Repulsive interlamellar interaction induced by addition of colloidal particles

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The effects of colloidal particles confined between lamellar membrane slits on interlamellar interactions have been investigated by small-angle neutron scattering. On addition of colloidal particles to a lamellar phase composed of a non-ionic surfactant, the first lamellar peak becomes sharper and higher-order peaks appear. Thus the colloidal particles suppress undulation fluctuations of lamellar membranes by their steric hindrance, which results in a repulsive interlamellar interaction. As the interlamellar distance decreases, the position of the Bragg peak shifts towards higher q [where q is the magnitude of scattering vector, given by $q = (4\pi/\lambda)\sin\theta$, where 2θ is the scattering angle and λ is the wavelength] and the peak intensity weakens. This tendency is completely opposite to the behavior of non-ionic surfactant lamellar phases, where the interlamellar interaction is governed by the Helfrich interaction. A phenomenological free-energy model is proposed based on the restriction of membrane fluctuations by colloidal particles. This model describes the experimental results well.

1. Introduction

Soft matter forms a variety of mesoscopic structures using a large number of internal degrees of freedom. These structures easily transform to other morphologies by applying external fields, such as a shear flow, an electric field and so on. In this study, we propose another type of the external field, *i.e.*, the addition of guest components, which affects the mesostructures through the entropic interactions between the host mesostructures and the guest components. For example, the most familiar entropic interaction induced by the addition of guest components is a depletion interaction (Asakura & Oosawa, 1954). This is an attractive interaction between host particles caused by a reduction of the free volume of guest components. Another example is reported for a system of lamellar membranes confining polymer chains (Ligoure *et al.*, 1997). Ligoure *et al.* have shown that the addition of polymer chains into lamellar membrane slits induces a reduction of the smectic compressibility and finally brings a lamellar–lamellar phase separation. In this case, the adjacent membranes overlap their depletion zones to increase the free volume of the added polymer chains. This results in a rise of the effective attractive intermembrane interaction.

In a previous paper, we have shown that the addition of colloidal particles suppresses the undulation fluctuations of membranes and results in an effective repulsive intermembrane interaction (Imai *et al.*, 2004). Thus the excluded volume effect of the colloidal particles produces another kind of entropic interaction compared with the case of polymer chains. In this article, we reveal the nature of the repulsive interaction induced by the addition of colloidal particles.

2. Experiments

We investigated a ternary mixture of water, non-ionic surfactant $C_{12}E_5$ and colloidal particles. $C_{12}E_5$ (purity > 98%) was purchased from Nikko Chemicals Inc. and used without further purification. The colloidal particles obtained from Magsphere Inc. were polystyrene latex with 160 Å diameter. The colloidal particles were used after dialysis for 1–2 weeks to remove excess surfactants and preservatives. By small-angle neutron scattering (SANS), we confirmed that the dialysis did not affect the stability of the colloidal particles. The ternary mixture samples for scattering measurements were prepared as follows. The surfactant $C_{12}E_5$ was added to the colloidal particle suspension at room temperature (isotropic micelle phase). After homogenization, the samples were transferred to the cells for scattering measurements and the temperature was set at 330 K for the measurements. The morphological changes of surfactant mesophases were followed by the SANS technique using the SANS-U instrument at JRR3-M at Tokai (Okabe *et al.*, 2005). For the SANS measurements, a neutron beam having a wavelength $\lambda = 7.0$ Å with 10% resolution was collimated by a simple pinhole collimator system and irradiated the sample with a beam size of 5 mm in diameter. The scattered neutrons were detected by a two-dimensional position-sensitive detector having a 65×65 cm (128×128 pixels) area. The sample-to-detector distances were 4, 8 and 12 m, which covered the magnitude of the scattering vector q [$q = (4\pi/\lambda)\sin\theta$, where 2θ is the scattering angle] range from 0.002 to 0.1 Å^{-1}. The samples were sealed within quartz cells and then mounted on a sample changer which controlled the sample temperature from 273 to 353 K with $\pm$ 0.1 K accuracy. The scattering patterns obtained were corrected for non-uniformity, the background scattering and the incoherent scattering intensity from protonated substances, and then transformed to an absolute scale using a secondary standard of Lupolene.

3. Results and discussion

First, we show the characteristic phase behavior of the lyotropic lamellar membrane and colloidal particle mixture systems. Fig. 1
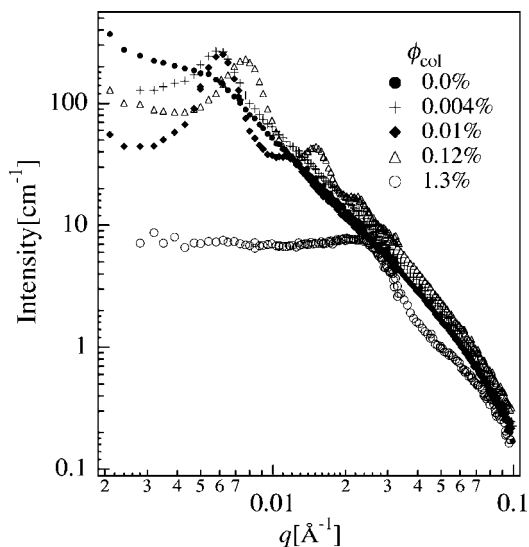
Figure 1
SANS profiles of the lamellar phase at ϕ_{C12E5} = 3.1% for different values of ϕ_{col}.

shows a series of SANS profiles as a function of the volume fraction of colloidal particles, ϕ_{col}, at a constant volume fraction of $C_{12}E_5$, ϕ_{C12E5} = 3.1%. It should be noted that the scattering profile without colloidal particles does not show any characteristic lamellar peaks because of the large membrane fluctuations. The addition of an extremely small amount of colloidal particles causes the emergence of the first Bragg peak and sharpens it. Thus, the presence of the colloidal particles suppresses the undulation fluctuations, which results in a repulsive intermembrane interaction. On adding further colloidal particles, the lamellar peaks shift to higher q at $\phi_{col} \simeq 0.13\%$, indicating a phase separation. At $\phi_{col} \simeq 1.3\%$ the SANS profile suddenly changes. The Bragg peaks characteristic of the lamellar phase disappear and the scattering intensity in the low-q

region decreases considerably. Recently we found that this new scattering profile can be described by a model scattering function for a prolate micelle. Thus the lamellar-to-micelle transition is induced by the addition of colloidal particles.

In addition to the lamellar–micelle transition induced by the colloidal particles, we found a unique behavior of the SANS profiles depending on the interlamellar distance. Without any guest components, the scattering profile from the dilute lamellar phase does not show significant changes even if we increase the surfactant concentration ϕ_{C12E5} as shown in Fig. 2(a). For convenience, each profile is shifted along the intensity axis. This result is due to the large amplitude of the membrane fluctuations.

In the presence of the colloidal particles, on the other hand, the scattering profiles from the dilute lamellar phase show a remarkable ϕ_{C12E5} dependence as shown in Fig. 2(b). At $\phi_{col} = 0.01\%$ and $\phi_{C12E5} = 3.1\%$, the scattering profiles from the mixture show a strong first Bragg peak and a weak second peak due to the repulsive interaction induced by the colloidal particles. As the volume fraction of $C_{12}E_5$ increases, the position of the Bragg peak shifts towards higher q and the peak intensity weakens. Thus the regularity of the lamellar membranes decreases with the decreasing interlamellar distance. This is completely opposite to the normal dilution behavior.

It is believed that interlamellar interactions of non-ionic surfactant membrane systems are governed by the Helfrich mechanism (Helfrich, 1978) arising from the steric hindrance of the adjacent undulating membranes. This Helfrich interaction potential per unit area is given by

$$F_{Hel} = \frac{(k_B T)^2}{32\mu\kappa} \frac{1}{\bar{d}^2}, \tag{1}$$

where $\bar{d}$ is the interlamellar distance given by $\bar{d} = d - \delta$ (d is the lamellar repeat distance and δ is the bilayer thickness), T is the temperature and κ is the bending modulus of a single membrane. A
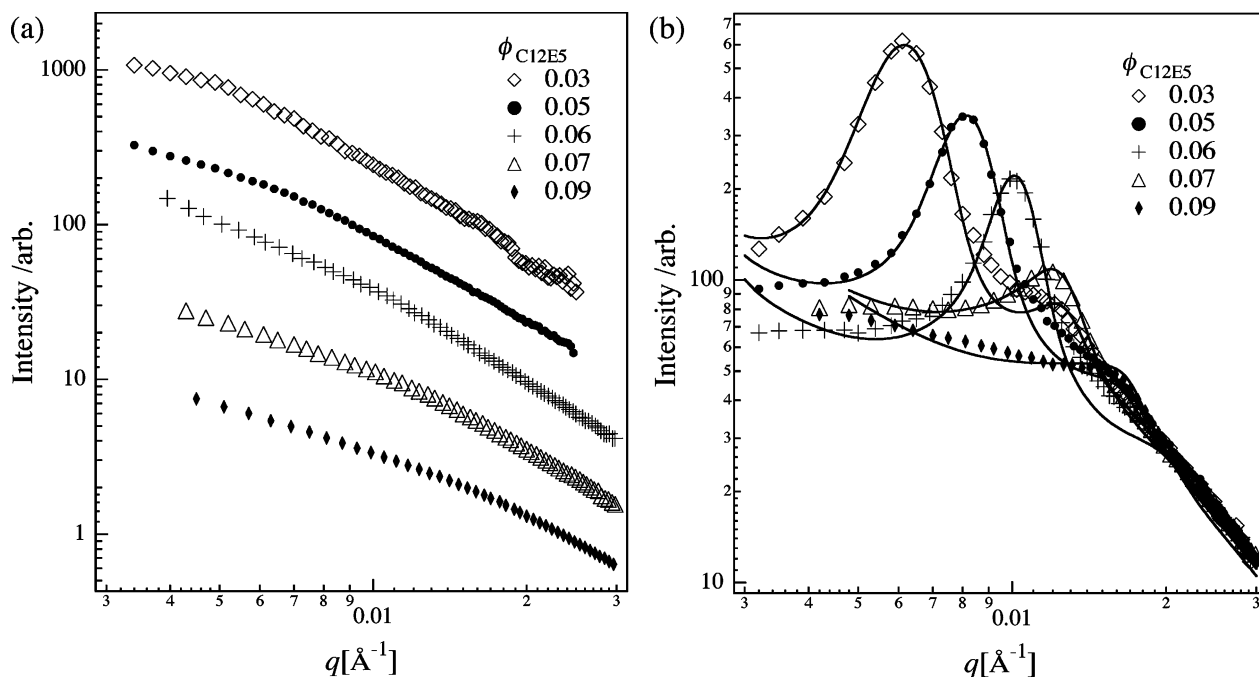

Figure 2
SANS profiles of the lamellar phase for different values of ϕ_{C12E5}: (a) lamellar phase without any guest components and (b) lamellar phase in the presence of colloidal particles ($\phi_{col} = 0.01\%$).

numerical factor, μ, is related to the local displacements of membrane $u(r)$ by the geometrical expression

$$\langle u^2(r)\rangle = \mu \bar{d}^2. \tag{2}$$

Whether the interlamellar interaction is governed by the Helfrich mechanism or not is easily examined by the simple geometrical relation

$$\eta = 2\pi\left(\frac{\mu}{3}\right)^{1/2}\left(\frac{\bar{d}}{d}\right)^2. \tag{3}$$

Here η is the Caillé parameter (Caillé, 1972) defined by

$$\eta = \frac{q_0^2(k_BT)}{8\pi(K\bar{B})^{1/2}}, \tag{4}$$

where K is the bulk bending modulus, $K = \kappa/d$, $\bar{B}$ is the layer compression modulus and q_0 is the position of the first Bragg peak: $q_0 = 2\pi/d$. We have confirmed that for the $C_{12}E_5$/water system the simple relation given by equation (3) holds and we obtained $\mu = 0.26$ (Imai et al., 2004). Thus by increasing the surfactant concentration ϕ_{C12E5}, the Caillé parameter η decreases, obeying the relation given by equation (3).

In order to elucidate such a characteristic behavior, we estimated the Caillé parameter from the SANS profiles of the lamellar phase with a model scattering function for the undulating lamellar structure proposed by Nallet et al. (1993),

$$I(q) = \frac{2\pi}{d}\frac{P(q)S(q)}{q^2}. \tag{5}$$

Here $P(q)$ and $S(q)$ are the form factor and the structure factor, respectively, expressed as

$$P(q) = (2\Delta\rho^2/q^2)\left[1 - \cos(q\delta)\exp(q^2\sigma^2/2)\right] \tag{6}$$
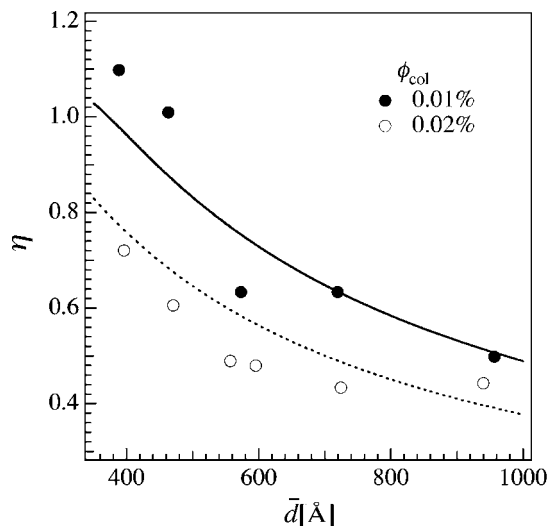
and

$$S(q) = 1 + 2\sum_{n=1}^{N-1}\left(1 - \frac{n}{N}\right)\cos\left[\frac{qdn}{1 + 2\Delta q^2 d^2\alpha(n)}\right]$$
$$\times \exp\left\{-\frac{2\Delta q^2 d^2\alpha(n) + \Delta q^2 d^2 n^2}{2[1 + 2\Delta q^2 d^2\alpha(n)]}\right\}\frac{1}{[1 + 2\Delta q^2 d^2\alpha(n)]^{1/2}}, \tag{7}$$

where N is the number of lamellar layers, Δq is the width of the resolution function assuming a Gaussian profile and $\Delta\rho$ is the contrast of scattering length densities between the surfactant and the solvent. In this model the correlation function for undulating lamellae $\alpha(n)$ in equation (7) is given by

$$\alpha(n) = \langle|u_n - u_0|^2\rangle/2d^2 = (\eta/4\pi)[\ln(\pi n) + \gamma], \quad n \gg 1, \tag{8}$$

with Euler's constant $\gamma = 0.5772$.

The scattering profile from the lamellar membranes without colloidal particles ($\phi_{C12E5} = 3.1\%$) is well described by the model function with the following fitting parameters: $\delta = 28$ Å, $\Delta\rho = 4.62 \times 10^{-6}$ Å^{-2}, $\Delta q = (11.87 \times 10^{-7} + 1.80 \times 10^{-3}q^2)^{1/2}$ Å^{-1} (Glinka et al., 1986) and $\eta = 1.8$ (the fitting result is not shown here). This indicates that Nallet's model is suitable for describing the experimental SANS profiles.

The fitting results of the lamellar membranes confining colloidal particles are shown by the solid lines in Fig. 2(b). Here we ignore the contribution of the SANS intensity of colloidal particles because of the very low concentration, $\phi_{col} \simeq 0.01\%$. The model scattering function describes the experimental SANS profiles and we plot the deduced Caillé parameters for the systems at $\phi_{col} = 0.01\%$ and 0.02% as a function of the interlamellar distance $\bar{d}$ in Fig. 3. It is notable that η decreases significantly as $\bar{d}$ increases. This result is completely opposite to the case of normal lamellar membranes without any colloidal particles. Without any guest components, η increases with an increase of $\bar{d}$ obeying equation (3), thus the Helfrich repulsive interaction potential decreases as $\sim 1/\bar{d}^2$. By confining the colloidal particles, however, the value of η decreases with an increase of $\bar{d}$.

In order to explain the observed experimental results, we derive an expression for the steric repulsive interaction potential based on the Helfrich formalism. We assume that the membrane fluctuations are restricted by the steric hindrance of the colloidal particles. This restriction of the membrane fluctuations induces the entropic repulsive interlamellar interaction. We consider that the degree of suppression of the membrane fluctuations is proportional to the volume fraction of the colloidal particles (number density of colloidal particles). For a confined system, the effective volume fraction between lamellar slits may be modified by the strength of the confinement $\bar{d}/R$. Then we introduce an effective volume fraction of the colloidal particle in the lamellar slits χ_{col} given by

$$\chi_{col} = \phi_{col}(\bar{d}/R)^m, \tag{9}$$

where the exponent m is an unknown parameter and determined from the experimental results. Then the restriction of the membrane fluctuations is expressed by a function of χ_{col},

$$|u(r)| \leq \bar{d}f(\chi_{col}). \tag{10}$$

This function $f(\chi_{col})$ must satisfy the following asymptotic conditions: (i) $f(\chi_{col}) \rightarrow \bar{d}$ for $\chi_{col} \rightarrow 0$ and (ii) $f(\chi_{col}) \rightarrow 0$ for $\chi_{col} \rightarrow \infty$. In order to satisfy these conditions, we adopt a trial function given by

$$f(\chi_{col}) = \tan h^{n/2}(1/\alpha\chi_{col}), \tag{11}$$

where n controls the nature of the trial function and α is a numerical constant. Using this function, the restriction of the membrane fluctuations is expressed by

Figure 3
Caillé parameters η as a function of the interlamellar distance $\bar{d}$. Experimentally obtained η values are represented by circles and the theoretical predictions based on equation (17) are indicated by a solid line for $\phi_{col} = 0.01\%$ and a dotted line for $\phi_{col} = 0.02\%$.

$$\langle u^2(r) \rangle = \mu \bar{d}^2 \tan h^n \left(\frac{R^m}{\alpha \phi_{col} \bar{d}^m} \right). \qquad (12)$$

Following the Helfrich formulation, the free energy of the steric interaction per unit area of membrane is given by

$$F_{col} = \frac{(k_B T)}{32 \mu \kappa} \frac{1}{\bar{d}^2 \tan h^n (R^m / \alpha \phi_{col} \bar{d}^m)}. \qquad (13)$$

For $\alpha \chi_{col} \ll 1$ $\left[\tan h^n (R^m / \alpha \phi_{col} \bar{d}^m) \rightarrow 1 \right]$, this equation coincides with the expression of the Helfrich given by equation (1).

In the case of a lamellar phase containing guest components, the layer compression modulus is expressed by (Ligoure *et al.*, 1997)

$$B = d \left\{ \frac{\partial^2 F}{\partial \bar{d}^2} - \frac{\left[(1/\bar{d})(\partial F / \partial \phi_g) - (\partial^2 F / \partial \bar{d} \partial \phi_g) \right]^2}{(\partial^2 F / \partial \phi_g^2)} \right\}, \qquad (14)$$

where ϕ_g is the volume fraction of the guest components in the solvent layer. We can derive the layer compression modulus, using equations (13) and (14),

$$B_{col} = \frac{(k_B T)^2 d}{32 \mu \kappa \bar{d}^4} \frac{g(\chi_{col})}{h(\chi_{col})}, \qquad (15)$$

$$
\begin{aligned}
g(\chi_{col}) = {} & -3 \bar{d}^2 \phi_{col}^2 - 2mn^2 (R^m / \alpha)^2 + 2m^2 n^2 (R^m / \alpha) \\
& + 2(-1 + m) mn (2R^m / \alpha) \cosh(2 / \alpha \chi_{col}) \\
& + n(R^m / \alpha) \bar{d}^m \phi_{col} \sin h(2 / \alpha \chi_{col})(3 - 4m - m^2) \\
& - 3(R^m / \alpha) \bar{d}^m \phi_{col} \sin h(4 / \alpha \chi_{col}) \\
& + 3 \bar{d}^{2m} \phi^2 \cosh(4 / \alpha \chi_{col}),
\end{aligned} \qquad (16)
$$

$$
\begin{aligned}
h(\chi_{col}) = {} & 2 \phi_{col} \bar{d}^m \sin h(1 / \alpha \chi_{col}) \cosh(1 / \alpha \chi_{col}) \tan h^{-n}(1 / \alpha \chi_{col}) \\
& \times \left[-n(R^m / \alpha) - (R^m / \alpha) \cosh(2 / \alpha \chi_{col}) \right. \\
& \left. + \phi \bar{d}^m \sin h(2 / \alpha \chi_{col}) \right].
\end{aligned} \qquad (17)
$$

Substitution of equation (14) into equation (1) gives the Caillé parameter η_{col},

$$\eta_{col} = 2\pi (2\mu)^{1/2} \left(\frac{\bar{d}}{d} \right)^2 \left[\frac{h(\chi_{col})}{g(\chi_{col})} \right]^{1/2}. \qquad (18)$$

The theoretically predicted $\bar{d}$ dependence of η is plotted in Fig. 3 with a solid line for $\phi_{col} = 0.01\%$ and with a dotted line for $\phi_{col} = 0.02\%$. Our theoretical model describes the SANS data well using $n = 0.75$, $m = 2.3$ and $\alpha = 1200$. Taking into account the fact that this theoretical model describes the experimental ϕ_{col} dependence of B_{col} well (Imai *et al.*, 2004), we consider that our free-energy model is suitable for the description of membrane and colloidal particle mixtures.

4. Conclusion

We investigated the interlamellar interaction induced by the addition of colloidal particles and found that the presence of the colloidal particles suppressed the undulation fluctuations of membranes. Thus the addition of colloidal particles induces an repulsive interlamellar interaction like the Helfrich interaction. The repulsive interaction increases with an increase of the interlamellar distance. This unique behavior is described well by the free-energy model based on the restriction of membrane fluctuations due to the colloidal particles.

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