LYOTROPIC LIQUID CRYSTALS
I. SPECIFIC STRUCTURES

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Abstract. This review synthesizes the most valuable recent information on lyotropic liquid crystals topic, laying on 70 international publications. It presents a general description of the lyotropic behavior from the micellisation process to the specific liquid crystals ordered structures conception. Thermodynamic conditions are detailed too. A succinct classification of the lyotropic liquid crystals, upon both geometrical configuration of the structures and the hydrocarbon chain conformation, is also presented.

Key words: liquid crystals, lyotropic, structure, phase transition, review.

1. INTRODUCTION

Liquid crystals, also named "mesophase", are organic substances that pure, or in aqueous solutions, are capable to reach a special state of aggregation, intermediary between liquid state and solid state. They preserve both the flow proprieties of a liquid and the ordering of a crystal and present multiple anisotropies. The existence domain, also named "mesomorphic" is very well defined by two distinct temperatures situated at its limits; the lower one is the *melting point* at the solid state border and the higher one is the *clearing point* upon which the isotropic liquid state begins.

Pure organic substances, providing liquid crystals reach the mesomorphic domain by varying temperature and have been named Thermotropic Liquid Crystals (TLC). Other organic substances, in aqueous solutions, reach the mesomorphic domain by varying temperature and concentration and have been named Lyotropic Liquid Crystals (LLC).

Depending on of molecular ordering, these two types of liquid crystals may form a number of specific structures [1, 2]. Hence the transition from the solid state to the liquid isotropic state is not a single one, but a succession of transitions passing by several thermodynamically stable phases. The microscopic investigation (texture observation) may be considered one of the most important methods for the identification and the ulterior classification of this large number of different liquid crystalline phases.

Certain steric conditions for molecules are necessary to provide TLC [3]. Molecules have to be rather long and to dispose of: some planar regions; some double or triple bounding which means a rigid zone corresponding to the molecular long axis; some polar groups and some weak dipolar groups at one of the ends. A specific structure of a TLC molecule consists of at least two benzene cycles interconnected by a rigid group and bounded to flexible lateral groups.

The molecules giving TLC are able to orient themselves with the long axis parallel to a certain direction, defined by the $\vec{n}$ versor, also named *director*. By consequence, they

can exist in a series of different structures such as nematic, smectic or cholesteric phases [4]. Each of them is defined by some ordering particularities: the nematic phase has a molecular parallel ordering but the structure is not stratified; the smectic phase has a planar stratified structure and the cholesteric phase has a helicoidally structure. TLC are of a great interest as a research topic in physics and chemistry and have found applications in many other domains such as optical devices, nondestructive testing of materials and medicine (tissues thermography).

Molecular species able to form LLC, also called amphiphilic or surfactants, have two distinct parts very much unlike as solubility. One part is hydrophilic, with a high solubility in polar solvents, while the other one is hydrophobic, with a high solubility in hydrocarbon. This part of the molecule consists of long linear or ramified hydrocarbon chains with or without benzene cycles. This is a good reason to imagine such a molecule as a little sphere representing the hydrophilic "head" continued with a long zigzag "tale" representing the hydrophobic chain. Conforming to the nature of the hydrophilic part, the amphiphilic molecule may belong to one of the following types: ionic, nonionic, or zwitterionic.

In solution, at certain concentrations, the amphiphilic molecules form aggregates with different shapes, which become structural units and by ordering lead to specific structures, such as lamellar, cubic, hexagonal, nematic or cholesteric. Like for thermotropic, lyotropic ordering is characterized by the $\vec{n}$ director.

Parameters describing the lyotropic mesomorphism are investigated by multiple experimental techniques such as optical microscopy in polarized light, neutron scattering or fluorescence quenching. Complementary investigations about molecular organization and motion in LLC can be obtained from X-ray structural analysis and from magnetic resonance studies of deuterated compounds.

The main lyotropic surfactants are of two types: soaps and phospholipids. Lately, LLC have become very important in the biomedical research too [5, 6], because of the great number of living structures implied: cell membrane and vesicles [7], myelin [8], muscles and red cells [9], nucleic acids [10, 11, 12], etc.

For a long time, the study of TLC and LLC was independently performed and made the interest of the colloidal chemistry research. Physicists too have shown very much interest to this area and they started a sustained and profound comparative study, finalized by a large number of publications.

In this paper, only the lyotropic liquid crystals field will be investigated.

In Section 2, the aggregation process is discussed in terms of temperature, concentration and packing parameter; thermodynamic conditions are also detailed. In Section 3, the classification of the LLC based upon the geometrical configuration of the aggregates ordering in different structures and the conformational aspect of the hydrocarbon chain are presented.

2. MICELLAR SOLUTIONS

Temperature, as an important parameter, conditions the appearance of a certain phase, both in thermotropic and lyotropic liquid crystals, but because lyotropics are solutions of at least two compounds, temperature is not the determinant parameter, but the concentration. Further discussions about lyotropics imply water as high polarity solvent [13] and whenever solutions will contain more than two compounds, it will be specified.

Up to a certain concentration named *critical micelle concentration* (CMC), lyotropics did not yet aggregate, the molecular disorder still existing. At the CMC value, a spontaneous organization network of the amphiphilic molecules begins and molecular aggregates of colloidal sizes appear; they have been called "association micelles". But the solution did not yet show liquid crystals behavior and is called "isotropic micellar solution" (IS). If the concentration increases more, lyotropic specific structures appear with a structural order even up to three dimensions and the solution becomes an anisotropic one, more or less viscous. Only in this case, the micellar solution is a liquid crystal.

The micellar aggregates contain a large number of monomers depending on the chemical composition of the surfactant, the aggregate shape, the temperature and the concentration.

Experimental observations, performed by fluorescence quenching [14], NMR [15], and small angle scattering measurements [16], give an aggregation number N of ~60 for monovalent surfactant with 11 methylene groups in the alkyl chain and ~80 for divalent surfactant with 14 methylene groups. Typical surfactants from the first kind, as SDS (sodium dodecylsulphate $C_{12}SO_4Na$), can have the aggregation number between 50 and 100.

The micellar aggregation is a dynamical process that supposes reversibility; each second, some 10^3 to 10^6 monomers are taking part to the aggregation and in the same time, about 0.1 to 10^2 micelles are breaking up. Both processes rates are related to the CMC value and become faster as this one increases. The micelle lifetime is about 10^{-2} to 10 seconds [17, 18]. Both local molecular dynamics (flexions, torsions, isomeric rotations) and surface diffusion effects are superposing. The density of the medium essentially governs fast motions, while slow motions are more related to the local structural parameters. Development of macroscopic investigations, such as conductivity measurements or infrared spectroscopy of water and polar head bonds, can help the interpretation of molecular dynamics.

Temperature also, must be taken into account for micelle aggregation, because it introduces a new condition: it has to be lower than a certain value, known as the "point Krafft" (PK), listed in Table 1 [19], together with the CMC values for various surfactants. In Table 1, substances in the first five lines are nonionic surfactants and in the last three lines are ionic surfactants; C_n represents the number of carbon atoms of the alkyl chain and EO_n represents the number of the ethylene oxide groups of the polar head.

Table 1.
Typical CMC values for some usual surfactants.

Surfactant	Krafft temp. ˚C	CMC mol dm^{-3}
C_8EO_6	25	9.9×10^{-3}
$C_{10}EO_6$	20	9.5×10^{-4}
$C_{12}EO_6$	25	6.8×10^{-5}
$C_{12}EO_8$	25	7.1×10^{-5}
$C_{14}EO_8$	25	9.0×10^{-6}

$C_8 SO_4 Na$	25	1.3×10^{-2}
$C_{12} SO_4 Na$	25	8.3×10^{-3}
$C_{16} SO_4 Na$	25	2.1×10^{-4}

Remark that, the CMC values reduce by a factor of 10 for each addition of two CH_2 groups to the alkyl chain for nonionic surfactants and of four CH_2 groups to the alkyl chain for monovalent ionic surfactants.

The CMC was determined from conductivity and pH measurements and it has been found that it is considerably higher for bivalent ionic surfactants than for monovalent analogues containing the same number of methylene groups in the alkyl chain, probably depending on the increasing electrostatic repulsion between the polar headgroups [20]. For charged surfactants, the electrostatic interactions are often the dominating factor in determining the properties of the systems. Comparison between monovalent and divalent amphiphilic molecules behavior in lyotropic solutions, demonstrates that physicochemical differences become important.

Under the CMC value, some physical parameters such as density, electrical conductibility, osmotic pressure and boil temperature increase with concentration, but present suddenly a significant variation upon the CMC value, as in Fig. 1, [21].

At concentration higher than CMC value, most of the monomers form a film at the water surface till saturation. After that, a new equilibrium is established and the micellisation process generalizes in the bulk.
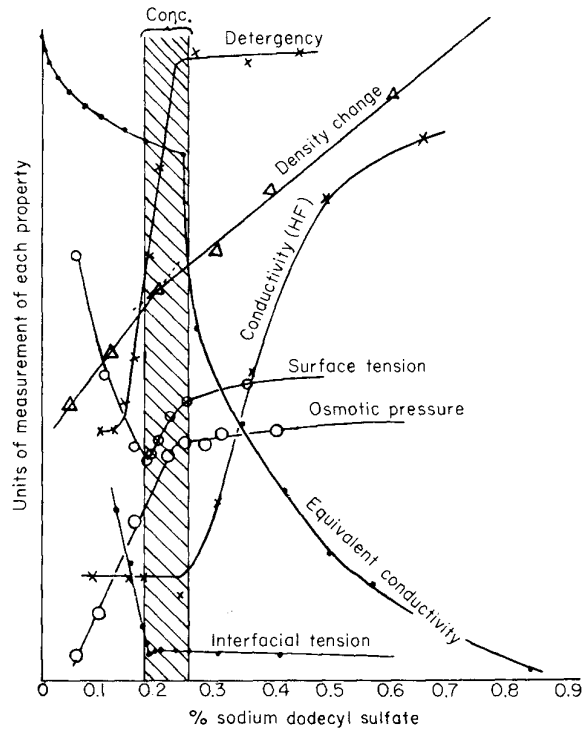
Fig. 1 - Sodium dodecyl sulphate physical properties behavior before and after reaching the critical micellar concentration (hatched zone)

The amphiphilic molecules free energy [22] may decrease considerably by forming large aggregates (N>40). Chemical exchanges between monomers and micelles can be described by the chemical potential equilibrium:

$$\mu_1^0 + k_B T \ln \chi_1 = \mu_m^0 + \frac{k_B T}{N} \ln \frac{\chi_m}{N} \tag{1}$$

where μ_1^0 and μ_m^0 are chemical standard potentials for a free monomer and for a monomer in a micelle, respectively; χ_1 and χ_m are the molar fractions of monomers and micelles, respectively; the logarithmic terms are the entropies of the mixtures in water and in micelles and N is the aggregation number.

Supposing N is constant and known, one can determine the molar fraction of the micelle and the CMC value by imposing the condition that the monomer concentration is maxima:

$$\text{CMC} = \chi_1^{\,max} = \exp\left[-\frac{\mu_1^0 - \mu_m^0}{k_B T}\right] \qquad (2)$$

The shape of the aggregates in isotropic micellar solutions is ordinary spherical (globular) as shown in Fig. 2.
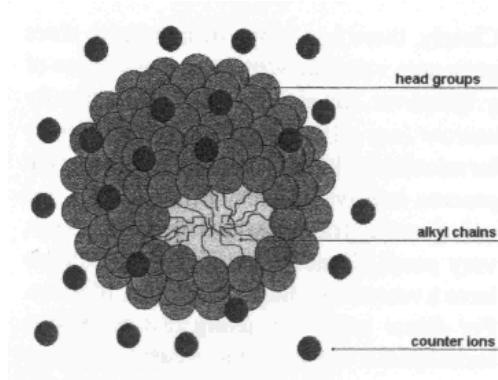

Fig. 2 - Spherical micelle

In a mesomorphic state, aggregates can have different other shapes, such as cylindrical, rod-like or disc-like.

In aqueous solutions micelles are called *normal,* meaning that the head of the amphiphilic molecules are in contact with water molecules, while the hydrocarbon tails entirely occupies the interior of the micelles. Below a certain specific water content which appears to be determined by the maximum capacity of the hydrophilic groups for binding water, the two parts of the amphiphilic molecule interchange position and micelles become *reversed*. The same molecular arrangement also occurs at any concentration in all the solutions with nonpolar solvents.

The aggregation shapes are submitted to a geometrical constraint; one of the three dimensions must be limited by the value *2l*, where l is the amphiphilic molecule length in complete extension. That is why, the most convenient shape is the spherical one, but also rods, lamellae or discs are available.

To classify and study those structures, the introduction of a packing parameter P is imposed:

$$P = \frac{v}{al} \qquad (3)$$

where v is the molecular volume and a is the medium area of the cross section of the polar head.

For an amphiphilic micelle with a spherical shape of radius r, the total micellar area A and the volume V are:

$$A = Na = 4\pi r^2 \quad \text{and} \quad V = Nv = \frac{4}{3}\pi r^3 \quad \text{hence} \quad a = 3\frac{v}{r} \qquad (4)$$

Making the same calculation for a cylindrical micelle of radius r or a lamellar one of width $2r$ and ignoring the edge effect, the possible values of the medium area of the cross section of the polar head a and the packing parameter P are:

$$a \geq 3\frac{v}{r} \quad \text{and} \quad P < \frac{1}{3} \quad \text{for spherical aggregates (radius } r\text{)} \quad (5)$$

$$a \geq 2\frac{v}{r} \quad \text{and} \quad P < \frac{1}{2} \quad \text{for cylindrical aggregates (radius } r\text{)} \quad (6)$$

$$a \geq \frac{v}{r} \quad \text{and} \quad \frac{1}{2} < P < 1 \quad \text{for lamellae or discs (width } 2r\text{)} \quad (7)$$

For molecules with a certain hydrocarbon chain length, the packing pattern strongly depends on the size of the polar head. All shapes just mentioned are possible if the values a are large enough; if not, only the disc shape is available. The great flexibility of the hydrocarbon chains, make impossible the estimation of the smallest values for r which implies certain difficulties to precisely define the maximal values for a.

Both theoretical and experimental observation [23] show that surfactants with the head composed by many groups regularly form spherical micelles, those composed by less groups form rods and those composed by even less groups, form discs. At the CMC, the entropy favors the aggregation and smaller aggregates are preferred, i.e. spheres to rods and rods to discs.

The micellar aggregation is the result of a complex process, called *the hydrophobic effect*, which describes the interaction between nonpolar surfactants and water. It is well known that nonpolar surfactants are almost insoluble in water and generally have a very small degree of solubility.

A thermodynamic analyze of the process shows that the immersion of hydrocarbon in water at room temperature, can be always associated to an increasing entropy, a decreasing to zero enthalpy and a resulting high positive free energy.

In a series of recent publications [24, 25, 26], this matter is discussed in detail. They consider the hydrophobic effect as a result of two contributions; the first one imposed by the surfactant ordering around water molecules and the second one imposed by the creation of a cavity in water, sufficiently large to include the nonpolar chains.

The first contribution is associated with negative entropy, because water molecules, in the vicinity of a nonpolar compound have less possible configurations than the "free water" and are not able to built hydrogen bridges with the solute. The strong hydrogen bridges between water molecules themselves justify small values of the enthalpy.

The second contribution is justified by the high energy required by the construction of the nonpolar cavity in the water. On one hand, the energy value is large because of the higher degree of cohesion between water molecules through the hydrogen bridges and on the other hand, because of the smaller dimension of water molecules in comparison with those of the surfactant. The strong bounding created by the hydrogen bridges that water provides, leads to a very high ordered aqueous structure.

.   The hydrophobic effect is very weak for nonpolar solutions, because of the repulsion that arises between water molecules and hydrocarbon or any other nonpolar groups. Otherwise, the ordering shall increase, reducing the entropy.

The specific micelle shape, closing inside the hydrocarbon tails of the amphiphilic molecules, favors the creation of a hydrocarbon zone, far from the water molecules.

Hence, both thermodynamic conditions implied in the micellar stability are solved; the minimization of the hydrophobic interactions and the maximization of the hydrophilic interactions as well.

In aqueous solutions, the micellar surface is rather rough, because the heads of the amphiphilic molecules overcross the ideal geometrical micellar surface for about 0.2-0.5 nm. The existence of small volumes between the polar heads increases the possibility of counterions bounding.

The number of counterions in the diffuse layer decreases because of the very strong bounding between them and amphiphilic ions of the surfactant, which contribution to the micellar superficial potential is of a great importance. That distribution favors the sudden decrease of the molar conductance and of the electrical conductibility near the CMC value.

In nonpolar solvents, because of their small electrical permittivity, the micellar aggregation becomes more difficult. The interactions with the solvent are weaker and the micelle aggregation pattern is of the *reversed* type; the polar heads form the micellar core while the alkyl chains form the micellar surface, contacting the nonpolar solvent.

The polar core of the *reversed* micelles develops cohesion on the behalf of the dipolar bounding and the hydrogen bridges, in complete opposition with the hydrocarbon core of the *normal* micelles, where the mainly spherical shape supposes high osmotic pressure which confines the hydrocarbon tails and make them have different proprieties than the free surfactant molecules.

In nonpolar solutions, the micellisation process does not begin at the CMC value, but upper and the number of the micelles is rather smaller than the *normal* micelles formed in a polar solvent. The number of *reversed* micelles could increase only in the presence of small quantities of water to solve the bounding of the polar groups.

In conclusion, decreasing the surfactant concentration under CMC, leads to the micelle dissociation and the solution turns up to the initial isotropic liquid state; at CMC, micellar solutions appear, but they are not yet liquid crystals because of ordering absence; increasing concentration leads to the extension of the micellar ordering till completely ordered phases appear, which really means the liquid crystal state. Temperature constraints are also imposed.

3. LYOTROPIC ORDERING

In order to identify all the lyotropic phases, there are some important methods of investigation, such as polarized light microscopy, X-ray scattering and RMN spectroscopy. Here are the different phases revealed by these   methods; lamellar *L*, cubic *I* or *V*, hexagonal *H*, nematic *N*, cholesteric *Ch* and some intermediate ones.

All of them, with one exception, are birefringent and present typical textures; the cubic phases are isotropic (like micellar solutions) so, they cannot be detected in polarized light investigation, but they have also a high viscosity, which make the difference. There is a particular phase, not yet mentioned named *gel,* where both the surfactant and the water have a very slow mobility, while mobility of all the other phases is high, like as liquids.

Every phase distinguishes from another by the specific long distance symmetry of the arrangement of the micellar aggregates and by the micellar surface curvature. Excepting the lamellar phase, with a planar molecular arrangement, all the other phases can be considered as continuous in the polar region, at least.

Lyotropic phases can be found in a *normal* or a *reversed* state and the index 1 or 2 respectively, will be attached to the appropriate phase symbol.

One can found for the lyotropic phases, different other names belonging to the usual soap manufacture terms, due to the direct application of that kind of amphiphilic in practical life.

By adding water to an amphiphilic crystal, the crystalline structure turns into a lamellar *normal* one, also called *neat soap*. If the water addition process continues, the cubic *normal* phase also called *viscous isotropic* appears followed by the hexagonal *normal* phase also called *middle soap* and then the micellar isotropic liquid state, presenting association micelles, is obtained.

Not all amphiphilic surfactants have the same phase succession as presented here, but the hydration process always finalizes by the isotropic liquid state for all of them.

Amphiphilic aggregates are always associated in such a structure to fulfill the free energy minima. The main forces implied in these structures are electrostatic and dispersive. The dispersive are generally weak forces, but sometimes they may govern the ordering interactions between molecules. The electrostatic are attractive forces between ions or dipoles (ion-ion, dipole-dipole, and ion-dipole). Increasing temperature may destroy these arrangements.

Depending on temperature and concentration, all lyotropic phases can occur in the same solution passing by multiple phase transitions.

In this section, the lyotropic ordering is discussed in two distinct paragraphs; in the first one (3.1), the main characteristics of all mentioned phases are detailed, while in the second one (3.2), a supplementary phase typology is revealed by means of the multiple conformational states of the hydrocarbon chain, symbolized by $\alpha, \beta, \beta', \delta, \alpha\beta$ and γ.

3.1 Specific Structures

3.1.1. Lamellar structure – *Neat soap*

The structural unit for the lamellar phase is the simple and double layers. It has to be mentioned that the bilayer, as a repetitive unit, forms the main matrix of the biological membranes that contain phospholipids as lyotropic compounds and not soaps.

The ordered bilayer structure is formed by amphiphilic molecules disposed in bi-dimensional infinite layers, delimited by water layers, all of them having a parallel disposition. The ionic heads of the molecules are contacting the aqueous medium, while the hydrocarbon chains are interdigitating in order to avoid water. The bilayers are disposed one under another through the third dimension, periodically alternating with water layers, like in Fig. 3 [27].

Because the bilayer ordering is not disturbed by the gravitational effect, the repetitive vertical distance between layers is constant. This phase is not a viscous one and the bilayers can slip easily one on the other. The specific optical characteristics of its textures make easier the identification of this phase.

The optical axis is parallel to the long axis of the molecules of the layers; the phase can be optically uniaxial, positive or negative, depending on the temperature values.
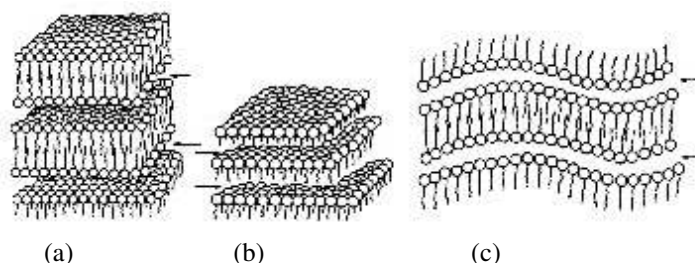
(a)   (b)   (c)

Fig. 3 - Lamellar structure: (a) bilayer, (b) monolayer, (c) rippled bilayer; arrows indicate water layer location.

The usual investigation method for the lamellar phase is the X-ray scattering that gives the following results [28]: the width of the double layer is of 30-40 Å, smaller than the double of the amphiphilic molecule length; the width of the intercalated water layers is of about 20 Å. These figures vary with temperature and concentration in the limits of the lamellar phase. The hydrocarbon chain folding configuration or the tilt angle of the molecules in the layer determines the width variation.

3.1.2. The cubic structure – *Viscous Isotropic*

As the name of the structure indicates, in that case, micelles arrange themselves in a cubic pattern and show always three different packing forms: cubic, cubic face centered and cubic body centered. There are two distinct micellar aggregation shapes: the first one is spherical and forms the *I* phase while the second one is rod-like, interconnected in a three-dimensional scheme and form the *V* phase. Considering also the *normal* and the *reversed* arrangements in both *I* and *V* phases, finely they are four different cubic structures in discussion.

From an optical point of view, cubic phases present no texture, because they are isotropic and can be distinguished from the isotropic micellar solutions only by their high viscosity.

The cubic phases *I* and *V* can be correctly identified one from another by their precise location among other phases. In the hypothesis of increasing progressively the surfactant concentration, the *I* phase location is between the isotropic micellar solution and the hexagonal one, while the *V* phase location is between the hexagonal phase and the lamellar one.

The *I* phase has the simplest configurations; all three mentioned packing forms are present for instance in the $C_{12}EO_{12}$/water solution in a *normal* I_1 arrangement. For that nonionic surfactant solution, a polyhedral representation in all three packing forms (see Fig. 4 [29]) has been appropriate.

<center>(a)   (b)   (c)   (d)</center>
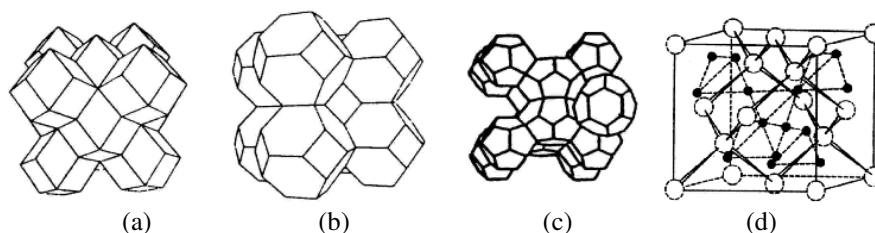
Fig. 4 - Cubic phases in a polyhedral micellar arrangement

Configuration (a) has been the subject of several hypotheses concluded as the following one: the polyhedral volume consists in two spherical micelles and six disc micelles. This packing network is convenient with the energetic stability condition too.

Configurations (b) and (c) are very well described by considering identical micelles with quasispherical shape proposed by Seddon [30].

There are surfactants that form the cubic I phase in a *reversed I_2* arrangement; micelles are supposed to be spherical, of two different sizes, disposed in the (d) configuration [31].

In all *reversed* structures, the packing constraint $r<l$ for spherical micelles, does not work any more because of the external disposition of the hydrocarbon tails. That is why, two different micelle sizes are allowed to grow and to coexist in the same solution.

In the V phase, the three-dimensional lattice consists of short rod-like micelles with the face curvature facing water (V_1), or the nonpolar solvent (V_2). They form three interesting bicontinous network (see Fig. 5)

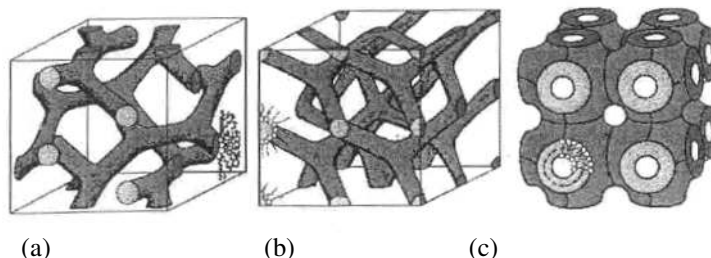<center>(a)   (b)   (c)</center>

Fig. 5 - Cubic phases with "bicontinous" structure

For the (a) network in Fig. 5, Luzatti [32] supposes that both surfactant and water form short cylinders that couple together three by three and form two independent interdigitating branches.

Luzatti and Tardieu [33] propose for the (b) network in Fig. 5, two tetrahedral interwoven ramifications, arranged in a double diamond structure, and for the (c) network in Fig. 5, they propose long water cylinders joined six by six in a cubic pattern.

<center>3.1.3. Hexagonal structure – *middle soap*</center>

If increasing solvent concentration in the cubic phase, the hexagonal phase occurs and forms *normal* structures H_1, or *reversed* structures H_2, according to the solvent polarity.

Micelles are very long aggregates, rod-like, which can have circular, square, rectangular or hexagonal cross sections. These rod-like aggregates are the structural unit of that structure.

With no respect to the continuous medium nature, rods disperse with their long axis in a parallel disposition, creating hexagonal, tetragonal or orthorhomboidal patterns.

The amphiphilic molecules arrangement is a radial one, around the rod long axis, with the polar groups exposed to the exterior in the H_1 structure, or with the hydrophobic tails exposed to the exterior in the H_2 structure; the continuous medium is water and hydrocarbon, respectively. Both the *normal* and the *reversed* types are shown in Fig. 6.
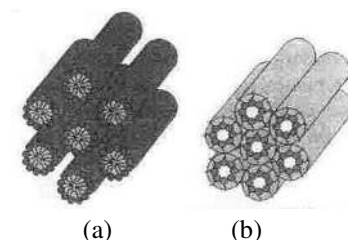

(a)   (b)

Fig. 6 - Schematic representation of a *normal* (a) and *reversed* (b) hexagonal phase

Using X-ray scattering [34], it has been found that normal rods have a diameter of 1.3 to 2 bigger than the hydrophobic chain length. The dimension of the separation zone between rods is in the 0.8-3 nm ranges for the *reversed* type, and up to 5 nm for the *normal* type. Both types show similar optical textures and present a higher viscosity in the hexagonal phase than in the lamellar phase.

3.1.4. The nematic structure

Certain solutions of lyotropic surfactant present nematic structures, like thermotropic nematics, i.e. orienting themselves in external magnetic field or under mechanical stress and showing typical Schlieren textures when observed in polarized light.

Lyonematic structures were discovered by Lawson and Flaut [35] by adding the corresponding alcohol to aqueous solutions of ionic surfactants with 8 and 10 carbon atoms of alkyl chain. Many ionic ternary solutions such as SDS/decanol/water, sodium decylsulphate (SdS)/decanol/water and potassium laurate (KL)/decanol/water, form nematic structures in a relatively narrow concentration/temperature range. Other ionic surfactants, as short chain fluorocarbon derivatives, show nematic phases in binary structures with water. The most extensively investigated example of these compounds is the cesium per-fluoro-octanoate (CsPFO).

Surfactants that give nematic phase usually have the polar head group of the type SO_4^-, CO_2^-, $N(C_5H_{10})^+$ or $N(CH_3)^+$; their alkyl tails have over 8 carbon atoms and are of no ramified type.

An example of nonionic surfactant that forms a nematic structure in a binary aqueous solution is the $C_{16}EO_8$. Recently it was shown [36] that other nonionic surfactants, such as hexapolyethilenoxi triphenil derivatives, present lyonematic phases.

Aggregates in the nematic phase are finite and anisotropic, due to the one-dimensional ordering characterized by the director $\vec{n}$, and present an important translational disorder.

There are two different micelle shapes in nematics, as in Fig. 7 [37]:

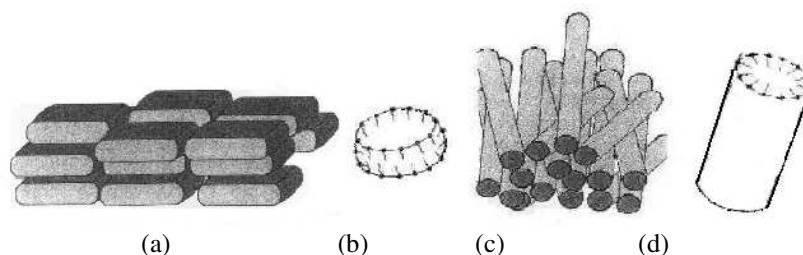(a)   (b)   (c)   (d)

Fig. 7 - Representation of nematic phases: (a) discotic micelles like rounded bricks; (b) cross section in a discotic micelle showing amphiphilic molecules distribution; (c) rod-like calamitic micelles; (d) cross section in cylindrical micelle showing amphiphilic molecules distribution

Concluding the experimental observations, three types of nematic phases are implied: the nematic discotic phase N_d, the nematic calamitic phase N_c and the nematic biaxial phase N_{bx}.   Both N_d and N_c phases are optically uniaxial and the oriented samples investigations revealed that N_d is uniaxial positive and N_c is uniaxial negative [38, 39, 40].

The discotic phase is formed by planar disc micelles and is related more to the lamellar phase, because micelles are built like *rounded bricks* or *ruler shaped,* rather than circular discs. The calamitic phase is formed by rod-like short micelles, and is related to the hexagonal phase.

In a concentration/temperature representation, the biaxial nematic phase always occurs between N_d and N_c phases. By consequence, some authors are presenting it as a mixture of the two types of micelles found in that ones. The N_{bx} phase has been found by Yu and Saupe [41] in the ternary solution KL/decanol/water in a narrow temperature domain at a constant decanol concentration of 6.24% and has been studied in detail by Galerne *et al* [42, 43, 44].

According to experimental observations, it has been found that the following five lyonematic solutions only, present all three nematic phases:
-    potassium laurate/decanol/water [45, 46]
-    sodium decylsulphate/decanol/water [47,48]

- potassium laurate/decylammonium chloride/water [49,50]
- sodium decylsulphate/decanol/water/sodium sulphate [48]
- sodium dodecylsulphate/decanol/water [51]

The evidence of all three nematic phases was confirmed by conoscopic microscopy and RMN spectroscopy, after adding deuterated water in small quantities.

The microscopy in polarized light shows typical nematic Shlieren textures; a planar texture for the N_c phase (as a monocrystal cut parallel to the optical axis) and a homotropic texture for the N_d phase (as a monocrystal cut perpendicular to the optical axis). In order to improve the understanding and study of the nematic textures and their dependence on concentration, Neto *et al* [52] proposes the *gradient concentration method* that better indicates the phase succession.

Lyotropic nematic structures are located between the well ordered phases (lamellar, cubic, hexagonal) and the completely disordered phases (micellar isotropic solutions).

Recently, the N_c phase of the KL/decanol/water solution was X-ray investigated [53] and it has been found that the micelle section is elliptical instead of being circular, as the random distribution of potassium laurate and decanol molecules around the micelle long axis, indicates.

Extending this theory, the general geometric shape of a nematic micelle can be described by an ellipsoid with three axes, l_1, l_2, l_3 . In this case, discotic and calamitic micelles appear only in the geometrical conditions $l_1 \sim l_2 > l_3$ and $l_1 > l_2 \sim l_3$, respectively. The director $\vec{n}$ has the orientation of the l_3 axis in the N_d phase and of the l_1 axis in the N_c phase. The N_{bx} phase is considered to have rhombohedra micelles with two axes and is characterized by two perpendicular directors, $\vec{n}$ and $\vec{m}$. The first one describes the long axes ordering and the second one describes the short axes ordering [54, 55]. According to the theory that the N_{bx} phase could be a mixture of calamitic and discotic micelles, then $\vec{n}$ and $\vec{m}$ directors would characterize their own directors, respectively, as well as the global micelles ordering [56, 57]. In the N_c phase micelles rotate around the long axes, in N_d phase they rotate around the short axes, while in the N_{bx} phase all rotations are frozen.

Further measurements on lyotropic nematic phases [58] have revealed a more interesting approach of this controversial subject. Within a large interval of temperature and concentration, the micelles mainly preserve two axes of symmetry and have, on average, the form of curved platelets (orthorhombic with three axes). Thus, only the different spatial and thermal orientational fluctuations of the platelets make the differentiation between phases, so that their resulting macroscopic symmetries become related to the probability distribution of orientation of the axes. That requires two directions, denoted by $\vec{\vec{n}}$ and $\vec{\vec{m}}$ (headless vectors) associated with the Euler angles (β, γ) and α, respectively. The probability distribution of the longest orthorhombic axis to be oriented in the direction $\vec{\vec{n}}$ is expressed by P (β, γ) $= \int P(\vec{n}, \vec{m}) d\alpha$. Figure 8 [58] shows the isotropic and nematic configurations in terms of this probability.

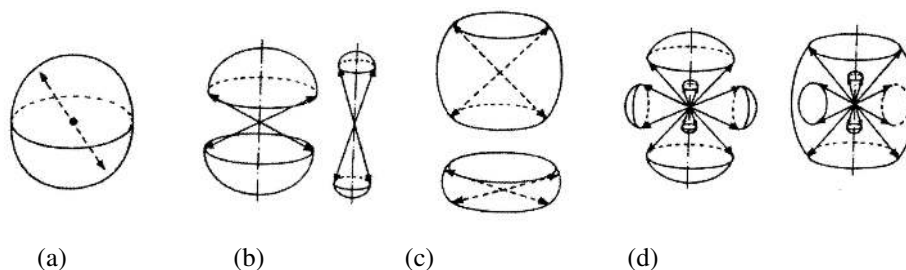(a)   (b)   (c)   (d)

Fig. 8 - Probability distribution (indicated by a double arrow) of the longest orthorhombic axis to be oriented in a given direction $\vec{n}$, in the (a) isotropic, (b) N_c , (c) N_d and (d) N_{bx} phase. In (b) and (c) the pair of figures symbolizes the evolution from the isotropic-like to the rod-like (b) and disc-like (c) configurations of $P(\vec{n})$; in (d), the two possible representations of $P(\vec{n})$ that possess three maxima (left) and three minima (right), illustrate the intermediary character of N_{bx} phase symmetry with respect to N_c and N_d phases symmetries

Nematic calamitic (b) and nematic discotic (c) representations in Fig. 8 can be equivalently replaced by revolution ellipsoids and the nematic biaxial (d), by an ellipsoid with three different axes, perfectly concordant with the other descriptions mentioned before. According to the X-ray and neutron diffraction measurements [59], the biaxial phase produces by a simple change of the micellar shape assumed to transform from a flat disc (N_d) or an elongated cylinder (N_c) to a biaxial ellipsoid (N_{bx}). This micelle shape malleability can also be the explanation of the fact that calamitic structure turns easily into a discotic one by adding only 0.3% sodium sulphate in the SDS ternary solution.

As mentioned by Hendrix [54] and Veracini [60], nematics can also be classified by their orientation in a magnetic field and then belong to one of the two following types: to the type I, if the director orients parallel to the magnetic field, having positive anisotropy of the magnetic susceptibility, or to the type II, if the director orients perpendicular to the magnetic field, having negative anisotropy of the magnetic susceptibility.

Changes of the relative concentration of the nematic solutions compounds imply changes of the anisotropy of the magnetic susceptibility sign [61]. The sign inversion can be attributed to both the change of the molecular susceptibility sign and the change of the micellar aggregation state.

As for thermotropics, when adding very small quantities (even under 0.1% in weight) of an optical active substance to lyonematics, they reach a new structural ordering and turn into *twisted* nematics, conserving only the initial micelle shape, while the structure becomes twisted in a spiral, like cholesterics. The optical active substance has to be water-soluble and to have bounding capacities, like all the lyotropic solutions compounds.

Experiments demonstrate that the sign of the optical activity of the added substance and the sign of the induced optical activity in the nematic structure are not related [62]. RMN spectroscopy revealed that the variation of solution composition induce dimensional changes of the micelles. It was found that the path of the spiral structure follows nearly this variation: it increases with increasing amphiphilic concentration and decreases with decreasing decanol concentration.

The study of lyotropic nematics is very important for biophysics too, because of the great number of biological systems presenting nematic structures. In this case, the surfactant, in adjunction with proteins, is organized in simple or multiples bilayers with the hydrophilic head pointing outwards; *normal* and *reversed* vesicles form as well.

3.2. Hydrocarbon Chain Conformation

3.2.1, *Liquid-like* conformation: α type

The α-type conformation of hydrocarbon chain shows a high disorder in the hydrocarbon region, liquid-like, as it is shown in Fig. 9 [63]. However, the average of the chain orientation is perpendicular to the amphiphilic-water interface and improves with the decreasing section of the polar head localized in the interface.

Even if X-ray scattering is not very suited for liquids investigation, it supplies several valuable arguments that support the liquid-like conformation theory of lyotropics [64]. Here are some of them: as for liquids, a diffuse band is observed in the large angles scattering; in the nonlamellar phases, for geometrical considerations, the hydrocarbon disordered chains appear to be folded in an irregular way, in smaller spaces, than in the bilayers; in the lamellar phase, the width of the bilayers decreases by about 30% and a delocalization of the CH_3 groups is observed, when passing from a more rigid conformation to an α-conformation.
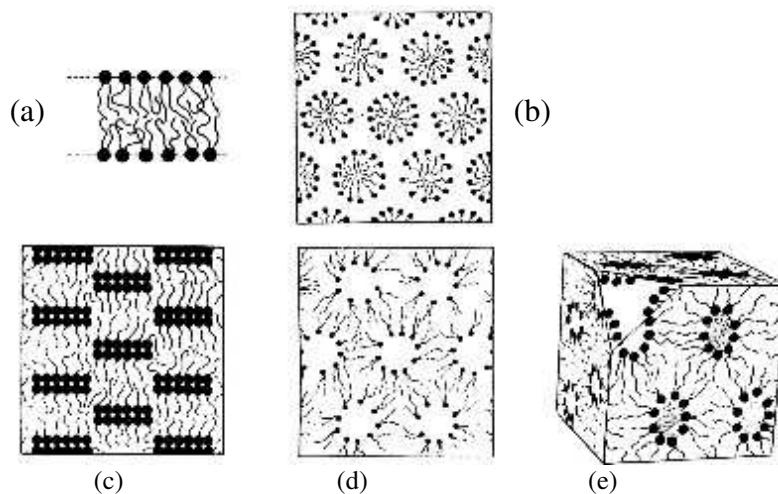

Fig. 9 - *Liquid-like* conformation:
(a) *normal* lamellar phase; (b) *normal* hexagonal phase; (c) *reversed* lamellar phase;
(d) *reversed* hexagonal phase; (e) *reversed* cubic phase

All the phases having chains in liquid-like conformation, display a peculiar temperature effect when raising temperature. It consists in decreasing values of the bilayer thickness (in the lamellar phase), or of the micelle diameter (in the nonlamellar phases) with an unusually high linear thermal coefficient (of the order of $-10^{-3} K^{-1}$) [64].

3.2.2. O*rdered* conformation: β, β' and δ type

At not so high temperature, the hydrocarbon chains become very ordered. That implies that only rotations around the molecule axis are allowed. The aqueous medium instead, is in a liquid-like conformation, without mobility restrictions, having very rapid rotational and translational movements.

In the lamellar phase, where amphiphilic are organized in bilayers, all three conformation types, β (parallel), β' (tilted) and δ (coiled into helices), are possible as Fig. 10 [65] shows.
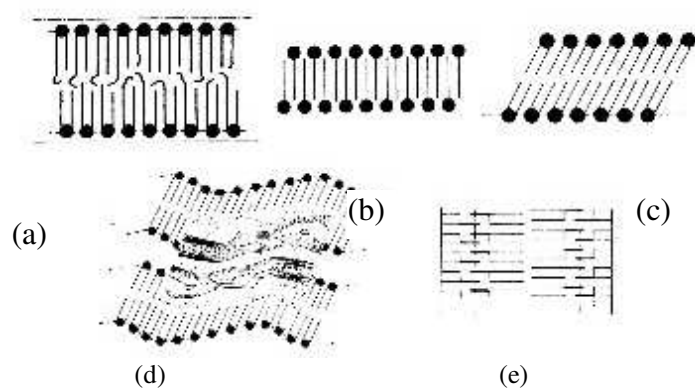

Fig. 10 - Lamellar phase with chains in *ordered* conformation:

(a) structure of the L_β phase with stiff and parallel chains; (b) structure of potassium soap (gel phase) with interdigitating parallel chains; (c) structure of the $L_{\beta'}$ phase with tilted extended chains; (d) two-dimensional periodic structure of a rippled lamellae with chains in β' conformation;(e) structure of the L_δ phase with a tetragonal lattice where the light lines represent the hydrocarbon chains coiled into helices with their axis perpendicular to the lamellae and the heavy lines represent the polar groups if two adjacent layers in registry

Such conformations have been observed in the lamellar phase in many lyotropic solutions with amphiphilic molecules presenting one or two (different) alkyl chains.

A rectangular lattice was observed with Rb soap, at low temperature and a square lattice L_δ, with a side of 4.8 Å, was observed in dry lecithin [66], both with chains perpendicular to the lamellae. In the L_δ, phase, the polar heads are ordered in a two-dimensional lattice, with the same symmetry as the hydrocarbon chains.

A hexagonal lattice (side 4.8 Å) appears most frequently with chains in β or β' conformation in synthetic lecithin. The thickness of the bilayer is related to the alkyl chain with CH_2 groups in extended trans-trans configurations; in the δ conformation, the

thickness of the bilayer is smaller because chains are coiled into helices. That demonstrates that the complete elongation of the chains does not determine the two- dimensional ordering.

The rotational disorder is present in all configurations, except the rectangular lattice, where it may be partially frozen.

In β and β' conformations, the CH_3 groups of two adjacent hydrocarbon layers are in registry in the middle of the bilayer and form a thin liquid-like zone [20, 67]. Concerning the polar heads, a two-dimensional ordering was not yet revealed.

Lamellae in β' conformation, represented in Fig. 10(d), are all distorted [66] because the distortion propagates from layer to layer. The lattice is two-dimensional, one dimension being the lamellar repeating distance and the other, the common periodicity of the distortion which is of hundreds of Angstroms. A very strong correlation was observed between lamellae; it may be intermediated through the water layer by the forces between polar head groups.

Even if strong long range interactions were observed in all three conformations in discussion, interactions at molecular level seems not to exist and three-dimensional ordering do not appear.

3.2.3. *Mixed* conformation: α β and γ type

Phases appearing at high surfactant concentrations have the hydrocarbon chains in a very rigid, ordered β conformation and the transition to the more fluid disordered α conformation supposes the existence of mixed domains, even for chemically homogenous chains. For example, during the $\alpha \rightarrow \beta$ conformation transition of the diacyl lipids, a segregation process of the heterogeneous chains takes place; the longest and the most saturated chains organize themselves in β microdomains, while the other chains remain in the α conformation. So, the α β chain conformation is a disordered mosaic of α and β domains, as it is shown in Fig. 11 [68, 69] (a):
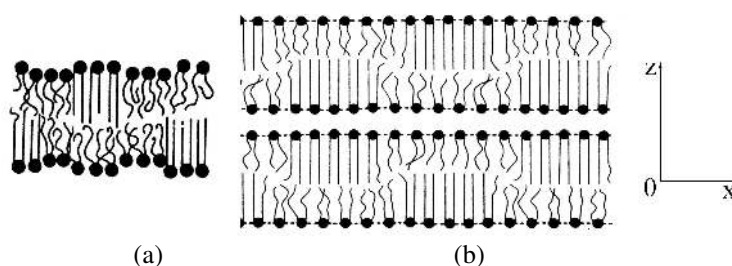

(a)   (b)

Fig. 11 - *Mixed* conformations: (a) lipid lamellae of the $L_{\alpha\beta}$ phase representing a disordered α and β mosaic; (b) lipid bilayers of the L_{γ} phase representing an ordered α and β mosaic

Both α and β conformation microdomains are similar with those of infinite domains appearing in L_α and L_β phases. The dimension of the α β microdomains is estimated to be of the order of hundreds of Angstroms.

Sometimes, at high surfactant concentrations, the microdomains are organized in a two-dimensional lattice depending on the lamellar periodicity along z-axis and on the length of α and β conformation microdomains along the x-axis. That is the case of the γ conformation of the hydrocarbon chains, shown in Fig. 11(b). This kind of lattice involves the existence of very strong interactions between lamellae, created by the polar head groups [70]. In Fig. 11(a), the water layers separating amphiphilic bilayers are sufficiently thick to hinder such interactions.

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