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ABSTRACT

Lyomesophases that orient in presence of magnetic fields are made of finite cylindrical micelles (type I) or finite planar micelles (type II). An analysis of the possible orienting mechanisms in these lyomesophases is presented. Quantitative estimates are made for the diamagnetic mean susceptibility and anisotropy of the micellar interior and of the solvent medium of typical lyomesophases. It is seen that both the molecular diamagnetic anisotropy of the hydrocarbon chains, which tends to align the chains perperndicular to the field, and the diamagnetic form anisotropy, which tends to align the major axis of the ellipsoids in the direction of the field, could in principle be responsible for the observed orientation; however the micellar units must be elastically coupled together, since the magnetic energy of a single micelle is smaller than thermal fluctuations.

A review of available information about the state of conformational order of the hydrocarbon chains in lyomesophases shows that the degree of parallelism among chains ensures that shape anisotropy of the micelles is negligeable in front of molecular diamagnetic anisotropy, which must be responsible for the orientation of these lyomesophases. The concept of order parameter for these lyomesophases is analysed; it is seen that a splitting in two order parameters, one relating the molecular average axis to the local micellar director $\vec{n}$ (S_{int}) and the other relating $\vec{n}$ to the bulk director $\vec{N}$ (S_{ext}) is convenient. The difficulties in applying elastic continuum theory to these lyomesophases are discussed.

1. INTRODUCTION

Lyotropic liquid crystals formed by binary lipid-water systems, ternary systems (lipid-water-alcohol) and several multicomponent systems have been widely studied and several types of structures have been discovered [1-4]. The most common lyomesophases are the neat soap (lamellar) and the middle soap (cylindrical micelles with hexagonal order in two dimensions).

Lyomesophases that orient in presence of magnetic fields have been known for more than a decade [5,6]. These magnetically oriented lyomesophases have been explored with NMR technique [7-9], and have been classified [7,9] as types I and II depending on whether the phase director orients parallel or perpendicular to $\vec{H}$. The two types can be identified by the NMR spectra obtained with sample spinning on an axis perpendicular to $\vec{H}$, since type I mesophases do not preserve their orientation in this condition while type II phases do preserve it. Type I phases are slow to respond to orienting forces in a magnetic field while type II phases are more mobile and orient more rapidly in a magnet; however characteristic times are much larger than for thermotropic nematics and both types I and II may present residual magnetic orientation in the absence of magnetic fields. The study of these lyomesophases is receiving increasing attention [10-22].

From small angle X-ray diffraction studies on oriented samples, the proposed structure is of finite planar micelles [11-15] (platelets) for type II and finite cylindrical micelles [15-16] for type I lyomesophases. It has been argued [9,13,15] that the observed orientation agrees with the expected orientation of carbon chains in magnetic fields due to diamagnetic anisotropy. On the other hand the observed orientation is the same that should be expected from the shape anisotropy of the micellar ellipsoids and it has been suggested [15] that the two processes have converging effects. However no quantitative estimate has so far been made.

Magnetic orientation in thermotropic nematic phases has been widely explored [23,24]; it is due to an anisotropy of the magnetic susceptibility resulting from diamagnetic properties of anisotropic molecules, mainly aromatic rings. The diamagnetic molecular anisotropy is rather small and magnetic orientation occurs because a very large number of molecules are elastically coupled together, resulting a magnetic energy for the bulk sample reasonably larger than thermal fluctuations.

While in thermotropic nematics spontaneous alignment occurs in the presence of magnetic fields, magnetically oriented thermotropic smectic mesophases can be obtained only by cooling in magnetic fields through the nematic-smectic transition [25-27]. Studies of magnetic alignment of the usual lamellar and hexagonal lyomesophases are scarce. NMR results [28] indicate that most lamellar phases do not spontaneously orient in the presence of magnetic fields of 14 kG ; however, if the phases are heated above the melting point and then very slowly cooled in the magnetic field, some of the phases orient and maintain their orientation for at least 24 h .

Magnetic orientation of particles in a solute can occur individually. Suspensions of various biological membrane systems such as retinal rod outer segments, chloroplasts and purple membranes have been known to show magnetic-field induced orientation [29,30]. This effect is attributed to molecular diamagnetic anisotropy which sums up when molecules are oriented within a membrane or biological unit. However, the magnetic orientation observed in biological membranes is oposed to that expected from the diamagnetism of the lipid bilayers: while hydrocarbon chains should orient perpendicular to $\vec{H}$, and therefore

with $\vec{H}$ in the plane of the membrane, the observed orientation is with $\vec{H}$ normal to the membrane plane. Therefore magnetic orientation of biological membranes has been attributed to the diamagnetism of oriented membrane proteins, which cancel the small effect of the carbon chains.

In the case of lyotropic mesophases there are finite anisotropic micelles that ressemble the biological units, with planar or curved lipid bilayers, but that also may be coupled together elastically as the anisotropic molecules of thermotropic mesophases.

In this paper the possible orienting mechanisms in these lyomesophases are analysed to establish which are the determinant factors producing magnetic orientation; in particular the effects of diamagnetic molecular and shape anisotropy are compared and it is verifyed in which conditions the magnetic energy is larger than thermal fluctuations.

A review on available information about the conformational state of the chains is also presented; this is particularly important since the carbon chains that should be responsible for the diamagnetic anisotropy are considered to be in a disordered-liquid state in lyomesophases [1,4], what would make questionable the additivity of the anisotropy to produce a macroscopic response.

These lyomesophases have been classified as nematic mainly because of the spontaneous magnetic orientation and because textures visualized in a microscope ressamble nematic textures [15,18,21]; an analysis of the concept of order parameter for these lyomesophases is performed and the possibility of applying elastic continuum theory to these lyomesophases is discussed.

2. ORIENTATIONAL EFFECTS IN MAGNETIC FIELDS

2.1. General Considerations

The magnetic induction $\vec{B}$ due to the presence of a magnetic field $\vec{H}$ and an induced magnetization $\vec{M}$ is given in the CGS system by

$$\vec{B} = \vec{H} + 4\pi\vec{M} = \vec{H} + 4\pi\chi\vec{H} = \mu\vec{H} \quad ,$$

where μ is the magnetic permeability and χ the magnetic susceptibility of the medium per unit volume ($\mu = 1 + 4\pi\chi$). For a paramagnetic medium $\chi > 0$ while for a diamagnetic medium $\chi < 0$.

When there is molecular anisotropy χ becomes a tensor of second order with different components for different directions in relation to $\vec{H}$ and with an average value $\bar{\chi} = 1/3\ (\chi_a + \chi_b + \chi_c)$, a, b and c being the principal axes of the molecule. For uniaxial nematic liquid crystals there are only two different components in the directions parallel and perpendicular to $\vec{H}$, respectively $\chi_{\parallel}$ and $\chi_{\perp}$, with an average value $\bar{\chi} = 1/3\ (\chi_{\parallel} + 2\chi_{\perp})$ and an anisotropy $\Delta\chi = \chi_{\parallel} - \chi_{\perp}$.

The magnetic energy for a uniaxial medium of volume V and director $\vec{n}$ is given by [23,24]:

$$U = -\frac{V}{2}\left[\chi_{\perp} H^2 + \Delta\chi(\vec{n}\cdot\vec{H})^2\right] \quad .$$

For the configurations $\vec{n} \parallel \vec{H}$ and $\vec{n} \perp \vec{H}$ we have

$$U_{\parallel} = -\frac{V H^2}{2}\chi_{\parallel} \qquad \text{and} \qquad U_{\perp} = -\frac{V H^2}{2}\chi_{\perp} \quad .$$

For diamagnetic substances the configuration of minimum energy is the one with smaller absolute value of χ .

The energy difference between the two configurations is

$$\Delta U = U_{\parallel} - U_{\perp} = -\frac{H^2 V}{2}\Delta\chi \quad .$$

For most thermotropic nematics $\Delta\chi > 0$ and the nematic axis prefers to lie along the magnetic field.

The above expression applies for the χ of one molecule when V is the molecular volume. Since the magnetic couplings between neighbouring molecules are very small χ is, to a reasonable approximation, simply a sum of individual molecular responses. When there are N molecules together with a degree of correlation expressed by an order parameter S , the energy difference is

$$\Delta U = -\frac{H^2}{2} VNS\ \Delta\chi \quad .$$

The quantity VNS can be considered as an effective volume V_{ef} where the diamagnetic anisotropy is summed up or alternatively the quantity $S\Delta\chi$ can be considered as the effective diamagnetic anisotropy per unit volume. For a monocrystal S=1 while for a typical nematic liquid crystal $S \sim 0.6$. When ΔU is much larger than the thermal energy orientational effects are observed; this happens with thermotropic nematic samples where $N \sim 10^{22}$.

Another source of orientation in presence of a constant $\vec{H}$ is form anisotropy, when a magnetically isotropic object of anisotropic shape is placed in a medium of different magnetic susceptibility. This possibility will be discussed for lyomesophases after the determination of typical values of χ , with a quantitative analysis of the effects of molecular anisotropy and form anisotropy.

A third possibility of orientation, due to anisotropy and inhomogeneities of the applied magnetic field, has a negligible influence in the case considered here, of rather small magnetic fields without provocated gradients in definite directions. This effect depends on HdH/dx , dH/dx being the gradient of H along the x direction, while the other effects depend on H^2 .

2.2. Molecular Diamagnetic Anisotropy

In the determinations of molecular diamagnetic susceptibilities it is useful to define a susceptibility per unit mass of a medium of density ρ as $\chi_m = \chi/\rho$ and the atomic or molar susceptibility $\chi_M = A\chi_m = A\chi/\rho$, where A is the atomic or molecular weight.

The determination of χ for a mixture of diamagnetic substances is made through the additive Wiedemann's law

$$\chi_M = \sum_i x_i \ \chi_{Mi}$$

where x_i are the molar fractions and χ_{Mi} the values for the pure components.

Theoretical exact calculations are possible only for very simple molecules. Therefore χ_M of molecules are calculated from known atomic values χ_A and constitutive contributions λ due to the chemical bonds (Pascal's constants) according to

$$\chi_M = \Sigma \chi_A + \Sigma \lambda \quad .$$

Tables with χ_A and λ for such calculation can be found in several references [31-34]. From an empirical point of view, for hydrocarbons the atomic values have been adjusted to give agreement with results for paraffins with $\lambda=0$; additive λ values are proposed for double and triple bonds and for specific radicals.

Measurements of the principal diamagnetic susceptibilities and of diamagnetic anisotropies have been performed by Londsdale [35] for several aliphatic and aromatic compounds; the measured values have been correlated with molecular dimensions, electronic configurations, optical polarizabilities, magnetic birefringence and other physical properties whenever possible. A theoretical treatment for the anisotropy exists only for the case of molecular rings.

Aromatic compounds possess stronger diamagnetic anisotropy, with larger χ in the direction of smaller refractive index, normal to the molecular plane, and therefore align with $\vec{H}$ parallel to the plane of the carbon ring. Typical values for nematogens [36] are $\bar{\chi}_m \sim -5 \,.\, 10^{-7}$ emu/g and $\Delta\chi/\bar{\chi} \sim 0.2 - 0.3$.

Aliphatic compounds of long chains, with satured single bonds, possess smaller diamagnetic anisotropies [35] ($\Delta\chi/\bar{\chi} \sim 0.1 - 0.2$) with larger χ in the direction of larger refractive index, corresponding to the length of the chain, and therefore align with $\vec{H}$ perpendicular to the molecular length.

Calculations of $\bar{\chi}$ and $\Delta\chi$ are now presented for the molecules of interest in the case of two typical lyomesophases:

Type II SDS (Na decyl sulfate 37 wt%/water 53 wt%/Na sulfate 5 wt%/ decanol 5wt%);

Type I LK (K laureate 33.6 wt%/water 64.1 wt%/KCℓ 2.3 wt%).

Table 1 gives the average molar diamagnetic susceptibilities $\bar{\chi}_M$ calculated from atomic values and constitutive constants found in the literature [31-34]; the precision of these values is about 3%. The table gives also an estimate of the percentual diamagnetic anisotropy, calculated assuming that the anisotropy comes only from the hydrocarbon chains and using the measured anisotropy for stearic acid [35].

From these calculated values and using the known value for water (-13.10^{-6} emu/mol) and the phase compositions, it is possible to calculate the average volumetric susceptibility for the micellar interior and for the solvent medium, admitting that the alcohol is inside the micelle, as usual, and that the salt is in the solvent. Results do not differ sensible for the two lyomesophases and typical values are $\overline{\chi} = - 6 .10^{-7}$ emu/cm^3 for the micellar interior, with $\Delta\chi/\overline{\chi} = 0.1$ and $\chi = -7 .10^{-7}$ emu/cm^3 for the solvent medium.

Since the hydrocarbon chains are expected to have a preferential direction perpendicular to the lipid-water interface, the molecular diamagnetic anisotropy should align cylindrical micelles with their axis parallel to $\vec{H}$ and planar micelles with the plane of polar heads containing $\vec{H}$. This is exactly the type of orientation that is observed.

The magnetic interaction energy for one amphiphile molecule with typical volume of 500 $\mathring{A}^3$ and $\Delta\chi = 0,7 .10^{-7}$ emu/cm^3 in a field of 2 KG comes out to be $\Delta U_{mol} = 7 .10^{-23}$ erg, exceedingly small when compared to the thermal energy.

For orientation to occur it would be necessary

$$\Delta U_{mol} = \frac{H^2}{2} V_{ef} \Delta\chi = 10 \ kT \quad .$$

At room temperature, the condition is

$$V_{ef} = S N V = 3 .10^{-12} \ cm^3 \quad .$$

For a typical amphiphilic molecule therefore it

would be necessary $SN \cong 0.6 .10^{10}$ molecules coupled together.

Let us admit for the moment the more favourable case of amphiphile molecules in the extended chain conformation, in which case the order parameter S for the molecule has a clear meaning. Even in the case $S=1$ it is necessary that a very large number of molecules be coupled together to produce orientation.

To estimate the number of molecules in a micelle it is necessary to estimate the micellar dimensions. There are some discrepancies in the estimate of the micellar size, but one can say that the number of molecules per micelle is expected to be $\sim 10^2$ for the smaller estimate [15] and of $\sim 10^3 - 10^4$ for the larger estimate [13,16]. In any case it is clear that a single micelle would not be able to align in a magnetic field of 2 KG due to thermal fluctuations.

Another way to discuss the possibility of individual micellar orientation is by calculating expected relaxation times for orientation of individual particles in a medium of viscosity η, as it is usually made for biological particles magnetically orienting in a solute. For such case the relaxation time for orientation is given by [29,30]:

$$\tau = \frac{r}{\Delta\chi \ V H^2}$$

where r is a coefficient of rotational friction of the ellipsoid.

For orientation to occur the relaxation time τ must be such that the brownian dislocation for independent particles

$$\overline{\Delta\theta^2} = \frac{2 \, kT}{r} \Delta t$$

must be much smaller than $\pi/2$ for $t \sim \tau$.

This condition comes out to be equivalent to the previous condition $\Delta U >> kT$ and leads to the same minimum value for the volume V_{ef} .

It must concluded therefore that for orientation due to molecular diamagnetic anisotropy to occur the micelles must be elastically coupled together in a way analogous to thermotropic liquid crystals. This is in agreement with X-ray results that indicate collective reorientation of the micelles [16].

2.3. Form Anisotropy

The problem of orientation of an ellipsoid of magnetic permeability μ_2 in a medium of magnetic permeability μ_1 in presence of a constant magnetic field $\vec{H}$ has been treated rather completely [31,32,37-39]. The magnetic energy of an ellipsoid of volume V is

$$U = \frac{V}{8\pi} (\mu_2 - \mu_1) \vec{H}^{loc} . \vec{H}$$

where $\vec{H}^{loc}$ is the local field inside the ellipsoid, given by

$$H_i^{loc} = H_i - D_i M_i \qquad \text{with} \qquad i = x,y,z \quad .$$

D_i are demagnetizing factors. Calling a, b and c the semiaxis of the ellipsoid $(a \geq b \geq c)$, the factors D_a , D_b and D_c where given by Osborn [38] as a function of (a/c) in analytical expressions for special cases and tabulated as a function of (c/a) and (b/a) . These factors vary between 0 and 4π , with $D_a + D_b + D_c = 4\pi$. Ellipsoids of revolution are prolate when $b=c$ and oblate when $b=a$.

When the ellipsoid is placed in presence of a

constant magnetic field $\vec{H}$ the three directions of his principal axes are directions of equilibrium but only the situation $\vec{a} || \vec{H}$ is of stable equilibrium, and this does not depend on the sign of $(\mu_2 - \mu_1)$; the components of the torque on the ellipsoid are such that they turn the major axis in the direction of the field by the shortest way [31,32,37]. The energy of the configurarions with the major axis $||$ and $\perp$ to $\vec{H}$ are:

$$U_{||} = \frac{V}{8\pi} \frac{(\mu_2 - \mu_1) H^2}{1 + D_a \chi_2} \qquad\qquad U_{\perp} = \frac{V}{8\pi} \frac{(\mu_2 - \mu_1) H^2}{1 + D_c \chi_2}$$

Remembering that $\chi << 1$, the energy difference between the two configurations is given by

$$\Delta U = U_{||} - U_{\perp} = \frac{V}{2} H^2 (\chi_2 - \chi_1)(D_c - D_a) \chi_2$$

The largest energy difference occurs for highly asymmetrical ellipsoids, when $a >> c$; in this case $D_a = 0$ and $D_c = 4\pi$ for oblate spheroids and $D_c = 2\pi$ for prolate ellipsoids.

From the micellar shape anisotropy it is expected that the larger ellipsoid semiaxis orients in the direction of $\vec{H}$, what would also give the observed orientations of cylinders with their axis parallel to $\vec{H}$ and disc-like platelets with $\vec{H}$ in the plane.

For $\Delta U_{form} >> kT$ orientational effects due to form anisotropy may be observed. Taking the largest possible value for ΔU_{form} this implies

$$2\pi (\chi_2 - \chi_1) \chi_2 H^2 V = 10 \ kT \quad .$$

At room temperature and typical values of diamagnetic substances $(\bar{\chi} \sim 10^{-6} , \chi_2 - \chi_1 \sim 10^{-7})$ the necessary condition is

$H^2 V \sim 1 \, (G^2 \, cm^3)$.

For the magnetic fields necessary to orient lyomesophases ($H \sim 2$ KG) this condition will be fullfilled for oblate ellipsoids with $a = b \sim 10^{-2}$ cm, $c \sim 10^{-3}$ cm and for prolate ellipsoids with $a \sim 2.10^{-2}$ cm, $b = c \sim 2.10^{-3}$ cm. This means that for small values of $\vec{H}$ only macroscopic particles may present orientational effects due to shape anisotropy. Micellar particles with $V \sim 10^8$ Å^3 would require impossible high fields ($H \sim 10^8$ G) to orient in function of shape anisotropy.

There is still the possibility that the individual micellar ellipsoids are elastically coupled together, so that a very large number of them would reach a magnetic energy larger than thermal fluctuations. The number N of elastically coupled micellar units necessary to build a macroscopic answer would need to satisfy $SNV \sim 10^{-6}$ cm^3 , S being an order parameter for the micellar ellipsoids. This conditions could be satisfied by the macroscopy samples investigated.

This elastic coupling is also the mechanism that makes possible diamagnetic orientation due to molecular diamagnetism. To decide whether the two processes may compete or have converging effects it is necessary to compare ΔU_{mol} due to molecular anisotropy with ΔU_{form} due to form anisotropy.

Let us consider a micelle with N anisotropic molecules, of anisotropy $\Delta\chi$ and average susceptibility $\bar{\chi}$, in a solvent medium of susceptibility χ_o . The volume of the micelle will be NV_o , where V_o is the volume of one molecule.

$$(\Delta U)_{form} = \frac{N V_o}{2} H^2 (\bar{\chi} - \chi_o) \, 4\pi \, \bar{\chi}$$

$$(\Delta U)_{mol} = \frac{S N V_o}{2} H^2 \, \Delta\chi$$

where S is an order parameter describing the degree of order among molecules within a micelle.

The ratio between the energy differences is

$$\frac{(\Delta U)_{mol}}{(\Delta U)_{form}} = \frac{S \, \Delta\chi}{\bar{\chi} - \chi_o} \, \frac{1}{4\pi \, \bar{\chi}} \quad .$$

As it has been seen in the previous item $\Delta\chi \sim \bar{\chi} - \chi_o$ and as $\bar{\chi}$ is very small ($\sim 10^{-6}$) it results $\Delta U_{mol}/\Delta U_{form} \cong 10^5 \, S$. Therefore $\Delta U_{mol} >> \Delta U_{form}$ except in the case of almost completely uncorralated molecules, when S goes to zero. This would be the case for anisotropic molecules in the isotropic liquid state.

Therefore if the hydrocarbon chains are in a completely disordered state, as it is accepted by some authors [1,4], form anisotropy would play a role in the orientation of these lyomesophases.

To decide whether the determinant orientation mechanism is molecular diamagnetic anisotropy of the hydrocarbon chains or shape anisotropy of the anisotropic micelles it is fundamental to discuss in detail the state of conformational order of the hydrocarbon chains, a rather controversial subject.

3. CONFORMATIONAL STATE OF HYDROCARBON CHAINS

3.1. The Disordered-Liquid Hypothesis

The hypothesis of carbon chains in a highly disordered conformational liquid state in all lyotropic mesophases has been adopted [1,4] from the evidence of X-ray diffraction at high diffraction angles: in the gel phases, at lower temperatures, typical diffraction lines indicate a two dimensional packing of the stiff and fully elongated hydrocarbon chains, while in the liquid crystalline state only a diffuse band at 4.6 Å appears, as in liquid paraffins. This fact, together with the measured negative thermal coefficient of the bilayer thickness $(-10^{-3}/^{o}C)$, of the same type as in rubber, led to the postulation of a highly disordered type of chain conformation, although it is usually assumed that the average chain orientation is perpendicular to the lipid water interface. That is a picture rather confused needing some clarification.

The diffuse band at 4.6 Å, which has been taken as evidence of conformational disorder along the chain length, indicates in reality the break down of the close packing and of the two dimensional order in the plane perpendicular to the chain axis.

Pure paraffin crystals C_nH_{2n+2} exist in four crystalline modifications [40]: even chains exist in a triclinic form from C_{18} to C_{26} and in a monoclinic form from C_{26} to C_{36} while odd chain lengths are orthorrombic. There exists still an hexagonal or quasi-hexagonal state which results from the occurrence of a first order phase transition at a temperature of a few degrees below the melting point; this form exists for even chains from C_{20} to C_{36} and for odd chains from C_9 to C_{41}. This phase transition has been, since the earlier work of Müller, associated with rotation of the stiff molecule around its axis and has been considerably studied [40].

The earlier work on paraffins [41] shows that the expansion of the c axis, along the chain length, is one order of magnitude smaller than that of the a and b axes and it is considered that the chain length is not much changed on melting. The a and b axes have an expansion ratio of 3.5 and the chain molecule has no radial symmetry about the chain axis. At the first order phase transition in the solid state the 110 and 200 reflections become indistinguishable from each other, in an hexagonal close packed structure.

On melting the crystalline reflection is substituted by a diffuse band, but is is admitted [42] that there is no drastic change in chain length. The large decrease in density is attributed to the larger volume required by a square packing, which is no longer resistent to shear, and therefore this form is liquid. Long spacings disappear in the liquid state but the chains are believed to stay roughly parallel to each other over short distances.

Therefore the picture of a liquid paraffin moiety shall not be confused with a highly disordered state of chain conformations. The random coiled polymer chain model is applicable [43] only to chains of sufficient length $(n > 1000)$ that are not perturbed by external forces, which is not at all the case of the rather short hydrocarbon chains under severe restrictions of packing of polar heads in these lyotropic liquid crystals.

Even linear polymers, that may take up a very large number of conformations by varying the angles of rotation around the bonds of the skeleton, stabilize in defined conformations [44] due to van der Waals interactions between nonbonded atoms. The trans-planar conformation of polyethylene corresponds to a minimum energy situation, while other polymers stabilize in helical conformations, all determined mainly by intra-molecular interactions. The uniform helices might be further stabilized in the crystal by the more favourable packing, but such polymers retain their most stable conformation, at least in short sections of the chain, also in the noncrystalline state.

Results for the structure and rotational isomerization of free short hydrocarbon chains $(n \leq 7)$ in the gas state [45] show that neither the random coiled nor the rigidly extended models apply. Trans and gauche conformations are present with probabilities related to the average free energy difference between the two conformations (~600 cal/mol). The lower stability of the gauche conformation is believed to result principally from steric repulsions between hydrogens in the gauche form.

Laser vibrational scattering studies in polymethylene chains [46] have shown that in the liquid state the all-trans conformation dominates for short chains ($n \leq 8$) but becomes vanishing small in favour of chain shortened forms as n increase. However, optical anisotropies of liquid polymethylene chains for n=1 to 44 revealed [47] anomalies ascribed to an intermolecular effect in the liquids, namely chain alignment in a parallel ordering.

Therefore to have a real picture of the conformational state of the paraffin chains in lyotropic liquid crystals it is necessary to analyse the specific constraints imposed by close packing and the possible sequences of trans and gauche conformations energetically favoured. For this it is worthwhile to review what is known about the state of hydrocarbon chains in micelles in isotropic solutions, about the chain order profile in lyomesophases obtained from NMR, and about the well studied melting transition of membrane bilayers.

3.2. Micelles in Isotropic Solutions

It is admitted [48] that in isotropic solutions micelles contain chains having both all-trans and partially gauche conformations, but the former predominates; chains in micelles possess more gauche conformations than chains in the crystalline state but fewer than those or surfactant molecules in solution.

Laser Raman scattering [49] has shown that the percentage of the all-trans form of the surfactant molecules in aqueous solutions increases with an increase in the concentration, with a remarkable change at the critical micellar concentration; the all-trans form is more stable in the micelles than in the monomolecular dispersion state.

The micellar change or growth into larger structures at high concentrations of surfactants or in the presence of added electrolyte is a well established phenomenum [50]. With increase of amphiphile concentration there occurs in the isotropic solution a transition from spherical to cylindrical micelles. Laser Raman scattering evidence [50] gauche and all-trans forms in the micellar core, but the studies show a greater ordering of the HC chains in the rod shaped compared to the sphere shaped aggregates.

The picture inside micelles is one of atoms adjacent to the polar head group in a rigid structure while there are liquid like structures associated with the C atoms towards the ends of the chains.

Recent studies [51] propose partial movements out from and back into micelle without the monomer leaving the micelle. The picture emerging from these calculations is one of a very dynamic micellar surface with frequent and rather large protusions of monomers out from the hydrophobic core. The surface of the micelle is proposed to have a very high degree of roughness.

It has been argued [4] that in nonlamellar phases the chains must be folded in a fairly irregular way to fill uniformly the oddly shaped volume offered to them. However, packing of actual models of hydrocarbon chains is spherical [48] and cylindrical [52] micelles is a difficult task both for all--trans and for chaotically disordered chains. The conclusion drawn from the geometrical packing is that there must be water penetration into the micelles untill the first 4 to 6 carbons. Folding does not eliminate aqueous cavities within the micelle;

it reduces the CH_2-water contact, but less than one might think.

3.3. The Chain Order Profile in Lyomesophases

The NMR study of amphiphilic molecules with deuterated methylene groups in lyotropic liquid crystals gives the order parameter of the C-D bonds of these groups with respect to the external magnetic field. The profile of the order parameter has been obtained for lyotropic mesophases of types I and II [7-9,17] as well as for lamellar and hexagonal ones [53]. Differences due to overall motions of the molecule result in lower absolute values in the measured splittings for types I and II mesophases, but the chain profile is essentially the same for all types of structure and the disorder increases in very similar way from the polar head towards the methyl ends of chains. The order decreases from the polar head to the third carbon atom, then it stays almost constant in the middle part of the chain and finally shows a rapid decrease for the terminal 2-4 segments. This profile has been interpreted in terms of local behavior dominated by water-surfactant interactions for the first carbons and by interchain interactions for the rest of the chain.

The profile of order obtained in lyomesophases is neither that of an all-trans configuration of the fully extended chain, existent in the solid state, nor that of a highly disordered chain as proposed for lyomesophases since the early works on structure determination [1,4]. Typical order parameters S_{C-D} range form 0.05 to 0.2 .

3.4. The Transition in Membranes

Biomembranes and phospholipid bilayers present a thermally induced phase transition known to involve a change in the state of the hydrocarbon chains in the interior of the bilayer [54,55]; this transition is considered to be analogous to the gel-liquid crystalline transition in lipid bilayers and involves a change from a highly ordered state with the chains in almost all trans conformations to a more disordered state with some gauche rotations in the chain bonds. The profile of the order parameter of the C-D bond for phospholipid bilayers in the disordered state is of the same type as for lyotropic mesophases.

Two types of conformational changes may be considered [55]:

1) isolated gauche conformations - these are highly improbable except in the central part of the bilayer, since close to the polar head interface it disrupts the parallel packing of the hydrocarbon chains;

2) formation of a kink sequence ($g^{\pm}$ t $g^{\mp}$)- Trans sequences before and after the kink remain parallel to each other. The formation of a kink introduces only a small local defect into the bilayer, but the length of the chain is reduced by 1.25 Å .

Collective tilt of the hydrocarbon chains in the disordered state with a lifetime longer than 10^{-6} sec is excluded from experimental results [55].

Recent statistical mechanical models for this transition make extensive use of the idea of kinks [55-57]. If it is assumed that the kink is not localized at a certain segment but is fluctuating up and down the chain, the model [55,56] leads to a constant order parameter for all segments; however the probability of a kink decreases in the central part of the bilayer.

The more coherent model [55,56] accepts that in about two thirds of the bilayer cross section coupled gauche rotations (mainly kinks) are preferred in order to facilitate a mostly parallel packing of the chains, leading to the picture of disordered chains in an ordered bilayer. In the central part of the bilayer the steric constraints are relieved and the probability of simple gauche conformations increases. The calculated [55,56] fraction of trans bonds is 0.7 and of gauche bonds is 0.3 . These figures are common to many models for this order-disorder transition [54,57].

For a hydrocarbon chain with $n=10$ this could correspond to one fluctuating kink in the middle part of the chain and a single gauche more to the chain end.

Summing up all this discussion, it can be concluded that the so-called "disordered" state of the hydrocarbon chains corresponds, for all structural types of lyotropic mesophases, to a situation of rather parallel hydrocarbon chains, with kinks in the middle part of the chains and bending at the end, with a resulting shortening of the chain length and increase of area per molecule.

Coming back to the discussion of the previous item it is possible now to conclude that the effect of the shape anisotropy of the micelles is negligeable in front of the molecular diamagnetic anisotropy of the methylene groups, which must be the determining factor for the magnetic orientation of these lyomesophases.

4. ORDER PARAMETER IN LYOTROPIC NEMATICS

It is necessary to discuss now the meaning of the order parameter S in the case of flexible molecules in a flexible micelle.

For a rigid molecule with cylindrical symmetry the order parameter of an atomic bond, such as S_{C-D} , can give the molecular order parameter S_{mol} in relation to the magnetic field, or in relation to the director if the angle between $\vec{n}$ and $\vec{H}$ is known. In this case the microscopic order parameter coincides with the macroscopic order parameter S .

For a flexible molecule the proportionality does not hold anymore and in particular it does not hold when S_{C-D} varies along the chain. The limitation of this approach has been discussed recently [58] in connection with NMR results in flexible thermotropic nematogens. In a more exact approach a single ordering matrix cannot describe the orientational order for non-rigid mesogens and it would be necessary to describe each conformation adopted by a molecule with a separate ordering matrix.

However, in a first approach to the problem of nematic lyotropics, it is reasonable to accept the existence of an average value S_{mol} possible to obtain from the chain order profile of S_{C-D} . In particular, since in these lyomesophases the diamagnetic anisotropy comes from the methylene groups, the value of S_{mol} obtained from S_{C-D} shall give a reasonable estimate of the order parameter related to the diamagnetic anisotropy of the macroscopy sample.

This order parameter S_{mol} refers to all fluctuations of the molecular average axis, including those of the micellar unit as a whole.

On the other hand, for these lyomesophases the basic unit is the anisotropic micelle and it is meaningfull to define a micellar director as the symmetry axis of the micellar unit. This is a simplification, since the micelles are also flexible and dynamically changing entities, but in a first approach it is possible to define a local micellar director $\vec{n}$ as the average symmetry axis of the micelle. This director $\vec{n}$ will be the cylinder axis in the case of cylindrical micelles and will be normal to the planar bilayer in the case of planar micelles.

It is then possible to define an external order parameter as

$$S_{ext} = \frac{1}{2} \langle 3 \cos^2 \theta - 1 \rangle \quad ,$$

where θ is the angle between the local micellar director $\vec{n}$ and the bulk director $\vec{N}$, defined as the average value of $\vec{n}$.

A definite direction $\vec{N}$ may result from interactions that tend to orient the mesophase, such as applied external fields or sample walls. In the case of a sample oriented in an external magnetic field $\vec{N}$ may be parallel to $\vec{H}$ (type I lyomesophases with $\Delta\chi > 0$) or perpendicular to $\vec{H}$ (type II lyomesophases with $\Delta\chi < 0$).

The two order parameters S_{mol} and S_{ext} are related through

$$S_{mol} = S_{int} S_{ext} \quad ,$$

where S_{int} is the order parameter relating the fluctuations of the average molecular axis to the average local micellar director $\vec{n}$.

Since there is an intrinsic order among amphiphilic molecules within a micelle S_{int} is a well defined quantity for given conditions of the lyomesophases, even in the absence of external fields. It is expected that S_{int} varies with the mesophases composition, since it is known that the degree of conformational order of the chains varies with the amount of water as well as with the presence of additives and the specific polar heads and counter ions.

The advantage of making this separation is that S_{ext} may be experimentally obtained from X-ray diffraction results in oriented samples, since this technique gives information about the orientational order of the diffracting unit [59,60]; the X-ray method does not give a very accurate result but can give approximate values for this order parameter. Besides, many macroscopic properties of the lyomesophases are related to S_{ext} and in fact any attempt to apply elastic continuum theory to these lyomesophases must consider the field of the local micellar director $\vec{n}$ and not the individual molecular axis.

Other properties, however, that depend on interactions at the individual molecular level, will be sensitive to S_{mol}.

The order parameter S_{int} is not directly measurable, but can be compared with results for S_{mol} in conditions where $S_{ext} \cong 1$, for instance, classical lamellar and hexagonal mesophases. Information about S_{int} may also be obtained from ratios of NMR splittings [17,61] that cancel S_{ext}.

However the two order parameters S_{int} and S_{ext} are not independent quantities. For instance, magnetic alignment occurs because there is a $S_{int} \neq 0$, but the resulting S_{ext} will depend also on the coupling between the micelles and the particular characteristics of the solvent medium.

To have some orders of magnitude, values of S_{mol} obtained for lipid bilayers [53,55] are of the same order as those obtained for phospholipid bilayers [55] with a typical value of 0.4 in the plateau. Nematic lyotropics present order parameters about 30% to 60% lower [17,21]. This would give as typical orders of magnitude $S_{int} \sim 0.4$, $S_{mol} \sim 0,25$ and $S_{ext} \sim 0.6$.

From our experience with X-ray diffraction, this is a reasonable estimate for S_{ext}. In some conditions of very well aligned samples the order parameter S_{ext} may be higher than S

for thermotropic nematics, while the order parameter S_{mol} is in general lower in lyotropic than in thermotropic nematics.

5. COMPARISON BETWEEN THERMOTROPIC AND LYOTROPIC NEMATICS

One comes now to the question of whether these lyomesophases could be treated as normal nematics, specially in what regards the applicability of elastic continuum theory.

Textures seen in a polarizing microscope are very similar to those of thermotropic nematics, suggesting at least a qualitative similarity for both [15,18,21]. However quantitative differences are considerable, specially regarding relaxation times. Orientation times are 10^4 times larger for lyotropics, being typically of 0.1 sec for thermotropics and several minutes to hours or even days for lyotropics. The fact that the process of disorientation can have an almost infinite relaxation time, with a residual orientation in the absence of magnetic fields almost permanent, finds no counterpart in thermotropic nematics and is reminiscent of the behavior of smectic phases once aligned.

Relaxation times for thermotropic nematics are given by [24]

$$\tau_{rise} = \frac{\eta}{\Delta X^2 - K q^2} \qquad \text{(in presence of } \vec{H}\text{)}$$

$$\tau_{decay} = \frac{\eta}{K q^2} \qquad \text{(in absence of } \vec{H}\text{)} ,$$

where η is the medium viscosity, K an average elastic constant and q a wave vector of the perturbation, that can be approximated to $q \sim \pi/d$, d being the sample thickness.

An estimate has been made [21] that K should be two orders of magnitude smaller in lyotropics than in thermotropics, but this would not account for the residual orientation observed. The anisotropy ΔX can be one order of magnitude smaller in lyotropics, but this also does not explain the 10^4 difference in orientation times.

It must therefore be concluded that the elastic theory cannot be applied to lyotropics without adaptations. Some obvious differences regard the fact that the micellar size is much larger than the molecular size and this fact may turn difficult a continuum approach; however the textures for these lyomesophases show that this is not the more important point. Also for type II lyomesophases the theory developed for rods does not apply directly.

There is however still another difference between thermotropic nematics and these lyomesophases that seems to constitute a major difficulty for the application of the usual continuum theory.

Our X-ray diffraction results [11-14,16] have evidenced that one of the most basic characteristics of these lyomesophases is the formation of aggregates of micelles keeping only solvation water between micelles with seggregation of the excess disordered water. In other words, there is not in these lyomesophases a homogeneous distribution of the micelles in the solvent medium. The formation of these aggregates depends critically on interactions with the sample walls; an applied magnetic field has also the effect of nucleating such aggregates.

This phenomenon of aggregation of the micellar units occurs both because these lyomesophases are formed with excess water and because the addition of an electrolyte causes a screening of the eletrostatic repulsion between the charged micelles.

The effect of occurrence of the so-called tactoids in diluted gels has been observed undoubtedly by X-ray studies of the repeat distance in function of concentration [62]. In such case there occurs a mixture between a more concentrated phase and a more diluted one, very finely dispersed in one another. Even in more concentrated colloids the addition of electrolyte may cause flocculation.

The evidence accumulated by X-ray results in our laboratory for both types I and II mesophases clearly indicates that there is formation of aggregates of micelles, separated by the excess water, in a very delicate equilibrium, so that the hypothesis of homogeneous distribution of mass does not hold.

Moreover, within these aggregates there is a higher degree of order, with the formation of lamellar packing of platelets for type II and hexagonal packing of cylinders for type I.

It is possible that somewhat modified continuum theories, allowing for changes of the density, as it has been developed by de Gennes for the smectic phase [63] may have some success in describing these lyomesophases.

The next step in the study of these systems must be the analysis of the balance of forces between interacting micelles, including Van der Walls attractive forces, coulombian repulsion between charged micelles, in presence of high ionic strenght, and solvation forces.

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TABLE 1

Calculated molar diamagnetic susceptibility $\overline{\chi}_M$ and estimated percentual diamagnetic anisotropy $\Delta\chi/\overline{\chi}$.

molecule	$-\overline{\chi}_M/10^{-6}$ (emu/mol)	$\Delta\chi/\overline{\chi}$
Na decyl sulfate	165	9%
K laurate	155	10%
decanol	124	12%
Na_2SO_4	54	--
KCℓ	39	--