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Y. Hendrikx[a]; J. Charvolin[a]; P. Kekicheff[a]; M. Roth[b]
[a] Laboratoire de Physique des Solides associé au CNRS, Btiment 510, Université Paris Sud, Orsay, France [b] Institut Laue-Langevin, Grenoble, France

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Structural fluctuations in the lamellar phase of sodium decyl sulphate/decanol/water

by Y. HENDRIKX, J. CHARVOLIN and P. KEKICHEFF
Laboratoire de Physique des Solides associé au CNRS, Bâtiment 510,
Université Paris Sud, 91405 Orsay, France

and M. ROTH
Institut Laue-Langevin, 38042 Grenoble, France

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We present a neutron scattering study of oriented samples for the lamellar phase of the ternary mixture sodium decyl sulphate/1-decanol/water. Diffuse scatterings are observed, around the Bragg reflections and away from them, which show that the structure of this lamellar phase deviates from the periodic stacking of infinite homogeneous lamellae of water and amphiphilic molecules usually proposed for the structure of lamellar phases. The nature of this deviation evolves with the soap/decanol ratio, according to the location of the sample in the lamellar domain of the phase diagram. In the middle of the domain the deviation relates to the organization of the lamellar stacking, without apparent modification of the structure of the lamellae of amphiphiles. Moving away from the middle, for higher soap/decanol ratios, the structure of the lamellae appears to be randomly perturbed, eventually by the presence of a few water regions piercing them. When the boundary of the lamellar domain is approached, for still higher soap/decanol ratios, the density of these peturbations increases and they start to be correlated over limited distances, within the lamellae and from lamella to lamella. The local symmetry of these short range correlations is such that these perturbations may be seen as structural fluctuations which may be seen as precursors of the transformation of the lamellar phase into a neighbouring phase on the phase diagram. This phenomenon is discussed briefly in relation to the structural fluctuations of the relative concentrations of sodium decyl sulphate and decanol within the aggregates.

1. Introduction

The well-established description of lamellar phases of amphiphilic molecules in the presence of water is that of a periodic stacking along one dimension of alternate homogeneous lamellae of water and amphiphilic molecules with flat interfaces. This description emerged from textural studies, showing the existence of focal conics associated with a smectic order [1] and from X-ray scattering studies of polycrystalline samples, exhibiting a set of Bragg reflexions in the ratio 1, 2, 3 . . . [2]. However recent X-ray and neutron scattering studies on oriented samples have suggested that some lamellar phases might have more complex structures. Indeed, observations of diffuse scattering, which was not detectable in the polycrystalline configuration, show that the quality of the lamellae stacking and the structural homogeneity of these lamellae may be questioned.

The first diffuse scatterings observed in lamellar phases were found away from the Bragg spots, with samples close to the boundary of the lamellar domain in the phase diagram. They were therefore associated with structural fluctuations announcing the change of symmetry of the phase. For instance, in the lamellar phase of decyl ammonium chloride/water/ammonium chloride, close to the lamellar–nematic transition, these diffuse scatterings were shown to result from a fragmentation of the lamellae of amphiphilic molecules into small oblate aggregates [3]. Similar behaviour was reported recently for the lamellar phase of caesium perfluoro-octanoate/water [4]. Such diffuse scattering was also observed in the lamellar phase of the more classical system, sodium dodecyl sulphate/water, in the vicinity of the biphasic domain separating the lamellar phase from a neighbouring phase with bi-dimensional symmetry [5]. Recently a second type of diffuse scattering, located around the Bragg spots, was also observed in the first system [3]. These diffuse scatterings are being analysed in terms of pretransitional fluctuations in the ordering of the oblate aggregates at the approach of the transition to the nematic phase [6]. In all these cases the lamellae of amphiphilic molecules are observed, or suspected, to be no longer infinite or homogeneous. They can be fragmented, or pierced by holes of various shapes, in ways which correspond to important modulations of the interfacial curvatures [7].

All of these are binary systems with only one ionic amphiphilic species, so that the modulations of interfacial curvatures are certainly to be associated with variations of the degree of dissociation of the ionic head groups of the amphiphilic molecules. Indeed we may expect that the degree of dissociation of the head groups is higher in curved interfacial regions than in flat regions. Such modulations might therefore be enhanced by mixing ionic and non-ionic amphiphilic species in the same system and this idea guided us towards the investigation of the lamellar phase of a ternary system made of an ionic amphiphilic species, sodium decyl sulphate, and a non-ionic one, decanol, in the presence of water [8]. We have studied the structure of the lamellar phase of this system following a particular line of its phase diagram [9]. Along this line the water content is maintained constant while the soap/decanol ratio is increased, moving from the middle of the lamellar domain towards its boundary with a biphasic domain separating the lamellar phase from a neighbouring rectangular phase. As expected we observed intense diffuse scatterings away from the Bragg reflections and around them, which we interpret as structural fluctuations evolving with the soap/decanol ratio.

2. Experimental

2.1. *Preparation and characterization of the samples*

The samples were prepared in sealed glass tubes by mixing together known amounts of sodium decyl sulphate (SdS, Merck p.p.a. 99 per cent), 1-decanol (C_{10}–OH, Fluka p.p.a. 99 per cent) and D_2O (99·8 per cent, CEN Saclay). The tubes were stored in an oven for several days and centrifuged back and forth several times to ensure the homogeneity of the samples. The temperature of the oven during the homogenization was maintained below 40°C in order to prevent the hydrolysis of SdS into decanol. The composition of the samples, in weight and mole per cent, together with the soap/decanol molar ratio, (SdS/C_{10}–OH), are given in the table. All of the experiments were carried at 23°C.

The samples were first identified from their textures under a polarizing microscope. They all show the focal conics and oily streaks characteristic of one-dimensional lamellar phases [1, 10]. This lamellar structure was then confirmed by X-ray scattering studies of polycrystalline samples. We used a Guinier camera with monochromatic Cu,Kα_1 radiation of wavelength λ = 1·54 Å. The samples were contained between

Composition of the samples.

Sample	Weight per cent SdS	Weight per cent C_{10}–OH	Weight per cent D_2O	Mole per cent SdS	Mole per cent C_{10}–OH	Mole per cent D_2O	SdS/C_{10}–OH (molar ratio)
1	19·24	30·49	50·26	2·66	6·94	90·40	0·38
2	29·28	20·52	50·20	4·09	4·72	91·19	0·87
3	33·23	16·55	50·22	4·66	3·82	91·52	1·22
4	35·17	14·56	50·26	4·94	3·36	91·70	1·47
5	39·19	10·53	50·28	5·52	2·44	92·04	2·26

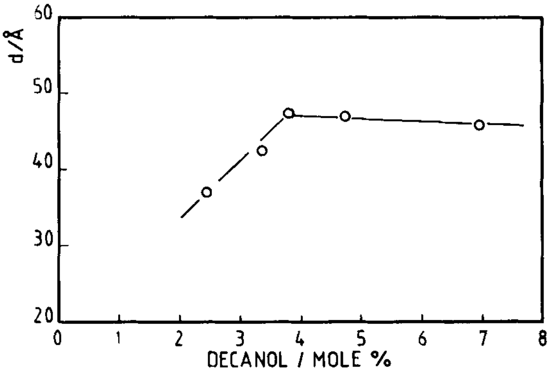


Figure 1. Periodicity of the lamellar phase, d, as a function of decanol in mole per cent.

mica sheets separated by a teflon spacer of thickness 0·7 mm; the whole cell, whose tightness was ensured by a set of joints and mechanical clamping, was placed in a thermostated enclosure. Two Bragg reflections in the ratio 1 : 2 were observed with all samples. The parameter of the lamellar stackings d, deduced from the positions of these reflections, is plotted as a function of the decanol in concentration in figure 1.

2.2. *Study of oriented samples by neutron scattering*

Oriented samples are needed to obtain a complete picture of the reciprocal space in order to locate the diffuse scatterings with respect to the Bragg reflections. Monocrystalline domains of a lamellar phase are usually obtained by squeezing or flowing the phase in between closely spaced parallel glass plates [11]. X-rays are strongly absorbed by glass but quartz plates are transparent to neutrons. We have chosen therefore to work with quartz plates using neutron scattering [5]. Samples of oriented lamellar phases were obtained by flowing each sample between a stack of quartz plates with a regular spacing of 50 μm between the plates. The whole stack was contained in a sealed quartz cell whose section was 10 mm × 5 mm. The experiments were performed at ILL in Grenoble on spectometer D17 provided with an XY multidetector. The sample–detector distance was 140 cm, the wavelength $\lambda = 10{\cdot}23$ Å and the wavelength spread $\Delta\lambda/\lambda = 5$ per cent. We worked with protonated SdS and decanol in D_2O so that the scattered intensity depended on the contrast of the amphiphilic molecules with respect to D_2O and therefore on the relative distribution of amphiphiles and water and not on that of soap and alcohol [13].

Most of the experiments were performed with the scattering geometry shown in figure 2. The incident beam is nearly parallel to the layers of the phase, i.e. nearly

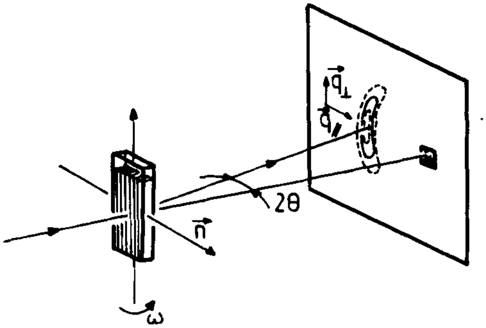


Figure 2. Scattering geometry reported from [5]. The incident beam is nearly parallel to the layers of the lamellar phase. The horizontal axis is along the director, **n**, of the lamellar phase and the symmetry axis of reciprocal space. The scattering vectors are along **n** ($\mathbf{q}_\parallel$) and perpendicular to **n** ($\mathbf{q}_\perp$). The Bragg reflections are recorded along the **n** direction. The angle between the scattered and incident beams is 2θ. The sample may be rotated about its vertical axis by an angle ω.

perpendicular to its director, **n**, so that the scattering vectors are in a plane containing **n** and the Bragg reflections are recorded along the **n** direction. In some cases the sample was rotated along its vertical axis by an angle ω in order to explore other planes of reciprocal space.

Special care must be exercized in analysing the spectra as some scatterings observed on the diffraction patterns correspond to artefacts associated with the sandwich method used to obtain oriented samples. We have listed the following effects:

Specular reflection. When the incident beam is quasi-parallel to the lamellae of the sample, i.e. quasi-parallel to the quartz plates, critical reflection on the quartz plates gives rise to intense scattering spots near the beam stop along the **n** direction; this reflection disappears when the sample rotated about its vertical axis [12].

Imperfect orientation of the sample. The lamellae of the sample may be partially disoriented when they are between quartz plates which are not perfectly parallel to each other so that the scattering of the Bragg reflection is distributed in a crescent-shaped spot centred on the origin of the spectrum.

Multiple scattering. As the oriented samples are thick (5 mm of mesophase in the scattering geometry shown in figure 2) the probability of multiple scattering is not negligible; in particular the neutrons may undergo two successive coherent diffractions which result in scattering along the incident beam in the vicinity of the beam stop [5]; in this case a way to remove multiple scattering is to rotate the sample about its vertical axis over a small angle ω so that the optimal Bragg reflection conditions are no longer fulfilled.

Absorption band. When the neutrons have their trajectories parallel to the quartz plates, they cross 5 mm of mesophase and are partly absorbed by it; this produces an extinction in the direction parallel to the plates, i.e. in the plane perpendicular to **n** [5].

Typical examples of patterns which contain scattering due to imperfect orientation of the sample and multiple scattering are shown in figures 3 (*a*) and (*b*). Scatterings due to specular reflection are present in figures 4 (*a*) and (*c*), respectively on the left and right side of the beam stop along the horizontal axis of the figures; the absorption band is evident in figure 4 (*c*).

We shall describe and analyse only the diffuse scatterings for which we have no doubt about their structural meaning, disregarding any scattering which might contain some component of artefactual origin.

3. Diffuse scattering

3.1. *Description*

We have chosen to describe the scattering patterns obtained for samples 1, 4 and 5 because they illustrate the evolution of the diffuse scatterings in the lamellar phase as a function of its increasing soap/decanol molar ratio. They are shown in figures 4 (*a*), (*b*) and (*c*); the scattering geometry is that of figure 2. The horizontal beam is parallel to the vertical layers of the phase (i.e. $\omega \sim 0$), so that the horizontal axis of the figures is along the director $\mathbf{n}$ of the lamellar sample and the symmetry axis of reciprocal space. The intense reflections centred on this axis are the first-order diffractions of the lamellar phase.

The pattern shown in figure 4 (*a*) is obtained with sample 1 located in the middle of the lamellar phase, soap/decanol ratio = 0·38. In addition to the Bragg reflection we shall consider only the diffuse scattering associated with its base along $\mathbf{q}_{\parallel}$ (horizontal axis of the figure). So far we do not consider the diffusion along $\mathbf{q}_{\perp}$ as it contains an important contribution resulting from the imperfect orientation of the sample. The pattern shown in figure 4 (*b*) is obtained with sample 4 located between the middle and the phase boundary of the lamellar domain, soap/decanol ratio = 1·47. Here too the Bragg reflection has a broad base and, besides this diffuse scattering around the Bragg reflection, diffuse scattering is observed around the origin whose intensity increases when $\mathbf{q} \rightarrow 0$. We have made sure that this diffuse scattering cannot be ascribed to multiple scattering. The pattern shown in figure 4 (*c*) is obtained with sample 5 located in the vicinity of the boundary of the lamellar domain, soap/decanol ratio = 2·26. The broadening of the base of the Bragg reflection is much less important than in the preceding spectra but diffuse lateral scattering streaks are observed along $\mathbf{q}_{\perp}$ which were absent in the latter. The intensity profile of these streaks is modulated and exhibits three maxima. Moving from the left to the right hand side, along the direction of a streak, a first maximum appears inside the trace of the crescent of the Bragg reflection, then a second, partially masked by the absorption band along the vertical axis. (The minimum observed between these maxima cannot result from an artefactual absorption band; indeed an absorption band would imply a local reduction of the lowest intensity level.) The third maximum which is symmetric to the first is not apparent on the figure because of the position of the detector.

It should be observed that the large crescent centred on the origin in figure 4 (*a*) obtained with sample 1, due to imperfect orientation of the sample, has disappeared in figures 4 (*b*) and (*c*) obtained with samples 4 and 5 and that the profile of the Bragg reflections of samples 4 and 5 differs from that of sample 1; in particular, the base of the Bragg reflection of sample 1 seems to be broadened along $\mathbf{q}_{\perp}$, but it is difficult to discriminate the associated diffuse scattering from the scattering due to imperfect orientation.

3.2. *Analysis*

As we have noted the scattering concerns the amphipiles/solvent distribution only. In the case of sample 1, with a low soap/decanol ratio of 0·34, the unambiguous diffuse scattering is located around the Bragg reflection and no similar scattering can

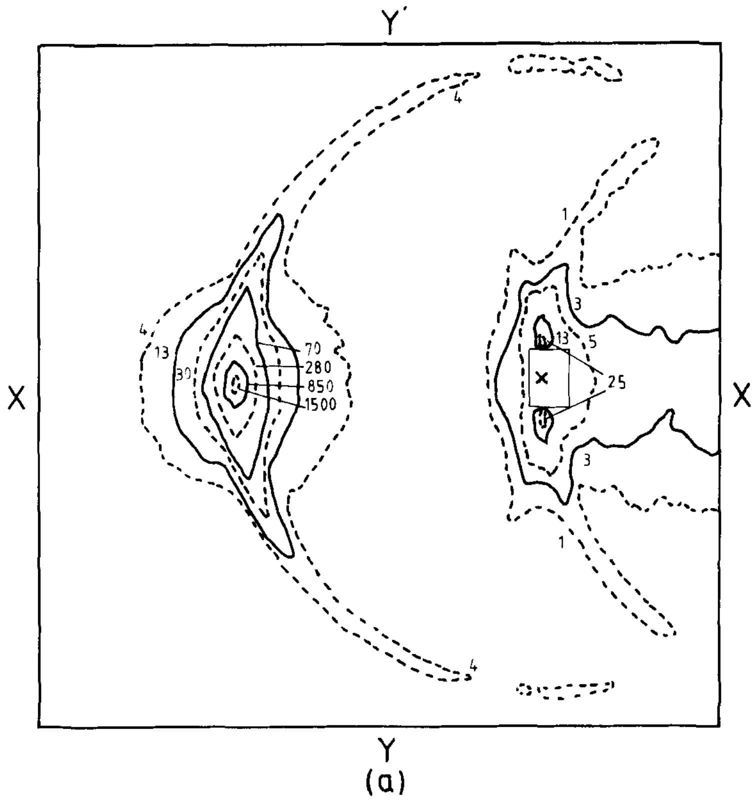
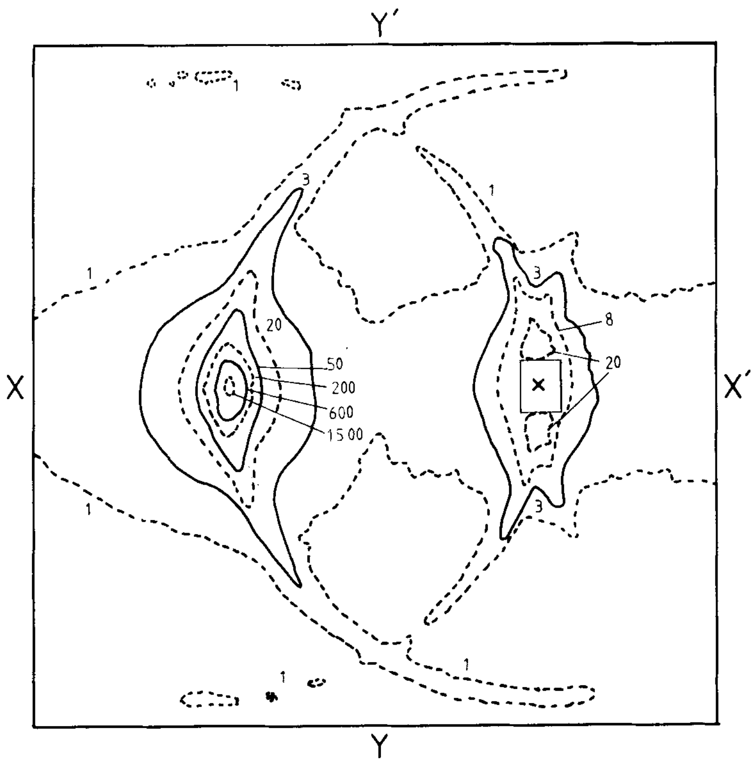


Figure 3. Scattering patterns obtained with sample 1; molar SdS/C_{10}–OH ratio = 0·38. Scattering geometry with respect to figure 2: (*a*) $\omega = 2°$; (*b*) $\omega = 6°$. The origin of the spectra is indicated by the cross on the beam stop level. The intensity levels are in arbitrary units. *Imperfect orientation of the samples*: the Bragg reflections are broadened according to a large crescent centred on the origin of the spectra; however a cross-section taken at half height of the Bragg peaks reveal disorientations of the order of 4°. *Multiple scattering*: crescent shaped scatterings are observed along the incident beam, in the vicinity of the beam stop, since the neutrons undergo two successive diffractions; both diffractions concern the first Bragg reflection.

be seen around the centre of the pattern. This diffuse scattering results therefore from displacement disorder which corresponds to fluctuations of the periodic stacking of the layers [14]. This may occur if, for instance, the thickness of some homogeneous amphiphilic or aqueous lamellae differ from the thickness of the other lamellae. In the case of sample 4, with an intermediate soap/decanol ratio of 1·47, there is still a diffuse scattering around the Bragg reflection but a diffuse scattering is also apparent around the origin which indicates the presence of a substitution or density disorder in addition to the displacement disorder [14]. As the scattering length density of the soap and the decanol can be considered equal these fluctuations can be associated with more or less pronounced inclusions of water within amphiphilic lamellae [15]. In the case of sample 5, with a high soap/decanol ratio of 2·26, the diffuse scattering around the Bragg reflection is less pronounced, that scattering around the origin has disappeared, but diffuse lateral scattering streaks are present. They indicate that a structural modulation occurs in all amphiphilic lamellae. Following this scheme the lamellae are no longer homogeneous but perturbed by water inclusions and the position of the diffuse

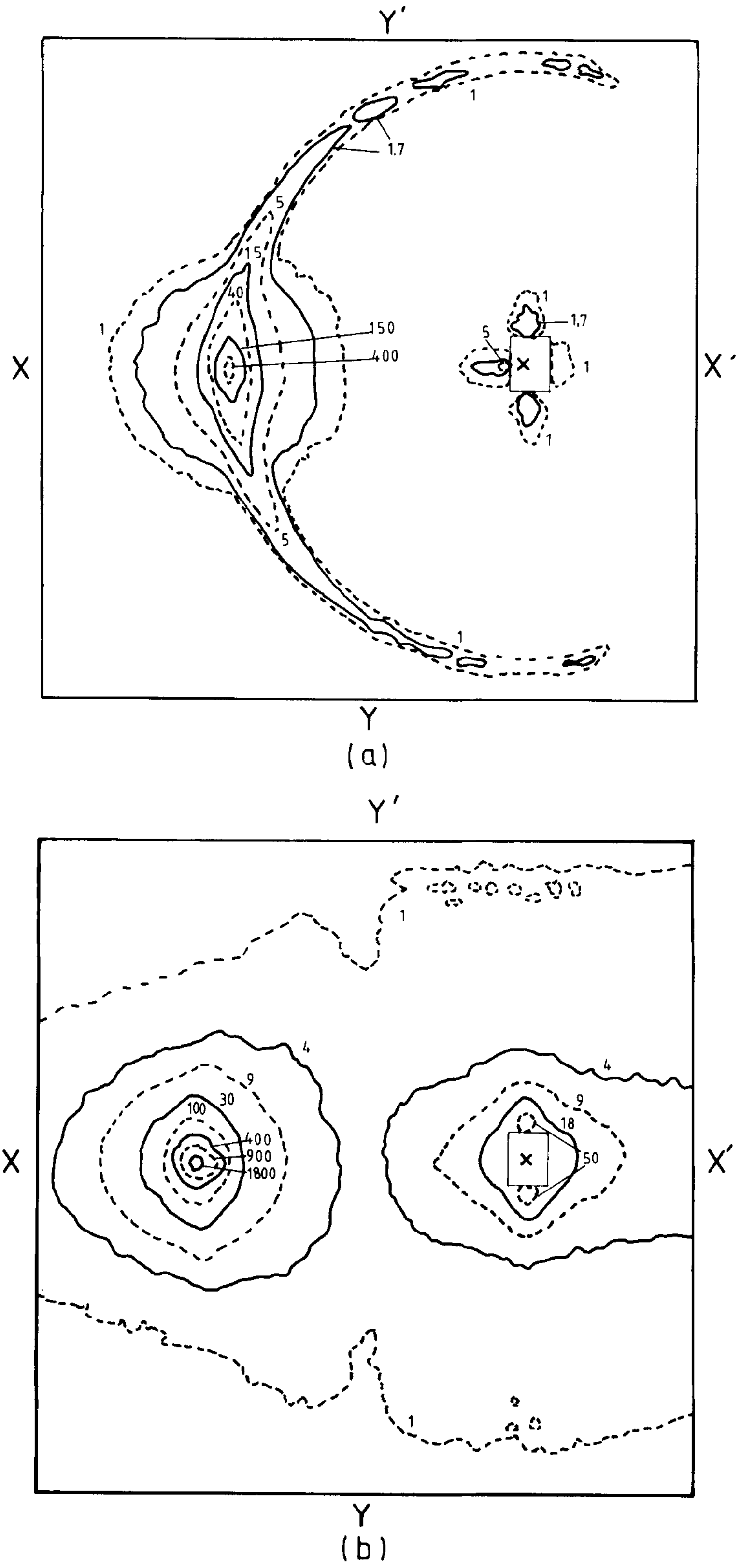


(b)

scattering streaks shows that the water regions are correlated in the layers over an average distance equal to $(q/2\pi)^{-1} \sim 88$ Å. Moreover the maxima in the intensity profile of the streaks reveal that correlations exist between the organization of the water regions over a few adjacent layers.

4. Discussion

Our data show that the structure of the lamellar phase of the SdS/$C_{10}OH$/water system deviates from that usually proposed for lamellar phases. The nature of the deviations appears to be dependent on the soap/decanol ratio. At low soap/decanol ratios the structure of the phase approaches that usually proposed for lyotropic lamellar phases. The phase is made of infinite homogeneous amphiphilic lamellae separated by water sheets and the only deviation we have considered concerns the lamellar stacking. However it might be that the particular profile of the Bragg reflection is due not only to imperfect orientation of the sample but also originates from undulation modes in the lamellae related to the elastic properties or compressibility of the lamellae. We have insufficient experimental data to discuss both phenomena at the moment. When the soap/decanol ratio increases, amphiphilic lamellae are affected by the presence of water regions which may be pores or channels piercing them. We might find in them a reason to explain the perturbation of the lamellar stacking which can still be observed. These water regions are randomly distributed and are somewhat separated from each other. Their occurrence is in good agreement with the decrease of the periodicity of the phase shown in figure 1, as some of the water which should normally belong to the water sheets is included in the


Y'
X
X'
Y
1
1.7
5
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40
150
400
1
1.7
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×
1
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1
Y'
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1800
4
9
18
50
×
1

(a)

(b)

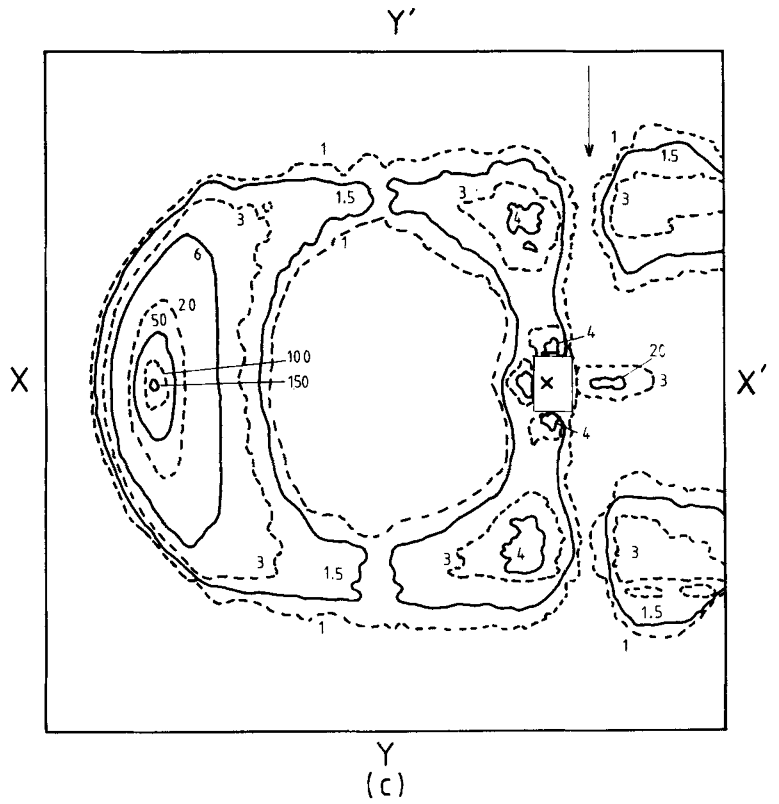

Figure 4. Scattering geometry as in figure 2, $\omega \approx 0$. The origin of the spectra is indicated by the cross on the beam stop level. The intensity levels are in arbitrary units. (*a*) Scattering pattern obtained with sample 1; molar SdS/C$_{10}$–OH ratio = 0·38. Diffuse scattering is observed around the Bragg reflection. (*Imperfect orientation of the sample*: the Bragg reflection is broadened according to a large crescent centred on the origin of the spectrum; *specular reflection*: intense scattering spot on the left side of the beam stop along the **n** direction.) (*b*) Scattering pattern obtained with sample 4; molar SdS/C$_{10}$–OH ratio = 1·47. Diffuse scattering is observed around the Bragg reflection and around the origin; the intensity of the latter increases when $\mathbf{q} \rightarrow 0$. (*c*) Scattering pattern obtained with sample 5; molar SdS/C$_{10}$–OH ratio = 2·26. Diffuse lateral scattering streaks are observed along $\mathbf{q}_\perp$; their intensity profile is modulated. (*Specular reflection*: intense scattering spot on the right side of the beam stop along the **n** direction; *absorption band*: the arrow indicates the extinction of scattered intensity along $\mathbf{q}_\perp$, i.e. in the plane perpendicular to **n**.)

amphiphilic lamellae. When the soap/decanol ratio is such that the lamellar phase is near the boundary of the lamellar domain, i.e. in the vicinity of a biphasic region, these density fluctuations affect all the lamellae and are correlated within a lamella and from lamella to lamella over limited ranges. Indeed the two maxima in the intensity of the lateral scattering streaks could be organized along vectors which belong to a lattice in reciprocal space. This array of spots corresponds either to a three-dimensional short range organization of discoidal aggregates or to a two-dimensional short range organization of cylindrical aggregates. The latter seems more probable as the neighbouring ordered phases beyond the biphasic region are two-dimensional rectangular phases whose aggregates are infinite ribbons [9].

5. Conclusion

We have looked for structural fluctuations induced in the lamellar phase of the ternary system, SdS/C_{10}–OH/D_2O, by the variation of the relative concentrations of the soap and the alcohol along a particular line of the phase diagram. Our neutron scattering data show the appearance of fluctuations of scattering length density in the lamellae above a given SdS/decanol ratio. We propose that these fluctuations are due to the presence of water pores or channels in amphiphilic lamellae, connecting the two water lamellae on either side of them. As the soap/decanol ratio increases the density of these water regions in the amphiphilic lamellae increases and they start to be correlated within each lamella and from lamella to lamella over limited distances, as the phase boundary as approached. Owing to the very nature of our experiments, neutron elastic scattering experiments, we cannot decide if we are dealing with dynamic or static fluctuations.

From a purely local point of view these water pores or channels piercing the amphiphilic lamellae must be associated with highly curved interfacial amphiphilic/water boundaries within the lamellae. As expected, this certainly involves the substitution of decanol molecules with non-ionic polar heads by SdS molecules with ionic polar heads. Local fluctuations of the relative concentrations of both amphiphiles should make possible the coexistence of domains with different interfacial curvatures [8].

From a more structural point of view the fact that these water regions show some local organization with a lower symmetry than the lamellar one, when the boundary of the lamellar domain is approached, suggests that they are precursors of the transformation of the lamellar phase into a neighbouring phase.

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[8] Indeed, in previous studies of this system, we had observed that aggregates with strongly inhomogeneous interfacial curvature are often present in its isotropic, nematic and rectangular phases and that the modulations of interfacial curvatures are related with inhomogeneous distributions of sodium decyl sulphate and decanol molecules. Hendrikx, Y., Charvolin, J., and Rawiso, M., 1984, *J. Colloid Interface Sci.*, **100**, 597. Alperine, S., Hendrikx, Y., and Charvolin, J., 1985, *J. Phys. Lett., Paris*, **46**, 27.

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[15] It could also be argued that this substitutional disorder originates from the inverted situation, where water lamellae might be perturbed by amphiphilic molecules connecting two amphiphilic lamellae through one water lamella. However, as the phases observed for very high soap/decanol ratio are ordered two-dimensional rectangular and hexagonal phases with amphiphilic aggregates dispersed in a continuous water medium [9], we dismiss this situation.