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Structural defects of a lamellar lyotropic mesophase : a neutron scattering study

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Résumé. — Contrairement aux images couramment admises, la géométrie plate n'est pas la configuration de plus basse énergie libre pour les bicouches de SDS dans la phase lamellaire SDS/eau. Par diffusion de neutrons aux petits angles, nous observons une figure de diffusion diffuse, qui s'ajoute aux taches de diffraction caractéristiques de toutes les phases lamellaires. La diffusion diffuse loin du faisceau incident est produite par un arrangement de défauts de structure, dont la pseudopériode est de 60 Å à l'intérieur d'une lamelle. La diffusion diffuse près du faisceau incident est causée par des défauts de texture, de dimensions plus grandes que 200 Å.

Abstract. — Contrarily to previous expectations, the flat geometry is not the configuration of lowest free energy for the bilayers of SDS in the lamellar phase of SDS/water. Indeed, neutron scattering reveals an unusual pattern of *diffuse* scattering at small angles, in addition to the regular diffraction spots of a layered mesophase. The diffuse scattering away from the beam is produced by an array of *structural* defects, with a pseudo-period of 60 Å within one layer. The diffuse scattering around the beam is caused by *textural* defects, with dimensions larger than 200 Å.

1. Introduction.

Mixtures of amphiphilic molecules with water form a variety of mesophases which are regular arrays of structural elements such as bilayers, rods, ribbons, etc. [1]. The « simplest » of these mesophases are the lamellar phases, where amphiphilic bilayers are separated by thin water layers. These phases are noteworthy because of their similarity with biological membranes. An implicit assumption in most studies of the lamellar phases so far is that the layers are infinite and flat. Yet there has already been some evidence that this assumption may not always hold. In the lecithin-water system, corrugated structures are found when some or all of the amphiphilic molecules are in the rigid, extended configuration [2]. Although this was acknowledged, it was still assumed that the flat geometry should be the structure of lowest free energy whenever the chains of the amphiphilic molecules are liquid like, i.e., when the amphiphilic bilayer is a 2-dimensional liquid. More recently, M. Holmes and J. Charvolin found structural defects

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in a lamellar phase whose chains are liquid like [3]; these defects were described as pores or channels which interrupt the bilayers. However their mesophase is very close to a lamellar-to-nematic transition, where the bilayers break up into small disks; thus despite these findings it could still be maintained that « regular » lamellar phases should nevertheless conform to the flat geometry.

In the present paper we show that spontaneous structural defects exist also in a common lamellar phase. This is the « L_x » phase of the SDS/water system in the terminology of Luzzati *et al.* [4]. This phase is formed at high SDS concentrations (above 70 % wt.) and high temperature (above 53 °C). The structure of this phase is defined by its reciprocal space which is observed in scattering experiments. The reciprocal space contains the classical features of a lamellar « L_x » phase :

— a linear array of spots along the symmetry axis of the phase; these spots are the Bragg reflexions which correspond to the repetition (33 Å) of the bilayers, they are spaced by $2\pi/33 = 0.19 \text{ \AA}^{-1}$;

— a diffuse ring in the equatorial plane normal to the symmetry axis. This ring corresponds to the average distance (4.5 Å) between neighbouring chains within one SDS bilayer; this ring is diffuse because the chains are liquid like; it is located at $2\pi/4.5 = 1.4 \text{ \AA}^{-1}$.

In this study we show that the reciprocal space of SDS/water actually contains some additional regions of diffuse scattering. These diffuse structures imply the existence of spontaneous structural defects in this lamellar mesophase : the flat geometry is not the configuration of lowest free energy for SDS bilayers in the L_x phase.

2. Methods.

2.1 SAMPLES. — In order to achieve a good contrast in neutron scattering the mesophases were made of protonated SDS and deuterated water, as described previously [5]. They were contained in quartz cells which were closed tightly and sealed with a polyurethane glue. With thick (1 mm) cells, non oriented samples were obtained. Oriented samples were prepared by pushing a mesophase into a stack of 40 thin quartz plates, with regular spacings of 50 μm between the plates : the flow of the mesophase through the stack produced an orientation of its layers parallel to the plates; this orientation was maintained by the anchoring of the SDS layers on the plates. An excess of the mesophase was added on top of the stack, to act as a buffer against a possible loss of water; the whole unit was contained in a sealed fluorimeter quartz cell.

2.2 SCATTERING GEOMETRIES. — Figure 1 shows the geometries used for oriented samples.

(i) Incident beam parallel to the layers : the scattering vectors of the collected neutrons are in a plane which contains the symmetry axis of the mesophase, with the Bragg diffraction spots, and one line of the equatorial plane.

(ii) Incident beam normal to the layers : the scattering vectors of the collected neutrons give a picture of the equatorial plane.

(iii) Tilted sample : this geometry selects a plane of the reciprocal space whose normal is tilted by an angle ω with respect to the symmetry axis of the mesophase.

2.3 MULTIPLE SCATTERING. — Only neutrons scattered by simple coherent scattering events give a correct picture of the reciprocal space. Because the oriented samples used in this work are thick, the probability of multiple scattering is not negligible. Most of the double scattering events are coherent \times incoherent events, because the samples contain a majority of H nuclei, which have a very large cross section for incoherent scattering. Such events only add a flat background to the scattered intensity, at the expense of the coherently scattered intensity. This effect is trivial, except for neutrons scattered parallel to the quartz plates in geometry (i) above. In this geometry, neutrons which remain in between 2 quartz plates must cross 5 mm of mesophase,

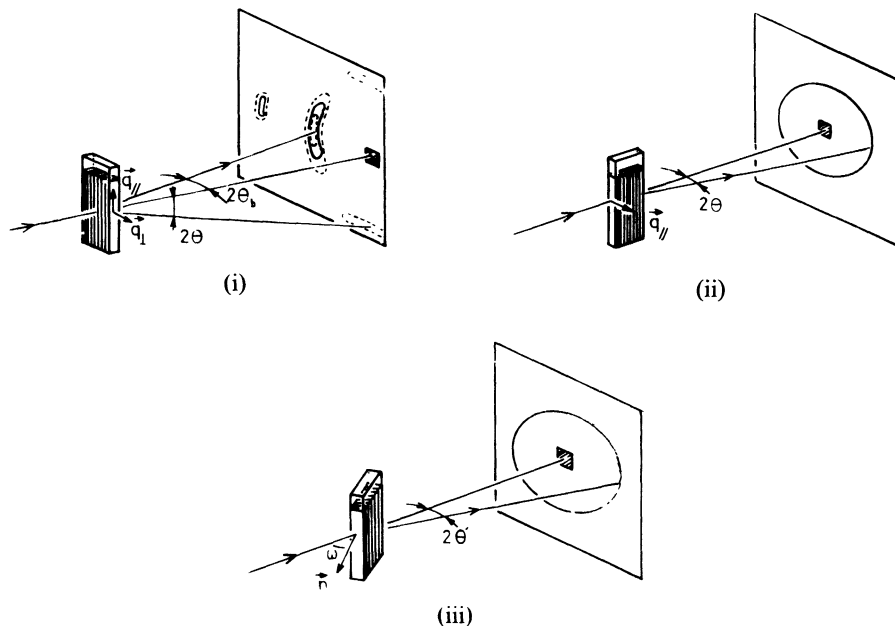


Fig. 1. — Scattering geometries. (i) Incident beam parallel to the layers of the mesophase : the neutrons collected on the detector describe a plane of the reciprocal space ; this plane contains the symmetry axis of the reciprocal space (horizontal axis) with the Bragg diffraction spots and one line of the equatorial plane (vertical axis). (ii) Incident beam normal to the layers : the neutrons collected on the detector have their scattering vectors \mathbf{Q} in the equatorial plane of the reciprocal space. (iii) Tilted sample.

whereas in other directions the neutrons must cross 4 mm of quartz plates and only 1 mm of mesophase. This produces an extinction in the directions parallel to the plates, i.e. in the equatorial plane of the reciprocal space. This problem can be circumvented by tilting the sample by 2° , so that the direction of extinction is moved outside the detector ; such a small tilt remains compatible with the observations of Bragg scattering spots, because the layers of the mesophase are slightly disoriented with respect to the plates.

Then there is the problem of those neutrons which undergo 2 successive coherent diffractions : these events are rare except when each diffraction corresponds to the first Bragg diffraction order. They can result in scattering either along the beam or at the position of the second diffraction order. Neither of these effects is relevant for the present work, which is based on the observation of diffuse scattering outside the regions of Bragg diffraction.

2.4 INSTRUMENTS. — Experiments on unoriented samples were performed on the spectrometer PACE at the reactor ORPHEE of LLB in CEN-Saclay. A double graphite monochromator was used, yielding a narrow distribution of wavelengths ($\Delta\lambda/\lambda = 1\%$ around $\lambda = 5 \text{ \AA}$); this was important to prevent an overlap of the peaks in the isotropic average of the scattering pattern. Experiments on oriented samples were performed on PAXY at the same institution. Because no isotropic average is performed in this case, a higher flux is required ; this is achieved with a mechanical wavelength selector ($\Delta\lambda/\lambda = 6\%$ around $\lambda = 3.8 \text{ \AA}$). The lower resolution is not a problem because the various regions of scattering correspond to different azimuthal directions. Some experiments were also performed at ILL, in Grenoble, on the multidetectors D16 ($\Delta\lambda/\lambda = 1.5\%$ around $\lambda = 4.5 \text{ \AA}$) and D17 ($\Delta\lambda/\lambda = 5\%$ around $\lambda = 10.4 \text{ \AA}$).

3. Results.

3.1 DIFFUSE SCATTERING AWAY FROM THE BEAM. — As mentioned in the introduction, we find that the L_α phase of the SDS/water system produces a large amount of diffuse coherent scattering at small angles, in a region of reciprocal space where flat bilayers should not scatter. This is already obvious in the spectra of unoriented samples, where a large hump appears around $Q = 0.11 \text{ \AA}^{-1}$ (Fig. 2). Yet this hump was missed by previous investigators [4]. This can be explained in 3 ways. Firstly, the hump is intense at 55 °C, near the lower temperature limit of the L_α phase, but as temperature rises it becomes broader (65 °C) and eventually merges with the background (Note that Luzzati *et al.* [4] worked at 76 °C). Secondly, it also becomes broader when small amounts of dodecanol are present with the SDS; such amounts can easily be produced at high temperature by an autocatalytic hydrolysis of SDS. Thirdly, the use of a linear collimation in X-ray scattering can obscure all the diffuse features which are near the inside edge of an intense line (the first order of diffraction).

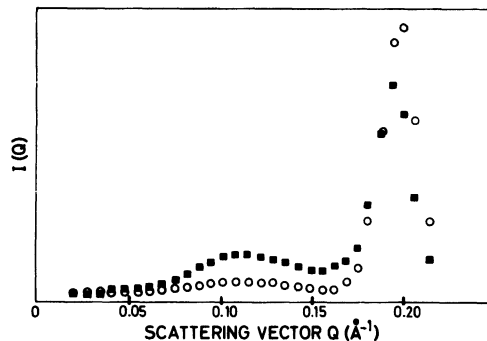


Fig. 2. — Radial scattering curve for an unoriented sample made of 70.08 % SDS and 29.92 % D_2O . The hump at $Q = 0.11 \text{ \AA}^{-1}$ is produced by diffuse scattering from structural defects. Its magnitude decreases with a rise in temperature : squares 55 °C; circles 64 °C. The peak at 0.19 \AA^{-1} is the first order Bragg diffraction of the layers; its width is controlled by the resolution of the experiment, in this case $\Delta\lambda/\lambda = 6 \%$. Spectrometer PACE with a mechanical wavelength selector; similar results were obtained with a monochromator.

This diffuse scattering reflects the existence of correlations over a range of 60 \AA ; a more precise picture of these correlations in the reciprocal space is provided by the experiments on oriented samples. Figure 3 shows two maps of the XY detector of PAXY, obtained in geometry (i) of figure 1, where slices at two different intensity levels have been isolated : here the layers are vertical and normal to the figure; the incident beam is also normal to the figure, and the axis of symmetry of the reciprocal space is the horizontal axis of the figure. The large crescent centered on this axis is the first diffraction order of the layers; this crescent is wide because the cross section of the detector is taken at low intensities, whereas the peak intensity is very high; actually a cross section taken at half height of this peak would reveal disorientations on the order of 2 degrees. The horizontal stripes correspond to the hump seen at $Q = 0.11 \text{ \AA}^{-1}$ in figure 2. Because the reciprocal space in this picture has a symmetry of revolution around the horizontal axis, these stripes must be a section of a cylinder of revolution around this axis. This is confirmed by experiments in the other geometries of figure 1 : with the beam along the axis of symmetry of the mesophase, the

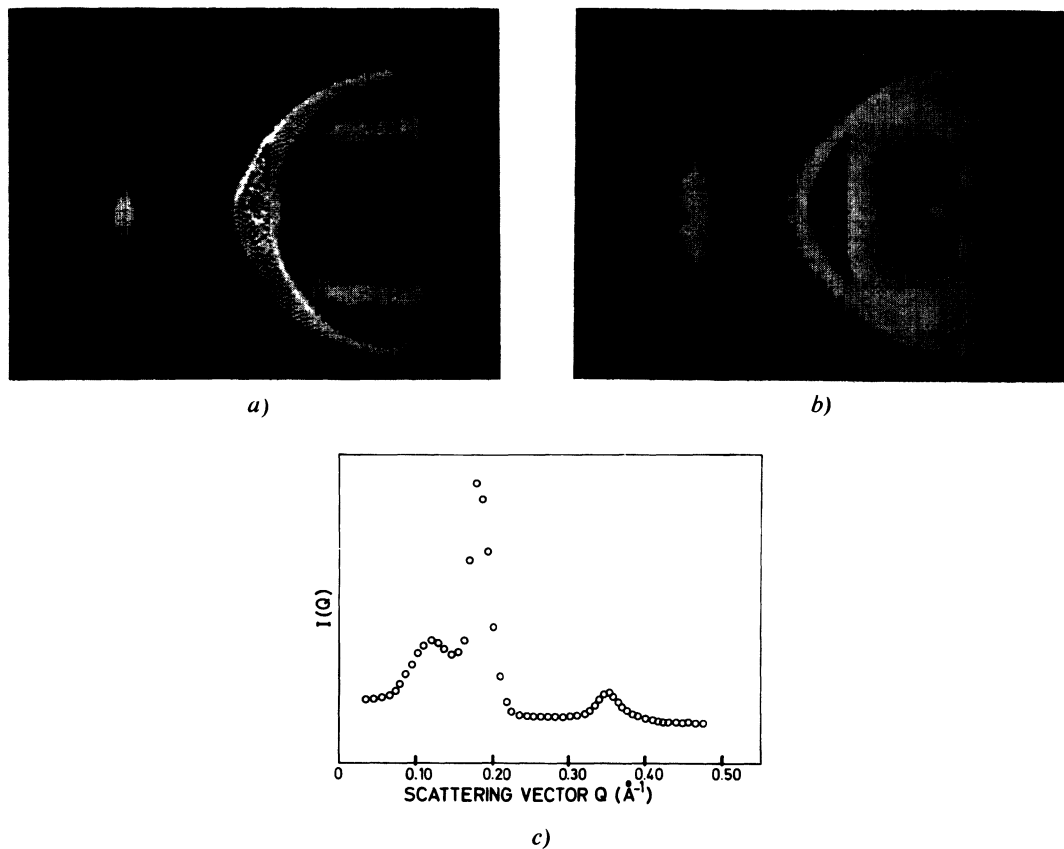


Fig. 3. — (a) A slice at constant intensity of the scattering pattern observed with PAXY; scattering geometry as in Fig. 1(i). The sample is a lamellar phase made of 70.01 % SDS and 29.99 % D_2O at a temperature of 64°C ; it is oriented by a stack of vertical quartz plates. The horizontal axis is the axis of symmetry of the reciprocal space; on this axis are, from right to left, the beam stop, the 1st diffraction order of the layers and the 2nd order. In slices made at lower intensity levels, a cross of diffuse scattering appears around the beam stop. The horizontal stripes are the section of a tube by a radial plane; it is argued that they are caused by diffuse scattering from structural defects in the layers. (b) A slice at a lower intensity level of the same scattering pattern. The cross around the beam is produced by textural defects. (c) Isotropic regrouping of the same scattering pattern; the horizontal stripes give rise to the hump at $Q = 0.11 \text{ \AA}^{-1}$; the diffraction orders are at 0.19 \AA^{-1} and 0.38 \AA^{-1} .

section of this cylinder by a plane normal to the axis is observed, i.e. a circle (Fig. 4a); tilting the sample yields an ellipse (Fig. 4b) whose axes are consistent with the dimensions measured in figure 4a (see geometry (iii) of Fig. 1).

An apparent discrepancy between the spectra of unoriented samples and those of oriented ones is the area covered by the region of diffuse scattering. In figure 2 this region appears extremely broad, with a half width of 0.06 \AA^{-1} . In figures 3a, b and 4 the diffuse scattering seems confined to the sections of a thin tube. In fact, these sections correspond to a level just below the peak intensity of this diffuse scattering; this peak intensity is much lower than that of the first diffraction order. A cross section at a lower intensity level reveals that the region of diffuse scattering broadens considerably; in all cases its half width is much broader than the resolution of the experiment. Finally an average over all azimuthal directions in the detector yields a radial scattering curve

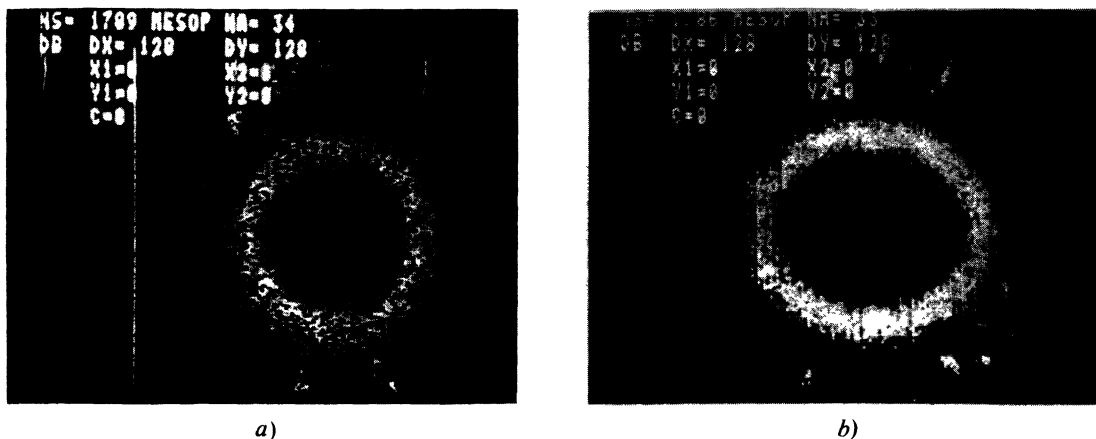


Fig. 4. — Same as Fig. 3, but with the last 2 geometries of Fig. 1. (a) A slice at constant intensity in the equatorial plane of the reciprocal space, obtained with the geometry (ii) of Fig. 1. The ring is another section of the tube already seen in Fig. 3a, but this time by the equatorial plane. (b) The elliptical ring is a section of the tube of the reciprocal space by a tilted plane, as indicated by geometry (iii) of Fig. 1.

(Fig. 3c) which is quite similar to the curve obtained for unoriented samples (Fig. 2) although the angular averages are not the same in both cases.

3.2 TEMPERATURE BEHAVIOUR. — At 55 °C, near the lower limit of the lamellar phase, the region of diffuse scattering is made of 2 identical rings around the axis of symmetry. The section of each ring by a plane containing this axis yields a set of 2 dumbbells (Fig. 5). The radius of the rings is 0.10 \AA^{-1} , and their spacing along the axis of symmetry is 0.06 \AA^{-1} . When the temperature is increased, the rings progressively merge into a tube (65 °C); then the tube becomes thicker and

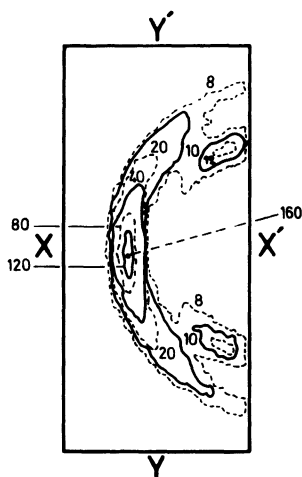


Fig. 5. — Contour map obtained on D16 with the same sample and geometry as in Fig. 3, but at 55 °C. The beamstop is outside the detector, to the right of the figure; the large crescent on the left is the first order of diffraction. The tube of diffuse scattering, whose radial section gave the horizontal stripes in Fig. 3, has been replaced by 2 rings around the horizontal axis. The radial section of one of these rings shows up here as a set of 2 dumbbells located at 0.10 \AA^{-1} from this axis; the other ring is located at $2 \times 0.06 \text{ \AA}^{-1}$ to the right of this one.

longer at still higher temperatures (75 °C). In real space this evolution means that at « low » temperatures the structural defects which cause the diffuse scattering are correlated across 2 or 3 bilayers; the Q vectors of these correlations are tilted with respect to the axis of symmetry; at high temperatures all correlations between adjacent bilayers are lost.

3.3 CONCENTRATION OF SDS. — All the results presented above were obtained with samples containing 70 % SDS and 30 % D₂O by weight. This composition is close to one boundary of the L_x phase, which extends from 69 % SDS, 31 % D₂O to 81 % SDS, 19 % D₂O; it is also near the maximum water content of the phase that the pattern of diffuse scattering is most distinctive. As the water content is lowered, the region of diffuse scattering becomes broader, indicating a loss of the interlayer correlations for the structural defects observed at 60 °C, and at higher temperatures a loss of the correlations within one layer (Fig. 6).

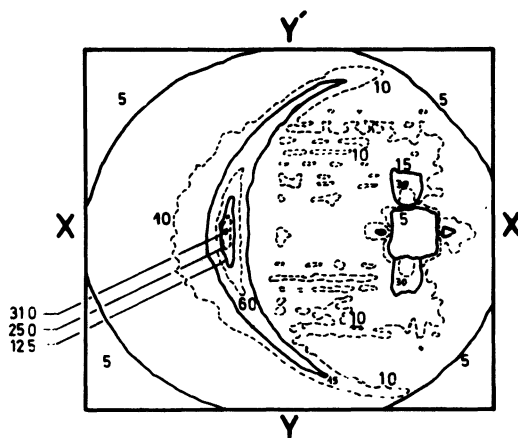


Fig. 6. — Same geometry as in Figs. 3 and 5, but for a mesophase with low water content (SDS 77.16 %, D₂O 22.84 %) and at high temperature (70 °C). The tube of diffuse scattering caused by structural defects has merged with the background. The cross around the beam is produced by textural defects.

3.4 DIFFUSE SCATTERING NEXT TO THE BEAM. — In addition to the stripes at $Q = 0.11 \text{ \AA}^{-1}$, the spectra of oriented samples also show some diffuse scattering next to the beam. This scattering appears as a cross extending in the directions parallel and normal to the symmetry axis (Fig. 6); in the range $0.03 \text{ \AA}^{-1} < Q < 0.07 \text{ \AA}^{-1}$ its intensity is comparable with that of the stripes at $Q = 0.11 \text{ \AA}^{-1}$. In the direction of the symmetry axis, this scattering can contain a contribution from double scattering on the 1st order of diffraction (see Sect. 2); however this possible artefact does not explain the angular dependence of the observed scattering. In the direction normal to the symmetry axis, the scattering next to the beam must be produced by large anisotropic defects in the sample ($Q < 0.03 \text{ \AA}^{-1}$, thus $d = 2\pi/Q > 200 \text{ \AA}$). These defects must be elongated in the direction normal to the layers, and very thin in the directions parallel to the layers.

4. Discussion.

Our results can be summarized as follows. Samples prepared at « high » water content (30 %) within the lamellar phase of the SDS/water system produce a characteristic pattern of diffuse scattering. This scattering is confined to small regions of reciprocal space away from the regular diffraction spots of the lamellar structure; therefore it can be analysed in terms of defects which break the symmetry of this structure. Two classes of defects can be distinguished, depending on the regions of reciprocal space which are considered.

4.1 TEXTURAL DEFECTS. — For the diffuse scattering observed next to the beam ($Q < 0.03 \text{ \AA}^{-1}$), the relevant spatial scales ($d > 200 \text{ \AA}$) are much larger than the period of the layers (33 \AA). Such scales correspond to the texture of the sample rather than to its structure. Isotropic scattering in this range can be produced by trivial defects such as bubbles or voids; however the anisotropic scattering observed in the oriented samples must be produced by specific defects which are elongated along the symmetry axis of the mesophase. So far we do not know whether these defects are the same as those found in bulk samples, or whether they are induced by the flow of the mesophase through the stack of quartz plates during sample preparation. It is important to note that the same defects are observed through the whole concentration and temperature ranges of the lamellar phase.

4.2 STRUCTURAL DEFECTS. — The diffuse scattering away from the beam corresponds to a pseudo-period of 50 \AA , comparable with the period of the layers. Therefore it must be produced by a change in the equilibrium structure of the mesophase. At high temperature or low water content, the region of diffuse scattering is elongated in the direction normal to the layers; in real space it represents correlations between defects in directions parallel to the layers. The dimensions of these defects along the normal to the layers match the thickness of the bilayers; their average separation within one layer must be close to 60 \AA . At low temperature and high water content the diffuse scattering concentrates in smaller regions located in directions tilted at an angle of 60° from the normal to the layers. In real space this represents correlations between defects which are staggered in adjacent bilayers. The range of these correlations is related to the dimensions of the regions of diffuse scattering; it does not exceed 2 or 3 bilayers.

This evolution with temperature may hold a clue for understanding these spontaneous deformations of the lamellar phase. Indeed, the structural defects appear to become organized near the boundaries at high water concentration or low temperature of the lamellar phase. Beyond these boundaries, a mesophase made of SDS rods separates out [6]; these rods are packed on a rectangular lattice, and it is likely that their section is rectangular as well. Thus the structural defects can be seen as heterophase fluctuations of the rods in the lamellar phase; an attractive picture would be a local corrugation of a few layers, so that each layer could be described as an array of rods assembled and fused in a staggered configuration.

At this point it is appropriate to draw a comparison with other lamellar phases which depart from the flat geometry. As mentioned in the introduction, regular corrugated structures have been found in lecithin/water systems; however such structures are only observed when some or all of the amphiphilic chains are in the rigid extended configuration; lamellar phases with the same composition but liquid chains have flat layers. Therefore the driving force for the deformation of these layers differs from that in the SDS/water system.

The observation of diffuse scattering away from the beam in DACl/water/ NH_4Cl by Holmes and Charvolin seems more closely related to our observations in SDS/water [3]. However, closer inspection reveals that the nature of the defects and the mechanism for their formation are again quite different from those in SDS/water. Firstly, the defects in DACl have a strong effect on the average curvature of the hydrocarbon/water interfaces, whereas those in SDS/water do not. Indeed, the orientational order parameter of the DACl molecules is lower by a factor of 2 in a mesophase with defects as compared with a mesophase without them. Yet in SDS/water, the change is only by 25%, and can be accounted for by a change in the average thickness of the layers. Secondly, the defects occur in DACl at a much higher water content, near the boundary to a nematic phase where the layers break up into small disks.

Despite these differences, a unified description might be found if a « natural curvature » can be defined for the amphiphile/water interfaces. This would be the curvature which the interface would take spontaneously if it were not constrained by the necessity to build a periodic structure. This hypothetical quantity expresses the balance of forces at the interface : hydration « forces », electrostatic repulsions, hydrophobic « forces », etc... For each mesophase, there is a narrow

range of conditions where this natural curvature would be near zero; then the flat geometry is the configuration of lowest free energy for the bilayers. Other conditions may be encountered, where this natural curvature is significantly different from zero, and yet not large enough to match the average curvature of other mesophases, such as those made of rods. Then the free energy of the lamellar phase may be lowered by the introduction of defects which change the average curvature of the interfaces.

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