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Dynamic Light Scattering of A Lyotropic Liquid Crystal Lamellar Phase and A Sponge Phase

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DYNAMIC LIGHT SCATTERING OF A LYOTROPIC LIQUID CRYSTAL LAMELLAR PHASE AND A SPONGE PHASE

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Abstract We measured the fluctuations of a lyotropic liquid crystal lamellar (L_α) phase in dilute surfactant concentration and a sponge (L_3) phase by dynamic light scattering technique. We observed the concentration fluctuation induced by the thermal undulation of layers in the L_α phase and obtained the dependence of the effective rigidity k_c of layers on the repeat distance d, which reflected the fluctuation-induced layer softening. In the L_3 phase, two kinds of fluctuation modes were observed.

INTRODUCTION

The nonionic surfactant $C_{12}E_5$ in aqueous solution aggregates to form bilayers with smectic order called a lyotropic liquid crystal lamellar (L_α) phase. The layer separation d is determined by the surfactant volume fraction Φ as $d \cong \delta / \Phi$ where δ is the layer thickness ($\approx$ 3.75 nm), and increases up to nearly half of the wavelength of light with decreasing Φ[1]. The steric repulsion between layers[2] caused by the thermal fluctuations or undulations of the fluidly flexible, accordingly crumpled, layers stabilizes a widely spaced smectic order of the highly swollen L_α phase. Therefore, the experimental determination of the bending rigidity k_c controlling the thermal fluctuation is important for clarifying the properties of smectic crumpled layers. The value of k_c has been reasonably estimated to be of order the thermal energy, $k_B T$, by various scattering experiments such as the X-ray scattering[3], SANS and static light scattering[1], and dynamic light scattering[4]. Theoretical efforts have also been devoted to the estimation of k_c for the crumpling layers and it has been predicted that the thermal undulations of the crumpling layers decrease the rigidity k_c. This is fluctuation-induced layer softening[5,6,7]. The effective bending rigidity decreases logarithmically as

$$k_c = k_0 - \frac{\alpha k_B T}{4\pi} \ln\left[\frac{d-\delta}{\delta}\right] \tag{1}$$

where k_0 is the local bending rigidity. The value of the numerical factor α has an ambiguity, it is predicted to be either one[5,6] or three[7].

Further decreasing Φ, there occurs a phase transition to an L_3 phase, the so-called "anomalous isotropic phase". The structure of this phase has a bicontinuous topology, in which bilayers are randomly aligned and multi-connected to separate the solution into two connected subspaces. The characteristic length observed from the scattering experiment[1,8] corresponds to the average size $\bar{d}$ of solvent passages. The shear viscosity measurement indicates that the L_3 phase shows a Newtonian flow behavior[9], which implies that the bilayers move freely in spite of their multi-connected structure. The investigations of the L_3 phase have been so far mostly focused on its structure and not on its dynamical properties.

In this study, we detect the fluctuation modes in both the highly swollen L_α and L_3 phases by a dynamic light scattering (DLS) technique. If the layer separation d of the swollen L_α phase becomes large, the logarithmic correction term in k_c given by Eq. (1) would be large enough to observe the fluctuations due to the layer softening clearly. Thus, from the DLS measurement of the swollen L_α phase we estimate k_c and obtain its dependence on d to verify the layer softening. Further, we elucidate the details of fluctuation modes in the L_3 phase by the DLS measurements.

EXPERIMENT

The surfactant $C_{12}E_5$ was purchased from Nikko chemicals and used without further purification. The solvent was distilled water. The samples for the DLS measurement were aqueous solutions with 2 to 7 wt% of $C_{12}E_5$, corresponding to $d \cong 182-73$ nm for the L_α phase and with 0.5 to 0.7 wt% of $C_{12}E_5$ for the L_3 phase. We sandwiched the samples of the L_1 phase in a sealed cell between two glass plates separated 0.1 mm by a Teflon spacer. A homeotropically aligned L_α phase was obtained by the following thermal treatment: the sample was heated, through the L_α phase, to the L_α-L_3 coexistence region, then cooled slowly (0.1°C per minute) down to 59°C. We observed the optical extinction under the crossed polarization and confirm that the sample was well aligned. The thermal treatment for the a L_3 phase was similarly the heating the sample up to the L_1-L_3 coexistence region and the slow cooling down to 59°C. The temperature was kept to 59°C during the DLS measurement. The geometry of the homodyne DLS measurement is schematically shown in Fig. 1, where the polarizations of the incident light (He-Ne laser with λ = 632.8 nm) and the scattered light are commonly vertical to the plane including the both wave vectors in order to observe concentration fluctuations alone[4]. We scanned the angle ϕ between the detector and the lazer beam from 10° to 35° with θ fixed to 36°.

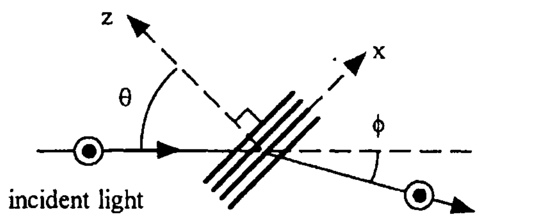

Fig. 1 The geometry of the DLS measurement.

RESULTS AND DISCUSSION

The correlation functions of the swollen L_α phase obtained from the DLS measurement were well-fitted to a single exponential decay function. The model for the hydrodynamics of the lyotropic lamellar phase are treated in Refs. 4 and 10. According to Ref. 4, for an oblique geometry with the wave vector $q = (q_x, q_y, q_z)$ satisfying $q_x q_z \neq 0$, the baroclinic coupling of layer displacements and concentration fluctuations is expected to be observed by DLS and the dispersion relation between the decay rate Γ and q is given as

$$\Gamma = \mu \frac{\overline{B} q_z^2 + K q_x^4}{q_z + \eta q^4} q_x^2 \tag{2}$$

where $\overline{B}$ is the layer compressibility modulus at constant chemical potential given by[2,11]

$$\overline{B} = \frac{9\pi^2}{64} \frac{(k_B T)^2}{k_c} \frac{d}{(d-\delta)^4}, \tag{3}$$

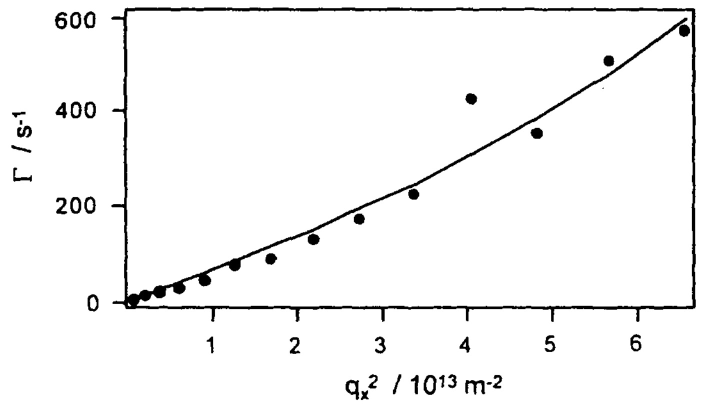

Fig. 2 The decay rate Γ of the L_α phase vs. q_x^2 (Φ = 2.0 wt%). The solid line is the best fitted curve.

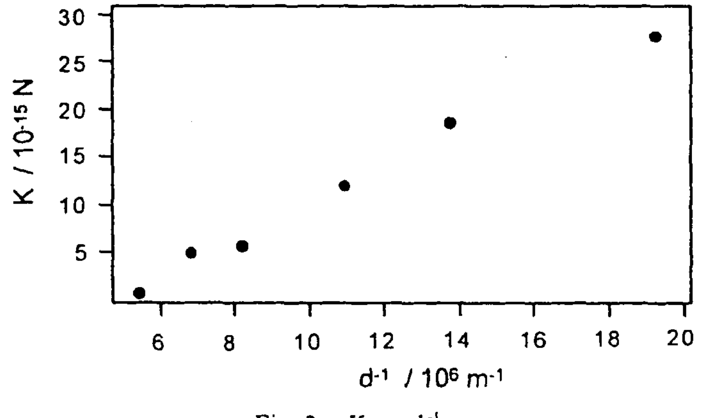

Fig. 3 K vs. d^{-1}.

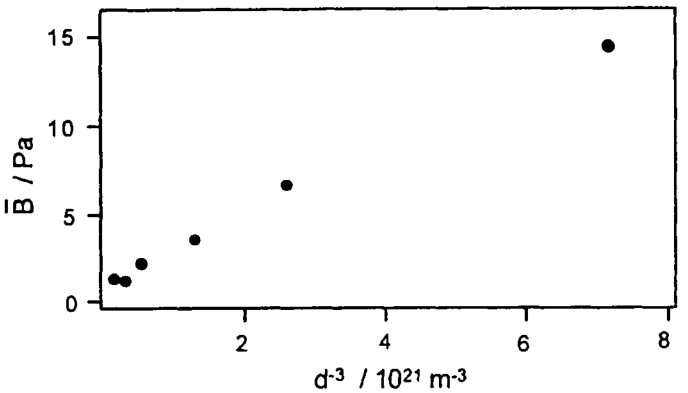

Fig. 4 $\bar{B}$ vs: d^{-1}.

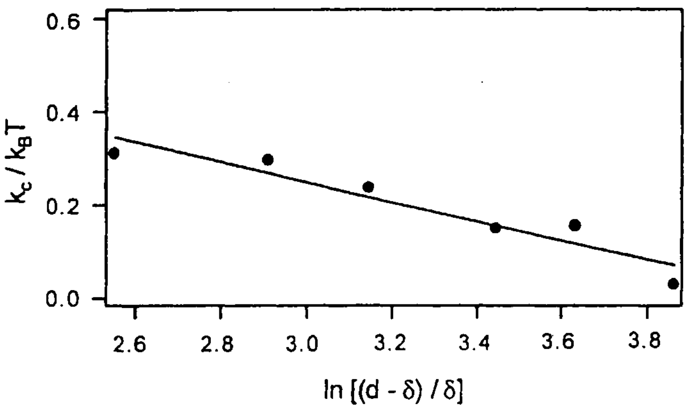

Fig. 5 k_c/k_BT vs. $\ln[(d - \delta) / \delta]$. The solid line is the best fitted curve.

and K (= k_c/d) is the bending modulus, μ (= $(d\text{-}\delta)^2/12\eta$) the slip coefficient and η the shear viscosity of the solvent. In Fig. 2, the decay rate Γ obtained from the DLS measurement are plotted against q_x^2. By using Eq. (2) as a fitting function, the values of K and $\overline{B}$ are evaluated as shown in Figs. 3 and 4, respectively. Then, we can obtain the dependence of k_c on d from K. Fig. 5 shows k_c plotted against the logarithmic correction term $\ln[(d\text{-}\delta)/\delta]$. The linear relation between k_c and $\ln[d/\delta\text{-}1]$ supports the fluctuation-induced layer softening mechanism. By using Eq. (1), we have $k_0/k_BT = 0.88$ and $\alpha = 2.6$, compared with k_0/k_BT = 1.3 obtained from SANS and static light scattering measurements for the same aqueous $C_{12}E_5$ solutions[1]. Furthermore, our result supports α equal to 3 and not to unity. Though k_c is estimated also from $\overline{B}$ by using Eq. (3), the values of k_c from $\overline{B}$ are about eight times larger than that from K and the value of α is equal to 20. The DLS measurements in other surfactant systems have also encountered a large discrepancy between the values of k_c estimated from K and $\overline{B}$[4]. The approximations in $\overline{B}$ in the calculation of the dispersion relation may be responsible for this discrepancy.

The correlation functions of the L_3 phase show two different decay times as observed in Ref. 12 and are best fitted with a double exponential function given as

$$\langle I(0)I(t)\rangle / \langle I(0)^2\rangle = B + \left[A_f \exp(-\Gamma_f t) + A_f \exp(-\Gamma_f t)\right]^2 \tag{4}$$

where Γ_f and Γ_s are fast and slow decay rates, respectively. Fig. 6 shows Γ_f and Γ_s plotted against ϕ. Fig. 7 shows that Γ_f is proportional to q^2. Since this relation implies the characteristic length ξ of fluctuations is smaller than q^{-1} (~ 400 nm) and further the average size $\bar{d}$ of passages is estimated to be larger than q^{-1}, the fast mode is ascribable to the fluctuations of a single membrane, i.e., ripples on the passages. Fig. 8 shows Γ_s plotted against q^3, indicating $\Gamma_s = \text{constant} \times \dfrac{k_BT}{\eta} q^3$. This result shows that ξ is much larger than q^{-1} and the slow mode may be ascribed to the concentration fluctuations of multi-connected but mobile layers, i.e., the Brownian motions of the passages.

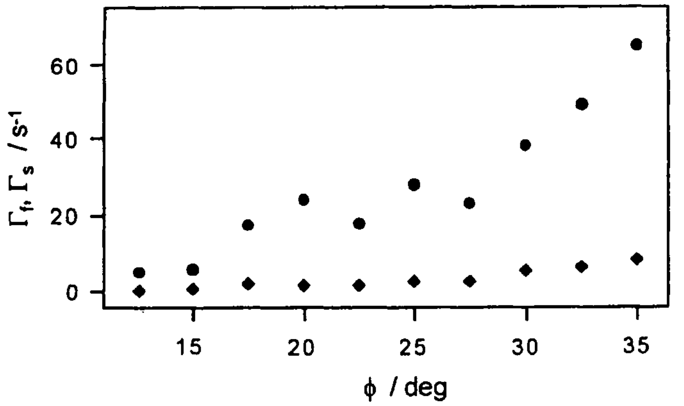

Fig. 6 Γ_f (●) and Γ_s (◆) of the L_3 phase vs. ϕ (Φ = 0.05 wt%).

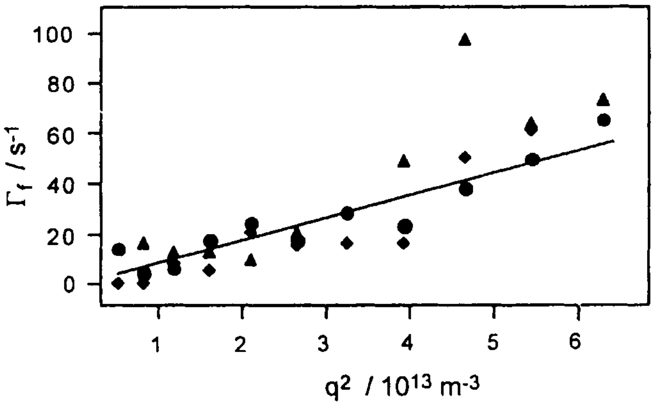

Fig. 7 Γ_f of the L_3 phase vs. q^2. Φ = 0.5 wt% (●), 0.6 wt% (◆), 0.7 wt% (▲). The solid line is the best-fitted curve for Φ = 0.5 wt%.

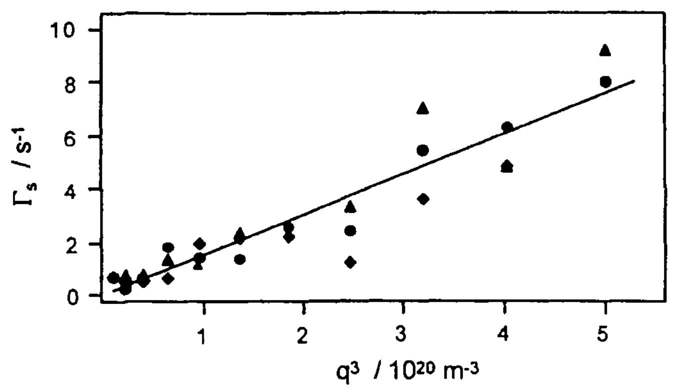

Fig. 8 Γ_s of the L_3 phase vs. q^3. $\Phi = 0.5$ % (●), 0.6 % (◆), 0.7 % (▲). The solid line is the best-fitted curve for $\Phi = 0.5$ %.

CONCLUSIONS

By DLS measurement of the baroclinic mode in the L_α phase, we estimate k_c from K and $\bar{B}$. Though there remains a large discrepancy of k_c from K and $\bar{B}$, the dependence of k_c on d estimated from K supports the fluctuation-induced layer softening and gives the value of α in favor of the result from the renormalization group calculation[7]. The fast and slow modes of fluctuations are observed in the L_3 phase. By DLS measurement of the fast mode, we estimate ξ is smaller than q^{-1}. We are planning a detailed measurement of the L_3 phase.

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REFERENCES

1. R. Strey, R. Schomäcker, D Roux, F. Nallet and U. Olsson, J. Chem. Soc. Faraday Trans., 86, 2253 (1990).
2. W. Helfrich, Z. Naturforsch., 33A 305 (1978).
3. D. Roux, F. Nallet, E. Freyssingeas, G. Porte, P. Bassereau, M. Skouri and J. Marignan, Europhys. Lett., 17, 575 (1992).

4. F. Nallet, D. Roux and G. Porte, Phys. Rev. Lett., 62, 276 (1989); J. Phys. France, 50, 3147 (1989).
5. W. Helfrich, J. Phys. France, 46, 1263 (1985).
6. L. Peliti and S. Leibler, Phys. Rev. Lett., 54, 1690 (1985).
7. L. Golubovic and T. C. Lubensky, Phys. Rev. B, 39, 12110 (1989).
8. G. Porte, J. Marignan, P. Bassereau and R. May, J. Phys. France, 49, 511 (1988).
9. P. Snabre and G. Porte, Europhys. Lett., 13, 641 (1990).
10. F. Brochard and P. G. de Gennes, Pramana Suppl., 1, 1 (1975).
11. S. Leibler and R. Liplowski, Phys. Rev. Lett., B35, 7004 (1987).
12. M. Kotlarchyk, E. Y. Sheu and M. Capel, Phys. Rev. A, 46, 928 (1992).