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Evolution of cylindrical structures in the system sodium decylsulphate/decanol/water

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The binary mixture sodium decylsulphate/water exhibits a hexagonal structure for a degree of hydration of about 50 per cent by weight. In this structure the amphiphiles build infinitely long cylinders which are organized on a 2D lattice of space group p6m. If, in such a mixture, sodium decylsulphate is progressively substituted by decanol, the hexagonal structure transforms itself successively into two rectangular structures. In these rectangular structures the amphiphiles also build cylinders, but these are organized on 2D lattices with space groups cmm and pgg, respectively. This evolution of cylindrical structures in the ternary mixture is also marked by a growth of the mean normal section of the cylinders. An analysis of these results is proposed, in which the growth is accompanied by a change in the normal section, from circular for the hexagonal structure to non-circular for the rectangular structures; this change occurs abruptly at the hexagonal–rectangular transition and is stabilized by an important fluctuation of the relative concentrations of the two amphiphiles within the cylinders.

1. Introduction

Cylindrical structures are currently observed in the liquid crystalline domains of most of the phase diagrams of amphiphilic molecules in the presence of a solvent [1–9]. In these structures the amphiphiles aggregate and build infinitely long cylinders organized on 2D lattices with various symmetries. Most often the symmetry is p6m, the so-called hexagonal structure, and the mean normal section of the cylinders is supposed to be circular or to have at least sixfold symmetry. Some examples of cylindrical structures are of a lower symmetry, for instance monoclinic, quadratic and rectangular, which suggest cylinders with non-circular sections also of lower symmetry. This article examines some aspects of the deformation of the section in relation to the overall symmetry changes in the case of the cylindrical structures of the system sodium decylsulphate/decanol/water [3–5, 10–12].

The choice of a complex system with two amphiphiles for such a study was driven by the following consideration. In simple binary systems, the sequence of cylindrical structures, when it exists, is observed on varying the solvent concentration whereas, in the case of the chosen ternary system, it is observed on substituting sodium decylsulphate by decanol at constant solvent concentration. In the first case, the changes are driven by the degree of solvation of the polar heads, whereas they are driven by the presence of alcohol groups at the interface in the second case, and we know more, in a more quantified manner, about the action of the second variable than about that of the first, from monolayer studies particularly [13].

First, experimental data on two aspects will be presented: the sequence of cylindrical structures of the system sodium decylsulphate/decanol/water and the variation of the mean area per molecule in a monolayer of sodium docosylsulphate

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with the addition of cetyl alcohol. Then three simple models will be considered to analyse the first set of data on the basis of the second. The correct agreement, which is obtained in between two of these models and the experimental data suggest the direction to follow in order to develop a more thermodynamical approach to this problem.

2. Experimental data

2.1. *Cylindrical structures of the system sodium decylsulphate/decanol/water*

The binary system water/sodium decylsulphate ($C_{10}H_{21}OSO_3Na$, hereafter called SdS) exhibits a cylindrical structure with p6m symmetry, the well-known hexagonal structure, in the medium concentration range of about 50 per cent by weight at room temperature [2]. When SdS is progressively substituted by decanol ($C_{10}H_{21}OH$), this hexagonal structure transforms successively into two rectangular structures, with space groups cmm and pgg, before the lamellar structure appears. The symmetries of the structures and their parameters were characterized by X-ray scattering experiments [3–5, 10], and the 2D lattices are shown in figure 1. The parameters of the structures are used to calculate the area of the unit cell from which, knowing the number of cylinders per cell and the concentration of paraffinic chains, the area Σ of the normal section of a cylinder of paraffinic chains can be determined; the area considered here is that occupied by the chains of the molecules exclusively, their polar groups being considered as parts of the solvent (see the Appendix). The variation of the area of the normal section of a cylinder of chains as the decanol content increases is presented in figure 2, as well as the sequence of the structures.

The area of the section of the paraffinic cylinders in the p6m structure without decanol is 544·23 Å^2, if the section is assumed to be circular this corresponds to a radius of 13·16 Å and a mean area per chain at the interface of 45·18 Å^2; then the area of the section increases regularly as the decanol concentration ϕ (mol%) in the amphiphilic medium increases. The transition from the p6m structure to the cmm one is marked by an important jump in the value of this area, from 674·25 to 845·03 Å^2; no polyphasic domain separating the two phases was detected, which means that, if there is one, it is quite narrow. The transition from the cmm structure to pgg is not marked by a similar jump, if any, in the value of the area of the section, a fact difficult to evaluate owing to the distribution of the data for the pgg structure; a narrow polyphasic domain separating the two phases was however detected in this case. Although the lamellar phase present at higher decanol concentrations is not the subject of this article, it is

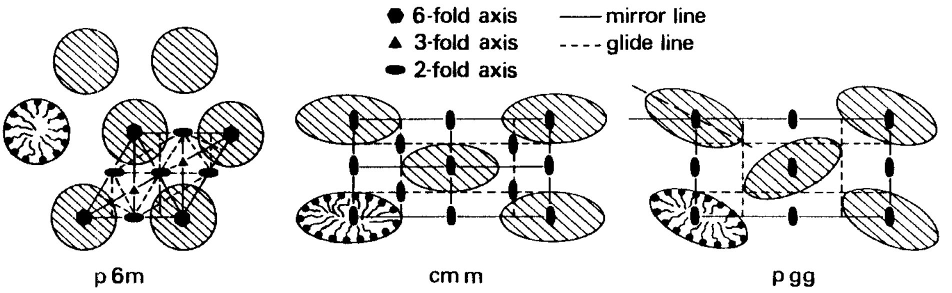

Figure 1. The p6m, cmm and pgg 2D lattices with their symmetry elements and their representations with motifs having the highest symmetries possible compatible with the observed intensities of the Bragg's spots [3–6].

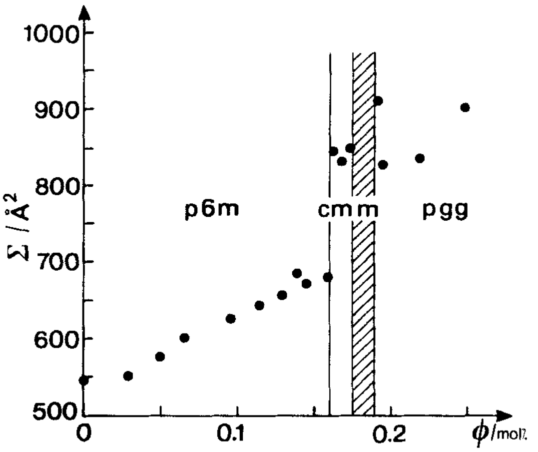

Figure 2. The variation of the mean area Σ of the section of the cylinders with the decanol content ϕ (mol%) in the aggregates and the sequence of the structures.

useful to notice that its structure is the usual one, i.e. with infinite and uniform lamella, for decanol concentrations higher than 0·45 mol% only; below this value, and in proximity to the rectangular structure, the uniformity of the lamella, and most likely their integrity, are perturbed by the presence of defects [12]. In the concentration range higher than 0·45 mol%, where the lamella are without defect, the area of their section is of course infinite; half the thickness of their paraffinic core is 11 Å and the mean area per chain at the interface is 27 Å^2.

The water content being kept constant, the cause of the evolution is to be found in the progressive substitution of SdS by decanol and, more precisely, as these two molecules have the same chain lengths, in the progressive substitution of OSO_3Na groups by OH groups at the interface. Obviously, as this substitution transforms a structure of cylinders with a mean area per chain at the interface of 45·18 Å^2 into a structure of flat lamella with a mean area per chain at the interface of 27 Å^2, this substitution affects the mean area per chain at the interface and/or the interfacial curvature. To go further, some knowledge about the variation of this area with alcohol content is needed and, fortunately, a study exists for a closely related system which provides useful information.

2.2. *Mean area per chain in an insoluble mixed monolayer*

This study concerns the influence of cetyl alcohol, i.e. hexadecanol ($C_{16}H_{33}OH$), on the properties of an insoluble flat mono-film of sodium docosylsulphate ($C_{22}H_{45}OSO_3Na$) spread at a flat air/water interface [13]. One of the results obtained is the variation under constant lateral pressure of the mean area σ per chain at the interface when the alcohol content ϕ increases; this is represented in figure 3. In the concentration range from 0 to 0·2 mol%, corresponding to that of the present study, the mean area decreases linearly with a constant slope. This linear behaviour corresponds to a faster decrease than that of the straight line joining the mean areas of the pure components and indicates that the mixture is not ideal. Interaction phenomena between the polar groups of the different molecules certainly occur, enhancing the decrease in the area in a manner hardly sensitive to the lateral pressure, i.e. to the state of compression of the molecules.

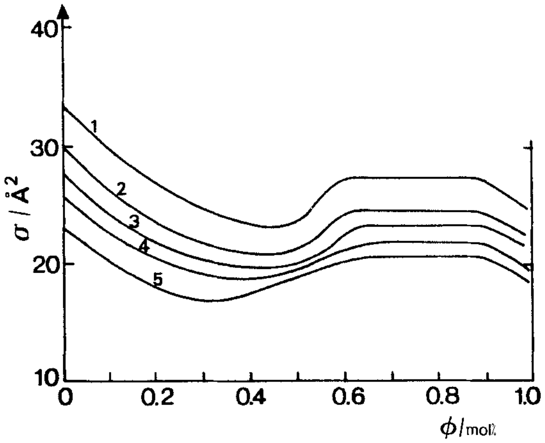

Figure 3. The variations of the mean area σ per chain in mixed monolayers of sodium docosylsulphate and cetyl alcohol under pressures Π at an air/water interface as the cetyl alcohol content ϕ (mol%) increases. ($\Pi = 4$, 12, 18, 24, 40 d cm^{-1} from 1 to 5) from [13].

Following this last remark, it is proposed to make use of the same linear behaviour in the case of the SdS/decanol structures studied in this article, although the volume occupied by the solvent is not semi-infinite, the interface is not flat and the mean area at the interface is larger. This linear behaviour may be written as $\sigma = -31\phi + 45{\cdot}18$, where 45·18 is the mean area per chain in the cylindrical structure without decanol and -31 is the slope measured on the curves of figure 3.

2.3. *Comment*

Thus, to study the evolution of the shape of the normal section of the cylinders of the cylindrical structures in the system SdS/decanol/water as SdS is progressively substituted by decanol, there exist two sets of data: one is the variation of the mean area σ per molecule at the interface and the other is that of the mean area Σ of the section. Models corresponding to different shapes will be developed, in which the variation of σ will be introduced in order to calculate evolutions of Σ which will be compared with the experimental behaviour. We must notice that Σ alone is not sufficient to discriminate between different shapes; to do so it would have been useful to determine the form factors of the cylinders but, owing to the small number of reflections observed in the scattering experiments, this cannot be done with sufficient accuracy. However, some qualitative information may be obtained from such determinations [3–6] and also, from the study of the distribution of the SdS and decanol in a cylinder [10, 11], the results suggest that the section becomes anisotropic when σ decreases.

3. Normal section of the cylinders

There are four microscopic parameters intervening in this problem of shape on a mesoscopic scale: the volume v of a chain, the area σ of this chain at the interface, its mean lateral area in the core of the paraffinic medium, which may be expressed as v/λ, if λ is its mean elongation, and, because of the presence of two molecules, their relative distributions in the section. The volume v is of course constant. The area σ and v/λ vary, but not necessarily in similar manners, as they depend on conditions prevailing in two media with different properties, i.e. the interface and the paraffinic medium; indeed this area gradient along the normal to the interface controls its mean curvature H following

$\sigma H = 2(\sigma - v/\lambda)/\lambda$ [14]. For instance a flat interface corresponds to $\lambda\sigma/v = 1$, a cylindrical one with a radius of curvature λ corresponds to $\lambda\sigma/v = 2$ and a spherical one with the same radius corresponds to $\lambda\sigma/v = 3$. Finally, a distribution of the two molecules, which modulates σ, may modulate H.

A first model will be considered which, ignoring the physico-chemical flexibilities of the system, is an attempt to find a geometrical configuration with respect to uniform values of σ and λ. Of course, there is no such solution in general and, even if distortions altering the uniformity are accepted, the area Σ of the section deduced from this model cannot fit the data; however it indicates the directions to be followed next. The second and third models take into account physico-chemical aspects, related to properties of the molecules and of their distribution within the section, in two extreme manners. The results are in rather good agreement with the data on either side of the jump in Σ recorded in figure 2, respectively, and this suggests the nature of the terms to be considered in a deeper analysis of the structures and their transitions in this system.

3.1. *Mapping of an ideal section (model 1)*

This model corresponds to a general approach recently developed to elucidate the geometrical foundation of the polymorphism of systems of amphiphiles [15]. The argument is that it is only when $\lambda\sigma/v = 1, 2$ and 3 that structures with uniform interfaces can be built in our euclidean space; they are the lamellar, hexagonal and micellar structures with flat lamella, circular cylinders and spherical micelles, respectively. When $\lambda\sigma/v$ has intermediate values, more complicated structures are observed and, among them, are the spectacular cubic structures which can be understood on a purely geometrical basis also [16]. The path followed in this approach is the following: ideal structures with uniform interfaces, with respect to σ and λ, and whatever the value of $\lambda\sigma/v$, can be built in non-euclidean spaces with positive curvatures and the mappings of these curved spaces on to our euclidean space, through a disclination procedure, obeying strict laws imposed by the curvature of the spaces and the symmetry of the ideal structures, provides geometrical configurations having the topologies and symmetries of the observed structures.

Ideal cylindrical structures with C_∞ symmetry can be built if the normal section of the cylinder is drawn on a curved surface with radius R, as shown in figure 4 [15, 17]. In this case $\lambda = R\theta$, the spherical cap of the section has an integrated gaussian curvature $\alpha = 2\pi(1 - \cos\theta)$, its perimeter and its area are $2\pi R \sin\theta$ and $2\pi R^2(1 - \cos\theta)$, and $\lambda\sigma/v = \theta(\sin\theta)/(1 - \cos\theta)$. After the disclination of angle α is introduced around the C_∞ symmetry axis of the ideal section, to map it on to the flat space, its perimeter and area

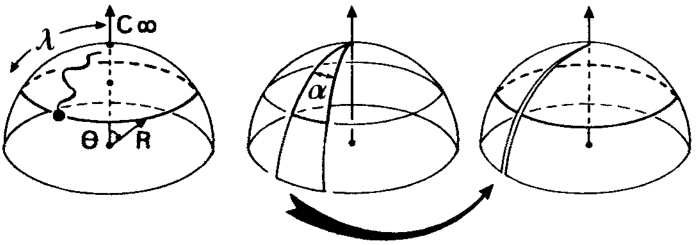

Figure 4. A cylinder normal section of radius λ drawn on a curved surface with radius R and the suppression of its curvature α by introduction of a disclination of the same angle, following a Volterra process.

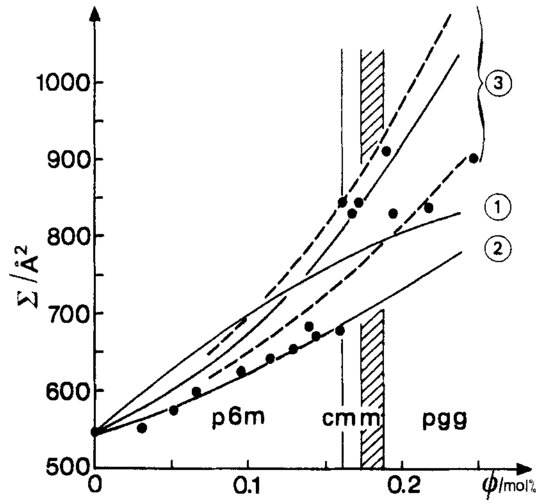

Figure 5. Comparison of the data of figure 2 with the results of the three models considered in the text and numbered as 1, 2, 3. In the case of model 3, the upper dotted curve corresponds to a concentration of decanol in the flat region on the cylinder $\phi_1 = 0{\cdot}45$ mol%, the intermediate full line to $\phi_e = 0{\cdot}5$ mol% and the lower dotted line to $\phi_1 = 0{\cdot}6$ mol%.

Table 1. Evolution of the normalized perimeter X and area Y as $\lambda\sigma/v$ decreases in model 1; r is the anisotropy ratio of an elliptical section, θ is in degrees.

θ	0	10	20	30	40	50	60	70	80
$\lambda\sigma/v$	2	1·995	1·98	1·95	1·92	1·87	1·81	1·74	1·66
X	1	1·009	1·04	1·08	1·136	1·19	1·24	1·275	1·287
Y	1	1·012	1·05	1·108	1·18	1·27	1·37	1·46	1·547
X^2/Y	1	1·006	1·03	1·05	1·09	1·115	1·122	1·113	1·07
r	1	1·105	1·275	1·39	1·525	1·61	1·64	1·6	1·45

become $(2\pi + \alpha)R \sin\theta$ and $(2\pi + \alpha)\, R^2(1 - \cos\theta)$. If those two quantities are divided by the perimeter and area of the section in the hexagonal structure without decanol, $2\pi\lambda$ and $\pi\lambda^2$, normalized perimeter $X = (\sin\theta)\ (2 - \cos\theta)/\theta$ and area $Y = 2(2 - \cos\theta)\ (1 - \cos\theta)/\theta^2$ can be defined, and values are given in table 1, together with those of $\lambda\sigma/V$. Thus the section of the cylinder is defined by its perimeter and area for different values of $\lambda\sigma/V$. When σ decreases from its value in the cylinder with circular section, $\lambda\sigma/V$ becomes smaller than 2, Y becomes larger than 1 and the area of the section increases but, as the ratio X^2/Y becomes larger than 1, the section cannot stay circular. The perimeter of the section becoming too large for its area, it might become elongated with a C_2 symmetry, for instance an ellipse, but this would be obtained at the price of a loss in the uniformity of the interfacial curvature. Values of axes and the anisotropy ratio for such ellipses can be determined from X and Y; their anisotropy ratios are given in the table. Other elongated shapes satisfying X and Y would give similar values. If the characteristics of the cylinders of the hexagonal structure without decanol, $\sigma = 45{\cdot}18$ Å^2 and $\lambda = 13{\cdot}16$ Å, and the relation between the mean area per chain and the decanol concentration, $\sigma = -31\phi + 45{\cdot}18$, are taken into account, the mean area Σ of the normal section of a cylinder in this model can be calculated and compared with the experimental data, as shown in figure 5. It appears that the general trend, the increase of Σ, is correct, but that the model does not fit any situation, hexagonal or rectangular; it lies just in between them.

The failure of this model lies indeed in its purely geometrical nature: an ideal structure was built in a curved space to give uniform values of σ and λ in a C_∞ symmetry and the flattening of the curved space by suppression of its intrinsic angular deficit α creates a new situation where the C_∞ symmetry is broken, or the interfacial curvature modulated, so that the constraints on σ and λ can no longer be respected. The molecules must therefore adopt configurations differing from that which they have in the ideal state. This implies that their physicochemical properties must be considered, particularly interaction and entropy terms. Unfortunately, the knowledge of all these terms is at the moment too limited for a detailed study from first principles; only empirical models can be developed in order to search for dominant terms. The next two models, which consider two extreme configurations, are of this type: one preserves the C_∞ symmetry, the other decreases it to C_2 by making different interfacial curvatures more favourable by an adequate choice for the distribution of the molecules within the section.

3.2. *Section with C_∞ symmetry (model 2)*

In this model the section remains circular and, therefore, the two molecules are uniformly distributed. A mean area σ per chain at the interface is then possible if the section has a radius $\rho = 2v/\sigma$, as the section is flat, so that $\Sigma = \pi\rho^2 = 4\pi v^2/\sigma^2$ as shown in figure 6. The result of this simple model is in correct agreement with the data of the p6m structure, but not with those of the cmm and pgg structures, as shown in figure 5.

One important feature of this model is that its validity is limited to values of ρ which are smaller than the length of an extended C_{10} chain in an all-*trans* conformation, i.e. $\rho < 14{\cdot}8$ Å; this limit would correspond to a value of σ of $40{\cdot}17$ Å^2 and to a value of the decanol content ϕ of 0·16 which is close to the end of the p6m structure. Beyond this limit the growth of the section is necessarily non-circular, keeping one dimension smaller or equal to 29·6 Å. At this point we might think to make use of model 1, with $\lambda = 14{\cdot}8$ instead of 13·16 Å, to study the deformation in the cmm and pgg structures, but the consequence would be a continuous variation of Σ, with only a change of slope at the transition, not a discontinuity as observed. A third model is needed beyond this point.

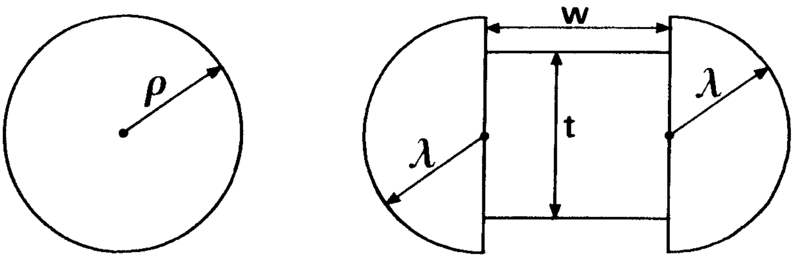

Figure 6. The circular section, with radius ρ, of model 2 and the non-circular section, with a flat central region of width w and thickness t and hemi-cylindrical lateral regions with radius λ, of model 3.

3.3. *Section with C_2 symmetry (model 3)*

A simple section with C_2 symmetry can be built assembling a central rectangular part with two lateral semi-circular edges, as shown in figure 6. It exhibits flat and curved interfaces along which the molecules cannot satisfy the mean area at the interface σ and the required chain elongation λ, simultaneously. This difficulty may be passed round in a simple manner, assuming that the central part of the aggregate is a piece of lamellar structure with an adequate decanol content ϕ_l and the edges are two half cylinders of the p6m structure without decanol. This is an important fluctuation of concentration which is indeed supported by experimental data [11]. Thus, the thickness of the flat central part being known to be $t = 22$ Å from the X-ray data in the lamellar phase, and the radius of the edges being $\lambda = 13{\cdot}16$ Å from those in the hexagonal phase, the width w of the central part is related to the global decanol content ϕ by $\phi(\pi\lambda^2 + wt) = \phi_l(wt)$. The area $\Sigma = \pi\lambda^2 + wt$ of the section can then be calculated as a function of ϕ, for different values of ϕ_l, and compared with the data, as shown in figure 5. The curves obtained for values of $\phi_l > 0{\cdot}45$ mol%, the limit corresponding to the beginning of the lamellar structure without defect, do not fit the points of the p6m structure, but are close to the distribution of the points of the cmm and pgg structures; in the case of the cmm structure $0{\cdot}45$ mol% $< \phi_l < 0{\cdot}5$ mol% and in the case of the pgg structure $0{\cdot}5$ mol% $< \phi_l < 0{\cdot}6$ mol%; these are reasonable values for regions of the aggregates having structures similar to a lamellar structure (at any rate, better controlled measurements of Σ should be made in order to ascertain this evolution of ϕ_l.

This model also has a limit of validity which is related to the fact that the flat region must have a size sufficient for it to be described as a lamellar structure. Assuming that two molecules in the width w correspond to this inferior limit and considering that one molecule occupies the lateral area of 27 Å^2 measured in the lamellar structure, then w must be larger than $4\sqrt{(27/\pi)}$ or ϕ larger than $0{\cdot}17$ mol%. This inferior limit is only slightly above the transition between the p6m and cmm structures.

4. Phase transitions

A summary of the analysis is given in figure 7. Starting from the section of the cylinder without decanol in the p6m structure, which is considered as the basic state to which all others are referred, the mean area of the section first grows isotropically, following model 1, then anisotropically, following model 2, when decanol is added. The p6m/cmm transition might be associated with the passage from one model to the other, i.e. from one shape to the other, whereas the cmm/pgg transition is not marked by such an obvious phenomenon.

4.1. *The p6m/cmm transition*

On the lower side of the transition, the mean section is circular, the two molecules are distributed uniformly within it and, as the area of the section increases with the introduction of decanol, the chains of the molecules are more and more stretched towards the upper limit of their all-*trans* conformation, corresponding to a decanol concentration $\phi = 0{\cdot}16$ mol%. The free energy of such a section, relative to that of the circular section without decanol, contains the dilution entropy of the different molecules and the stretching energy of their chains associated with their conformational entropy. The dilution term per molecule goes as $kT(\phi \log \phi + (1-\phi) \log(1-\phi))$, and stays finite therefore as ϕ increases, as shown in figure 8, whereas the stretching term diverges when approaching the limit of the all-*trans* conformation.

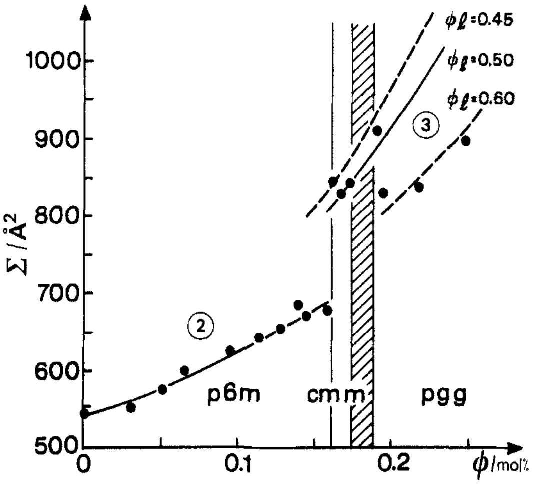

Figure 7. A summary of the analysis presented in this article; the curve corresponding to model 2 is stopped when the radius of the section becomes equal to the length of the stretched chain in an all-*trans* conformation, and the curves corresponding to model 3 start when the flat central region of the section has a width of the order of 2 times the lateral molecular size.

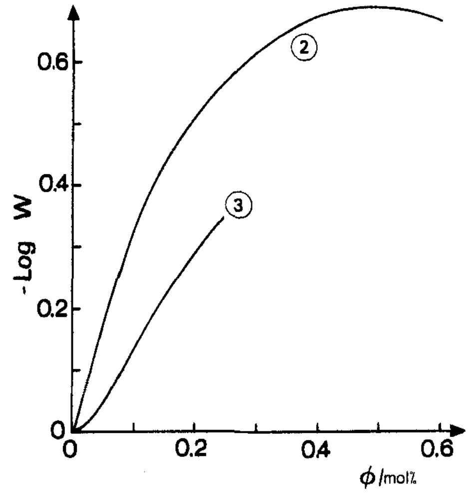

Figure 8. Variations of the dilution entropies (*w*) in models 2 and 3 when the decanol content ϕ (mol%) in the sections increases.

On the upper side of the transition, the mean section is elongated, it has a central region with flat interfaces limited by two lateral regions with curved interfaces, the local decanol concentration being 0·5 mol% in the first and 0 mol% in the second. Moreover, the width of the central region increases with the decanol content from its lower reasonable value, which corresponds to $\phi = 0{\cdot}17$ mol%, as the free energy of such a section, relative to that of the circular section without decanol, contains that of the central region with a lamellar character, that of the regions connecting it with the semi-circular edges, where the gradients of interfacial curvature are localized, and the dilution entropy of the molecules. The first two terms are difficult to

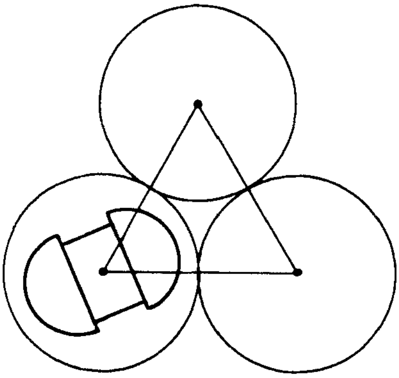

Figure 9. At the transition from the p6m structure to the cmm structure; the non-circular overall sections (including polar group and ionic layers) would interact if they stayed organized on the p6m lattice.

estimate at the moment, but certainly stay finite, and the last one, which goes as $kT(\log 0{\cdot}5)\,(wt)/(\pi\lambda^2+wt)$, as the decanol stays in the central region of area wt with a local concentration of $\phi_1=0{\cdot}5$ mol%, is smaller than its equivalent in the circular section, as shown in figure 8.

In this approach the transition between the two shapes must occur in their common domain of existence, i.e. for $0{\cdot}16\,\text{mol\%}<\phi<0{\cdot}17\,\text{mol\%}$, and is controlled by the competitions between the energy and entropy terms discussed above: when, on increasing the decanol content, the stretching energy of the chain in the isotropic section becomes too high, it is lowered by moving to the anisotropic section, but this is done at the price of a decrease in the dilution entropy of the molecules. The fact that a change of symmetry is associated with those changes in shape and area relates certainly to the fact that the growth of the long axis of the anisotropic section with constant thickness is proportional to its area and therefore faster than the growth in the size of the hexagonal cell containing it, which is proportional to the square root of this area, so that the sections start to interact. For instance, the largest dimension of a paraffinic section with an area $S=850$ Å^2 is 41 Å; if polar group and ionic layers of 4 Å thickness are added to it, this increases to 49 Å, which is also the value of the distance between cylinders on the p6m lattice for this concentration, as shown in figure 9.

4.2. *The cmm/pgg transition*

A single model, that of total segregation, gives a correct account of the variation of the mean area of the section in the two structures. In this approach, there is no qualitative change at the transition, but a quantitative one only, which is the continuous increase in the largest dimension of the section. It is therefore proposed that the symmetry change results from the evolution of the interactions between sections and, among the possible terms, a good candidate might be the quadrupolar term resulting from the density of charged OSO_3^- groups which is higher in the lateral regions of the section than in the central region, where the anionic groups are diluted with OH groups without charge. Such interactions are known to favour herring-bone organizations of quadrupoles with, in general, angles between quadrupoles on parallel rows close to $\pi/2$ [18]. In the system studied here, the angle is much smaller, not more than 15° [4, 5], suggesting the existence of a term opposing the reorientation of the

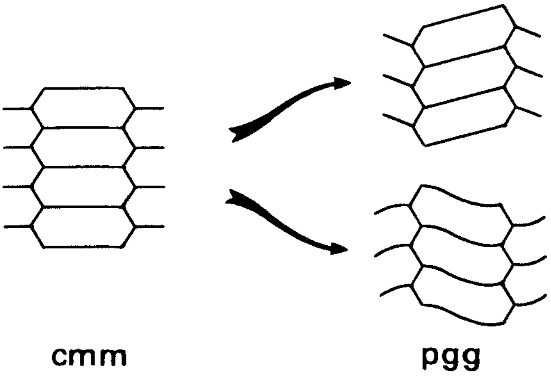

Figure 10. At the transition from the cmm structure to the pgg structure, the film of water separating the cylinders must suffer distortions from its flat equilibrium configuration with equal connecting angles of $2\pi/3$.

sections. This might be the distortion of the film of water separating the sections from its configuration in the cmm structure, which is an equilibrium one, as the films are flat and connected three by three at equal angles of $\pi/3$, as shown in figure 10.

5. Discussion

The evolution of the shape of the mean normal section of the cylinders built by amphiphiles in the hexagonal and rectangular structures of the system SdS/decanol/water when the decanol content increases and the mean area σ per chain at the interface decreases, was examined by considering three models. In the first of these models, it was shown that an ideal structure, respecting the value of σ imposed by the decanol content and the conformational state of the chains imposed by their entropy in a uniform manner, can be built in a curved space; the mapping of this curved space on to flat space destroys this uniformity, and the molecules must occupy different sites on the interface. This was formalized by saying that the section in flat space contains angular defects or disclinations. This model cannot take account of the observations and the reason for this most likely relates to the intrinsic limitation of a geometrical approach to a physical problem; indeed these defects represent a certain energy cost and the system may move away from the best geometrical configuration to decrease this cost. The second and third models represent two possible attempts in this direction.

In one case no new defect is introduced relative to the basic situation of the circular cylinder without decanol; the chains are simply stretched to fit the decrease in mean area σ per chain at the interface. The uniformity of the interface is maintained, at the cost of the stretching energy of the chains, and this is most likely favoured here by the gain in dilution entropy associated with the uniform distribution of the molecules. This type of relaxation, by a mere suppression of the defect, does not depend on the nature of the system, whether one or several amphiphilic species, and should be observed whatever the nature of the system. In the second case the energy of the defect is relaxed by a particular distribution of the amphiphiles which creates curved and flat interfaces similar to those of the basic hexagonal and lamellar structures which are free energy minima; this energy loss is obviously balanced by a dilution entropy decrease. This type of relaxation, by a redistribution of the amphiphiles, is specific for systems in which different species can be identified, either because the system is a mixture of several species or, in the case of one amphiphilic species only, because the polar groups may have different degrees of solvation or dissociation [6].

Finally, in this analysis, the shape of the sections is controlled by intra-aggregate constraints only and their ordering along lattices is controlled by steric and electrostatic forces between hard bodies; intra-aggregate and inter-aggregate terms are therefore considered as decoupled. We may suspect that this is a coarse approximation in such a 'soft' medium and that, in spite of the rather good agreement obtained between the results of the models and the observations, both should be refined. A thermodynamical approach to this problem was recently proposed within the frame of a 'cell' model [19].

Discussions with J. F. Sadoc (Laboratoire de Physique des Solides d'Orsay) are gratefully acknowledged.

Appendix

Two sets of experimental data, corresponding to two different batches of sodium decylsulphate, are used in this article. The concentrations of the samples, the symmetries of their structures and the parameters of their cells are given in tables A 1 and A 2, where the notations of the samples are those of the original articles [3, 4]. All these samples have about the same degrees of hydration, so that the sequences of structures are very close to that corresponding to a progressive substitution of SdS molecules by decanol molecules.

The parameters of the p6m structures with the same decanol content are not the same in the two tables; for instance, that without decanol has a parameter of 40·04 Å in table A 1 and 41·5 Å in table A 2. This is certainly to be related to the fact that tables A 1 and A2 correspond to two different batches of SdS which might contain different impurities or different quantities of the same impurity. One of the most common impurities of SdS is decanol produced by hydrolysis and, if it is assumed that the SdS of table A 2 is less pure than that of table A 1 and contains 4·96 per cent of molecules of decanol, the two sets of data can be put together in a coherent manner as shown in table A 3.

In table A 3, the area of the section of the cylinders occupied by the paraffinic chains only, the polar OH and OSO_3Na groups of the decanol and SdS molecules being considered as belonging to the polar area with water, was calculated with the following molecular volumes: OH = 20·3 $Å^3$, OSO_3Na = 67·8 $Å^3$, H_2O = 29·9 $Å^3$ and $C_{10}H_{21}$ = 297·3 $Å^3$ (obtained from molecular data in the *Handbook of Physics and Chemistry*).

Table A 1. Experimental data concerning the p6m structure in [10].

	Mol %				
Sample	H_2O	SdS	Decanol	Symmetry	Parameter/A
1	92·91	7·09	0	p6m	40·04
2	92·82	6·95	0·23	p6m	40·15
3	92·74	6·79	0·47	p6m	41·64
4	92·75	6·65	0·70	p6m	42·32
5	92·59	6·55	0·86	p6m	42·63
6	92·55	6·47	0·98	p6m	43·11

Table A 2. Experimental data concerning p6m, cmm and pgg structures in [4, 5].

	Mol %				
Sample	H_2O	SdS	Decanol	Symmetry	Parameters/A
a	93·15	6·85	0	p6m	41·5
b	92·8	6·65	0·698	p6m	44·1
c	92·67	6·58	0·74	p6m	43·8
d	92·69	6·46	0·84	p6m	44·0
e	92·58	6·53	0·88	cmm	37·5 111
f	92·57	6·49	0·93	cmm	37·5 109
g	92·56	6·46	0·97	cmm	36·6 114
γ	92·51	6·37	1·12	pgg	37·2 120
k	92·51	6·33	1·15	pgg	37·4 107
l	92·44	6·19	1·36	pgg	36·3 111
m	92·34	6·05	1·61	pgg	38·9 120

Table A 3. Coherent organization of the data of tables A 1 and A 2 (see text), with the concentration ϕ of decanol in the cylinder, the area Σ of the section of the cylinder and the radius ρ it would have if it was circular.

Sample		Symmetry	Cell area/Å^2	Σ/Å^2	ρ/Å
1	0	p6m	2776	544·2	13·16
2	0·032	p6m	2792	553·3	13·27
a	0·05	p6m	2981	576·0	13·54
3	0·065	p6m	3·3	600·0	13·82
4	0·095	p6m	3102	624·9	14·10
5	0·116	p6m	3147	638·0	14·25
6	0·131	p6m	3218	654·8	14·43
b	0·14	p6m	3368	680·3	14·71
c	0·146	p6m	3323	670·5	14·6
d	0·189	p6m	3353	674·25	14·65
e	0·163	cmm	4155	845·0	16·40
f	0·168	cmm	4088	833·0	16·3
g	0·174	cmm	4172	851·0	16·46
γ	0·192	pgg	4457	913·5	17·0
k	0·196	pgg	4009	822·0	16·2
l	0·22	pgg	4034	832·0	16·3
m	0·25	pgg	4331	901·5	16·9

References

[1] LUZZATI, V., MUSTACCHI, H., SKOULIOS, A., and HUSSON, F., 1960, *Acta crystallogr.*, **13,** 660. HUSSON, F., MUSTACCHI, H., and LUZZATI, V., 1960, *Acta crystallogr.*, **13,** 668.

[2] EKWALL, P., 1975, *Adv. Liq. Crystals*, **1,** 1.

[3] HENDRIKX, Y., and CHARVOLIN, J., 1981, *J. Phys. Paris*, **42,** 1427.

[4] ALPÉRINE, S., 1985, Third Cycle Thesis, Université d'Orsay.

[5] HENDRIKX, Y., and CHARVOLIN, J., 1992, *Liq. Crystals*, **11**, 677.
[6] KÉKICHEFF, P., 1991, *Molec. Crystals liq. Crystals*, **198**, 131.
[7] SEDDON, J., 1990, *Biochem. biophys. Acta*, **1031**, 1.
[8] GRUNER, S., TATE, M. W., KIRK, G. L., SO, P. J. C., TURNER, D. C., KEANE, D. T., TILCOCK, C. P. S., and CULLIS, P. R., 1988, *Biochem.*, **27**, 2853.
[9] THOMAS, E., REFFNER, J. R., and BELLARE, J., 1990, *J. Phys. Paris*, **51**, C7-363.
[10] HENDRIKX, Y., and CHARVOLIN, J., 1988, *Liq. Crystals*, **3**, 265.
[11] ALPÉRINE, S., HENDRIKX, Y., and CHARVOLIN, J., 1985, *J. Phys. Lett. Paris*, **46**, L-27.
[12] HENDRIKX, Y., CHARVOLIN, J., KÉKICHEFF, P., and ROTH, M., 1987, *Liq. Crystals*, **2**, 677.
[13] HENDRIKX, Y., and MARI, D., 1979, *Physico-Chimie des Composés Amphiphiles*, edited by R. Perron (C.N.R.S.).
[14] HOFFMAN, D., 1990, *J. Phys. Paris*, **51**, C7-197.
[15] SADOC, J. F., and CHARVOLIN, J., 1986, *J. Phys. Paris*, **47**, 683.
[16] CHARVOLIN, J., and SADOC, J. F., 1988, *J. Phys. Paris*, **48**, 1559 and **49**, 521.
[17] CHARVOLIN, J., and SADOC, J. F., 1988, *J. phys. Chem.*, **92**, 5787 and 1991, *Physica* A, **176**, 138.
[18] HOLDSWORTH, P. C. W., GINGRAS, M. J. P., BERGERSEN, B., and CHAN, E., 1989, *Physica scripta*, **39**, 613.
[19] HAGSLÄTT, H., SODERMAN, O., and JÖNSSON, B., 1992, *Liq. Crystals*, **12**, 667.