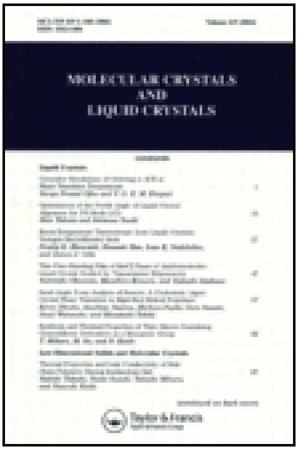

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From Cylinders to Bilayers: A Structural Study of Phase Transformations in a Lyotropic Liquid Crystal

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From Cylinders to Bilayers: A Structural Study of Phase Transformations in a Lyotropic Liquid Crystal

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The structural relations of the four intermediate mesophases between the hexagonal phase and the lamellar phase of the sodium dodecyl sulfate-water system are examined. The system manages to cross from a situation with homogeneously curved interfaces (cylinders) to another one with zero curvature (bilayers) in a nearly continuous way. The first step is the transformation of the cylinders into ribbons; then the ribbons become connected to each other at regular intervals to form a three-dimensional array of rods. Subsequently this array is distorted to give a layered structure where the layers are spaced as in a lamellar phase but retain the correlations of the cubic phase in the other directions. The final step is the transition to a system of flat layers. The only physical parameter which appears to change in a consistent way through this series of structures is the mean curvature of the interfaces. Comparison with other systems which adopt different solutions to transform a cylinder into a bilayer is discussed.

Keywords: lyotropic, phase transition, SDS

INTRODUCTION

The amphiphilic nature of surfactant molecules leads to self-aggregation in solution, so that they isolate hydrophobic from hydrophilic regions. Depending on the temperature and solution conditions, a variety of liquid crystal phases can be displayed.[1] Although disordered on atomic distances, highly organized structures possessing long-range order may form. The microstructure of the most common mesophases (micellar, hexagonal, and lamellar) are reasonably well-modeled by classical surfaces (viz., spheres, cylinders and planes, respectively). Complicated structures, such as the bicontinuous cubic phases,[2] require more exotic surface geometries, as the interwoven, but otherwise independent, three-dimensional networks of interconnected cylinders, of some systems in their earliest description.[3]

One of the generally unsolved problems is to rationalise the sequence of liquid crystal phase structures, which occurs when an external parameter (the temperature or the water composition) is varied. In particular, at compositions between the lamellar and hexagonal phases in two component systems, there usually lies a vast concentration region over which the systems cross from zero curvature (bilayers) to finite curvature (cylinders). In terms of local molecular surfactant geometry, the "surfactant parameter",[4] v/Al, which relates the chain volume per surfactant molecule v, to the average chain length, l, and head-group area per molecule, A, decreases from 1 (lamellar phase) to 0.5 (hexagonal phase). At both ends of the transformation, the interplay between inter- and intra-aggregate interactions sets easily a homogeneous curvature to the interfaces compatible with a separation between two neighbouring interfaces of the order of the length of an amphiphilic molecule. Thus, the Van der Waals forces between all the molecules, the electrostatic repulsions and solvation forces between the hydrated polar heads together with the forces between the aliphatic chains (water/oil surface tension)[5] set a mean curvature 1/R of the interface for the cylinders and zero for the bilayers. When the content of water becomes intemediate between these two extremes, the chain may be too flexible to fold inside the volume compatible with if the aggregate is a circular cylinder, and too stiff if the structure is composed of flat bilayers. Thus, the "desired" curvature is not any more compatible with this constraint, and the system tries to change the shape of its interfaces, by building an inhomogeneous curvature or a negative Gaussian curvature (saddle-splay structures, etc).[6] This basic problem behind the shapes of the interfaces, originally called the cumulative strain effect[1,7] has been analyzed in terms of frustration.[8] The transformation of a cylinder into a bilayer can occur in a variety of ways.

The system may undergo successive transitions through the intermediate mesophases whose aggregates have interfaces of inhomogeneous curvatures. This has been observed in a ternary system whose the mixture of two molecules of same chain length but different amphiphilic character creates a phase sequence whose symmetries of the mesophases are: hexagonal p6m/rectangular cmm/rectangular pgg/lamellar.[9] The inhomogeneity in the curvature of the interfaces results from the difference in the average surface area occupied by the two amphiphilic molecules.

When one decreases the number of degrees of freedom as in a binary system of nonionic molecules in water, one favours the building of cylindrical structures with homogeneous curvature. For example, it has been observed[10] that the transformation of a lamellar mesophase to a hexagonal one, occurs first by the fragmentation of the bilayers into cylinders organized with a local hexagonal order. These cylindrical fluctuations within the lamellae can turn into a long-range metastable hexagonal order before the formation of a cubic phase. Further, the decrease of correlations along the ⟨111⟩ directions of the cubic phase signals the rupture of the connected rods in the cubic structure and the progressive formation of indefinite and non-deformed cylinders of the hexagonal mesophase.

Because, ionic amphiphilic molecules can have different degrees of dissociation, they can segregate along the interfaces and thus provide a variety of aggregates with inhomogeneous interfacial curvatures. That what happens in the case of the dehydration of the binary system of sodium dodecyl sulfate (S.D.S.)/water where the shape of the aggregates changes in a nearly continuous way from the most hydrated mesophase, the hexagonal phase H_{α}, to the least hydrated mesophase, the lamellar phase L_{α}.[11–14] In this article we reexamine the structures of the intermediate mesophases which lie between these two extremes and their relations.

METHODS

Purity of the constituents and preparation of the samples have already been reported.[11-14] For the sake of consistency with N.M.R. and neutron scattering experiments,[12,14] the mixtures were made with D_2O.[11] Different techniques were used to investigate the mesophases of the SDS/water system. They have already been described in previous articles: differential scanning calorimetry,[11] optical microscopy,[12] N.M.R.,[12] small-angle scattering by X-rays[12,13] and neutrons.[14] The combination of isoplethal together with isothermal methods gave a quite precise picture of the phase behaviour of the lyotropic mesophases. All the results obtained required high sophistication of the techniques. For instance, small transition enthalpies were detected using large sample volumes scanned at very low heating rates in a high sensitivity flux type microcalorimeter.[11] The high fluxes of synchrotron radiation and neutron beams were used to determine unambiguously the symmetries of the mesophases studied in different configurations: powder[12,13] or surface-oriented samples.[14] Moreover, because a large number of different phases can lie in a narrow composition range, deliberately made samples with a spatial gradient in their composition were scanned by a point-collimation of the X-ray beam of a synchrotron source[13] giving an equivalent resolution in water concentration of about 0.05%.

RESULTS AND DISCUSSION

The phase diagram of the binary system sodium dodecyl sulfate (S.D.S.)/water was determined by the convergence of all the results obtained by the different techniques used.[11-14] Figure 1 presents an enlargement of the complete phase diagram (established in references 11 and 12) in the region of the concentrated mesophases. The intermediate region between the hexagonal H_α and the lamellar L_α phases contains a variety of four phases whose related structures to each other suggest that the system may undergo a nearly continuous transition from a planar geometry to a cylindrical geometry[12-14]—the driving external parameter of this transformation being the increase in the hydration of the mesophases.

1. Successive Transformation of the Lattices

Because of the large number of Bragg diffraction reflections, the shape and dimensions of the unit cell for every structure is determined unambiguously. The transformations of this unit cell through the series of mesophases are remarkable because they follow a nearly continuous path.

(i) The unit cell of the two-dimensional hexagonal phase H_α is progressively deformed: one of the edges becomes longer than the other and the angle between them decreases continuously.[13] No miscibilty gap between the two-dimensional monoclinic phase M_α and H_α is observed at high temperature.[11]

(ii) Although the phase transition to the next mesophase, the rhombohedral phase R_α, is first order, the transformation into a three-dimensional net-

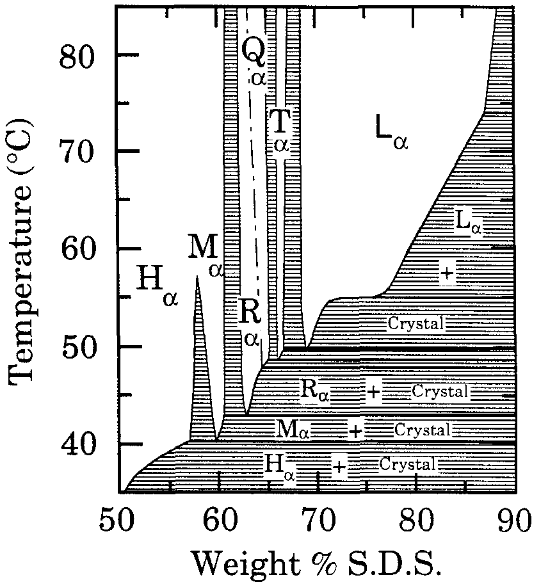

FIGURE 1 Binary phase diagram of the S.D.S.-deuterated water system described in detail in references 11 and 12. Luzzati's terminology[1] was adopted for the mesophases (the subscript α refers to a quasi-liquid state for paraffinic chains). They are labeled according to the symmetry of their lattice: H_α hexagonal phase; M_α, two-dimensional monoclinic phase; R_α, rhombohedral phase; Q_α, cubic phase; T_α, tetragonal phase; L_α, lamellar phase.

work induces a doubling of period in one direction of the space (the Bragg spots 10 and 01 of M_α turn into $\bar{2}11$ and $21\bar{1}$ of R_α).[13,14]

(iii) The continuous change of the dimensions of this rhombohedral unit cell yields to the cubic phase Q_α, which is in fact a particular case of the former structure (Figure 2).

(iv) The transformation towards the tetragonal phase T_α can be interpreted as a distorsion of the cubic phase Q_α. Since the Bragg spots 211 and 222 of the cubic network turn into 101 and 002 of the tetragonal structure, the edge length of the square base of the tetragonal unit cell is roughly equal to the half diagonal of the cube face while its height is equal to a third of the long diagonal cube.

(v) Finally, the transformation into the lamellar mesophase L_α is a discontinuous transition, but it occurs via strong heterophase fluctuations[14,15]: the thickness of the primitive unit tetragonal cell matches the repeat period of the bilayers[13] while Bragg diffraction spots of the tetragonal network progressively become diffuse in the lamellar phase.[14]

2. Relations between Consecutive Structures

It has been previously noticed that the diffraction patterns of oriented samples have many striking similarities[14] and evolve in a nearly continuous way despite an apparent large change in the symmetries of the networks. This indicates that the

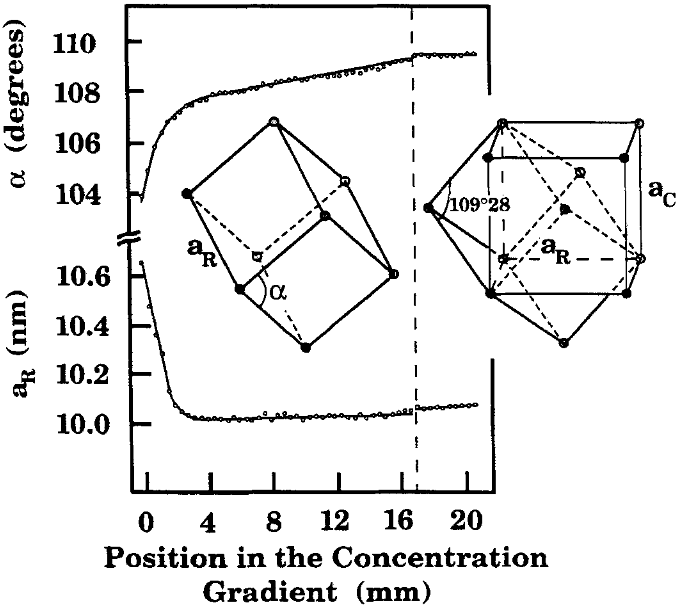

FIGURE 2 Transition from the rhombohedral phase R_α to the cubic phase Q_α. The sample contains a deliberately created spatial gradient in the concentration of water/S.D.S. and is scanned by a high collimated X-ray beam of a synchrotron source, allowing diffraction patterns to be recorded at concentration intervals of about 0.05%. The figure shows the edge length a_R and the angle α of the unit cell as functions of the sampled position in the concentration gradient. The composition range explored here is about 3%. At the higher concentrated surfactant limit, the angle locks at 109° 28 which is the value for the cubic phase; at lower S.D.S. concentration, the structure becomes more anisotropic as α decreases; the complete transition to a structure made of infinite ribbons would require $\alpha = 0$.

shapes of the aggregates vary nearly continuously throughout the concentration range.

The simple chemical and physical criteria that often lead to an estimate of the shape and size of the structure elements may grow into convincing arguments when applied to many different structures at once. Firstly, the dimensions of the structure elements must be consistent with the volumes occupied by the polar and the apolar moieties. Secondly, the distance from any point of the hydrocarbon regions to the polar/apolar interface cannot exceed the fully extended length of the hydrocarbon chains. Finally, the area per chain at the polar/apolar interface is expected to increase, or at least not to decrease, as temperature and water content increase, even when phase boundaries are crossed. This approach has been adopted successfully in the past.[1] In the case of the cubic phases, though, the structures often are too complex to yield to this simple approach and a pattern recognition technique based on the scattering data has been developed.[2] Unfortunately the large difference in the electronic densities of the polar heads and the lipidic chain of a S.D.S. molecule prevents firm conclusions by the use of this elegant method.[16]

The use of infinite periodic minimal surfaces (IPMS)[17] has turned out to be an important tool in the understanding of liquid crystalline phases, in particular cubic phases and microemulsions,[8,18-21] as the film built by the interfaces is supported by surfaces directly related to them. IPMS can be described as periodic non-intersecting surfaces with zero mean curvature and negative Gaussian curvature in all points of the surface, that is concave and convex curvatures balance each other everywhere. The polar heads, located on each side of the minimal surface, build a polar medium centered on such IPMS, and thus separate two lipidic-filled channel systems. The polar/apolar interfaces are approximately translationally parallel to the minimal surface and have a nearly constant mean curvature. The result is to partition space into fixed volume fractions such that the surface area is stationary with respect to area perturbations.[22] It has sometimes been suggested that the physical counterpart of this geometric property is the tendency to minimize the interfacial tension.

2.1 Structure of the cubic phase. This structure has the highest symmetry of all the intermediate mesophases. Because it can been reached through a continous deformation from the other structures which surround it, the determination of its structure is a key for understanding the other phases.

For this phase it has been demonstrated[13] that six space groups are crystallographically possible (Im3m; I432; I$\bar{4}$3m, Im3; I23; I$2_1$3). Among these possible space groups, the Im3m is remarkable because it matches the symmetry of the primitive surface P of Schwarz.[17] In this case it separates two interpenetrated systems of rods; the unit of each system is made of six rods which meet at right angles (Figure 3a). Further, diffraction on oriented samples has shown[14] that the three-fold axis ⟨111⟩ is a privileged direction of the cubic structure as indicated by the alignment of the Q_α mesophase along macroscopic surfaces, i.e. in a similar manner as the bilayers of the lamellar mesophase L_α. Moreover the Bragg diffraction spot 222 of the Q_α phase matches the first order of the L_α phase. These features suggest locally flat (lamellar) regions spaced with the same period and the choice of Im3m as space group is tempting. Indeed, the intersection of the four reticular planes perpendicular to each diagonal of a cube define the tetrakaidecahedron of Lord Kelvin[23] (Figure 3c). By curving this surface constituted by 8 hexagonal and 6 square flat faces, the Schwarz's P-surface is reobtained. In other words, the surface formed by the infinite periodic polyhedra built with either square or hexagonal flat faces meeting 6 by 6 or 4 by 4 at every vertex respectively is topological analogue of the P-surface.[24] On the P-surface, the planar points with a local Gaussian curvature equal to zero are the centres of the hexagons (point L in Figure 3a). That is, the planar points correspond to the apexes of the cube in the reciprocal space, i.e. the Bragg diffraction spot 222. Thus the vectors of the unit cell might be the axes of the rods whose connections are located on the apexes and the centre of the cube, and the external surfaces of these rods might consitute the pseudo-lamellar planes. Nevertheless, other mechanisms could be proposed to build a stratified structure.[9,10]

The nature of the constituent which fills the interior of the labyrinths can be determined, knowing that the experimental volume concentration is between Φ = 61.9 and 62.9% and that the cubic unit cell has an edge length a = 11.6 nm.[11-14] An estimate of the volume fraction of rod interiors is obtained by assuming that the rods are circular cylinders (radius R) joined by six at a tetrakaidecahedron

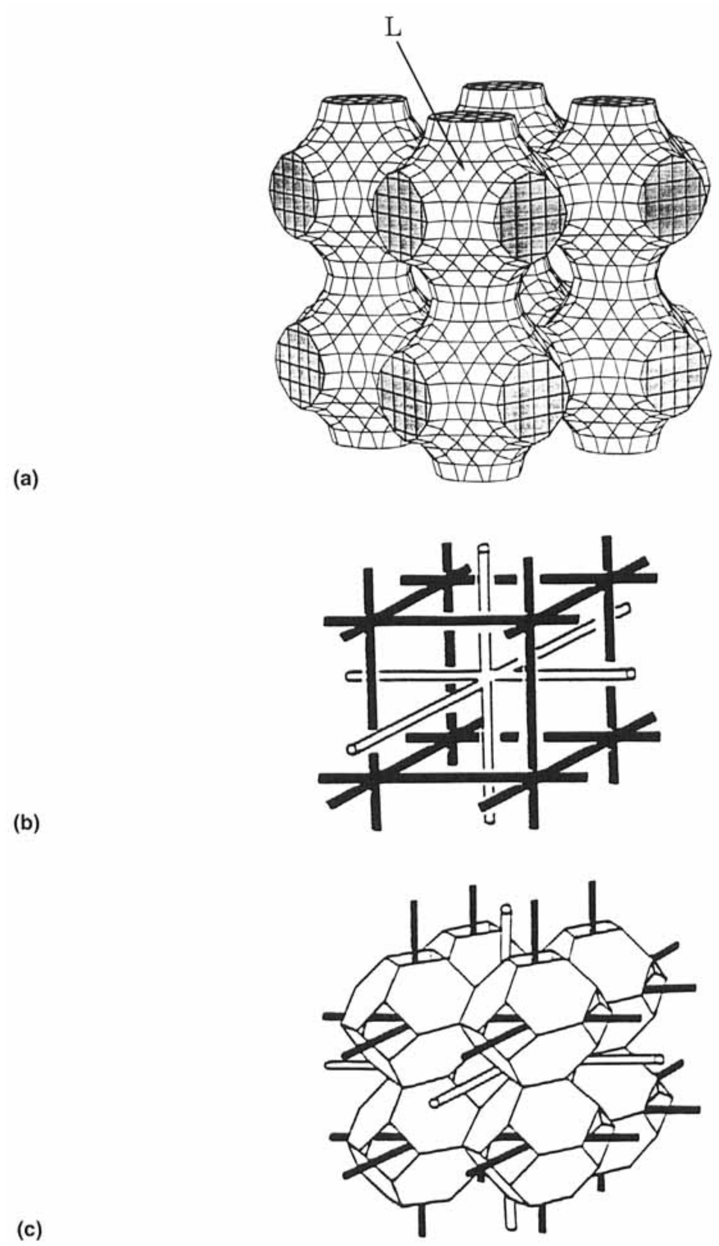

FIGURE 3 a) Representation of the Schwarz's minimal surface of type P. The point L is locally flat (Gaussian curvature equals to zero). The cubic structure observed in the S.D.S./water system may be related to the P-surface, in which case, the P-surface would support a film constituted by the polar medium and would separate two indefinite continuous and identical apolar subspaces. b) The two congruent labyrinths of the P-surface: they have a connectivity of 6 and are formed by the edges of simple cubic lattices, the vertices of one labyrinth being at the centres of the cubes of the others. c) A topological analogue of the P-surface: the tetrakaidecahedron of Lord Kelvin[23] contains 8 hexagonal and 6 square flat surfaces; all the edges have the same length; the two labyrinths (black and white) are also represented.

(edge length l; volume: $11.31 \times l^3$, Reference 25). Then the volume fraction of the rods is given by: $2x\{3x(a - 2\sqrt{2} \times l)x\pi R^2 + 11.31 \times l^3\}/a^3$. We set the radius of the rods equal to the extended length of a S.D.S. chain (about 1.8 nm, which is also the largest radius of a S.D.S. cylinder observed at the end of the H_α mesophase); this yields to $l = 2.2$ nm. In that case the model could be compatible with a structure related to the P-surface, consisting of two congruent lipidic labyrinths in a polar continuum. Note that a structure consisting of aqueous rods (radius 1.4 to 1.7 nm) in a hydrocarbon continuum would also fit the unit cell dimensions, since the volumes of polar and nonpolar regions are almost identical. However, in that case, the cubic mesophase would have a reversed topology which seems very odd in the phase sequence diagram since it would imply that the area per molecule does not follow a monotonic change as a function of the hydration. Thus, we prefer the structure involving nonpolar rods despite the occurrence of some voids in the middle of the connections of the rod (the longest cord in a tetrakaidecahedron is $\sqrt{10}/2 \times l$ (see Reference 25). The cost in energy to create these voids in the apolar medium may shed some doubts about the use of the P-surface as a candidate for the structure of the Q_α phase. Clearly, the structure will have to be checked against the measured structure factor[26] by calculating the relative amplitudes of the diffraction lines which it would produce. Further calculations using our data performed independently by V. Luzzati[16] and S. Hyde[27] have pointed out that the actual structure must have a topology of genus between three and six per unit cell and consequently the related surface might be more complicated that the P-surface.

2.2 Transformations between two-dimensional phases. The structure of the hexagonal phase H_α is made of S.D.S. cylinders whose radius increases as the concentration in surfactant increases as well. As while as this radius remains shorter than the extended length of a S.D.S. molecule, the p6m symmetry is conserved. When it reaches this value, simulation of our experimental diffraction patterns show that the cylinders are not perfectly circular, but slightly deformed[26] (Figure 4). This deformation might be induced by some segregation of S.D.S. molecules with different degrees of dissociation. This is an interesting example where the change of shape of the aggregates is not immediately related to the change of symmetry of the structure; nevertheless the random distribution of the slightly anisotropic cross-sections remains compatible with the conservation of a 6-fold axis symmetry (Figure 4) (this feature has also been observed in a ternary system[9]). Further dehydration increases the anisotropy of the cross-section of the aggregates because it allows the opposing surfaces to remain further from each other and thus decreases the (repulsive hydration and electrostatic) interaction energy, at the expense of curvature energy. At a certain point, the anisotropy of the ribbons is too large and the symmetry of the phase is lowered (phase transition to the M_α mesophase).[11–14]

2.3 Transformations between two-dimensional and three-dimensional phases. To some extent, similar arguments can be invoked to explain the transition to the next rhombohedral phase R_α. Indeed, at the upper end of the phase M_α, diffraction on oriented samples reveals diffuse scattering which may indicate a modulation along

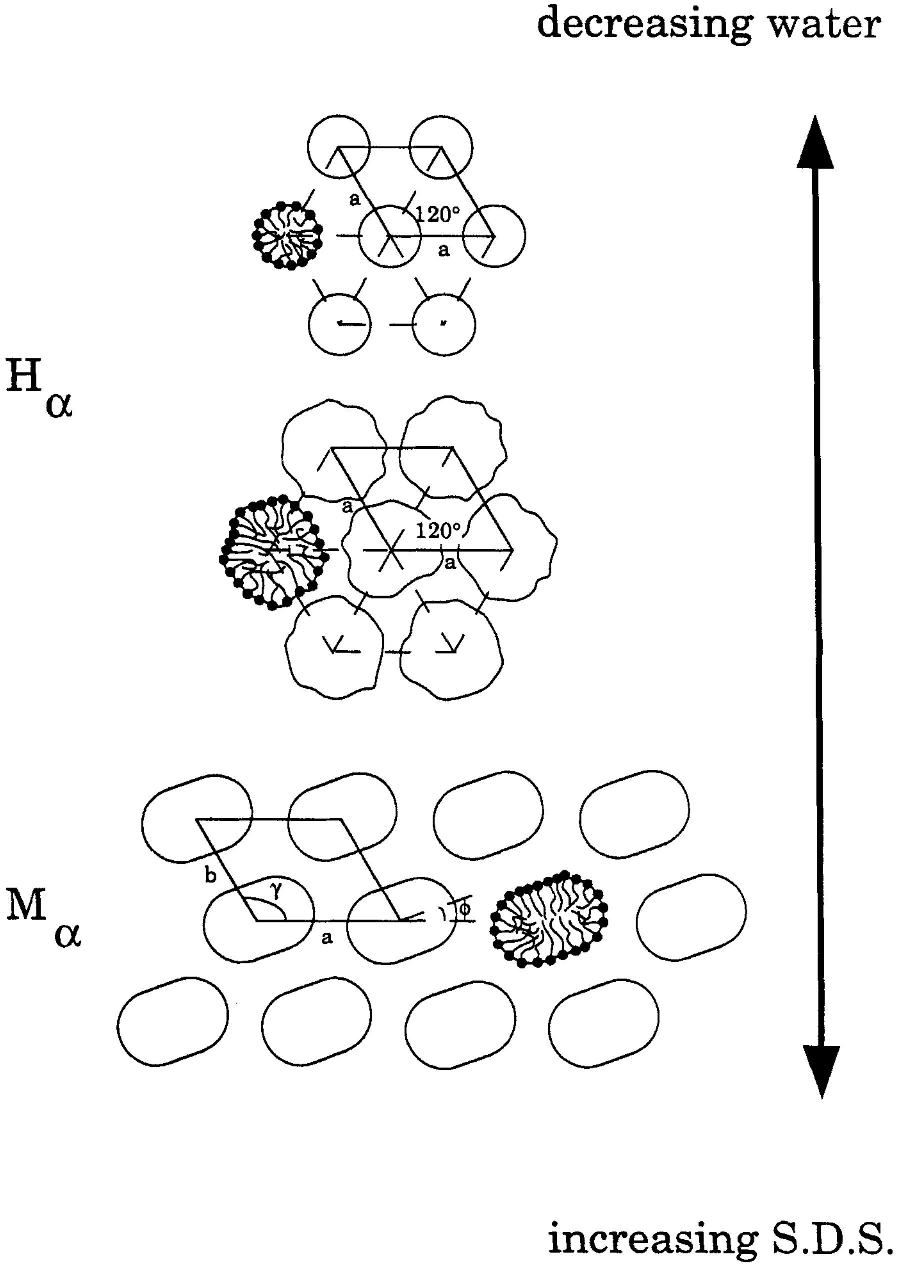

FIGURE 4 Transition between the two-dimensional hexagonal H_α and monoclinic M_α phase. Near the upper composition boundary of the H_α phase, the profile of the diffraction lines[13,14,26] indicates a change in the shape of the aggregates which is not immediately related to the loss of the p6m symmetry of the structure. Further dehydration increases the anisotropy of the cross-section of the aggregates and beyond a certain stage the anisotropy of the ribbons becomes too large; this results in a phase transition by lowering the symmetry of the structure (M_α mesophase). In real space the unit cell can be considered as a deformation of the parallelogram (or regular hexagon) of the H_α phase.

the length of the ribbons.[14] Further, simple calculations on the dimensions of the structure elements deduced from the volumes occupied by the polar and the apolar moieties indicate that the aggregates become very close together and would nearly touch each other (separated by about 0.5 nm).[13] Again, this configuration would be highly unfavorable because of the hydration and electrostatic repulsions between the polar groups of adjacent aggregates. It is much easier for the system to fuse the aggregates two by two and the observation of the doubling of the unit cell in one direction is consistent with this view.[13,14] However, the fusion is not straightforward since the modulation along the length of the ribbons in the M_α phase may be a precursor for their connections at regular intervals in the R_α phase. It is likely that the decrease in the mean curvature by introducing a saddle-splay geometry (negative Gaussian curvature) for the apolar/polar interface reduces the cost in energy and thus favours this new three-dimensional intermediate mesophase.

2.4 Transformations between three-dimensional phases. The cubic mesophase Q_α is a particular case of the rhombohedral R_α (the angle α is equal to 109.47°; cf Figure 2). Note the second order phase transition between these two phases[11] (Figure 1).

The tetragonal mesophase T_α is the one which allows the stratification of the structure before it is transformed into a stack of lamellae. Because the period of this phase is exactly twice times the period of the lamellar phase, it is likely that the unit cell contains two planes of rods. Then the stratification of the original cubic structure is achieved by lowering the coordination number of the vertices to 4. In that case each plane is a square lattice of rods, and these lattices are staggered on top of each other in the unit cell. Figure 5 shows a model to represent this structure, which has also been observed in other systems.[28,29] The volume fraction of rods, equals to $4x\{(a - 2R)x\pi R^2 + 4R^3\}/a^2c$ where the rods are supposed circular cylinders joined at a square junction region, is totally compatible with the surfactant dimensions, S.D.S. concentration (about 66 wt %) and unit cell dimensions (a = 7.61 nm; c = 6.72 nm[13]) of the T_α mesophase. Moreover, this proposed tetragonal structure is fully supported by order parameter and self-diffusion data in another system.[29]

2.5 Transformations between three-dimensional and one-dimensional phases. The last transition to be considered is that from the tetragonal T_α to the lamellar phase L_α. This tetragonal phase T_α approaches the lamellar structure through a layering whose period matches the repetition of the bilayers in the lamellar phase.[13] The flat layers are obtained by a progressive loss of correlations between rods in neighbouring layers, which occurs partly at the transition to the lamellar phase and partly through the range of the L_α phase[14,15] (Figure 6). The close structural relationship between the two phases was also observed in another system where no discontinuity in the diffusion coefficients was observed at the tetragonal/lamellar transition.[29]

3. Transition energies

Our thermal data[11] indicate that mesophase formation is weakly energetic compared to the micellization process by one or two orders of magnitude: the enthalpies

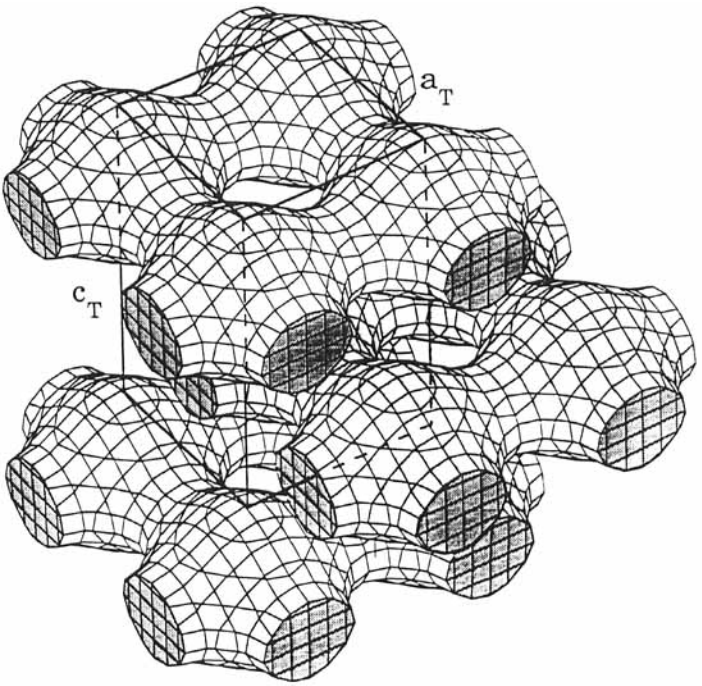

FIGURE 5 Representation of the structure of the T_α phase. The polar medium is continuous while the apolar medium is made of an infinite number of perforated sheets—each is constituted of finite and connected rods arranged in a square network: the centre of a square overhangs the vertex of the square below. The tetragonal structure is obtained by a stratification of the original cubic structure (see Figure 3).

associated with the invariant reactions involving mesophase formation range from 0.1 to 0.8 kcal/mole.

It has already been noticed[11] that the highest values are related to mesophase transformation involving the most important structural modifications due to a topology change in the apolar medium. For instance, the dimensional change in the surfactant aggregates when ribbons of the 2d-monoclinic phase merge two-by-two sideways, and also at regular intervals along their lengths to form two indefinite identical apolar subspaces in the 3d-rhombohedral phase is driven by both inter-aggregate forces (in order to fuse the aggregates) and also by intra-aggregate forces (in order to produce a modulation of the interface by introducing a saddle-splay geometry). In a similar way, the stratification of the cubic structure to form the tetragonal phase is obtained by rupture of some connections between the rods (compare Figures 3 and 5).

On the other hand, the transitions involving no topology change have the weakest cost in energy. This is the case of the progressive deformation of circular cylinders of the hexagonal phase into anisotropic flattened ribbons. Also, the rhombohedral phase appears as a distorsion of the cubic phase. Finally, the order/disorder transition between the tetragonal and lamellar phases appears to be intermediate between these two extremes.

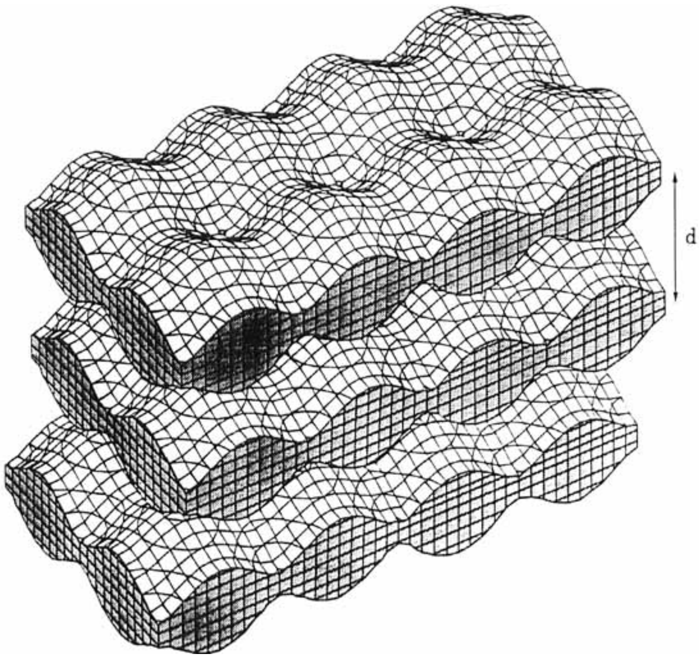

FIGURE 6 Representation of the structure of the L_α phase near the boundary at low SDS concentration. The bilayers are riddled with defects whose correlations resemble the tetragonal structure.[14] The ordering in rods or square lattices of the T_α phase still shows up as heterophase fluctuations in the lamellar phase. As one moves away from the transition boundary, these fluctuations progressively vanish and flat bilayers are achieved.

CONCLUSION

The relations between the structures of the mesophases in the S.D.S./water system show that the system manages to cross from a situation with homogeneously curved interfaces (cylinders) to another one with zero curvature (bilayers) in a nearly continuous way. At this stage the only physical parameter which appears to change in a consistent way through this series of structures is the mean curvature of the interfaces: this is largest for cylinders, smaller for ribbons, then presumably very small for the saddle-splay structures of the three-dimensional phases; then the transition to the lamellar phase sets not only the mean curvature but also the Gaussian curvature to zero. The transitions between the mesophases can be understood from changes in wedge shape,[4] either by increased thermal mobility along the hydrocarbon chain or a similar disorder induced by increased water content. 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 the degree of dissociation of the head groups is expected to be higher in curved interfacial regions than in flat regions. Such modifications might explain the richness of structures encountered in this system in order to transform a cylinder into a bilayer. In striking contrast, relatively poor solutions are adopted by other systems: the nonionic systems make an effort to build aggregates of homogeneous interfacial curvature[10] while others build only large heterogeneous curvature, without saddle-splay structures.[9] The variety of structures observed in the S.D.S./water system will certainly be encountered for other ionic surfactants of similar chain length, if these systems are investigated at a high enough resolution. It would be quite surprising if such complex systems were not capable of adjusting their structures in response to their main structural parameter—the hydration. Such complexity could be also enhanced by mixing ionic and non-ionic amphiphilic species in the same system and it seems likely that a range of new structures await discovery.

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