CRYSTALS OF INTERFACES : THE CUBIC PHASES OF AMPHIPHILE/WATER SYSTEMS

J. Charvolin

JOURNAL DE PHYSIQUE
Colloque C3, supplément au n°3, Tome 46, mars 1985

CRYSTALS OF INTERFACES : THE CUBIC PHASES OF AMPHIPHILE/WATER SYSTEMS

J. Charvolin

Laboratoire de Physique des Solides, Bâtiment 510, Université Paris-Sud, 91405 Orsay, France*

Résumé - Les interfaces sont les interfaces liquide/liquide formés par les molécules amphiphiles. Ils structurent l'espace en deux milieux: polaire et paraffinique. Dans certaines conditions cette organisation peut être périodique suivant 3 dimensions et de symétrie cubique. Ces cristaux cubiques sont tout à fait inhabituels dans le sens où leur ordre à longue distance n'est pas le résultat de la propagation d'un ordre moléculaire à courte distance. On peut les voir comme des cristaux formés par deux liquides séparés par un interface. Nous les considèrerons en relation avec le problème du partage de l'espace par des surfaces minimales périodiques.

Abstract - The interfaces are the liquid-liquid interfaces built by amphiphilic molecules. They organize space in two media: polar and paraffinic. Under certain conditions this organization may present a 3-d periodicity of cubic symmetry. Such cubic crystals are quite unusual in the sense that their long range order is not the result of the propagation of a short range order. They can be seen as crystals formed by two liquids separated by an interface. We shall analyze them in relation with the problem of space partition by periodic minimal surfaces.

I - INTRODUCTION

Amphiphilic molecules, such as soaps, detergents and lipids, are well known for their aggregation property when put in presence of water and for forming the structures of micellar and liquid crystalline phases with various degrees of order. The diluted micellar phases are disordered at long range and the concentrated ones may sometimes exhibit a long range orientational order of the nematic type. The more concentrated lyotropic liquid crystals are translationally ordered. Most often, in the latter case, large zones of the phase diagrams are occupied by structures ordered along 1 or 2 dimensions, such as the well known lamellar or hexagonal phases. There are also a few examples of phase diagrams where structures ordered along 3 dimensions can be found in rather narrow zones. We shall be concerned with these structures which, for cases known up to now, have a cubic symmetry. They are not to be confused with the 3-d crystalline states of amphiphilic molecules which are classical molecular crystals of complex symmetries. To make apparent the very particular nature of these 3-d structures, as well as the difficulties of their study, we shall briefly discuss one of them on the basis of its pictorial representation in fig.1.

---

*Laboratoire associé au CNRS (LA n° 2).

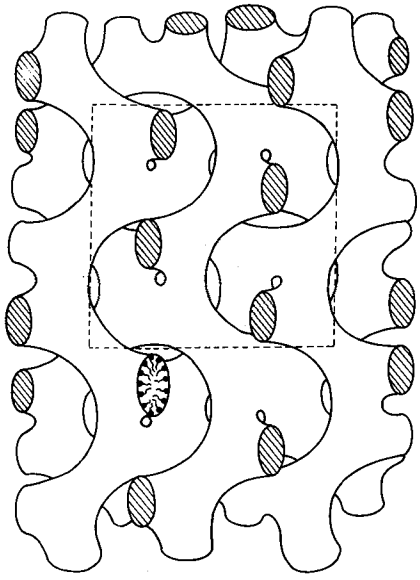

Fig. 1 - Schematic representation of the cubic structure built by the mixture potassium laurate/36% water in weight at 100°C. The diameter of a rod is 28 Å.

This is one of the first cubic structures which was established with some certainty[1]. In this structure the amphiphilic molecules aggregate in small cylinders which are joined 3 by 3 and build two 3-d lattices which are unconnected and mutually interwoven. These two infinite lattices of amphiphilic molecules are separated by one infinite aqueous medium.

This structure has body-centered cubic symmetry with spatial group I_{a3d}. At the local level the amphiphilic molecules are disordered and diffuse along the rods of the structure with a translational diffusion coefficient, $D \sim 2\ 10^{-6}\ cm^2 s^{-1}$, which is rather close to that of melted paraffins, $D \sim 10^{-5}\ cm^2 s^{-1}$ [2]. Such a structure is characterized by the coexistence of long range crystalline order and short range liquid-like disorder. It is therefore quite original and absolutely distinct from the crystals of amphiphilic molecules as its long range order does not result from the propagation of a short range order [3]. From the above description we might say that this phase is an ordered entanglement of two liquids separated by an interface. We shall follow this point of view, at a descriptive level, when we shall consider later on that the structures built by amphiphilic molecules in presence of water are organizations of interfaces between two continuous liquid media. However it must not be forgotten that the meaning usually conveyed to the term "liquid" is not applicable here globally because of the anisotropic molecular behaviors induced by the existence of the interface [4].

The structure presented above was determined by small angle X-ray scattering. It was a particularly favorable case because of the relatively large number of reflection orders observed, eight to ten. Since then other cubic phases have been discovered but the situation is not always so favorable and the number of observed orders can be insufficient to allow for an unequivocal characterization of a complex structure. On the basis of such limited data the solution proposed can only be but

one among several others possible. It is therefore necessary to argue with a larger set of data including those provided by other techniques. But, even then, there is always some degree of uncertainty left and in order to appreciate it we shall consider briefly the various methods used to characterize cubic structures.

II - METHODS

Direct observations

The 3-d phases appear very different from the 1-d and 2-d lamellar or hexagonal phases. They are very clear and optically isotropic whereas the latter are a bit translucid, scatter light and are optically anisotropic. Also they have a much stiffer consistency. At last, because of this consistency, they can not to be confused with the fluid disordered micellar phases which have similar optical properties.

Observation under the microscope

There is no texture visible under the polarizing microscope because of the optical isotropy and this approach might be thought to be of no help. However, in a few cases, it has been possible to obtain quite a noteworthy information when nucleation and growth of monocrystals of cubic phases can be observed [5]. For instance germs of a 3-d phase may grow as the polyhedra shown in Fig.2.

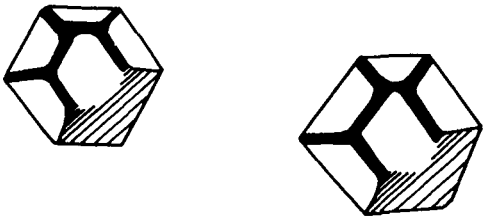

Fig. 2 - Polyhedra of a cubic phase separating from an isotropic solution in the sodium di(2 ethylhexyl)acetate/water system. Their size is about 10 μm (from a photograph in (5))

This observation examplifies the crystalline nature of the phase.

X-Ray scattering (3)

This method has been the most powerful one up to now. As always with lyotropic liquid crystals two regions are to be distinguished in the diagrams. At large angles, for values of $s = \frac{2\sin\theta}{\lambda}$ of about $(4.5\ \text{Å})^{-1}$, a diffuse band is observed which demonstrates the disordered state of the molecules in the structure. At small angles, in a range of s values from about $(10\ \text{Å})^{-1}$ to $(100\ \text{Å})^{-1}$, narrow Bragg reflections are observed which demonstrate the long range crystalline order of the structure. The number of orders observed varies from about 2 to 17 according to the system studied. In general it is not too high in hydrated systems, between 2 and 10, as the characteristic size of the scattering element, the thickness of the amphiphilic or aqueous media, is rather large and makes the structure factor decrease rapidly. It can be higher, up to 17, in anhydrous systems where the polar heads and ions of important electronic densities are localized in very narrow polar domains. The small angle region of a typical powder spectrum

is shown in fig.3.

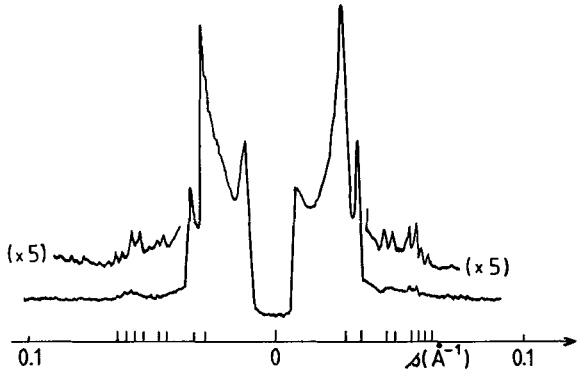

Fig. 3 - Microdensitometer trace of the X-ray powder diagram of the cubic phase of the mixture potassium laurate/36% water in weight at 100°C. Eight orders are visible. The camera is of the Guinier type.

All spectra can be indexed in a cubic lattice whose space group can be known in principle from the determination of the absent reflections. However errors are frequent because a reflection may be accidentally suppressed. One possibility is the fortuitous coïncidence of a zero of the structure factor with the position of an order of reflection. This can be detected by varying the conditions, temperature, water content, eventually the length of the paraffinic chain of the amphiphilic molecules, in order to change the structure factor or the parameter of the cell and to suppress the coïncidence. Another one is an imperfect distribution of monocrystalline domains which can be such that some reticular planes are not at the Bragg's condition for reflection. This may happen because of the ability of cubic phases to grow large monocrystals. However when the monocrystals are very large it may be possible to work with mono-domains [6]. Finally, there are a few examples of errors because of spurious reflections which force the indexing into a wrong direction. This happens when the sample is accidentally in one of the neighboring polyphasic zones surrounding the narrow cubic zone, then a superposition of spectra is analyzed as one unique spectrum. All these facts are major handicaps to correct indexing of the spectra. Once they are understood and eliminated a structural model can be proposed. This model should be tested by calculating the scattered intensity for the different orders and comparing them with the experimental ones. In the case where the number of orders is rather low the model is not always unique and more information must be looked for in order to make a selection. A first complementary information is provided by the examination of the structures and structural parameters of the neighboring phases in the phase diagram. When they are ordered phases they are ordered along 1 or 2 dimensions so that they can be characterized easily and their structural parameters well known. For instance their mean area per amphiphilic molecules at the interface, the convexity of their interface, the continuities of their aqueous and paraffinic media are known and these characteristics should show a monotonous behavior when going through the cubic phase separating them. Certain models can be eliminated that way. To go further complementary information can be brought by spectroscopic studies, particularly nuclear magnetic resonance.

Nuclear magnetic resonance

This technique sees the aqueous and paraffinic media of a cubic phase as isotropic liquids. This holds to the fact that the translational diffusion of the molecules along the interfaces, the normals of which are isotropically oriented, averages out all the non scalar interactions of the nuclei with their environment. The NMR signals in the cubic phases are therefore hardly different from those in the disordered micellar phases and not very sensitive to the details of the structures of isotropic phases [2]. However this drawback due to the translational diffusion can be turned into a positive advantage. Indeed a NMR technique was developed, the study of spin echos in an inhomogeneous magnetic field, which allows for the measurement of the translational diffusion of molecules when it occurs over distances of about 1 μm and for durations of a few milliseconds. The application of this technique to the problem of the cubic phases can therefore provide an important topological information about the extension of the aqueous and paraffinic media [8]. For instance it should allow one to choose between a cubic structure made of finite micelles, where the translational diffusion of the amphiphilic molecules is restricted on distances of about 30 Å, and a cubic structure of small rods connected to infinity such as the one drawn in fig.1., where the molecules may diffuse over large distances [9].

Electron microscopy (10)

This should be the most direct method, and rather well fitted if one compares its resolution with the characteristic dimension of the aggregates in the lyotropic phases. However it can not be used directly without preparation of the sample because of the damaging effects of the high vacuum and electron beam and because of the very low contrast of the amphiphilic molecules. Usual pretreatments which permit electron microscopic observations, chemical fixation and straining, modify the sample structure. It is possible to overcome some of these difficulties by cryofixation. In general the observation is indirect. The sample is quenched at low temperature, then fractured, eventually the surface is etched by evaporation of some water, and a heavy metal replica of the surface is made which is observed by electron microscopy. It must be ascertained that the structure of the sample has not been modified during the several steps of this procedure. One way consists in controlling it after quenching by X-ray scattering. This is being developed and the first photographs of cubic phases supported by such a control have just been published[10].One on them is shown in fig.4.

Such a photograph demonstrates unambiguously the crystalline cubic structure and should be of considerable help to analyze the structures as our understanding of fracture propagation in such materials develops.

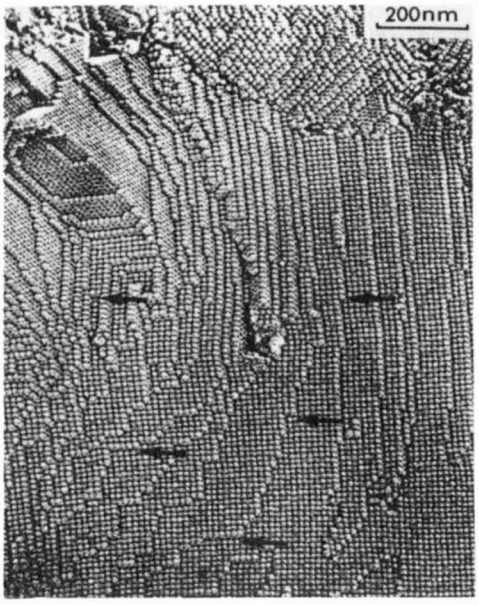

Fig. 4 - Freeze fractured electron micrograph of sunflower oil monoglycerides/cytochrome C/water cubic phase. Rotatory shadowed with W-Ta but contrast is reversed (shadows are black). Notice the different fracture planes through the phase. From reference (10).

III - PROPOSED STRUCTURES

We have classified the phases discussed in the literature according to the spatial group which can be deduced from the examination of their X-ray diagrams. The first two, I_{a3d} and P_{n3}, are considered as certain. The others I_{m3m}, P_{m3n}, F_{d3m} are still matters of discussion.

Group I_{a3d}

This is a body centered cubic lattice. It is quite widespread. It was seen for the first time in anyhydrous strontium soaps and the first cubic structure built with rods was then proposed (1a). It is represented in fig.5 where the rods are the locii of the strontium ions, the paraffinic chains of the soap molecules being disordered all around.

Since then similar cubic structures were found in egg lecithins containing a small amount of water (1b), in between lamellar and inverted hexagonal phases, and in potassium carboxylates and alkyl trimethyl ammonium bromides with higher water content (1c), in between lamellar and direct hexagonal phases. It is the latter case which is represented in fig.1 where the small soap cylinders have the rods of fig.5 for axes. It is quite noticeable that the locations of these cubic phases in the phase diagrams indicates that the same structure may exhibit different topologies. When the phase is present on the low water content side of the lamellar phase the two aqueous rod structures are imbedded in a continuous paraffinic matrix, when the phase is present on the high water content side of the lamellar phase the topology is inverted, the two rod structures of soap molecules are imbedded in a continuous aqueous matrix. Other structures, apparently simpler, were

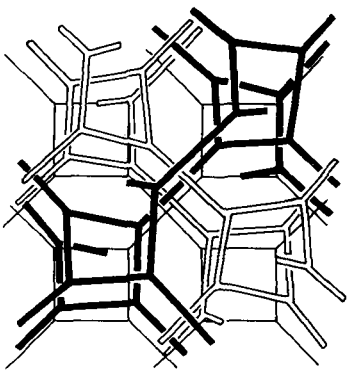

Fig. 5 - The cell of the cubic structure I_{a3d}, the rod are the axes of either water channels, at low water content, or soap cylinders, at high water content.

proposed for some above cases. They have been demonstrated to be incorrect. Nevertheless we think interesting to consider them to illustrate the use of NMR in this problem. An outdated proposal is that of the body-centered cubic I_{m3m} packing of sperical micelles shown in fig.6.

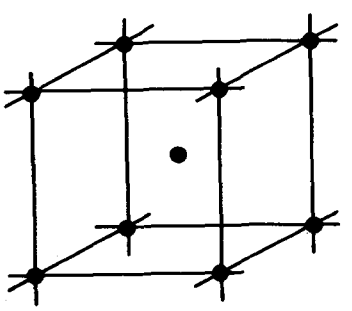

Fig. 6 - A body centered cubic array of spheres.

A more recent one[11] is that of the body centered cubic I_{a3d} packing of infinite straight cylinders shown in fig.7

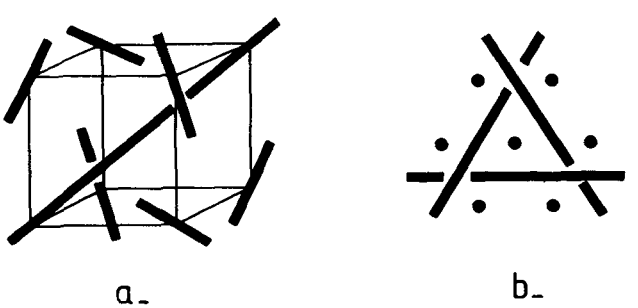

Fig. 7 - A body centered cubic array of infinite straight cylinders, a) perspective view, b) view down a trigonal axis.

Both can be rejected on the basis on crystallographical arguments[10,12], but, in addition, they would imply molecular behaviors which are not compatible with the NMR data. These data show that the amphiphilic molecules diffuse rapidly on macroscopic distances, which eliminates the structure built with finite micelles, and have an isotropic behavior, which eliminates the structure built with straight cylinders along which the molecules should have an uniaxial behavior [2]. It is however not impossible that the body centered cubic structure of infinite straight cylinders exists in certain systems as suggested by a recent NMR study of the hexagonal phase of the hexaethylene glycol dodecyl ether/water system [13].

Groups P_{n3} and P_{n3m}

These are primitive cubic lattices. Both groups were proposed but they look similar at low resolution and we shall use P_{n3} only since it is of highest symmetry. It was proposed first for a phosphatidyl ethanolamine/water system, the lipid having been extracted from insects[14]. More recently it was met in the glycerol monooleate/water system [15]. The structure is represented in fig.8.

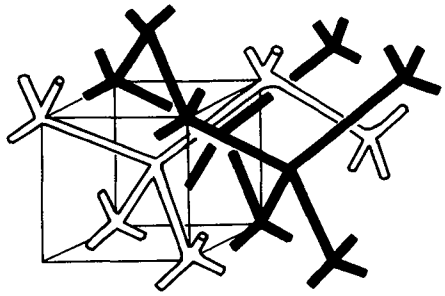

Fig. 8 - The cubic structure P_{n3}, the rods are the axes of water channels.

The rods are water channels which are connected four by four at tetrahedral angles. They build two unconnected but interwoven diamond lattices which are isolated from each other by a continuous bilayer of amphiphilic molecules of complex shape.

Group I_{m3m}

This is a body centered cubic lattice with infinite aqueous and paraffinic media. The structure is represented in fig.9.

We mention it because it recently appeared in the literature as being a possible candidate for the glycerol monooleate/water system discussed above [16]. It must be abandoned now as a better understanding of the phase diagram and a thorough analysis of the X-ray data have led to an indexing in perfect agreement with the one reported above[17]. There is therefore no X-ray evidence for I_{m3m} up to now. The interpretation of electron micrographs of prolamellar bodies in the membrane system of etiolated leaves of *Avena Sativa* suggests a structure which might have this space group [18]. However this is quite different a situation as the samples studied here are biological organites whose membranes contain not only lipids but many other biological molecules too.

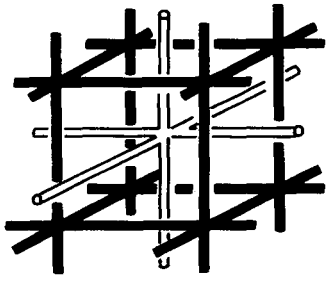

Fig. 9 - The cubic structure I_{m3m} with infinite aqueous and paraffinic media, the rods are the axes of the water channels.

Group P_{m3n}

This is a primitive cubic lattice. This phase is wide-spread. It was found first in Na-caprylate/organic solvents/water systems, it has been observed since then in dodecyl trimethylammonium chloride/water, egg lecithin/water, lauryl decaethylene glycol ether/water, sodium or potassium soaps/organic solvents/water systems. In all these cases the location of the phase in the phase diagram is in the water rich region, between the hexagonal and micellar phases. The structure has been proposed to consist of a 3-d network of rods of finite length, all crystallographically equivalent, which meet 3 by 3 at one end and 4 by 4 at the other to form the bars of a system of cages, each cage enclosing a spherical micelle; the rod and the micelles are paraffinic and imbedded in water [19]. This is a clathrate-type structure. It is represented in fig.10.

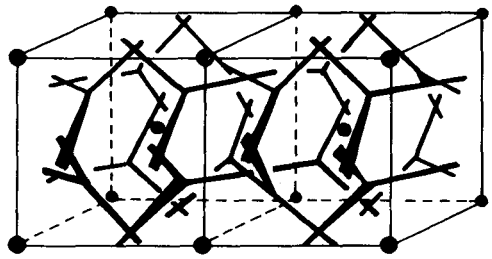

Fig. 10 - The "clathrate" structure P_{m3n}, the rods and dots are the axes and centers of the paraffinic rods and micelles.

This complex structure is not supported by recent NMR studies which do not detect the translational diffusion of amphiphilic molecules over long distances implied by the existence of an infinite network of connected rods [20,21]. This would be in favor of a structure of finite amphiphilic aggregates.

Group F_{d3m}

This cubic face centered lattice was mentioned for lipids extracted from *Pseudomonas Fluorescens* in presence of water and for Triton detergents in presence of organic solvants [14]. Systems presenting this symmetry are under investigation.

Remark about the terms of the description

We introduced the structures as crystals of interfaces separating the paraffinic and aqueous media but we represented them, from fig.5 to 10, as networks of rods which are the axes of these paraffinic or aqueous media. Indeed this is the most rigorous representation because the data essentially give access to the directions of symmetry. How can we deduce the geometrical shapes of the interfaces from the networks or rods? This may be relatively easy to do in rather descriptive manner when the rods are the axes of the soap aggregates. We know that their diameter can not exceed twice the length of a molecule, so we just increase it up to that value. This is what we did in fig.1 which was drawn only to make the nature of the phase perceptible. However this intuitive way of introducing the interfaces is not applicable when the rods are axes of water channels whose radii are not known. Moreover, it does not bring any new insight into the necessary principles which might control the structure of the phases. We have therefore chosen to discuss a notion which might be useful in this respect, that of partition surfaces in liquid media whose shapes may be defined on the basis of simple principles.

IV - PARTITION SURFACES

Such a notion is suggested by the examination of structures P_{n3} or I_{m3m} shown in fig.8 and 9. Here the rods are the axes of water channels organized in two interwovem aqueous media and separated from each other by one continuous medium of amphiphilic molecules with the liquid like behavior described in the introduction[22]. The central part of this bilayer, occupied by the methyl ends of the chains, defines a geometrical surface with the physical properties of a liquid film which partitions space in two cells which are everywhere in contact. This partition surface has a superficial tension, which minimizes the total area, it also experiences equal pressures on both sides as the cells are at equilibrium, so that its curvature has to be zero everywhere. These conditions impose certain types of surfaces which were indeed considered by physicists and mathematicians at the end of the last century after Plateau'work on soap films. For instance Lord Kelvin showed that space can be filled and homogeneously partitioned into equal and similarly situated cells by a polyhedron, the α - tetrakaïdekahedron, which is derived from the ortho-tetrakaïdekahedron shown in fig.11 by slight curving of the edges and warping or the faces in order to keep their internal tensions balanced.

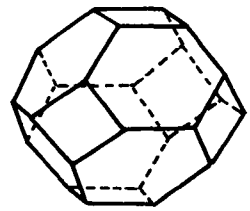

Fig. 11 - An ortho-tetrakaïdekahedron. This space-filling polyhedron has 8 hexagonal faces and 6 square faces.

This α-tetrakaïdekahedron does not fit our purpose as it concerns finite closed cells but we quote it because an assembly of such polyhedra is a simple illustrative solution to the key ideas of our problem: the

faces build a minimal partition surface, their curvature is null, the tensions are balanced between hexagonal and square faces, which meet 3 by 3 at dihedral angles of 120°, and along the edges, which meet 4 by 4 at angles of 109°28'. We quote it also because it was used to visualize the surfaces in I_{m3m} cubic structures, as shown in the inset of fig.14. If such a visualization is topologically correct it is incorrect as far as the physics of film is concerned because the necessity to open some faces of the α-tetrakaïdekahedra to make the cells communicate destroys the balance of the tensions in the films. On the other hand the problem of infinite 3-d cells was implicitly considered by Schwarz and Neovius when they calculated periodic minimal surfaces with null curvature and submitted to various boundary conditions[24]. These surfaces which partition space in a bicontinuous manner were recently re-introduced to support an argument in favor of bicontinuous structures in the middle phases of microemulsions [25]. If their role is necessarily limited in this case, because microemulsions are disordered while the surfaces are ordered along 3-d lattices, these periodic surfaces have been thought to be relevant to the problem of cubic phases. For instance we suggest in fig.12,13,14, in the cases of P_{n3} and I_{m3m} structures, that space might be partitionned in two aqueous regions by surfaces similar to those calculated by Schwarz.

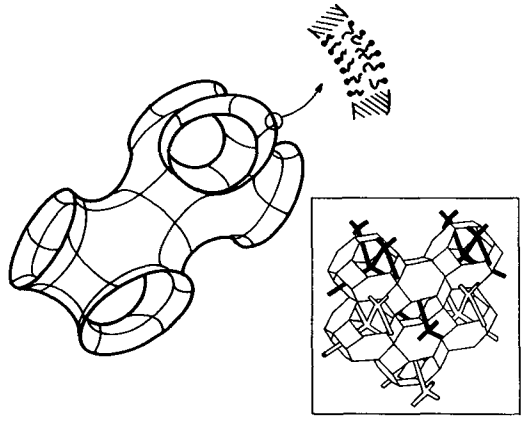

Fig. 12 - Part of the surface separating the water channels in the structure P_{n3}. It was drawn from the compact packing of tetrakaïdekahedra opened on four hexagonal faces shown in the inset and used only as a guide for the eye.(see the text). The surface looks close to Schwarz's tetrahedral minimal surface.

An element of a surface calculated by Schwarz shown in fig.13 might fit in the P_{n3} structures because of its symmetry and because the total surface is obtained by the juxtaposition of such elements along a cubic lattice.

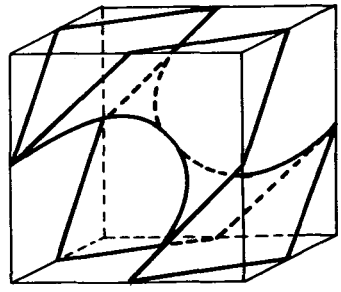

Fig. 13 - An element of a Schwarz's surface with might fit in structure P_{n3}. The straight lines on the faces of the cubic cell are the boundary conditions on which the surface is defined. The infinite surface is obtained by juxtaposing such element along a cubic lattice.

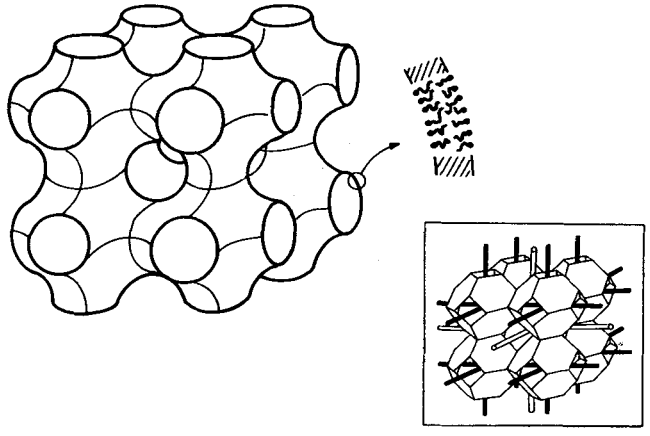

Fig. 14 - Part of the surface separating the water channels in the structure I_{m3m} (the existence of which has not been firmly established yet). It was drawn from the compact packing of tetrakaïdecahedra opened on their square faces shown in the inset and used only as a guide for the eye (see the text). The surface might be Schwarz's periodic minimal surface.

In order to bring out this idea of partition surface we considered cubic phases of the inverted type, where water channels are separated by one continuous paraffinic bilayer. In the case of phases of the direct type, where paraffinic channels are imbedded in a water matrix, the equivalent surface is to be looked for in this matrix, for instance the surface along which the effects of the anisotropic fields[26] of the two facing amphiphile/water interfaces balance each other.

This analogy between crystalline cubic phases and periodic minimal surfaces, although attractive at this coarse level of a first approach and useful to feel the nature of the problem, should not be pushed further at the moment. The reasons are that the mathematical bases of

the two problems are different and therefore their solutions are not necesseraly the same. Schwarz and other mathematicians calculated minimal surfaces for boundary conditions defined in an unit cell and were concerned with such surfaces which can pack periodically keeping their properties of minimal surfaces (see fig.13). Also the finite surfaces defined by the boundary conditions in the unit cell are stable with respect to small displacements and this property is kept for the infinite periodic surface as the boundary conditions of the unit cells are implicitly maintained. If we now suppress the boundary conditions in the unit cells, as it should be the case for the amphiphilic film in the cubic phase, it is not obvious at all that the periodic minimal surfaces remain stable. Finally the surfaces considered by the mathematicians are isolated surfaces, i.e.they do not interact, but those of the physical system strongly interact through attractive Van der Walls forces and repulsive electrostatic and hydration forces[26].

In spite of some morphological similarities between their solutions the mathematical and physical problems appear fundamentally different. Particularly if in the first case extrinsic boundary conditions determine the morphology of the structure they don't exist in the second case and we must look for a substitute. In the next paragraph we shall consider the possible role of the spontaneous monolayer curvature in this respect.

V - MONOLAYER CURVATURE

We have considered an infinitely thin geometrical surface which we identified in the case of inverted phases with the locus of the CH_3 of the bilayer. In principle this surface has zero curvature but this does not imply that the curvature is zero for each monolayer of amphiphilic molecules on either side of it. Indeed, as shown in fig.15 where we consider the curvature of a surface parallel to a saddle surface with zero curvature, the curvature at the amphiphile/water interface is different from zero.

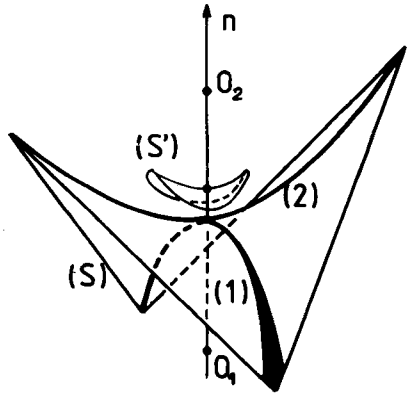

Fig. 15 - A saddle surface S with principal sections 1 and 2, the centers of curvature O_1 and O_2 are on the normal n, the curvature of the surface $R_1^{-1} - R_2^{-1}$ is zero as $R_1 = R_2 = R$. A parallel surface S' at a distance ℓ has a non zero curvature $(R_1+\ell)^{-1} - (R_2-\ell)^{-1} \sim - 2\ell\, R^{-2}$.

If we try to estimate its value with the structural data, i.e.with $\ell = \ell_o$ the molecular length and $R \sim 2\, \ell_o$, we find $|C| \sim 1/2\, \ell_o$ which is

intermediate between that of a lamellar phase, $|C| = 0$, and that of a hexagonal phase, $|C| \sim 1/\ell_o$. The same would be valid for direct phases of the same type where the surface with zero curvature is within the aqueous medium between the paraffinic rods, a parallel surface moving away from it to fit on the amphiphile/water interface sees its curvature increasing from zero to a value which is that of the curvature of the interface itself. Thus the building of a cubic structure may be seen as a way chosen by an amphiphile/water system to accomodate a weak homogeneous curvature in each monolayer. This point can be better appreciated by examining the locations of cubic phases relative to that of lamellar and hexagonal phases in the phase diagrams. To do so we refer to the hypothetical phase diagram shown in fig.16. It represents that of an amphiphile/water system presenting almost every known phase except those existing on the low water content side, a complicated region which can not be schematized in a simple way.

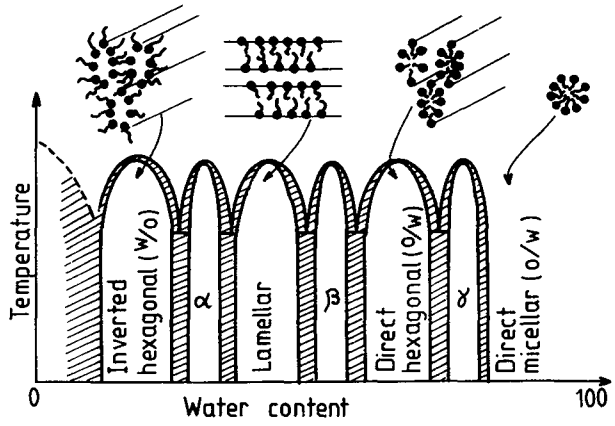

Fig. 16 - An hypothetical amphiphile/water phase diagram (hatched regions are polyphasic domains)

The interest of such a diagram is that it presents the phases in their natural order of occurence as the water content increases. A real phase diagram presents only a few of them, for instance the inverted phases for di-alkyl amphiphiles or the direct phases for mono-alkyl amphiphiles, but they always appear with increasing water content following the sequence given in fig.16. For instance an inverted hexagonal is before a lamellar phase, whereas a direct hexagonal comes after. When the cubic phases exist they are localized in the intermediate zones α, β, γ. In zone α, in between the inverted hexagonal and lamellar phases, the structures can be I_{a3d}(lipids) or P_{n3} (monoglycerides), with networks of water channels imbedded in a continuous medium of amphiphilic molecules. In zone β, in between the lamellar and direct hexagonal phases, the structure is I_{a3d} with a network of amphiphilic molecules imbedded in a continuous water matrix. In zone γ, in between the direct hexagonal and micellar phases, the structure proposed from x-ray data is P_{m3n} of the clathrate type, with rods and micelles, but we have seen that this structure is still a matter of debate, as NMR fails to detect the infinite network of rods, and we shall not consider it any longer. We see clarly on this phase diagram that increasing the water content increases the curvature. If we say that the curvature is negative on the low water content side of the lamellar phase and positive on the high water content side, it increases from $-1/\ell_o$ in the inverted hexagonal to 0 in the lamellar, then $1/\ell_o$ in the direct hexagonal and finally $2/\ell_o$ in the direct micellar phase.

The cubic phases I_{a3d} and P_{n3} with curvatures between 0 and $-1/\ell_o$, or $+1/\ell_o$, are therefore logically located in the intermediate zones α,β. But now why are complex cubic structures needed for realizing states of weak monolayer curvatures? A first understanding of this point can be found considering the driving forces for the curving of the monolayers and the constraint under which they exert their action. The curvature results in part from a competition in the amphiphilic layer between the electrostatic interactions of the polar heads, which tends to pull them apart when the water content increases, and the entropy of the paraffinic chains and their interactions which tends to keep them in an almost constant conformational state [4]. If only these local terms were considered every homogeneous curvature might be envisaged by simply curving the flat interfaces of the lamellar phase in a cylindrical of spherical manner, as shown in fig.17.

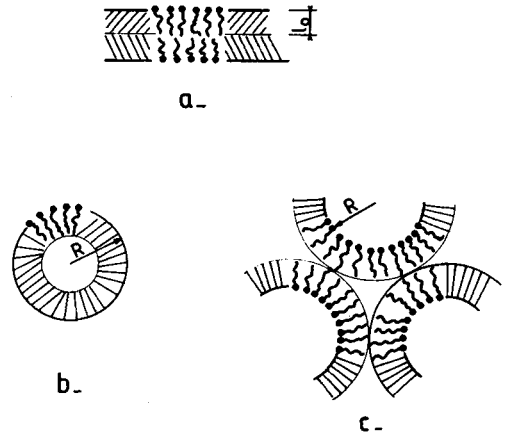

Fig. 17 - Deformations of the flat interface of a lamellar phase(a) into cylindrical ones, with positive curvature in (b), with negative curvature in (c). In both cases interfaces are to be created in the paraffinic medium. In (b) this interface disappears when $R \sim \ell_o$, direct hexagonal phase. In (c) the smaller R the easier it is for the chains to make it disappear by increasing their elongations fill the hole, inverted hexagonal phase.

However, except when the radius of curvature R is about the average molecular length ℓ_o, as in direct hexagonal or micellar phases, or small, as in inverted phases, the system must create new interfaces within the paraffinic layers which introduce a supplementary interfacial energy. The building of a minimal surface of the type of those discussed above might be therefore a way to accomodate a weak spontaneous monolayer curvature without an extra cost of interfacial energy.

Obviously, in this picture, the classical lamellar and hexagonal phases are examples of accomodation to zero and $\sim 1/\ell_o$ monolayer curvatures. When the conditions are such that the interfacial curvature is zero everywhere the only possible minimal partition surfaces are flat and the phase is lamellar. When the conditions are such that the interfacial curvature is about the inverse of the molecular length everywhere the aggregates are cylindrical, the minimal partition surfaces are to be organized in a honey comb structure [23] and the phase is hexagonal. We might also add, in an even more speculative manner, that

when the conditions are such that the interfacial curvature is about twice the inverse of the molecular length everywhere the aggregates are spherical micelles, the minimal surfaces are to be organized in α-tetrakaidecahedral structure [23] and a concentrated micellar solution must present the short range body centered cubic structure as shown by a recent experiment [28].

Finally the observation of other phase diagrams suggest that the formation of a cubic phase is not the only way possible for an amphiphile/water system to conciliate the constraint of a weak curvature with that of a compact paraffinic medium. Certain systems exhibit phases with rectangular symmetry instead of cubic phases in the same zones α, β [27]. Those rectangular phases, like the one shown in fig.18, are assemblies of infinite ribbons with non circular section. Here the curvature varies along the interface from about 0 in the central core of the ribbon to about $1/\ell_o$ along its edge, and it is the average value which is weak.

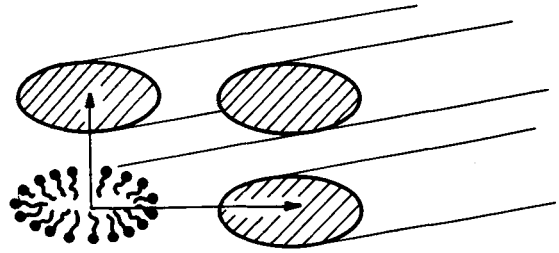

Fig. 18 - Schematic representation of a rectangular phase. The aggregates are infinitely long ribbons organized along a 2-d lattice with rectangular symmetry.

Such inhomogeneous solutions may be preferred in a system with two amphiphiles, as it has been shown that curvature fluctuations may be made more favorable by concentration fluctuations within the aggregates [29], or in ionic systems, where fluctuations of the ionic distribution might occur. Conversely non-ionic systems with only one amphiphile, where no such fluctuations may occur, are known to prefer the less inhomogeneous solutions of the cubic phases.

VI - CONCLUSION

There were two aspects in our presentation of the cubic structures formed by amphiphilic molecules. The first was a critical discussion of the existing structural data in the "Introduction" and in the paragraphs "Methods" and "Proposed Structures". The second was a somewhat conjectural search for a common principle underlying the apparent complexity of the structures, it was developped in the paragraphs "Partition surfaces" and "Monolayer curvature". In the first of these last paragraphs we started this approach recalling that the experimental evidences indicate that the aqueous and paraffinic media have liquid-like behaviors and that the cubic structures may be analyzed as two infinite cells of one medium separated by a film of the other (The cells are water cells and the film is paraffinic for the inverted structures, the cells are paraffinic and the film aqueous for the direct structures).There is therefore an analogy between the cubic phases and the problem of space partitionning by liquid films which can be solved by the introduction

of minimal surfaces with zero curvature separating cells with equal pressures. A certain number of such surfaces were calculated by mathematicians and it was proposed in the literature that some of them might fit in the structures proposed for the cubic phases. First it was not clear where those surfaces should be looked for. Obviously they are not to be confused with the amphiphile/water interfaces but rather would be the ideal surfaces in the partitionning films where the effect of the pressures in the two cells balance each other. Second although attractive this analogy must be considered with care if used to go beyond this simple approach. The two problems are indeed not similar. The surfaces in the mathematical problem are infinitely thin and non interacting surfaces whithout curvature elasticity and supported by well defined boundary conditions in their unit cell. The surfaces in the physical problem are associated with strongly interacting films of finite thickness which have a curvature elasticity and which are not supported by any boundary conditions. Those two problems do not have necessarily the same solutions. In the last paragraph "Monolayer curvature" we restricted our scope considering only the possible role of the spontaneous curvature of each monolayer on either sides of partition surface with zero curvature to build a particular structure. This monolayer curvature, which was not considered by the mathematicians, is the feature which distinguishes the amphiphilic medium from true liquids. It is imposed by the degree of hydration and the temperature of the system. Most likely this physical constraint, which acts under the necessity of keeping the compacity of the paraffinic medium, forces the system to choose one minimal partition surface among several others. It would now be tempting to study the local curvatures of the partition surface associated with the minimal free energy of curvature for a given spontaneous curvature in each monolayer. However the existing expressions of this energy are harmonic approximations which can not give account of the strong curvatures exhibited by the structures [30].

ACKNOWLEDGMENTS

We thank V.Luzzati and T.Gulik-Krzwicki (Centre de génétique moléculaire, CNRS, Gif sur Yvette) for fruitful discussions about structural determinations and for the authorization to reproduce the electron micrograph of a cubic phase in fig.4, B.Lawson and C.Margerin (Centre de Mathématiques, Ecole Polytechnique, Palaiseau) for their interesting comments about minimal surfaces.

REFERENCES

1. a. LUZZATI V. and SPEGT P.A., Nature 215, 701 (1967).
   b. LUZZATI V., GULIK-KRZYWICKI T. and TARDIEU A., Nature 218, 1031 (1968).
   c. LUZZATI V., TARDIEU A., GULIK-KRZYWICKI T., RIVAS E. and REISS HUSSON F., Nature 220, 485 (1968).
2. CHARVOLIN J. and RIGNY P., J.Chem.Phys. 58, 3999 (1973).
3. LUZZATI V., in *Biological Membranes*, edited by D.Chapman, Academic Press, New York (1967).
4. CHARVOLIN J., in *Polymorphism of liquid crystals*, H.Gasparoux editor, J.Chimie Physique 80, 15 (1983).
5. WINSOR P.A., in *Liquid Crystals and Plastic Crystals*, Vol.1, Gray G.W. and Winsor P.A. editors, Ellis Harwood Ltd, Chichester (1974).
6. BALMBRA R.R., CLUNIE J.S. and GOODMAN J.F., Nature 222 1159 (1969).
7. CHARVOLIN J., in *NMR IN LIQUID CRYSTALS*, Emsley J.W. Editor, Reidel Publishing Company (1984).
8. CHARVOLIN J. and RIGNY P., J.Magn.Reson. 4, 40 (1971).

9. BULL T. and LINDMAN B., Mol.Cryst.Liq.Cryst.28, 155 (1974).
10. GULIK-KRZYWICKI T., AGGERBECK L.P. and LARSSON K., in *Surfactants in Solution,* Mittal K.L. and Lindman B.editors, Plenum Press 1983.
11. SALUDJAN P.and REISS-HUSSON F., Proc.Natl.Acad.Sci USA 77, 6991(1980)
12. LUZZATI V., TARDIEU A. and GULIK-KRZYWICKI T., Proc.Natl.Acad.Sci, USA 78, 4683 (1981).
13. HENRIKSSON U. and KLASON T., J.Phys.Chem.87, 3802 (1983).
14. TARDIEU A., thesis, Université Paris Sud (1972).
15. LONGLEY W; and Mc INTOSH T.J., Nature 303, 612 (1983).
16. LINDBLOM G., LARSSON K., JOHANSSON L., FONTELL K. and FORSEN S., J.Am.Chem.Soc.101, 5465 (1979).
FONTELL K., Mol.Cryst.Liq.Cryst.63, 59 (1981).
17. LARSSON K., Nature 304, 664 (1983).
18. GUNNING B.E.S., Protoplasma 60, 111, (1965).
19. TARDIEU A. and LUZZATI V., Biochim.Biophys.Acta 219, 11 (1970).
20. ERIKSSON P.O., KHAN A. and LINDBLOM G., J.Phys.Chem.86, 387(1982), on the dodecycyl trimethylammonium chloride/water system.
21. CHARVOLIN J., TARDIEU A., unpublished results, on the potassium laurate/decanol/water system.
22. The liquid behavior of lipid membranes was also demonstr.by early cytologist, see the discussion by Y.Bouligand, in "*Liquid Crystals*" L.Liebert editor, Solid State Physics, suppl.14, 259, Academic Press (1978).
23. A discussion of the space-filling problem is given in the book by d'Arcy Thompson, "*On growth and Form*", Cambridge University Press.
24. SCHWARZ M.A., *Gesammelte Mathematische Abbandung,* Vol.1, Springer, Berlin (1890).
NEOVIUS E.R., *Minimalflächen,* Frenkel J.C., Helsingfors, (1883).
25. SCRIVEN L.E., Nature 263 123 (1976) and in *Micellization, Solubilization and Microemulsions,* Vol.2, Mittal K.L., Plenum Press, New-York (1977).
26. Including the long range forces associated with water polarization, MARCELJA S. and RADIC N., Chem.Phys.Lett.42 129 (1976).
27. HUSSON F., MUSTACCHI M. and LUZZATI V., Acta Cryst.13, 668 (1960).
28. CABOS C., DELORD P. and MARTIN J.C., J.de Phys.Lett.40, 407(1979).
29. HENDRIKX Y., CHARVOLIN J. and RAWISO M., J.Coll.Interface Sci.100 597 (1984).
ALPERINE S., HENDRIKX Y. and CHARVOLIN J., to be published in J. Physique Lettres.
30. HELFRICH W. course 12 in "Physics of defects", Les Houches 1980, R.Balian Editor, North Holland, (1981).