Sequence of Phase Transformations in the Ternary Lyotropic System Sodium Decyl Sulfate/2-Octanol/Water

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Abstract. — An oriented hexagonal phase of the ternary lyotropic system sodium decyl sulfate/2-octanol/water transforms into a lamellar phase. The transformation occurs in several steps due to a decrease of the water content by slow evaporation in the course of time while the 2-octanol/sodium decyl sulfate molar ratio remains constant. The following sequence is identified by small angle X-ray scattering studies: hexagonal phase → hexagonal phase coexisting with a rectangular phase → cubic phase → cubic phase coexisting with a lamellar phase. Epitaxial relations between the different phases are pointed out. The diffraction pattern of the lamellar phase exhibits in addition to the characteristic reflections of the latter, diffuse scattering which corresponds to density fluctuations within the amphiphilic bilayers. According to the Bragg reflections the cubic phase is a centred one and we propose a new model for this phase. The structure reminds us of that of the cubic phase which space group is Im3m, but the rods of both sub-lattices are no longer cylinders as in Im3m but ribbons and therefore the space group is Im3.

Résumé. — Une phase hexagonale orientée du système lyotrope ternaire, décyl sulfate de sodium/2-octanol/eau, se transforme en une phase lamellaire suite à une lente évaporation de l'eau au cours du temps tandis que le rapport molaire 2-octanol/décyl sulfate de sodium reste constant. La transformation se fait en plusieurs étapes. La séquence suivante est identifiée par diffraction de RX aux petits angles: phase hexagonale → phase hexagonale en coexistence avec une phase rectangulaire → phase cubique → phase cubique en coexistence avec une phase lamellaire → phase lamellaire. Des relations épitaxiales entre les différentes phases sont mises en évidence. Le cliché de diffraction de la phase lamellaire présente en plus des réflexions caractéristiques de cette phase, de l'intensité diffusée en dehors des réflexions de Bragg qui résulte de fluctuations de densité dans les bicouches d'amphiphiles. En accord avec les réflexions de Bragg, la phase cubique est centrée et nous proposons un nouveau modèle pour cette dernière. La structure rappelle celle de la phase cubique dont le groupe d'espace est Im3m, mais les tiges des deux sous-réseaux ne sont plus des cylindres comme dans la Im3m mais des rubans et dans ce cas le groupe d'espace est Im3.

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1. Introduction

The earliest reported sequences of phase transformations which occur between the hexagonal and lamellar structure in lyotropic systems, were observed in binary systems of ionic amphiphilic molecules in the presence of water by increasing the amphiphile concentration [1, 2]. In particular, in the sodium dodecyl sulfate/water system, as well as two dimensional hexagonal and monoclinic phases, rhombohedral, cubic and tetragonal three dimensional phases have been identified as the soap concentration increases, before reaching the lamellar phase [3–5]. Binary systems of non-ionic amphiphiles in the presence of water show a much simpler sequence of phases either by increasing the amphiphile concentration or increasing the temperature [6, 7].

In previous studies we have investigated the structural phase transformations induced by the addition of a non-ionic surfactant, 1-decanol, to the hexagonal phase of the binary sodium decyl sulfate (SdS)/water system. Most of the results are summarized in reference [8]. This system is very similar to that studied in the present paper and therefore we recall some important features of the ternary sodium decyl sulfate/1-decanol/water phase diagram which we have explored. As a matter of fact this phase diagram has guided us on the one hand in the preparation of our samples, on the other hand in the interpretation of our results. As shown in Figure 1, moving along line A, the water content remains constant and the SdS molecules are progressively substituted by decanol molecules. The sequence of phases, when the decanol/soap (SdS) molar ratio increases appears to be at room temperature: two dimensional hexagonal phases, two dimensional rectangular phases with different symmetries and finally the one dimensional lamellar phase. The decanol molecules may be seen as the driving force for the above phase transformations. It is important to note that the hexagonal phase of the binary SdS/water system is made of infinite cylinders with homogeneous interfacial amphiphile/water curvature. When the SdS molecules are progressively substituted by decanol molecules, the section of the cylinders becomes anisotropic and above a threshold concentration of decanol, the sixfold symmetry of the hexagonal lattice is broken and the hexagonal phase transforms into rectangular phases with different symmetries. The aggregates of the rectangular phases are infinite ribbons with inhomogeneous interfacial amphiphile/water curvature between 1/R (infinite cylinders with circular section of the hexagonal phase) and 0 (infinite flat bilayers of the ideal lamellar phase). When the decanol concentration is still further increased, the lamellar domain is reached. At the lower boundary of the lamellar domain (Fig. 1, sample 1), the amphiphilic bilayers are pierced by water pores or channels correlated over limited distances within the lamellae and over a few adjacent lamellae. Local fluctuations of the relative concentration of both amphiphilic species should make possible the coexistence of domains with different interfacial amphiphile/water curvature [9–12]. In the middle of the lamellar domain, the lamellae are infinite amphiphilic bilayers without density fluctuations.

In this paper we discuss an unexpected sequence of phase transformations which occurs in the ternary SdS/2-octanol/water system. Our first purpose was to detect the additional distortions induced in the cylindrical structure elements of an hexagonal phase when optical active (-) 2-octanol is used (instead of 1-decanol) compared to those detected in an hexagonal phase with identical composition as the previous one but prepared with the racemic 2-octanol. It has already been shown that the structure elements of an hexagonal phase are not perfect infinite cylindrical aggregates [13, 14]. Fluctuations occur along the cylinders and we expect that in the presence of the chiral 2-octanol compound, the aggregates should most probably be twisted. Such deviations manifest themselves by diffuse scatterings in addition to the Bragg reflections characteristic of an ideal hexagonal lattice. These deviations are not detectable in polycrystalline samples and contrary to our studies discussed above we started with an SdS/2-octanol/water oriented hexagonal phase. By chance, a slow evaporation occurred in
The capillary containing the oriented hexagonal phase and we could follow the evolution of the structure of the sample using X-ray diffraction: an unexpected sequence of phase transformations was observed. The results concerning the effect of chirality, will be presented in a forthcoming paper.

The observed sequence of phase transformations which we are interested in, is the following: an hexagonal phase transforms into a lamellar phase owing to the slow evaporation of water while the 2-octanol/SdS molar ratio remains constant. This transformation occurs in several steps: hexagonal phase $\rightarrow$ hexagonal phase in coexistence with a rectangular phase $\rightarrow$ cubic phase $\rightarrow$ cubic phase in coexistence with a lamellar phase $\rightarrow$ lamellar phase. The same sequence is observed with the racemic and optical active (-) 2-octanol. The structures obtained in the ternary system SdS/1-decanol/water enable us to interpret some diffraction patterns obtained in the present study. We started with an SdS/2-octanol/water hexagonal phase which composition is the same as that of a SdS/1-decanol/water hexagonal phase reported in Figure 1 and denoted as $\alpha$. Obviously a cubic phase also exists in the ternary SdS/1-decanol/water system, but it probably extends over a very narrow domain and so far we haven’t identified it. The diffraction pattern of the lamellar phase shows diffuse scattering streaks similar to that observed in the vicinity of the lower boundary of the lamellar domain in the SdS/1-decanol/water system. If we assume that the thickness of the amphiphilic bilayer, $d_a$, in the SdS/2-octanol/water system is equal to that of the lamellar phase located in the phase diagram SdS/1-decanol/water system (Fig. 1, sample 1), we can calculate the composition of the lamellar phase in the SdS/2-octanol/water system. It appears that the starting sample or hexagonal phase which transforms into a lamellar phase has lost 25% water in weight while the 2-octanol/SdS molar ratio remains constant. The composition of the lamellar phase should correspond to that of sample $\beta$ reported in Figure 1 along line B. Epitaxial relations are pointed out between the different identified structures: hexagonal, rectangular, cubic and lamellar. To our knowledge, these relations are observed for the first time. The set of reflections obtained for the cubic phase indicates the latter is centred and analogous to the cubic phase identified in the binary sodium dodecyl sulfate/water system, and we presumed at first, that the space group was the Im3m one [3–5]. In that case the structure should be compatible with one of the
minimal surfaces defined by Schwartz [15], i.e. the type “P” surface [16]. So far this structure has only been observed in a few other amphiphilic and thermotropic systems [17,18]. This structure is made of two systems of interpenetrated rods of amphiphilic molecules embedded in a continuous water medium: each system is formed by six rods, parallel to the vectors of the cubic cell, which meet at right angles at the apex of the cell for one of the two systems, and in its center for the other one [19]. We propose that the centred cubic phase which is identified in the sequence of phase transformations in the ternary sodium decyl sulfate/2-octanol/water system presented in this paper is made up of two systems of interpenetrated rods as described above, but the rods are no longer cylinders but ribbons so that the space group is no longer Im3m but Im3.

2. Samples

The samples are prepared in sealed glass tubes by mixing together known amounts of SdS (Merck purity 99 percent), 2-octanol (racemic, Fluka purity 98 percent, or optical active, Aldrich purity 99 percent) and water. The tubes are stored in an oven for several days and centrifuged until perfect homogenization is achieved. The composition of sample α (Fig. 1) with racemic 2-octanol, which is identical to that with optical active (-) 2-octanol is the following: 48.34% SdS, 4.45% 2-octanol and 47.21% H₂O in weight per cent. The molar 2-octanol/SdS ratio is 0.184.

3. Experimental Methods

3.1. Oriented Samples. — Monodomains of the hexagonal phase are obtained by squeezing the phase in flat Lindeman capillaries and thereafter, sealing the extremities of the capillaries. The flat capillaries are not from commercial origin. We obtain them by heating Lindeman capillaries, placed between two brass plates (one of them is provided with grooves), in an oven at 580 °C during two hours. Thereafter the oven is turned off and the capillaries cool slowly in the oven until room temperature is reached. In this way we succeed in obtaining capillaries with two parallel flat walls. Their thickness is ~ 0.3-0.4 mm and their width ~ 2 mm.

3.2. Textures. — The nature of the samples is first identified by observing their textures in polarized light. The samples are smeared between glass plates and observed under a polarizing microscope (Olympus) equipped with a camera. Thereafter they are observed in the same manner but enclosed in flat capillaries. Finally the enclosed samples are stored during several weeks at room temperature in order to obtain oriented samples, i.e. monodomains. The sequence of phase transformations was first observed in a flat capillary by X-ray diffraction experiments. The phase transformations are due to a slow evaporation of water. We tried to observe this sequence under the polarizing microscope. Therefore a sample of the hexagonal phase was smeared between glass plates, and in order to make sure the water should evaporate very slowly, the edges of the glass plates were coated with paraffin.

3.3. Structures. — The structures of the samples are obtained by small angle X-ray diffraction. We use the following notation: s = 2 sinθ/λ, where s is the scattering vector, λ the wave length and 2θ the angle between the scattered and incident beam. Once the nature of the samples smeared between glass plates has been qualitatively identified by their textures, the structure of the polycrystalline samples are studied with a Guinier camera [20] with linear collimation and monochromatic Cu-Kα₁ radiation, λ = 1.5405 Å. A set of narrow reflections is observed on the photographic films. The angles of the reflections give access to the symmetry,
hexagonal in the present case, and the parameters of the unit cell. The oriented samples which are the purpose of our study are investigated using a rotating anode equipped with a XY multidetector [21]. This detector quickly allows us to visualize the diffraction pattern and to define the orientation of the sample after a short X-ray exposure. The orientation of the sample contained in a capillary, placed vertically on a goniometric head, can be modified. Moreover the capillary can be translated vertically and horizontally, so that the sample can be explored at different levels. It can also be rotated along its vertical axis. Once the suitable orientation and position are reached, the detector is replaced by a photographic film. The radiation here is also the monochromatic Cu-Kα one, the section of the X-ray beam is \( \sim 1 \text{ mm}^2 \) and the sample-film distance = 24.5 cm.

4. Results

4.1. Textures. — Our samples smeared between glass plates exhibit a texture typical of a cylindrical phase [22]. The texture of the samples just after they have been pushed in a capillary is illustrated by photograph (a) in Figure 2. A fan-like texture is observed which is characteristic of two dimensional packing of infinite cylindrical aggregates [23, 24].

Photographs of oriented samples are shown in Figures 2b and 2c. Large domains of fine streaks parallel to each other are observed. The cylinders of the hexagonal phase are oriented parallel to each other and their director is along the long axis of the capillary, i.e. perpendicular to the observed parallel narrow streaks [25–28].

Finally, in Figure 3 one can see that when water evaporation occurs very slowly, isotropic faceted domains of a cubic phase nucleate on the glass surfaces within a cylindrical phase, probably a rectangular one.

4.2. Structures. — We will only deal with the experiments performed with the rotating anode. They were carried out at room temperature, \( T = 24 \pm 1 \text{ °C} \).

We started with the diffraction pattern of an oriented sample identified as a hexagonal, Hα, phase (powder pattern obtained with the Guinier camera). The composition of the sample (α) is given in Section 2. One must keep in mind that the results described below were obtained with this sample whose structure was transformed in the course of time due to a decrease of its water content through slow evaporation. The sequence of phase transformations was achieved after several days. Therefore it is important to remember that the patterns which are obtained and compared with each other, result from a continuous evolution of the sample composition.

The orientation of the sample with respect to the X-ray beam is fixed so that the diffraction pattern Figure 4a corresponds to a plane of the reciprocal space where only the 10 reflection can be detected (X-ray beam perpendicular to the director of the Hα phase). The same picture is obtained for each rotation of 60° around the vertical axis of the capillary. When the capillary is translated vertically one can see in Figure 4b that an other part of the sample is investigated. As a matter of fact, at this level the sample is less oriented because the 11 reflection, which corresponds to the second order of a powder pattern of the Hα phase is visible (the first and second order are in the ratio 1, \( \sqrt{3} \)). Moreover a reflection appears which is not compatible with the Hα structure, i.e. the Hα phase coexists with an other phase. If we come back to the original position of the capillary (Fig. 3a), we are in the presence of two monodomains, as shown in Figure 4c, each of which belongs to a particular phase. We still have two intense spots corresponding to the 10 reflection of the Hα phase; the lattice parameter of the latter is \( 43.5 \pm 1 \text{ Å} \). The other intense spots correspond to the reflection already observed in Figure 4b. They are intense and based on our study of the SdS/1-decanol/water system [8], we assume that they correspond to the 11 reflection of a rectangular phase: the scattering vector
Fig. 2. — Photographs of the textures of the samples with hexagonal structure. (a): just after they are been pushed into a flat capillary; (b) and (c) after several weeks: oriented or monocrystalline samples. Magnification: (a) and (b), 1 cm $\sim$ 73 $\mu$m; (c), 1 cm $\sim$ 130 $\mu$m. Polarizer and analyzer are crossed and parallel to the edges of the photographs.
is larger than the scattering vector of the 10 reflection of the Hα phase and of the same order of magnitude as that observed for the above mentioned rectangular phase. We recall that above a threshold concentration of 1-decanol the sixfold symmetry of the Hα phase in the SdS/1-decanol/water system is broken and that this phase transforms into a rectangular one. The aggregates of the rectangular phase are infinite ribbons with rather anisotropic sections instead of cylindrical aggregates. We assume that the same phenomenon occurs in the SdS/2-octanol/water system. In the present case the 2-octanol/SdS molar ratio remains constant but due to the slow evaporation of water, the absolute concentration of 2-octanol increases.

Maintaining the capillary in the same position (Figs. 4a and c), the diffraction pattern of an oriented cubic phase appears. Two diffraction patterns of the cubic phase are shown in Figures 5a and b. The monodomains are not the same in both pictures. As a matter of fact the diffraction pattern in Figure 5b has been obtained when the capillary (or the sample) is rotated by about 18° with respect to its initial orientation. The diffraction spots lie on circles which are drawn in Figures a' and b'. Their position are in the ratio $1, \sqrt{3}, \sqrt{4}, \sqrt{5}, \sqrt{6}, \sqrt{7}$. The circle where the 200 reflections should appear is also drawn on both figures (position $\sqrt{2}$).

According to Kékicheff et al. [3–5] the 200 reflections are very weak and therefore they are not visible. At least two domains give rise to the diffraction patterns presented in Figure 5. The Bragg spots 110, 211, 220 and 321 of the plane of each monodomain perpendicular to a [111] axis are indexed as in Figures 5a' and b'. In this orientation no 200 reflections are expected. In Figure 5a' the indexed spots are due to one domain which is orientated with a threefold axis parallel to the incident beam and a [220] axis roughly parallel to the capillary axis, while the grey spots belong to the monodomain whose index is given in b'. Reciprocally, in Figure 5b' the indexed spots are due to the other domain which is orientated with a threefold axis parallel to the incident beam (at 18° from the previous orientation in Fig. 5a) and a [211] axis roughly parallel to the capillary axis, while the grey spots belong to the monodomain whose index is given in a'. Some reflections on the diffraction patterns shown in Figures a and b lie on the fifth and sixth circle drew in Figures 5a' and b'. However these reflections are not drawn because they do not originate from the two domains clearly identified.
Fig. 4. — Diffraction patterns. (a) oriented hexagonal phase; (b) hexagonal phase in coexistence with another phase; orientation as in (a) but part of the sample which is less oriented than the previous one in (a); (c) position and orientation of the sample as in (a); two well oriented monodomains: hexagonal phase in coexistence with a rectangular phase.
Fig. 5. — Diffraction patterns of the cubic phase. (a) plane of a monodomain perpendicular to a [111] axis; the orientation of the sample is the same as that in (a), Figure 4; (a') indexing of the pattern; (b) the sample is rotated by about 18° around its vertical axis; plane of another monodomain than that shown in (a) which is also perpendicular to a [111] axis; (b') indexing of the pattern. (●) black spots present in the patterns; (〇) white spots absent from the patterns; (△) grey spots belonging to another monodomain: in (a'), they belong to the monodomain indexed in (b') and in (b'), they belong to the monodomain indexed in (a').

The indexing of the reflections is assessed by plotting the reciprocal spacings, $s_{hkl}$ of the observed Bragg reflections versus $(h^2 + k^2 + l^2)^{1/2}$ according to the relation $s_{hkl} = 1/a(h^2 + k^2 + l^2)^{1/2}$ with $a$ being the cubic lattice parameter. The lattice parameter $a$ of the cubic phase is $109 \pm 1 \text{ Å}$.

The coexistence of the cubic phase with a lamellar phase is apparent in the diffraction pattern shown in Figure 6a. This diffraction pattern has been obtained when the capillary (or sample) was in its original position, cf. Figures 4a and c and Figure 5a. The indexing of the pattern is shown in Figure 6a'; as in the previous patterns of the cubic phase (Fig. 5), some Bragg spots
of the cubic phase which coexists with the lamellar phase can not been indexed because the cubic crystal is not a perfect single crystal. The 222 reflections of the cubic phase lie on a circle which corresponds, as will be confirmed by the next diffraction pattern, to the 001 reflection of the lamellar phase. This circle is strongly reinforced along the horizontal axis of the picture, i.e., along the director of the lamellar phase.

Finally the cubic phase transforms into a lamellar phase whose diffraction pattern is shown in Figure 7. This pattern corresponds to that of an oriented lamellar phase. The intense Bragg spots centred on the horizontal axis are due to the first order of the lamellar phase; the second order is also apparent: the first and second order are in the ratio 1, 2. The parameter of the lamellar phase is $31.5 \pm 1$ Å. Besides the Bragg reflections, diffuse lateral scattering streaks
are observed which are typical of density fluctuations. Moreover the intensity profile of these streaks is modulated. This pattern is reminiscent of that obtained in the SdS/1-decanol/water system [8].

5. Discussion

Two points will dominate this discussion: one concerns the structural evolution of sample α along line B drawn in the phase diagram in Figure 1. The other one concerns the model proposed for the identified cubic phase.

5.1. Structural Evolution of Sample α. — The results of our study show that an oriented hexagonal phase, Ha, of the SdS/2-octanol/water system transforms into an oriented lamellar phase, La, in several steps.

The phase transformations result from a slow water evaporation of the Ha sample while the 2-octanol/SdS molar ratio remains constant. In order to interpret our results we refer to the phase transformations observed in the SdS/1-decanol/water system [8], which from a chemical point of view is very similar to that described in the present paper.

Therefore we ascribe the reflections which appear in coexistence with the reflections of the initial pure Ha phase to the 11 reflections of a rectangular, Ra, phase (Figs. 4b and c). It has been shown that one phase transforms into another via an epitaxial growth [7]. Thus an epitaxial relation must exist between the (10) planes of the Ha phase and the (11) planes of the Ra phase although the spacing between the planes is not the same: $s_{10}(Ha) = (36 \pm 1 \text{ Å})^{-1}$; $s_{11}(Ra) = (31.5 \pm 1 \text{ Å})^{-1}$.

Obviously we missed the pure rectangular phase and the biphasic region where the rectangular phase coexists with the cubic, Qα, phase before the pure cubic phase is obtained (Figs. 5a and b). An epitaxial relation exists unambiguously between the (11) planes of the Ra phase and the (222) planes of the Qα phase. The spacing between the 11 and the 222 reflections is the same: $s_{11}(Ra) = s_{222}(Qα) = (31.2 \pm 1 \text{ Å})^{-1}$. Surprisingly, in the cubic phase diffractions pattern, Figure 5, there are no intense 222 Bragg spots corresponding to the 11 spots of the rectangular phase. This is probably due to the fact that the cubic phase first nucleates on the glass surfaces of the capillary and not in the bulk. This was observed under polarizing microscope when the sample preparation was such that the water evaporation could only occur very slowly as described in Sections 3.2 and 4.1. As was also noticed by Kékicheff [5], the [111] axis is a privileged direction of the cubic structure and the reticular planes perpendicular to this direction are parallel aligned to the glass surfaces. This orientation is that of the crystallites which give many strong spots in Figure 5. Owing to the ratio between the circles where the Bragg spots of the monocrystals of the cubic phase are located, Figures 5a’ and b’, and the fact that for all the reflections $h + k + l = 2n$, we may conclude that the cubic phase is a centred one. Moreover at first, based on the same arguments as those used by Kékicheff [5] in the case of the sodium dodecyl sulfate/water cubic phase, we assumed that the space group of the identified centred Qα phase in the SdS/2-octanol/water system was Im3m.

The diffraction pattern in Figure 6a shows that the cubic phase coexists with a lamellar phase before the pure Lα phase is formed. Here also, an epitaxial relation exists between the (222) planes of the cubic phase and the (001) planes of the lamellar phase. The spacing between the 222 reflections and the 001 reflections is the same: $s_{222}(Qα) = s_{001}(Lα) = (31.5 \pm 1 \text{ Å})^{-1}$.

Looking to the diffraction pattern of the pure oriented Lα phase in Figure 7, one can see that the Bragg spots characteristic of a periodic lamellar stacking are along the horizontal axis of the picture, i.e. along the director of the Lα phase. Moreover diffuse scattering streaks for scattering vectors, in the plane perpendicular to the director of the phase, are observed
and the intensity profile of these streaks is modulated. Such diffuse scatterings indicate that the amphiphilic bilayers are affected by density fluctuations. In the present case the density fluctuations are due to water regions which may be pores or channels piercing the amphiphilic bilayers. These water regions affect all the lamellae: they are correlated within a lamella and from lamella to lamella over limited regions. This diffraction pattern reminds us of that already observed in the SdS/1-decanol/water system [8].

If we assume that the thickness of the amphiphilic bilayer of the SdS/2-octanol/water system, \( d_a \), is equal to that of the lamellar phase of the SdS/1-decanol/water system (Fig. 1, sample 1), we may calculate the composition of the lamellar phase. With \( d_a = 18.6 \text{ Å} \), the composition of the sample at this stage is the following: 59.20% SdS, 54.44% 2-octanol and 35.36% \( \text{H}_2\text{O} \). The sample with this composition is sample \( \beta \) reported along line B in Figure 1. Sample \( \beta \) has lost 25% water in weight compared to the initial sample \( \alpha \). Of course this composition is only approximative. Indeed, due to the slow evaporation of water a concentration gradient in the capillary takes place and the calculated concentration doesn't correspond to that of each part of the sample. Obviously, besides the lamellar monodomain, monodomains of other phases exist with different composition. Nevertheless we will use the concentration of the lamellar phase we have calculated, in order to illustrate the model we propose for the cubic phase in Section 5.2

5.2. Model Proposed for the Cubic Phase. — The cubic phase, space group \( \text{Im}3\text{m} \), is sketched in Figure 8a. The structure is made up of two systems of interpenetrated rods. Each system is formed by six rods, parallel to the vectors of the cubic cell, which meet at right angles at the apex of the cubic cell for one of the two systems, and in its center for the other one [19]. The volume occupied by the rods corresponds to that occupied by the amphiphilic molecules. The rods are cylinders with homogeneous interfacial curvature, i.e. with circular section. Knowing the parameter of the cubic cell, \( a = 109 \text{ Å} \), and taking the radius of the cylinders, \( R = 13 \text{ Å} \), (keeping in mind that the length of a fully elongated chain of sodium decyl sulfate is \( \sim 14 \text{ Å} \) [29]), we are able to calculate the volume fraction occupied by the amphiphilic molecules per cubic cell. It appears that the volume fraction occupied by the amphiphilic molecules is \( \sim 22\% \) of the total volume of the latter. In other words, if we assume that the composition of the cubic phase is roughly equal to the composition of sample \( \beta \), and knowing the concentration of both amphiphilic molecules and their respective molar specific
volume, it appears that the amphiphilic molecules occupy in fact ~ 61.5% of the total volume of the cubic cell, 38.5% is filled by water.

It is clear that cylinders of amphiphilic molecules do not satisfy the effective volume fraction occupied by the latter in the cubic cell. The cylinders occupy a volume much smaller than that imposed by the concentration of amphiphilic molecules in the sample. The cubic phase appears between a rectangular phase where the aggregates of amphiphilic molecules are ribbons and a lamellar phase with "defects", where the bilayers are most probably made of ribbon-shaped aggregates of amphiphilic molecules [8, 30]. Therefore we have considered another model with rods which are no longer cylinders with circular section but ribbons. The cubic phase made of two systems of interpenetrated ribbons is sketched in Figure 8b. The space group is no longer Im3m but Im3. This space group is still compatible with the experimental X-ray diffraction data. In order to calculate the volume occupied by the ribbons (or the amphiphilic molecules), we take ribbons whose section is made of a rectangular part, 19 Å width and 26 Å thickness, capped with two circular parts with \( R = 13 \) Å, as sketched in Figure 8c. The thickness of the rectangular or flat part of the section of the ribbons, 26 Å, which is equal to the diameter of its circular parts and that of the previous considered cylinders, is in agreement with the thickness of the amphiphilic bilayers made from infinite homogeneous amphiphilic lamellae, (without "defects"), observed in the SdS/1-decanol/water system. The thickness of such bilayers is \( \sim 25 \) Å [8]. The volume occupied by such ribbons of amphiphilic molecules is now \( \sim 43\% \) of the total volume (instead of 22% with cylinders). This volume fraction is still smaller than the expected one but already much more satisfying.

Fig. 8. — Centred cubic phase. (a) space group Im3m: two systems of interpenetrated rods; (b) space group Im3: two systems of interpenetrated ribbons. (c) representation of the section of a ribbon.
However, the composition of the cubic phase must differ from that of the lamellar phase, (the water content of the cubic phase is in principle higher) and this promotes a decrease of the volume fraction occupied by the amphiphilic molecules. Moreover, we can adjust the parameters of the section of the ribbons and thus easily increase the available volume for them. There is a favorable interplay between both factors. Therefore we may infer the model we propose for the cubic phase is correct.

6. Concluding Remarks

Epitaxial relations have been pointed out between monodomains of the following phases: hexagonal, rectangular, cubic and lamellar. To our knowledge these epitaxial relations are observed for the first time.

We propose a new model for a centred cubic phase, made of two systems of interpenetrated ribbons. The ribbons have inhomogeneous amphiphile/water curvature between $1/R$ (cylinders with circular section) and 0 (flat bilayers).

In order to precise this model and to be able to give a more quantitative description of the ribbons, we look for a pure cubic phase whose composition is known.

Finally measurements of the absolute or relative intensity of the diffraction lines of a powder pattern will enable to test the computed structure factor of the cubic phase and to prove the validity of our proposed model.

References