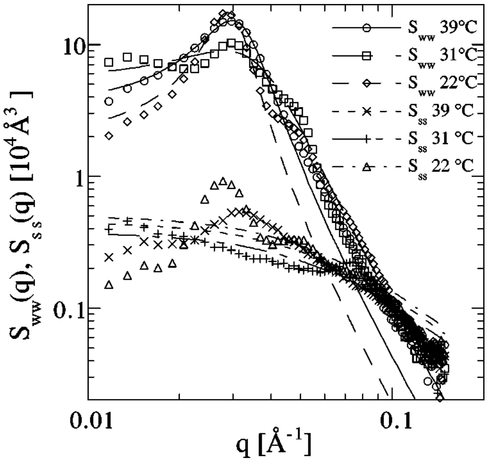

FIG. 3. The partial structure functions $S_{ww}(q)$ in place of $\chi_q^{\psi\psi}$ in Eqs. (11) and $S_{ss}(q)$ in place of $\chi_q^{\phi\phi}$ in Eqs. (12) at different temperatures determined from the SANS experiment. The approximate values of the parameters q_1, q_0, κ_0, κ_1, and κ_ϕ are determined from the fitting to Eqs. (11) and (12).

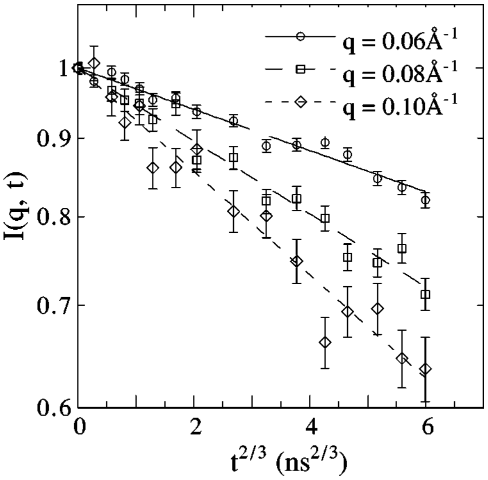

FIG. 4. Normalized intermediate correlation functions $I(q,t)$ obtained from the NSE experiments at JRR-3M in the low-temperature bicontinuous microemulsion phase of the bulk contrast sample of the $C_{12}E_5$–n-octane–water system at 21 °C (open circles, $q=0.06$ Å $^{-1}$; open squares, $q=0.08$ Å $^{-1}$; and open diamonds, $q=0.10$ Å $^{-1}$). The lines are fitting curves to Eq. (1) with $\beta=2/3$ in Zilman-Granek theory.

C1-2 port of JRR-3M, JAERI [28] using bulk and film contrast samples at room temperature. We used the partial structure functions of water-water correlation $S_{ww}(q)$ in place of $S^{\psi\psi}(q,0)$ and surfactant-surfactant correlation functions of $S_{ss}(q)$ in place of $S^{\phi\phi}(q,0)$. The approximations by Eqs. (11) and (12) to them are shown in Fig. 3. The approximate values of the parameters q_1, q_0, κ_0, κ_1, and κ_ϕ are determined from the approximations and are given in Table I.

IV. EXPERIMENTAL RESULTS

A. Analysis with Zilman-Granek theory

The results of our present NSE experiments analyzed in terms of Zilman-Granek theory have been published previously [23,24]. The dynamic structure factor obeys a stretched exponential law of Eq. (1) with $\beta=2/3$ as shown in Fig. 4 for the $C_{12}E_5$–water–n-octane system over the range $0<t<15$ ns and $0.03<q<0.17$ Å $^{-1}$. The results are independent not only whether the system is in microemulsion, lamellar, or droplet phase, but also whether the samples are in bulk or film contrast, because the behavior reflects only the single-membrane dynamics. The relaxation rate Γ_Z obtained from the fitting to Eq. (1) with an index $\beta=2/3$ are shown in Fig. 5 over the range $0.03<q<0.17$ Å $^{-1}$. The value of Γ_Z increased as q^3 particularly well at q higher than 0.08 Å $^{-1}$. These results support the theory presented by Zilman and Granek [14,15]. Equation (1) with an index $\beta=3/4$ was tested by Seto *et al.* for a network of wormlike micelles $C_{16}E_7$–heavy water binary system and a good agreement was obtained [29,30].

Figure 6 shows that the bending modulus κ estimated in the bicontinuous microemulsion and the lamellar phases of the $C_{12}E_5$–water–n-octane system using Eq. (3), where we put $\gamma_\kappa=1$ and used three times the value of average solvent viscosities for $\eta_\kappa(=3\eta_{solv})$ taking the local dissipation at the interface between the membrane and the solvent into consideration in the same way as Farago *et al.* did in their study of dynamics in droplet microemulsions [13]. Here η_{solv} is the simple average of the solvent viscosity, the average viscosity of heavy water and protonated n-octane for bulk contrast sample, and the average viscosity of heavy water and deuterated n-octane for film contrast at different temperatures.

The value of κ estimated is nearly the same as that estimated from dynamical light scattering in the $C_{12}E_5$–hexanol–water system at room temperature [21,22]. The value of κ in Fig. 6 decreases monotonically with increasing temperature independently of the mesoscopic structure and the scattering contrast. At q lower than 0.08 Å $^{-1}$, the decay rate Γ_Z deviates from the q^3 dependence and depends on the mesoscopic structure and the scattering contrast. Since the Zilman and Granek theory is considered to be

TABLE I. The parameters in the partial structure functions Eqs. (11) and (12) for $C_{12}E_5$–water–n-octane from SANS experiment.

Temperature	Bulk contrast				Film contrast		
(°C)	q_1 (Å $^{-1}$)	q_0 (Å $^{-1}$)	κ_0 (Å $^{-1}$)	$\hat{\kappa}_0=\kappa_0/q_0$	κ_1 (Å $^{-1}$)	κ_ϕ (Å $^{-1}$)	$\hat{\kappa}_\phi=\kappa_\phi/q_0$
39 [HTM]	0.029	0.030	0.021	0.70	0.045	0.088	2.9
31 [MTL]	0.049	0.030	0.027	0.90	0.051	0.085	2.8
22 [LTM]	0.017	0.030	0.018	0.60	0.043	0.079	2.6

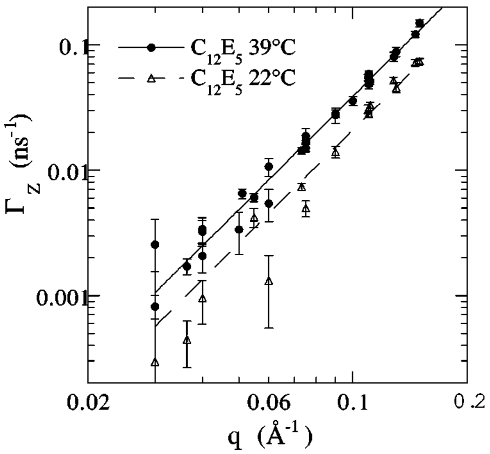

FIG. 5. The dependence of the relaxation rate Γ_Z on q obtained from the fitting to Eq. (1) with $\beta = 2/3$ in Zilman-Granek theory in the LTM (open triangles) and HTM phase (full circles) of the film contrast sample of the $C_{12}E_5$–n-octane–water system. The lines are fitting curves to Eq. (2) with $\beta = 2/3$.

applicable to the dynamics of a single membrane at q higher than $1/\xi$ where ξ is a typical size of the mesoscopic structure, the collective motions of the membranes that are not considered in the Zilman and Granek theory may play an important role in the dynamics at lower q.

B. Analysis with Nonomura-Ohta theory

The result of the NSE measurement analyzed with Nonomura-Ohta theory has been published elsewhere [32]. The normalized correlation functions $I^b(q,t)$ and $I^f(q,t)$ using bulk and film contrast samples, respectively, were calculated. An example is shown in Fig. 7 at the temperature 39 °C for bulk sample. Since the theory of Nonomura and Ohta applies well to small correlation time t and small wave number q, we have restricted to the data in the ranges of $0 < t < 5$ ns and $0.05 < q < 0.15$ Å^{-1} to obtain the decay rate Γ_{11} and Γ_{22} in Eqs. (5) and (6) of simple exponential dependence. Deviations from the simple exponential decay at larger t and larger q is evident as shown in Fig. 7. The deviations is not surprising because of the inherent character of the Nonomura-Ohta theory that should be applicable at smallest q limit.

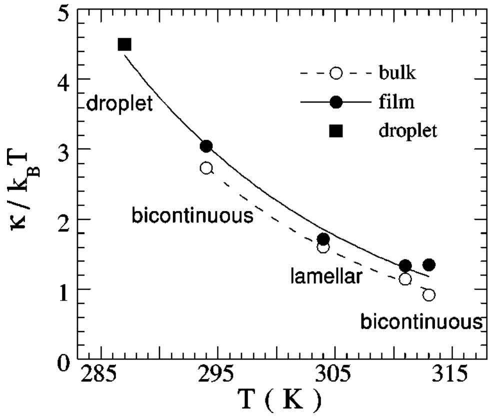

FIG. 6. The dependence of bending modulus κ of the membrane on the temperature T obtained from NSE experiments of the bulk (open circles) and film sample (full circles) in the $C_{12}E_5$–n-octane–water system using Eqs. (2) and (3) with $\beta = 2/3$ in Zilman-Granek theory. κ in the droplet phase at 287 K is the result obtained by Farago *et al.* [13]. The lines are a guide for the eye.

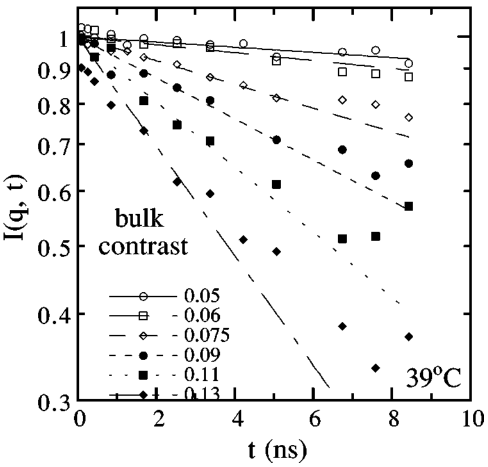

FIG. 7. Correlation function $I(q,t)$ of bulk contrast sample $C_{12}E_5$–water–n-octane at 39 °C for a range of $0 < t < 9$ ns. The insert shows the wavenumber q in unit of Å^{-1}. The full or dashed lines are fitting to a simple exponential Eq. (5) using data for a smaller range $0 < t < 5$ ns in Nonomura-Ohta theory. Deviations from the simple exponential decay at larger t and larger q are evident.

The decay rates for bulk contrast sample Γ_{11} and that for film contrast sample Γ_{22}, respectively, are calculated from the correlation functions $I^b(q,t)$ and $I^f(q,t)$. The result at 39 °C is shown in Fig. 8. Similar results were obtained at 31 °C and 22 °C.

We have fitted the decay rate data Γ_{11} and Γ_{22} to Eqs. (7) and (8). For this analysis we have calculated the functions $N(x,y)$ and $z\Omega(x/z)$ as a function of x, where parameters $x \equiv \hat{q} = q/q_0$, $y \equiv \hat{\kappa} = \kappa/q_0$, with particular values of $y = 0.5$, 0.7, 0.9 and $z \equiv \hat{\kappa}_\phi = \kappa_\phi/q_0$ with particular values of

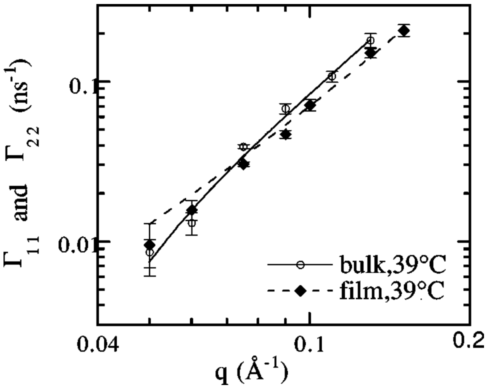

FIG. 8. The decay rates Γ_{11} and Γ_{22} from bulk and film contrast samples of $C_{12}E_5$–water–n-octane at 39 °C in double logarithmic scale. The full and dotted curves are fitting to Eqs. (7) and (8) in Nonomura-Ohta theory.

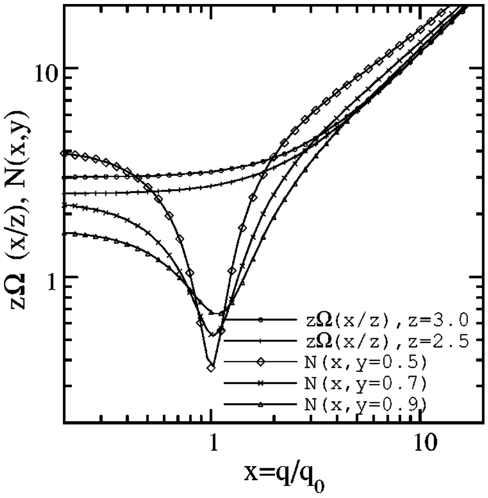

FIG. 9. The functions $N(x,y)$ and $z\Omega(x/z)$ as a function of $x \equiv \hat{q} = q/q_0$ proportional to the decay rate for bulk and film contrast, where $y \equiv \hat{\kappa}_0 = \kappa_0/q_0$ and $z \equiv \hat{\kappa}_\phi = \kappa_\phi/q_0$ in Eqs. (7) and (8).

$z = 2.5$, 3.0 as shown in Fig. 9. We approximated these functions by ninth order polynomials of x and used them for fitting to the experimental values.

It is to be stressed that there are no adjustable parameters except viscosities η_0. The viscosities η_0 are thus obtained from the fitting to the decay rate of the NSE data for bulk sample Γ_{11} and that for film contrast sample Γ_{22}, respectively, at different temperatures. The obtained values of viscosities η_0 are given in Table II and displayed in Fig. 10. These values are about ten times those for light and heavy water and n-octane and are in agreement with a literature value for the amphiphilic system with one-third amphiphile concentration [4], in which a value of kinematical viscosity $\nu = 4.8$ mm$^2/s$ at 31.7 °C is given from the static measurement for a similar bicontinuous system with 7% weight fraction (6.2% volume fraction) of $C_{12}E_5$, which can be converted to a viscosity value of 4.1 mPa s.

C. Analysis with Granek-Cates theory

The normalized correlation functions $I^b(q,t)$ and $I^f(q,t)$ for extended ranges of $0 < t < 10$ ns and $0.03 < q < 0.15$ Å^{-1} were compared with Eq. (13). For this analysis we have used $F(z)$ as a function of z by the approximation Eq. (16) in a form of stretched exponential function with a power of $\beta' = 0.517\,06$ over the range $0 < z < 0.3$. The decay rate Γ_G's were then calculated for the bulk and film contrast samples. The result of the fitting to Eq. (13) for the film contrast sample at 39 °C is shown in Fig. 11. The values of the decay rate Γ_G are shown in Fig. 12 for film contrast samples at different temperatures, where the expected linear dependence on q^3 is rather unsatisfactory. Similar data were obtained for the bulk contrast sample. The calculated values of the effective viscosities η_{eff} from the largest value of q that were used are given in Table II and displayed in Fig. 10. As in the analysis with Nonomura-Ohta theory, there are no adjustable parameters except viscosities η_{eff}. These values are about 12 times η_κ obtained from the analysis with Zilman-Granek theory and about five times η_0 obtained from the analysis with Nonomura-Ohta theory.

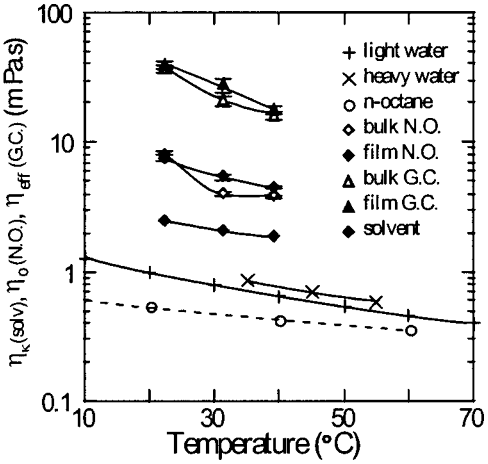

FIG. 10. The viscosities η_κ in Zilman-Granek theory, η_0 in Nonomura-Ohta theory, and η_{eff} in Granek-Cates theory of $C_{12}E_5$–water–n-octane involved in the present NSE analysis. They are compared with the viscosity η of other simple liquids; light and heavy water and n-octane.

It should be noted that viscosities η_0 were determined from Γ_{11} and Γ_{22} for the whole range of q that were used in analysis, while viscosities η_{eff} were determined from Γ_G at mostly the largest q that were used. At this value of q the condition of large q limit, $2\pi q/\kappa_0 \gg 1$, required for the applicability of Eq. (13) is well satisfied, because $q \sim 0.1$ Å^{-1} and $\kappa_0 \sim 0.021$ Å^{-1}. In this sense we can say that viscosities η_{eff} from Granek-Cates theory are determined at larger q than viscosities η_0 from Nonomura-Ohta theory.

In our present analysis in terms of Granek-Cates theory, we have picked out only Eq. (13), i.e., the ''critical'' term, which is strongly nonexponential and describes the response of the membrane to the correlations in the oil and water regions. For noncritical systems (as the one used here) there

TABLE II. Various viscosities $\eta_\kappa(=3\eta_{solv})$, η_0, and η_{eff} of $C_{12}E_5$–water–n-octane involved in the present NSE analysis.

	Zilman-Granek theory		Nonomura-Ohta theory		Granek-Cates theory	
Temperature (°C)	Bulk contrast η_κ (mPa s)	Film contrast η_κ (mPa s)	Bulk contrast η_0 (mPa s)	Film contrast η_0 (mPa s)	Bulk contrast η_{eff} (mPa s)	Film contrast η_{eff} (mPa s)
39 [HTM]	2.04 ± 0.03	2.22 ± 0.03	3.95 ± 0.08	4.64 ± 0.09	16.5 ± 1.0	18.2 ± 1.1
31 [MTL]	2.22 ± 0.03	2.40 ± 0.03	4.12 ± 0.20	5.57 ± 0.33	21.6 ± 1.8	28.3 ± 3.1
22 [LTM]	2.43 ± 0.03	2.64 ± 0.03	8.14 ± 0.66	7.74 ± 0.39	38.5 ± 2.7	41.0 ± 3.1

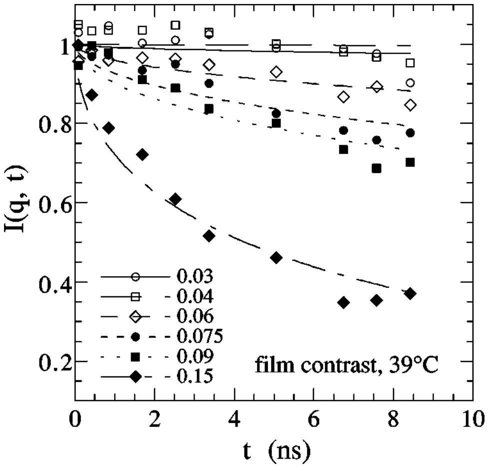

FIG. 11. Correlation function $I(q,t)$ of film contrast sample $C_{12}E_5$–water–n-octane at 39 °C for a range of $0<t<9$ ns. The inset shows the wave number q in unit of Å $^{-1}$. The various lines are fitting to a nonexponential function $F(z)$ in Eq. (13) of Granek-Cates theory.

is another term, describing the self-correlations in the surfactant. Its decay is exponential in time, and it can be nonnegligible. Fitting the experimental data to the full expression can be indeed quite a difficult job, but possible sometimes [31]. Moreover, the Granek-Cates theory describes primarily the dynamics at long wavelengths, $q<q_0$, so its use here for data in the region $q>q_0$ is a bit away from its region of applicability. In view of these, it is not too surprising that the fit to the Granek-Cates theory is not quite good.

V. DISCUSSIONS

A. Comparison of the three analyses

In our study on single-membrane dynamics in terms of Zilman-Granek theory (1) we used a value of viscosity three times the simple average of those for the solvent ($\eta_\kappa =3\eta_{solv}$). The result of our study on microemulsion dynamics in terms of Nonomura-Ohta theory (2) shows that the value of the effective viscosity is almost the same as literature value. It is eight times the simple average of those for the solvent and is 2.6 times those for Zilman-Granek theory ($\eta_0 \simeq 2.6\eta_\kappa = 8\eta_{solv}$). The viscosity obtained from our study in terms of Granek-Cates theory (3) that gives the nonexponential decay shows that the effective viscosity is five times greater than that from Nonomura-Ohta theory ($\eta_{eff} \simeq 5\eta_0 \simeq 12\eta_\kappa = 36\eta_{solv}$).

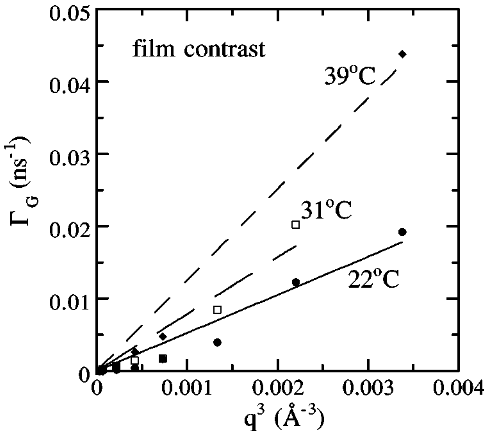

FIG. 12. The decay rates Γ_G from the film contrast samples of $C_{12}E_5$–water–n-octane at three temperatures 22, 31, and 39 °C as a function of q^3. The full or dotted curves are fittings to Eq. (14) in Granek-Cates theory determined mostly at highest q because of the deviation from the q^3 dependence.

To summarize, the three viscosities involved in the present analyses are (1) $\eta_\kappa(=3\eta_{solv})$ from Zilman-Granek, (2) $\eta_0(\simeq 2.6\eta_\kappa)$ from Nonomura-Ohta, and (3) η_{eff} ($\simeq 5\eta_0$) from Granek-Cates, where η_{solv} is the simple average of the solvent viscosity. These values are listed in Table II and plotted in Fig. 10.

It is to be noted that all the three theories have a common character that the decay rates Γ's are proportional to q^3 over the range of q in our present measurement. However, the prefactor to q^3 includes two physical constants of the system, i.e., bending modulus κ, and viscosity η_κ in Eq. (3) of Zilman-Granek theory. This is in contrast to the other two theories where the prefactors include only one physical constant: viscosities η_0 in Eqs. (7) and (8) of Nonomura-Ohta theory and η_{eff} in Eqs. (14) of Granek-Cates theory. This fact means that the viscosities in the latter two theories have something to do to compensate the effect of bending modulus, i.e., dissipations in the membranes. This is the main reason that the viscosities in the latter two theories are much larger than that in Zilman-Granek theory.

B. Relations between the three viscosities

In view of the three alternative analyses, all of which could reproduce the experimental normalized correlation function $I(q,t)$, the stretched exponential in Eq. (1) by Zilman-Granek with an exponent $\beta=2/3$ may be equated with the approximated stretched exponential function by Granek-Cates Eq. (17) with a constant $a'=3.4487$ such that

$$\Gamma_Z \simeq a'\Gamma_G \tag{19}$$

that leads to

$$\eta_{eff} \simeq \frac{a'\eta_\kappa}{6\pi\gamma_\alpha\gamma_\kappa}\left[\frac{\kappa}{k_BT}\right]^{1/2} \tag{20}$$

relating η_{eff} to η_κ and κ. For $\gamma_\alpha=0.025$, $\gamma_\kappa=1$, and $\kappa/k_BT=3$, we get $\eta_{eff}=12.7\eta_\kappa$. This rough estimate demonstrates the reason for 12 times larger viscosity obtained from the Granek-Cates theory than that obtained from Zilman-Granek theory.

Similarly, $I(q,t)$ in terms of simple exponential by Nonomura-Ohta, Eqs. (5) and (6) may be equated with the approximated simple exponential function by Granek-Cates Eq. (18) with a constant $a''=6.1978$ such that

$$\Gamma_{11} \sim \Gamma_{22} \simeq a''\Gamma_G \tag{21}$$

that leads to

$$\eta_{eff} \simeq a'' \eta_0 \frac{\hat{q}}{N(\hat{q},\hat{\kappa}_0)} \simeq a'' \eta_0 \frac{\hat{q}}{\hat{\kappa}_\phi \Omega(\hat{q}/\hat{\kappa}_\phi)} \tag{22}$$

relating η_{eff} to η_0, where $\hat{\kappa}_\phi = \kappa_\phi / q_0$. Since our numerical calculations show approximately that $\hat{q}/N(\hat{q},\hat{\kappa}_0) \sim \hat{q}/[\hat{\kappa}_\phi \Omega(\hat{q}/\hat{\kappa}_\phi)] \simeq 1/1.3 = 0.77$ [32] with the values $\hat{\kappa} = 0.7$ and $\hat{\kappa}_\phi = 2.5$ for the range $2 < \hat{q} < 4$ as shown in Fig. 9, we get $\eta_{eff} = 4.8\eta_0$. This rough estimate demonstrates the reason for five times larger viscosity obtained from the Granek-Cates theory than that obtained from Nonomura-Ohta theory.

C. Possible origins of the different viscosities

A possible interpretation for the three different viscosities involved in the present analyses can be based on the renormalization theory of viscosities [33,34] not quantitatively but qualitatively as follows. The key concept is that the bending modulus for larger wave vector q (i.e., smaller length scale) is larger and vice versa. This point must be reflected in the viscosity of the theory in which the bending modulus is not explicitly incorporated.

In Zilman-Granek theory the single membrane characterized by the bending modulus κ is thought to be embedded in the solvent of infinite extent. So it deals with the dilute limit of a membrane plaquette as in the same way as Milner and Safran's theory [10] deals with a single droplet. It is not a coincidence that both our analysis in terms of Zilman-Granek theory and Farago's analysis [13] in terms of Milner and Safran's theory took the viscosity of the dense system to be three times the average viscosity of the solvent and obtained reasonably good results. Therefore the local dissipation at the interface between the membrane and solvent in the dense system may be taken into account by the factor 3 in $\eta_\kappa = 3\eta_{solv}$.

In Nonomura-Ohta theory, where the simple exponential holds, the larger length scale corresponding to the smaller q than the other theories is involved. Therefore the bending modulus κ at this large length scale does not come into play so much, because of the smaller value of κ at larger length scale due to the renormalization, the bending modulus for smaller wave vector q is smaller. However, the whole system is affected only by the hydrodynamic fluctuation penetrating many interfaces between the membrane and the solvent. Thus the local dissipation at many interfaces between the membrane and solvent may be taken into account by the factor 2.6 in $\eta_0 \simeq 2.6\eta_\kappa$. It is to be stressed that this value of η_0 is very close to the literature value of viscosity in a similar system [4] as described before; it does not represent the viscosity of the solvent surrounding the membrane but represents the macroscopic viscosity of the system as a whole.

In Granek-Cates theory the smaller length scale corresponding to the larger q than Nonomura-Ohta theory is involved. Therefore the bending modulus κ at this length scale comes into play more; because of the larger value of κ at smaller length scale due to the renormalization, the bending modulus for larger wave vector q is larger. The whole system is affected not only by the hydrodynamic fluctuation at small length scale but also by the dissipation in the many membranes that have a large bending modulus κ. Therefore the larger effective viscosity from Granek-Cates theory as compared with the Nonomura-Ohta theory may be taken into account by the factor 5 in $\eta_{eff} \simeq 5\eta_0$.

VI. CONCLUSIONS

We have analyzed the intermediate correlation functions $I(q,t)$ obtained from NSE experiment in terms of the three dynamic theories: (1) Zilman and Granek, (2) Nonomura and Ohta, and (3) Granek and Cates theories. The result shows that the intermediate functions $I(q,t)$ for the range of $0 < t < 15$ ns and $0.03 < q < 0.2$ Å^{-1} are well fitted to a stretched exponential function in time $I(q,t) = \exp[-(\Gamma t)^{2/3}]$ for the bicontinuous microemulsion and the lamellar phases of the same system with the relaxation rate Γ increasing as q^3 in agreement with the theory (1) from which the bending modulus of the membrane κ was estimated. For more restricted range of $0 < t < 5$ ns and $0.05 < q < 0.15$ Å^{-1} the NSE result can be expressed by a simple exponential function in time in agreement with the theory (2) determined exclusively by hydrodynamic interactions and for intermediate range of $0 < t < 10$ ns and $0.03 < q < 0.15$ Å^{-1} by a nonexponential function in agreement with the theory (3), from both of which the effective viscosities of the system η were estimated.

The effective viscosity from the nonexponential η_{eff} is five times greater than that from the simple exponential η_0 that is almost the same as the literature value. The same viscosity η_{eff} is twelve times greater than that from the Zilman-Granek theory η_κ. The larger effective viscosity η_{eff} from Granek-Cates theory may be understood as the natural consequence of the renormalization of the bending modulus at larger q as compared with the result from Nonomura-Ohta theory, since the effective viscosity is a physical quantity determined not only by the viscosity of the solvent but also by the bending modulus of the membrane that is subject to the renormalization. These three analyses make up a coherent picture of the dynamical fluctuation of the mesoscopic structure in the ternary amphiphilic system.

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