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Dynamics of nano-sized colloidal particles in a swollen lyotropic lamellar phase of a nonionic surfactant has been studied by three methods of microrheology. By electrophoretic microrheology (EPM), we find two relaxation processes respectively relating to the fluctuation of membranes and topological defects in lamellar structure. By direct tracking of particles under a microscope and manipulating them with an optical tweezers, we obtained detailed information on diffusion of a particle at low frequencies. We observed the jump-trap motion of a particle and the non-Newtonian rheological behavior at low frequencies.

Keywords: colloidal particles; electrophoretic mobility; microrheology; optical tweezers; particle-tracking microrheology; swollen lamellar phase

1. INTRODUCTION

One can universally find spatio-temporal hierarchical structures in biological systems and these make it difficult to understand their macroscopic properties and functions as typical *complex fluids*. A lipid bilayer is one of the basic and common structures in biological systems. It is important to study the transport properties of nano-sized colloidal particles such as protein molecules in the

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matrices of bilayers in order to understand the dynamical aspects of living systems.

Recently, the local mechanical properties of complex fluids such as gels and polymer solutions have been intensively studied by analyzing the motion of probe particles dispersed in these complex fluids. They are often called *microrheology* [1,2]. In this study, we have applied three methods of microrheology to swollen lyotropic lamellar phase and studied the dynamics of particles whose sizes are a little bit smaller than the distance between membranes. We have applied a newly developed technique named electrophoretic microrheology (EPM) from 1 Hz to 10 kHz and measured the average complex mobility of the dispersed particles. The local motion of fluorescent-labeled particles has been studied directly under a microscope. We have also manipulated them with an optical tweezers in order to obtain detailed information on their dynamics at low frequencies.

2. EXPERIMENT

The polystyrene latex particles (Dow) whose diameter are $2a = 42\,\text{nm}$ or the fluorencent labeled polystyrene latex particles (Polyscience) whose diameter are $2a = 52\,\text{nm}$ were dispersed in a dilute lamellar phase of *n*-pentaethyleneglycol monododecylether ($C_{12}E_5$)-hexanol-water mixture. The surfactant bilayer in our system has small bending elasticity $\kappa \approx 0.8 k_B T$ at room temperature [3], and its lamellar structure is mainly stabilized by steric repulsion between undulating neighboring membranes.

In this study, we measured the complex electrophoretic mobility $\mu^*(\omega)$ of colloidal particles dispersed in lamellar phase by quasi-elastic light scattering under a sinusoidal electric field. We call this method electrophoretic microrheology (EPM) [4,5]. Since the complex mobility is inversely proportional to the complex viscosity, we can directly obtain the information on the frequency dependence of effective viscosity from EPM. The details of its principle and experimental setup have been discussed elsewhere [5,6].

The motion of fluorescent labeled particles in lamellar phase was directly observed under a fluorescent microscope (TE300, Nikon). The observed image was detected by a CCD camera and its center of mass was calculated by weighting the digitized intensity from the captured image.

We have studied the local mechanical properties of lamellar phase with optical tweezers. The Nd-YAG laser beam (Spectraphysics, wavelength: 1064 nm) is introduced to a inverting fluorescence microscope

and focused by a 100× oil-immersion objective lens (N.A. = 1.4). Garvano mirrors (X, Y direction) are used to change the position of a spot and the directions of mirrors are controlled by the electric field generated from a dual channel function generator (NF1946).

3. ELECTROPHORETIC MICRORHEOLOGY OF LAMELLAR PHASE

The local viscosity in lamellar phase can be obtained from the electrophoretic mobility of dispersed colloidal particles with use of generalized Smoluchowski equation [4]. When an ac electric field is applied, we can measure the frequency spectrum of complex mobility $\mu^*(\omega)$. Therefore we can measure the frequency dependence of effective viscosity by electrophoretic microrheology. A schematic frequency spectrum of $\mu^*(\omega)$ obtained is shown in Figure 1. There are two relaxation processes in $\mu^*(\omega)$ at around 1 kHz (HF relaxation) and around 1 Hz (LF relaxation). We divide the frequency region into I, II and III from higher frequencies. The mobility at the flat part in respective regions are named μ_{I}, μ_{II} and μ_{III}. The mobility μ_{III} is so small that we cannot measure its exact value by EPM. The mobility μ_{II} is about ten times smaller than that in aqueous solution μ_0. Even in the region I, the mobility μ_{I} is smaller than μ_0. Since the dispersed particles have frequency independent mobility in the frequency range we studied, the decrease of μ^* is originated from the increase of the effective viscosity of a particle in lamellar structure.

There are some possible reasons for decrease of μ in lamellar structure. One is that a particle is confined between membranes. It is

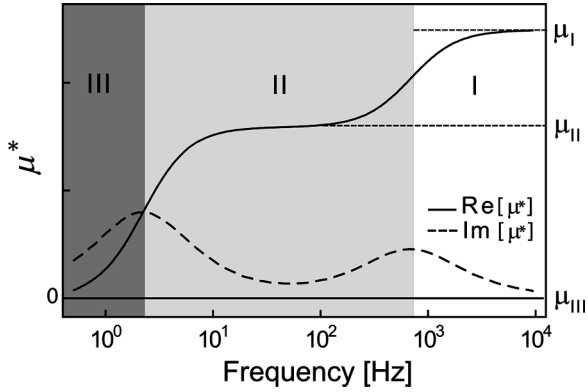

FIGURE 1 Schematic frequency spectrum of complex electrophoretic mobility μ^* in the lamellar phase of $\phi = 3.6\%$.

well known that such confinement increases the effective viscosity in macroscopic system [7]. As the intermembrane distance decreases, the effective viscosity increases. This static confinement is the main reason why the mobility μ_I is smaller than μ_0. The second reason is the fluctuation of a membrane. This also disturbs the free diffusion of a particle. This effect is a dynamic one depending on the characteristic time of membrane fluctuations. The relaxation frequency of the undulation fluctuation of membranes is of the same order as the HF relaxation. If the particle diffusion is slower than that fluctuation, a particle is exposed to flow caused by the fluctuation of a membrane. On the other hand, when the diffusion is much faster than the fluctuation, the motion of a membrane is "frozen" during the motion of the particle. Therefore the influence of membrane fluctuation becomes smaller in this case. This mechanism seems to be the plausible explanation of HF relaxation. The third one is the structural defects in lamellar phase. A particle is trapped within such defect sites, and it can only escape from them by thermal motion of colloids or self-reorganization of lamellar structure. The size of a trap site estimated from the LF relaxation frequency is as large as 1 μm. This indicates that there are structure defects or the barriers against the diffusion of a particle with such size. The slow diffusion of a colloidal particle is also confirmed by dynamic light scattering (DLS). The effective viscosity in the region III estimated by DLS is 1.4×10^4 times larger than one in pure water [5].

4. PARTICLE-TRACKING MICRORHEOLOGY

In the region III, the mobility $\mu^*(\omega)$ decreases to a very small value. This indicates that almost all particles are trapped within a space whose size is as large as several hundreds nm. The existence of trap sites is confirmed by direct observation of fluorescent particles dispersed in lamellar phase. Since the lamellar structure in this study is not macroscopically oriented, there must be defects at a scale larger than the period of lamellar structure. In fact, the vesicle-like structure or folded lamellar structure surrounded by perforated lamellar has been frequently observed by freeze fracture electron microscopy [8]. It is plausible that the trap sites for LF relaxation are composed of multi-lamellar vesicles which particles cannot move across. Even in the region III, particles can diffuse to longer distance if the reorganization of lamellar structure or renewal of trapping path occurs.

The motion of a particle is found to be completely different from that of a simple diffusion process. A particle stays at a certain site for a long time and suddenly jumps a distance as large as 1 μm. As the

concentration increases, the time spent at one site increases, and the number of such particles increases [9]. Similar trap-jump motion has been reported for the motion of colloidal particles in colloidal glasses [10] and in F-actin networks [11]. In those cases, a particle is trapped within a "cage" formed by crowding particles or entangled actin filaments, but can infrequently "jump" to different cages.

Figure 2 shows the temporal evolution of means square displacement (MSD) $\langle \boldsymbol{r}^2 \rangle$ in two dimension averaged over many particles for $\phi = 2.5\%$. If particles follow a pure diffusion process, $\langle \boldsymbol{r}^2 \rangle$ is proportional to the elapsed time t, and its slope gives the self-diffusion constant of particles. On the contrary, if particles are completely trapped within a "cage", $\langle \boldsymbol{r}^2 \rangle$ tends to saturate at a certain value. At $\phi = 2.5\%$, all particles are not in the same situation; some particles are trapped at a single site and some diffuse relative freely. In this case, the ensemble average of $\langle \boldsymbol{r}^2 \rangle$ over many particles shows so-called "sub-diffusive" behavior, and $\langle \boldsymbol{r}^2 \rangle$ follows the power law, $\langle \boldsymbol{r}^2 \rangle \propto t^{\alpha}$, where $0 \leq \alpha \leq 1$ [11]. At short time in Figure 2, $\langle \boldsymbol{r}^2 \rangle$ is well described by power function with $\alpha = 0.37$. On the other hand, it tends to follow normal diffusion process with $\alpha = 1$ at long time-scale. The measured diffusion constant at long time-scale is 1.3×10^4 times smaller than that in aqueous solution. This makes good agreement with that obtained by dynamic light scattering as mention in Section 3.

A direct observation of a particle's trajectory shows that the particle goes back and forth between a few sites and there seem to be a kind of connecting path between them. But at longer time-scale,

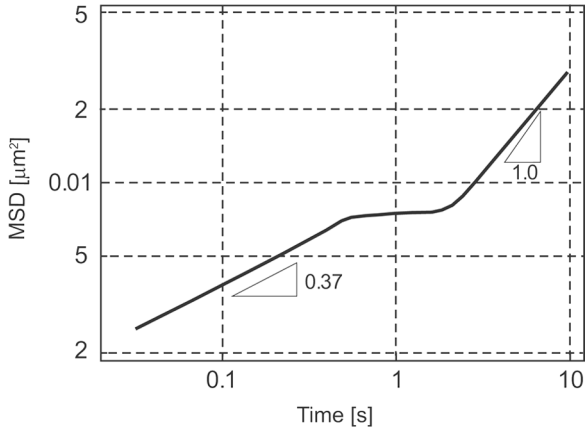

FIGURE 2 Temporal evolution of MSD of many colloidal particles in the lamellar phase of $\phi = 2.5\%$.

the connecting path will change, and a particle fluctuates along another new path. Therefore, transport of a particle in region III is governed by the reorganization and renewal of a path connecting trap sites. Such renewal process might be originated from the reorganization of lamellar structure or the dynamics of packing of vesicle-like structure.

5. OPTICAL TWEEZERS

Colloidal particles whose sizes are tens nm $\sim$ tens μm can be trapped and manipulated by the gradient force of light steeply converged if the refractive index of the particle is larger than that of solvent [12,13]. This is called an optical tweezers. A particle at the focal point of light suffers recovering force which is well approximated by a harmonic potential. We have demonstrated two experiments on the local mechanical properties of lamellar phase with an optical tweezers.

5.1. Yield Stress Measurement

By changing power of the beam, we have measured the minimum force necessary to move a trapped particle in lamellar freely to arbitrary directions. Since the size of a trap site is estimated about 1 μm from the EPM, we move a particle along a line whose maximum length is 3.2 μm with an optical tweezers. When the maximum of laser trapping force f_t is smaller than the minimum force necessary for the particle to escape from a trap site f_b, the particle will escape from the laser spot (Fig. 3(a)). In the opposite case, the particle follows the spot over the size of the trap site (Fig. 3(b)). In our experiment, we obtained the

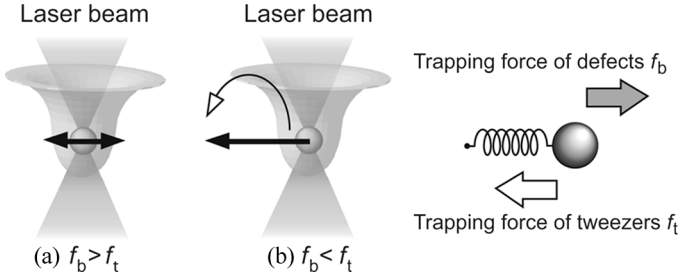

FIGURE 3 Yield stress measurement with an optical tweezers. (a) Trapping force f_t is smaller than yield stress f_b and a particle cannot escape from a trap site. (b) Trapping force f_t is larger than yield stress f_b and a particle escapes from a trapping site.

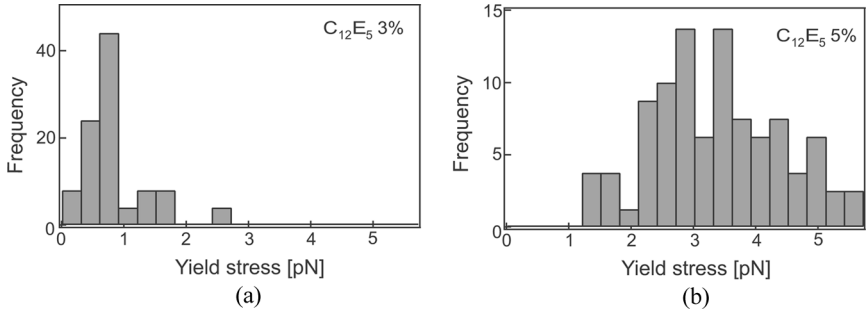

FIGURE 4 Distribution of yield stress measured by an optical tweezers. (a) $\phi = 3\%$, (b) $\phi = 5\%$.

minimum laser power at which a particle can follow the spot. In order to estimate the trapping force, it is necessary to know the relation between laser power and the trapping force. We have calibrated the trapping force with simple fluids, and the details of this method will be published elsewhere.

The distributions of the yield stress obtained for two concentrations ($\phi = 3\%$ and 5%) are shown in Figure 4. As the concentration increases, the distribution broadens and its average value increases. This indicates that a particle is more strongly trapped in more concentrated lamellar sample. This agrees with the dependence on concentration of the number of sites where a particle is trapped within constant time interval. By using the yield stress f_b, we can calculate diffusion constant in the region III as $D_{III} = D_{II}\exp(-\Delta U/k_B T)$, where ΔU is the potential barrier and D_{II} is the diffusion constant in the region II. The potential barrier can be estimated as $\Delta U = f_b^2/2k$, where k is the force constant of an optical potential (harmonic approximation). At $\phi = 3\%$, the potential barrier is estimated as $\Delta U = 7.3 \times 10^{-20}$ J and D_{III} is about 10^8 times smaller than that in pure water. This is much smaller than one obtained by light scattering. That is about 10^4 times smaller than that in pure water. Therefore, the diffusion process is not governed by the escape process due to thermal fluctuation and the trap potential is so deep that a particle cannot escape from it by thermal activation energy.

5.2. Viscosity Measurement

When we move a laser spot along a circular path in liquid and the rotation speed is low, an optically trapped colloidal particle follows

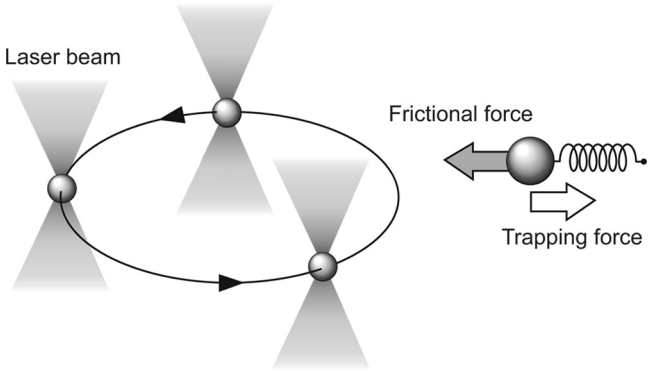

FIGURE 5 Viscosity measurement with an optical tweezers. Trapping force balances frictional force under the maximum speed v_{max}. At the speed greater than v_{max}, a particle goes out from the circular path.

the spot (Fig. 5) [14]. The particle also suffers frictional force $-\eta v$, where η is the viscosity of liquid and v is the speed of the particle. When the frictional force exceeds the trapping one by increasing speed, a particle will escape from the path. From the maximum speed v_{max} of a particle to follow the laser spot, it is possible to measure the maximum trapping force F_{max} at respective laser power as, $F_{max} = 6\pi\eta\, a v_{max}$, where a is the radius of a particle. There is linear relationship between F_{max} and laser power. Once we evaluate this relationship, we can obtain the effective viscosity in lamellar from the dependence of v_{max} on laser power.

In our experiment, at first step, we apply a sufficiently strong force to make particles escape from a trap site. After the particle starts moving, both speed and laser power is changed to find the maximum speed v_{max} at which the particle goes out the path. When the optical trapping force increases, the maximum speed v_{max} increases as is shown at the upper branch in Figure 6. In Figure 6, the region marked dark grey is one where a particle can be trapped by an optical tweezers. In simple fluids such as water, the boundary line between trap and untrap region is monotonic increasing function of laser power.

Since the laser power is proportional to the maximum of trapping force, v_{max} is proportional to the trapping force. This result indicates that lamellar solvent behaves as Newtonian fluid. The effective viscosity estimated from the slope of this branch is $8.2\,\mathrm{mPa \cdot s}$. This result makes good agreement with the effective viscosity in region II obtained by electrophoretic microrheology. In our experiment with

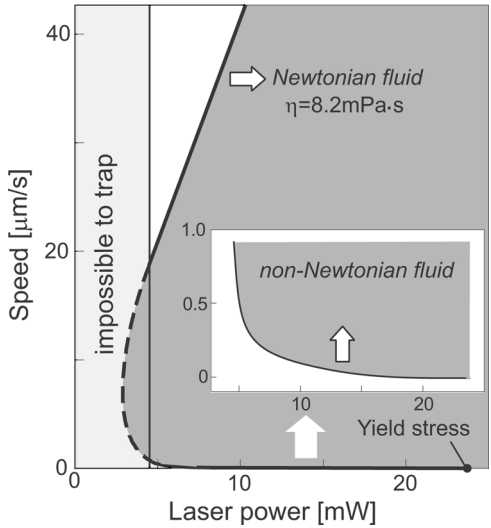

FIGURE 6 Dependence of maximum speed $v_{\max}$ on laser power (trapping force). The upper branch behaves as Newtonian fluid and the lower one as non-Newtonian fluid. The power corresponding to yield stress is also plotted as the point at zero velocity.

an optical tweezers, the structure of lamellar is forced to be smoothed by moving a particle along a small circular path. Therefore, the viscosity in such condition is understood as intrinsic one in ideal lamellar structure.

Unlike a particle in a simple fluid, a particle in a lamellar phase also escapes from the path when its speed becomes very low as shown at lower branch in Figure 6. In this part, the force necessary to trap monotonically increases with decreasing speed. This indicates that the lamellar behaves as non-Newtonian fluid. The main mechanism that governs the dynamics at low frequencies is the dynamics of defects in the lamellar structure. When the speed of the particle becomes smaller, the smoothed lamellar structure created by an optical tweezers will relax to defective one. Therefore, when the time period of rotation falls below the time necessary to close the path, more force is needed to move a particle. To estimate the relaxation time or characteristic time for the annihilation of a path, the laser power is plotted against its period. The data can be well ascribable as,

$$P_{\max} = P_{sat} - P_0 \exp\left(-\frac{t}{\tau}\right),$$

where P_{sat} is set to the power corresponding to yield stress f_b and τ is the relaxation time of a path in lamellar. The obtained best-fitted value of τ is $\tau \sim 100$ [s].

If the main mechanism of diffusion at low frequencies is the change or reconnection of a path, we can estimate the diffusion constant by using 1 μm as the size of a path. The calculated diffusion constant is 1.4×10^4 times smaller than one in water. This difference is due to the difference in effective viscosity. The extremely large value of viscosity agrees well with that obtained by light scattering and particle tracking measurement. More detailed information on structure of defects and mechanism of transport of a particle is necessary to clarify the slow dynamics in swollen lyotropic lamellar phase.

6. CONCLUSION

We have studied local mechanical property called microrheology of a swollen lyotropic lamellar phase by three microrheological methods. By electrophoretic microrheology, the spatio-temporal hierarchical structure in lamellar phase has been clearly demonstrated at the frequency range above 1 Hz. The dynamics of a particle between lamellae is controlled by two effects: one is the simple geometrical confinement between two membranes, the other is the fluctuation of a membrane. These two factors increase the effective viscosity to about ten times larger than that of water. At low frequencies under Hz, we have utilized the particle tracking microrheology and microrheology of an optical tweezers. From these experiments, we have obtained the extremely large effective viscosity due to the defective structure of lamellar phase. The diffusion at long-time scales is governed by the creation and annihilation of a path (or topological defects) in lamellar phase.

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