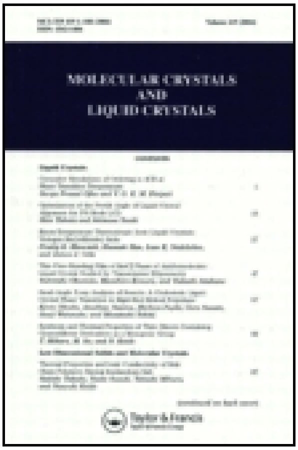

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Dynamic Light Scattering in a Sponge Phase of a Nonionic Surfactant

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Dynamic Light Scattering in a Sponge Phase of a Nonionic Surfactant

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The fluctuation of bilayers in the sponge (L_3) phase of the binary mixture of a nonionic surfactant, pentaethylene glycol dodecyl ether ($C_{12}E_5$), and water is studied by the dynamic light scattering spectroscopy. In concentrated solution, the autocorrelation function of the scattered light intensity shows almost a single exponential decay and the inverse of correlation time Γ is proportional to the square of scattering wavevector q. In dilute solution, the autocorrelation function shows a stretched exponential decay and the dispersion of Γ shows a crossover behavior from $\Gamma \propto q^2$ to $\Gamma \propto q^3$ as q increases. It is found that the dispersions of Γ *at* various concentrations and temperatures can be scaled into the universal curve. The results for dilute solution are compared with a recent theory concerning to the thermal fluctuation of membranes.

Keywords: nonionic surfactant; sponge phase; dynamic light scattering; thermal fluctuation; bilayers; bending modulus

INTRODUCTION

The surfactant molecules in solution aggregate into various kinds of objects, such as a sphere, a rod, a thread and a sheet[1]. As the concentration of surfactant increases, these objects spontaneously form more ordered structures such as hexagonal and lammelar phases. These ordered structures composed of surfactants are good examples of self-organizing systems and models of living systems. For the systems consisting of the soft low-dimensional objects such as threads and bilayers, the thermal fluctuation is important to determine their structure and dynamics in the three dimension. The dynamical properties of one-dimensional flexible objects such as polymers are extensively studied[2].

Quite recently, the structure and dynamics of the system composed of two dimensional aggregates such as polymerized membranes and fluid membranes of surfactants are also intensively studied theoretically and experimentally[3].

It is known that there are some kinds of structures made up of surfactant bilayers in solution. One of them is vesicle (L_1) phase where a bilayer forms a sphere enclosed the solvent inside. The other one is lamellar (L_α) phase which is a lyotropic smectic liquid crystalline phase and its structure is similar to that of the smectic A phase of thermotropic liquid crystals. At more dilute or higher temperature region bounded by the L_α phase in phase diagram, the isotropic phase made up of bilayers called sponge (L_3) phase has been recently discovered in some surfactant systems[4]. In this phase, the bilayers form multi-connected or sponge-like isotropic structure and this bicontinous structure is confirmed by small-angle neutron scattering (SANS)[5-7], electrical conductivity[5-7] and the direct observation by freeze fracture electron microscope[8]. Through the sponge phase is an isotropic phase, but a certain characteristic length scale is observed in the SANS spectra. This length is a little bit longer than the repeat distance of membranes in the L_α phase at the same concentration[7] and is regarded as the interlayer distance or the size of sponge cell in the L_3 phase.

The most researches on this phase are focused on its characteristic structure and the rather complex ternary or quasi-quaternary ionic surfactant systems are chosen as objects of study. In this paper, we studied the dynamical property of the sponge phase in a simple binary mixture of a nonionic surfactant and water by using dynamic light scattering spectroscopy. We mainly studied the extremely dilute solution where we can detect the fluctuation of a single membrane and compared the obtained results with the recent theory on the dynamics of membranes with finite size and rigidity at random orientations[9].

EXPERIMENT

A scattered light of He-Ne laser beam from a cylindrical sample cell was collected by the multi-mode optical fiber after passing through two focusing lens and 0.1-mm-diameter pinhole and fed into the photomultiplier. The intensity of the scattered light was photon-counted and its autocorrelation function was calculated and averaged on a personal computer. The scattering geometry used in our experiment was in homodyne regime. The obtained autocorrelation function $g(t)$ is analyzed as a stretched exponential decay function,

$$g(t) = 1 + A\exp\left[-2(\Gamma t)^{\beta}\right], \tag{1}$$

where the decay rate Γ is the inverse of correlation time τ, A is constant which depends on the experimental condition and β is the parameter characterizing the broadness of the distribution of correlation times. By changing the direction of the detector, we measured the wavenumber q dependence of Γ and obtained information on the dynamics of the sponge phase.

The nonionic surfactant we used in this study was pentaethylene glycol dodecyl ether ($C_{12}E_5$). In the binary system of $C_{12}E_5$ and water, the lamellar and sponge phases are stable even at a very low concentration and the distance between layers increases to that comparable to the wavelength of visible light[7]. So, the dilute solution of $C_{12}E_5$ is often iridescent due to the Bragg reflection from bilayers. The sample of $C_{12}E_5$ purchased from Wako Pure Chemical Industries was diluted with deionized pure water without further purification. The concentration of $C_{12}E_5$ was varied from 0.5% to 9% in the volume fraction and the measurements were performed at the middle temperature of the sponge phase for respective concentration.

RESULTS AND DISCUSSIONS

Concentrated Solutions

In the concentrated solution whose volume fraction ϕ is above 2%, the autocorrelation function $g(t)$ is well fitted to Eq. (1) with $\beta \approx 0.9$. The best-fitted values of β are almost constant at all wavenumbers we studied and show no apparent dispersion. We can regard this relaxation process to be almost single one. The wavenumber q dependence of Γ at various concentrations are shown in Figure 1. It is found Γ increases in proportion to q^2 and this indicates

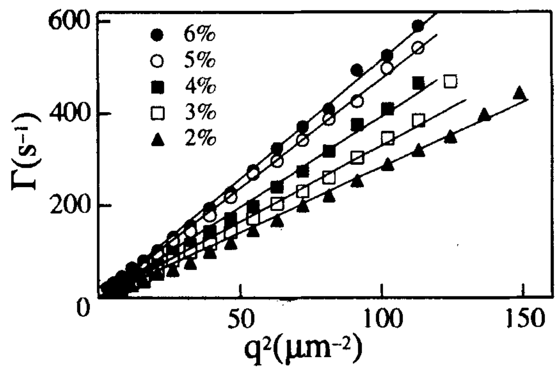

FIGURE 1 The wavenumber q dependence of Γ in the sponge phase of the concentrated solutions.

that the observed relaxation is the diffusion process. The diffusion constant D of each solution can be calculated from the slope of the best-fitted solid line in Fig. 1. As the diffusion constant linearly increases with the concentration of $C_{12}E_5$, the observed diffusion process is assigned to the cooperative diffusion of bilayers in the sponge structure. We can estimate the hydrodynamic radius ξ_H from D by using the Einstein-Stokes relation,

$$\xi_H = \frac{k_B T}{6\pi\eta D}, \tag{2}$$

where k_B is Boltzmann constant, T is absolute temperature, η is the viscosity of water. The calculated values of ξ_H for various volume fractions ϕ in the concentrated solutions are plotted as filled circles in Figure 2. The open circles in Fig. 2 represent the repeat distances d measured at the same concentrations in the L_α phase[7]. The value of ξ_H is almost a few times bigger than d and this indicates that the observed fluctuation are originated from that of sponge cell made up of surfactant bilayers.

Porte *et. al.*[10] showed that the hamiltonian of the bending elasticity in the sponge phase is scale invariant to the isotropic expansion of its scale and free

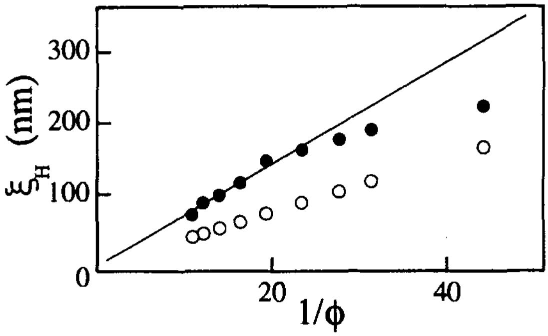

FIGURE 2 The volume fraction ϕ dependence of ξ_H of the sponge phase in the concentrated solutions.

energy density per unit volume is scaled as ϕ^3. They also discussed the scaling laws for the physical quantities in the sponge phase such as osmotic pressure, Kerr constant of electric birefringence, rotational relaxation time and cooperative diffusion constant. They predicted that the cooperative diffusion constant D_C is scaled as $D_C \propto \phi^{-1}$ and $\xi_H \propto \phi$. In our experiments, ξ_H increases in proportion to ϕ at higher concentrations, which is shown as a solid line in Fig. 2, but ξ_H goes down from this line at dilute concentrations.

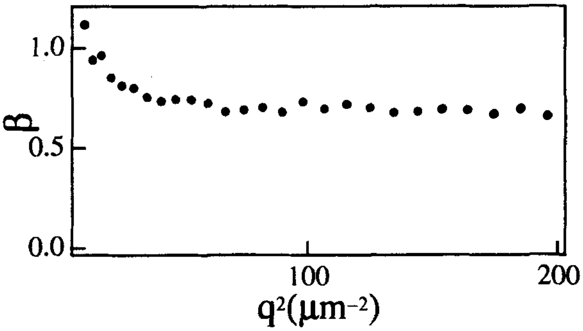

FIGURE 3 The wavenumber q dependence of β at ϕ =0.6%.

Dilute Solutions

In the dilute solution of $\phi \leq 1\%$, the obtained autocorrelation function $g(t)$ is also well fitted to the stretched exponential function of Eq. (1). But at large q, the best-fitted value of β decreases to about 0.7. In Figure 3, the wavenumber q dependence of β at ϕ=0.6% is shown as an example. The dispersion curve of Γ obtained at ϕ=0.6% is also shown in Figure 4. At small q, Γ increases in proportion to q^2 in the same fashion of the concentrated solution, but Γ increases in proportion to q^3 at large q. The similar crossover behavior in the dispersion of Γ for the cooperative diffusion is observed in the solution of flexible polymers[2] and the simple fluid near the critical point[11]. In these systems, the dispersion of Γ calculated by taking into account the hydrodynamic interaction between modes of fluctuation,

$$\Gamma = \frac{k_B T}{6\pi\eta\xi} q^2 F(q\xi), \tag{3}$$

where ξ is correlation length and $F(x)$ is called Kawasaki function defined as

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

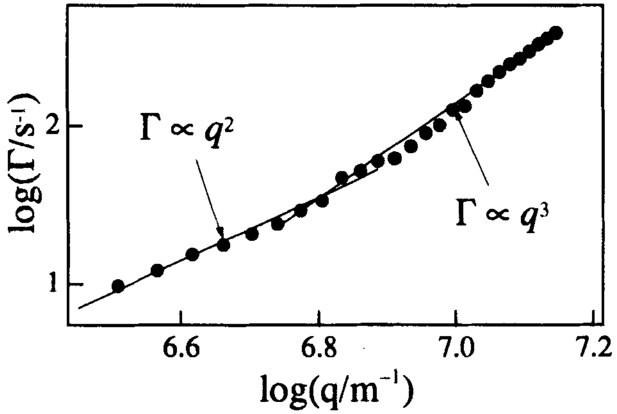

FIGURE 4 The wavenumber q dependence of Γ at ϕ =0.6%.

At the limit of $q\xi << 1$, the Eq. (3) reduces to the Einstein-Stokes relation of Eq. (2). At the limit of $q\xi >> 1$, it reduces to $\Gamma = (k_B T/16\eta)q^3$, which does not depend on the character of the fluctuating objects. The dashed line in Figure 5 is the calculated dispersion of Eq. (3) with $\xi = 570$nm which is estimated from the dispersion at small q. The theoretical dispersion of Eq. (3) is found to be quite different from the experimentally observed one plotted as filled circles in Fig. 5. The discrepancy lies in that the theoretical model neglects the rigidity of fluctuating membranes and it becomes important to the dynamical behavior at $q\xi >> 1$ region. So, we have to consider the bending modulus of a membrane to explain the results in dilute solutions.

Recently, Zilman and Granek[9] discussed the dynamical property of the ensemble made up of randomly oriented plaquettes with finite size ξ and bending modulus κ. They calculated the dynamical structure factor for this system by taking into account the thermal fluctuation of membranes and the hydrodynamic interaction between them. At the limit of $q\xi >> 1$, the structure factor $S(q,t)$ has a stretched exponential form,

$$S(q,t) \propto e^{-(\Gamma_q t)^{2/3}}, \tag{5}$$

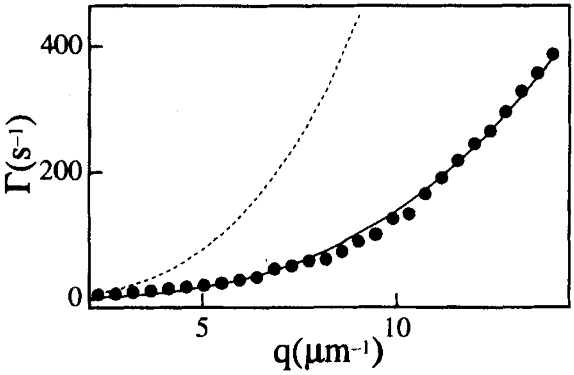

FIGURE 5 The comparison of the experimentally obtained dispersion of Γ at $\phi = 0.6\%$ with the theoretical one.

where

$$\Gamma_q = 0.025\left[1 - 3\ln(q\xi)\frac{k_BT}{4\pi\kappa}\right]\left(\frac{k_BT}{\kappa}\right)^{1/2}\frac{k_BT}{\eta}q^3 . \tag{6}$$

The predicted stretching exponent 2/3 in Eq. (5) is close to the experimental obtained value of 0.7. Except the logarithmic correction in Eq. (6), the decay rate Γ increases in proportion to q^3 and its slope depends on the bending modulus of a membrane κ. The best-fitted curve of Eq. (6) to the experimental result at $\phi=0.6\%$ with $\xi=570$nm and $\kappa=1.7k_BT$ is drawn as a solid curve in Fig. 5 and it seems to make a rather good agreement with each other. The estimated value of κ is a little bit larger than that calculated from the SANS and SLS spectra in the L_α phase of the same system, $\kappa=1.3k_BT$[7].

From Eq. (6), the wavenumber q dependence of Γ can be scaled into one universal curve at $q\xi \gg 1$. We try to plot the reduced value $\Gamma^* \equiv \Gamma/(T\phi^3/\eta)$ as a function of the reduced wavenumber $q^* \equiv q/\phi$ in Figure 6. All data in dilute solutions apparently arrange on the universal curve which shows the crossover behavior from $\Gamma^* \propto q^{*2}$ to $\Gamma^* \propto q^{*3}$. At the small q or large ϕ, the data goes away

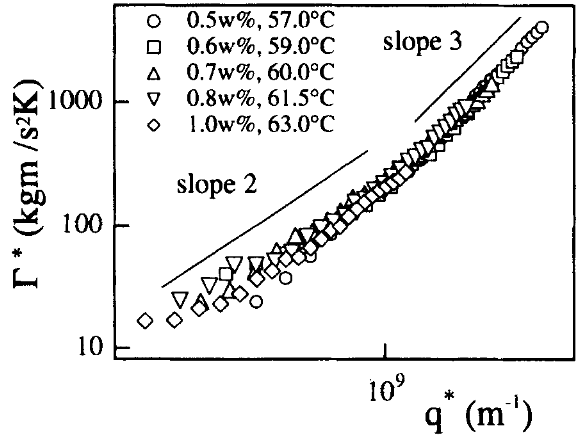

FIGURE 6 The reduced wavenumber q^* dependence of reduced Γ^* in dilute solutions.

from the master curve. This is mainly due to the breakdown of the scaling behavior predicted for the sponge in dilute solutions, which has been already discussed.

CONCLUSIONS

We have studied the dynamical property of the sponge phase in a binary system of $C_{12}E_5$ and water. In the concentrated solution, the scaling law for the sponge makes a good agreement with the obtained results. On the contrary, in the dilute solution, the dynamical property is governed by the nature of a single membrane with finite rigidity. We have shown the universal behavior in the wavenumber q dependence of relaxation rate Γ and succeeded in estimating the bending modulus κ in the sponge phase by using the theory of Zilman and Granek.

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