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Effect of Symmetry on a Three-Component Lamellar Phase: X-ray Scattering Study

R. Oda (*) and J.D. Litster

Department of Physics, Massachusetts Institute of Technology, Cambridge,
Massachusetts 02139, USA

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Abstract. — X-ray scattering data of a three-component lamellar phase composed of oil (octane), water and a non-ionic surfactant ($C_{12}E_5$) are shown for various surfactant concentrations as well as oil/water volume ratios, in order to study the periodicity of the layers as well as the effect of structural symmetry on their interactions and organization of the layers. The data are fitted with a recently proposed model which takes into account the geometry and the fluctuations of these repeated structures and gives a good fit for a highly fluctuating non-charged and non-oriented lamellar phase. The variation of the exponent η which characterizes the quasi-long range order indicates that the structure is more ordered for the most symmetrical system: *i.e.* for an oil/water ratio of 1.

1. Introduction

In solution, surfactant molecules concentrate at the interface between solvents of different polarities. In the case of a lamellar phase, depending on whether there are one or two solvents, they can form monolayer or bilayer structures periodically ordered along the direction perpendicular to the lamellar layer surfaces. This layered structure has various interesting characteristics: 1) these membranes are extremely flexible which allows us to study the dynamic fluctuation [1, 2]; 2) by changing the surfactant concentration or oil to water ratio [3], the periodicity or the symmetry of the system can be continuously varied, allowing to investigate the various intermembrane interactions [4–6]. Among these interactions, the important repulsive forces which stabilize an expanded lamellar structure are the electrostatic interaction (for ionic systems) and the steric interaction (also called the Helfrich interaction) which originates in the loss of entropy caused by confining a membrane between its neighbours [6]. X-ray scattering has been accepted as a very powerful technique to study the organization as well as the fluctuation of various self-assembled systems. In 1972, Caillé introduced [7] the structure

(*) Author for correspondence, *Present address:* Laboratoire d’Ultrasons et de Dynamique des Fluides Complexes (L.U.D.F.C.), CNRS URA 851, 3 rue de l’Université, 67084 Strasbourg Cedex France (e-mail: reiko@fresnel.u-strasbg.fr)

factor of infinitely large aligned thermotropic smectic-A liquid crystals by using a harmonic theory for the position of the fluctuating lamellar membranes. Ever since, the detailed analysis of the scattering spectra from the finite size powder samples of lyotropic lamellar phases has been attempted [8–12].

The goal of the work presented here was to investigate the structural difference between bilayer lamellae with only one solvent (water or oil) and monolayer lamellae where monolayers separate oil and water layers. A three-component lamellar phase composed of oil (octane), water and a non-ionic surfactant ($C_{12}E_5$) was investigated by X-ray scattering. First, we will describe the small angle X-ray scattering measurements performed on the lamellar phase with a powder texture. The data analysis was done using the structure factor and the form factor introduced by Nallet *et al.* [8]. Then we will discuss the variation of the order parameter η as a function of oil to water volume ratio. It was found that η shows a minimum and that the lamellar structure is more ordered (the penetration length is higher) for the monolayer system with equal volumes of water and oil, because of its higher compressibility.

2. Experimentals

The surfactant $C_{12}E_5$ was purchased from Fluka Chemical Co. with a purity $> 99\%$ and was used without further purification. Octane was also purchased from Fluka with a purity $> 99.5\%$. The phase diagram was established from microscope observations under crossed polarisers [13], and we found that at 33°C , lamellar (L_α) phase exists as a single phase for a large range of surfactant concentration as well as oil to water ratio. The experiments were therefore carried out for the following concentrations where all the samples were found to be in a one-phase region (L_α phase).

$$\gamma \equiv \frac{V_{\text{surfactant}}}{V_{\text{surfactant}} + V_{\text{water}} + V_{\text{oil}}} = 0.15, 0.20, 0.25, 0.30$$

$$\alpha \equiv \frac{V_{\text{oil}}}{V_{\text{oil}} + V_{\text{water}}} = 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8.$$

The scattering experiments were performed with a Rigaku RU2000 X-ray source, operated at 1 kW. The output was collimated in the horizontal direction by a gold-plated quartz mirror. A linear detector with 512 channels (99 channels/cm) was placed at 81 cm from the sample position. The beam path was in vacuum. The longitudinal resolution was $1.7 \times 10^{-3} \text{ \AA}^{-1}$ full width at half maximum. The out of plane resolution was determined by the acceptance of vertical slits and was $4.5 \times 10^{-3} \text{ \AA}^{-1}$. The samples were loaded and sealed in 1 mm diameter and $10 \mu\text{m}$ thick glass capillaries (Mark-Roehrchen). Because the capillaries had a size distribution, their diameters were measured again in the laboratory and only the ones with diameters of $1 \text{ mm} \pm 5\%$ were used. It was important that the samples stay in the powder-state without any long-range orientations in order to perform the spectra analysis, so we checked the samples with a microscope under crossed polarisers. Typically, samples had a birefringent mosaic texture of several microns. Leaving the samples in the capillaries may induce leek-like alignment of the lamellae due to the contact with the capillary walls, so samples were renewed every two days, and the “powderness” was also checked after the scans. Six capillaries were placed vertically in a sample holder, which could be moved horizontally. The temperature within the sample holder was controlled by a Neslab heat bath, with a temperature accuracy of $\pm 0.1^\circ\text{C}$. The peak intensity was normalized by the transmission of the direct beam. The background scattering from the pure solvent and the glass was measured and subtracted from the signal.

Fig. 1. — Normalized intensity profiles of various surfactant concentrations at $\alpha = 0.3$.

3. Results and Discussion

In this section, we will present the powder spectra obtained from the lamellar phases, as well as the analysis of these data based on the theory of the reference [8]. In Figure 1, normalized spectra are presented for various values of γ at fixed $\alpha = 0.3$. We remark that the measured spectra are quite broad (FWHM is about $0.01 \text{ \AA}^{-1}$) compared to the data found in the literature [10, 12] for similar quasi-Bragg peak position, q_0 . This can be interpreted as the following: contrary to the systems mentioned above, our system consists of a non-ionic surfactant and is stabilized only by steric interactions, therefore the fluctuation which broadens the spectra is much more important.

The scattering intensity of periodic systems can be calculated in terms of a form factor and a structure factor. Several works have been reported [9–12, 14] for the structure factor as well as the form factor of lyotropic lamellar phases in powder state. For our system, because of the broadness of the spectra, the usually accepted approximation which uses a density correlation function very close to the quasi-Bragg peak position in order to calculate the structure factor [10], turned out not to be an adequate approximation [15]. Instead, we have used a structure factor recently developed by Nallet *et al.* [8] (the Eq. (9) of [8]). In their calculations, they use a density correlation function which is valid throughout all q range and not only in the vicinity of the peak position. This allowed us to fit the broad spectra not only in the vicinity of the peak position, but throughout second order peaks. The number of lamellae (N in Eq. (9) of [8]) was chosen to be 100 in order to satisfy the condition $Nd\Delta q \gg 1$ where d is about $100 \text{ \AA}$ for $\gamma = 0.3$. This also corresponds to the birefringent texture of the powder sample (about microns) observed under the microscope.

We employ the simplified square profile as a form factor as used in [8],

$$P_z(q_z) = \frac{4}{q_z^2} (\rho_{\text{water}} - \rho_{\text{oil}})^2 \sin^2(q_z b/2), \quad (1)$$

where ρ_{water} and ρ_{oil} are electronic densities of water and oil (octane) respectively, where the density difference is $0.09 \text{ e\AA}^{-3}$, b is the thickness of a lamellar membrane as drawn in Figure 2. We shall emphasize that this b is not the dry lamellar thickness; *i.e.* two surfactant monolayers plus one sheet of oil (or water), since the form factor is determined based on the density profile. In this model, the electronic density of the hydrophilic part (*head group*) of the surfactant is assumed to be the same as that of water, while the density of the hydrophobic part (*tail group*)

Fig. 2. — Schematic illustration of a density profile along the normal to the membranes Z .

is assumed to be the same as that of oil. This assumption should not be too far from the reality since the chemical composition of the *tails* is $C_{12}H_{25}$, and the electronic density of the molecule which is the closest to this structure is that of $C_{12}H_{26}$ ($0.26 \text{ e}/\text{\AA}^3$) while octane (C_8H_{18}) has an electronic density $0.24 \text{ e}/\text{\AA}^3$. For the *head group*, the electronic density of the POE $[\text{CH}_2-\text{CH}_2-\text{O}]_n$ is 0.37 , while it is 0.33 for water. Therefore, b is described as a thickness of one sheet of oil (or water) plus twice the hydrophobic (or hydrophilic) part of the surfactant monolayers. While the latter is a constant, the former varies both with the surfactant concentration and the oil to water ratio.

Performing the powder averaging in the limit where $q \gg \Delta q$, the intensity can be written as (Eq. (17) of [8]):

$$I(\mathbf{q}) = 2\pi \frac{NL^2}{q^2} P(\mathbf{q}) S(\mathbf{q}) \quad (2)$$

where the structure factor $S(\mathbf{q})$ is defined in the equation (9) of reference [8], and the form factor $P(\mathbf{q})$ is shown above in equation (1) [16]. q^{-2} is the Lorentz factor for randomly oriented samples. With the proposed model, the number of free parameters is only 4: the membrane thickness b , the periodicity d_p , the order parameter η , and the scaling factor A . As it was mentioned above, the number of membranes N in the equation (14) of [8] was fixed to be 100. We also performed fittings with $N = 150$ and 300, but the differences in the obtained values were negligible. The fitting range was chosen as $q_0/2 \leq w \leq 2.5q_0$. The upper limit of q was chosen in order to simultaneously fit the first and the second harmonics, and the lower limit was chosen in order to avoid the excess scattering at small angle [17] which is not taken into account in reference [8]. Besides, the powder average which was done to obtain the equation (17) in [8] is only valid with the condition $q \gg \Delta q$.

This small angle excess scattering [17] originates in the concentration fluctuation, in the fluctuation of the membrane thickness, as well as in the membrane position. We will now briefly remark about this excess scattering. By taking the powder average and low q limit of the equation (5) of the reference [17], one gets,

$$I_{\text{SAXS}(q \rightarrow 0)} = \frac{1}{kT} \left(\frac{m}{v\rho} \right)^2 \kappa db^2, \quad (3)$$

Table I. — *The fitted parameters for all the spectra. α is the oil to water ratio, η is the undulation parameter defined by Caillé, b is the bilayer thickness, d_p is the lamellar periodicity.*

$\gamma = 0.15$	α	η	$b(\text{\AA})$	$d_p(\text{\AA})$
	0.2	0.976	52.2	194
	0.3	0.757	60.1	192
	0.4	0.551	71.4	199
	0.5	0.496	79.8	208
	0.6	0.517	79.4	202
	0.7	0.685	70.2	197
$\gamma = 0.20$	α	η	$b(\text{\AA})$	$d_p(\text{\AA})$
	0.2	0.849	23.9	138
	0.3	0.602	39.3	146
	0.4	0.458	52.9	149
	0.5	0.367	61.8	150
	0.6	0.395	61.9	150
	0.7	0.505	54.5	148
	0.8	0.684	36.4	131
$\gamma = 0.25$	α	η	$b(\text{\AA})$	$d_p(\text{\AA})$
	0.3	0.515	29.9	119
	0.4	0.403	33.4	124
	0.5	0.357	51.8	118
	0.6	0.271	42.6	119
	0.7	0.467	36.0	117
	0.8	0.636	34.9	116
$\gamma = 0.30$	α	η	$b(\text{\AA})$	$d_p(\text{\AA})$
	0.2	0.510	8.99	92.8
	0.3	0.380	23.3	96.7
	0.4	0.219	32.2	98.5
	0.5	0.197	39.6	97.9
	0.6	0.217	42.0	98.9
	0.7	0.394	37.9	94.7
	0.8	0.446	29.1	87.4

where m and v are the mass and volume of a surfactant molecule respectively, d is the distance between two membranes, and k is the bending modulus of a membrane. This excess scattering is expected to increase with the dilution since the lamellar periodicity increases. This was confirmed from the data shown in Figure 1.

In Figure 3, we show the fitted figures for $\alpha = 0.3$ and 0.5 for all the surfactant concentrations. In Table I, the parameters obtained from the fittings are shown. For a fixed surfactant concentration γ , the periodicity d_p as well as the membrane thickness b have a maximum at

around $\alpha = 0.5$ (water to oil ratio is 1) while the order parameter η has a minimum. In order to understand this variation in η as a function of oil to water ratio, we developed a model as described below. The bending rigidity of a monolayer film is supposed to be a half of that of a bilayer [18], and the interactions between the monolayers were assumed to be Helfrich-like. Then, the free energy of the system was written as a sum of two interactions, one between monolayers with a water layer in-between, and the other with an oil layer in-between. We will write these two interaction energies per area as V_w and V_o respectively, then the free energy density can be written as,

$$f(\phi_o, \phi_w) = \frac{1}{d_p} [V_o(d_p \phi_o) + V_w(d_p \phi_w)]. \quad (4)$$

Here, ϕ_o and ϕ_w are oil and water volume fraction, and $d_p \phi_o$ and $d_p \phi_w$ are the oil and water layers thickness respectively.

Nallet *et al.* have calculated the compression modulus for two-component lamellar phases [19] as well as three-component systems (doped-solvent lamellar phases) [20]. Following those expressions, we will now derive the expression for $\bar{B}$ for our system. Here we assume the monolayer to be incompressible, the smectic periodicity $d_p \approx d_{\text{monolayer}}/\phi_s$ to the first order approximation, where $d_{\text{monolayer}}$ is the monolayer thickness and $\phi_s = 1 - (\phi_o + \phi_w)$ is the volumetric concentration of surfactant. The free energy of the system then, is a function only of ϕ_o and ϕ_w . Therefore, it can be written as,

$$F = \int d^3x f(\phi_o, \phi_w). \quad (5)$$

The fluctuation around the equilibrium can be expressed by the expansion of f to the second order of the concentration fluctuations, which gives a simplified expression of equation (2) in the reference [20]. The free energy density can be written as,

$$f = f_0 + \frac{1}{2} \left[\frac{\partial^2 f}{\partial \phi_o^2} \delta \phi_o^2 + \frac{2 \partial^2 f}{\partial \phi_o \partial \phi_w} \delta \phi_o \delta \phi_w + \frac{\partial^2 f}{\partial \phi_w^2} \delta \phi_w^2 \right]. \quad (6)$$

The free energy density of a lyotropic smectic system was derived [2] as a function of the displacement vector $\mathbf{u}$ and the concentration variable δc , with elastic constants B , K_1 and χ ,

$$f = f_0 + \frac{B}{2} \left(\frac{\partial u}{\partial z} \right)^2 + \frac{1}{2} K_1 \left(\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} \right)^2 + \frac{1}{2\chi} \delta c^2 + C_c \delta c \frac{\partial u}{\partial z}. \quad (7)$$

Defining $\delta c = \delta \phi_o - \delta \phi_w$, and using $\partial u / \partial z = \delta d_p / d_p = (\delta \phi_o + \delta \phi_w) / \phi_s$, $\bar{B} = B - C_c^2 \chi$ and by comparing (4), (6) and (7), we get,

$$\begin{aligned} B &= \frac{d_p}{4} [W_w(1 - \phi_o + \phi_w)^2 + W_o(1 - \phi_w + \phi_o)^2]; & \chi^{-1} &= \frac{d_p}{4} [W_w + W_o] \\ C_c &= \frac{-d_p}{4} [W_w(1 - \phi_o + \phi_w) - W_o(1 - \phi_w + \phi_o)]; & \bar{B} &= d_p \frac{W_w \times W_o}{W_w + W_o}, \end{aligned} \quad (8)$$

where W_w and W_o are $\delta^2 V_w / \delta d_w^2$ and $\delta^2 V_o / \delta d_o^2$, respectively. Assuming that both V_o and V_w are Helfrich-like potentials [9], they can be written as,

$$V_o = A \frac{(kT)^2}{\kappa_{\text{mono}} d_o^2}, \quad (9)$$

$$V_w = A \frac{(kT)^2}{\kappa_{\text{mono}} d_w^2}, \quad (10)$$

Fig. 3. — Selected examples of the X-ray intensity profiles fitted to the equation (2): a) $\alpha = 0.15$, $\gamma = 0.30$; b) $\alpha = 0.15$, $\gamma = 0.50$; c) $\alpha = 0.20$, $\gamma = 0.30$; d) $\alpha = 0.20$, $\gamma = 0.50$; e) $\alpha = 0.25$, $\gamma = 0.30$; f) $\alpha = 0.25$, $\gamma = 0.50$; g) $\alpha = 0.30$, $\gamma = 0.30$; h) $\alpha = 0.30$, $\gamma = 0.50$.

Fig. 4. — The calculated (line) and measured values (●) for η for (a) $\gamma = 0.15$, (b) $\gamma = 0.20$, (c) $\gamma = 0.15$, (d) $\gamma = 0.30$.

where $A = 3\pi^2/128$ and κ_{mono} is the bending modulus of a monolayer. Substituting into (8), and using $d_o = d_p\phi_o$, $d_w = d_p\phi_w$, $d_w = d_p\phi_w$, we get,

$$\bar{B} = \frac{A(kT)^2}{\kappa_{\text{mono}}d_p^3} \frac{1}{\phi_o^4 + \phi_w^4}. \quad (11)$$

Now, we will assume that $K \equiv 2\kappa_{\text{mono}}/d_p$ is constant with variation of α from the following argument: for $\alpha = 0.5$, $K_{0.5} = \kappa_{\text{mono}}/0.5d_p$, while for $\alpha = 0.1$, $K_{0.1} = \kappa_{\text{bilayer}}/d_p = 2\kappa_{\text{mono}}/d_p = K_{0.5}$. Using again the definition of η , $\eta = q_0^2 kT/8\pi\sqrt{\bar{B}K}$ and also using $\phi_o = \alpha(1 - \gamma)$, $\phi_w = \alpha(1 - \gamma)(1 - \alpha)$, we get:

$$\eta = \frac{4}{3}(1 - \gamma)^2 \sqrt{\alpha^4 + (1 - \alpha)^4}. \quad (12)$$

In Figure 4, we show the η values obtained from fittings, as well as theoretically predicted values using equation (14) for each γ as a function of α , where there is no adjustable parameter. There is a good agreement between the two values specially for $\gamma = 0.25, 0.30$. The disagreement for the more dilute samples is probably caused by the excess scattering at $q \rightarrow 0$ mentioned above. Finally, from the definition of η above, the minimum of η at $\alpha = 0.5$ leads to the following conclusion: while the bending modulus is constant throughout all a values, the compressibility is higher when $\alpha \rightarrow 0.5$, *i.e.* when the monolayers are separated with equal thicknesses of water layer and oil layer. This maximal compressibility leads to a better alignment for the symmetrical monolayer – two solvent phase as opposed to the bilayer – one solvent phase.

4. Conclusions

Our success in fitting the broad spectra of powder samples of sterically stabilised lyotropic lamellar phases confirms the following two aspects. First, the structure factor has to be expanded not only around the quasi-Bragg peak position but through the entire q range in order to fit through the second harmonics, secondly the importance of incorporating the form factor which successfully describes the change in structure as well as dynamic characteristics as the water/oil ratio is varied. For the first time, our model attempted to describe the free energy of lamellae as a sum of Helfrich interactions between monolayers which have oil or water layers in-between. From this expression, one can calculate the order parameter η . The calculated values showed a good agreement with the measured results. η shows a minimum at around $\alpha = 0.5$, which indicates a better quasi-long range ordering for the case where the system consists of monolayers separated by equal amounts of water and oil. In conclusion, that as the system goes through the transition from monolayer lamellae to bilayer lamellae, while the bending rigidity K stays constant and the compressibility $\bar{B}$ decreases.

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membrane position is not modelled with the harmonic theory. They take into account the terms in the form factor originating from fluctuations which are ignored in our model when equation (2) was derived; *i.e.* the structure factor and the form factor of the scattering intensity function are not decoupled. These considerations are important for the systems close to a structural phase transition, where the bending rigidity lowers drastically, and the fluctuation of the bilayer structure dominates the organization mechanism. In this regime, therefore, it is not plausible to approximate the membrane fluctuation with a harmonic theory. However, this is not important for the case in the present article where the system is far from the phase transition and does not show the critical fluctuations. In the present case, while we do employ the structure factor which uses the correlation function which is valid through all the q value, we do not take into account the coupling of the structure factor and the form factor.

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