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A B S T R A C T

A study of a magnetically oriented lyomesophase formed by a quaternary system (Na decyl sulfate/water/decanol/ Na sulfate) is reported. Small angle X-ray diffraction measurements have been performed on unoriented samples and samples previously subjected to the action of magnetic fields ($\vec{H}$). Diffraction patterns show a diffuse inner halo at 80-140 Å and a sharp outer ring at 38 Å. They reduce to spots in the equator for oriented samples with the X-ray beam parallel to $\vec{H}$; no diffraction figure is produced for the X-ray beam perpendicular to $\vec{H}$. NMR spectra indicate that the director of the phase orients perpendicular to $\vec{H}$. These results show that this lyomesophase has a structure not previously encountered.

A model of finite planar micelles surrounded by water is proposed. In this model the micelles consist of a bilayer in the form of platelets, probably disk-shaped. These platelets align in presence of magnetic fields, with their plane parallel to $\vec{H}$, and further orientational restrictions are imposed by the container; they tend to be parallel and some periodicity appears in the direction of the director of the phase, perpendicular to the plane of polar heads. The mesophase satisfies the definition for nematics taking into account periodicities induced in nematic phases by magnetic fields.

I - INTRODUCTION

Lyotropic liquid crystals formed by binary lipid-water systems have been widely studied in unoriented mesophases; several types of uni, bi and even tridimensional structures have been discovered and studied by X-ray diffraction[1-4]. Ternary systems[5-7] (lipid-water-alcohol) and several multicomponent systems[8,9], presenting various mesophases over wide ranges of concentration and temperature, have also been studied by X-ray diffraction. The most common lyomesophases are the neat soap (lamellar) and the middle soap (cylindrical micelles with hexagonal order in two dimensions). Effects of orientation due to the container have been observed in lyotropic mesophases found in surfactant and lipid systems[10].

Quaternary systems, formed by a mixture of C_8 or C_{10} alkyl sulfates, the corresponding alcohol, sodium sulfate and water, produce mesophases that orient in magnetic fields and can be used as orientation matrix for NMR studies[11,12]. Magnetically oriented lyomesophases have been explored by Reeves and colaborators with NMR technique[13-19]. The study of ternary systems (detergents with decyl sulfate anion, decanol and D_2O), investigating the influence of detergent counterion and temperature variations, revealed the existence of two types of lyomesophases, seeming to be of a nematic type[18,19]; they have been classified as types I and II depending on whether the uniaxial nematic axis orients parallel or perpendicular to the magnetic field direction. Phase transitions have been observed as a function of composition and temperature; the addition of sodium sulfate to the ternary system leads to a type II mesophase[16,19]. Until recently[20,21]

no X-ray diffraction had been performed on these particular systems nor on magnetically oriented lyotropic liquid crystals.

Spontaneous alignment of uniaxial thermotropic nematic liquid crystals has been widely explored[22-24]; this phenomenon results from the anisotropy of the magnetic susceptibility, due to diamagnetic properties of anisotropic molecules. While in nematics spontaneous orientation occurs in the presence of magnetic fields, magnetically oriented thermotropic smectic mesophases can be obtained only by cooling in magnetic fields through the nematic/smetic 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 kilogauss; 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 hours.

This paper presents the study of a lyomesophase formed by a quaternary system (Na decyl sulfate/water/decanol/Na sulfate), that has the property of spontaneous orientation in the presence of magnetic fields. A particular and unusual characteristic of these magnetically oriented lyomesophases is that, in spite of being rather fluid, they remain oriented for several months after having been exposed to magnetic fields. In order to determine the structure of this lyomesophase, small angle X-ray diffraction has been performed on unoriented and oriented samples. NMR measurements have also been performed on the same sample.

II - EXPERIMENTAL

Quaternary lyomesophases were prepared with 37 wt% sodium decyl sulfate (prepared by sulfonation of 1-decanol[19]), 5 wt% sodium sulfate (commercial, highly pure), 53 wt% water (destilated) and 5 wt% decanol (destilated). The components were mixed to form a homogeneous phase by centrifuging at slightly elevated temperatures. Care was taken to avoid hydrolysis which occurs to an appreciable extent at temperatures higher than 60°C.

X-ray diffraction patterns were obtained by photographing technique using a small angle Rigaku-Denki diffractometer, operated with a 2 kW Cu tube, in a transmission geometry. The observable range is from 500 to 13 Å. Point and line focus were employed and CuK_α radiation was obtained with a Ni filter. Line focus has the advantage of higher intensity, but the diffraction figure can be interpreted only with the aid of point focus results, especially when orientational effects are present. Film measurements were made with a film measuring rule and by scanning the films on a microdensitometer. The higher angle region was explored with a Debye-Scherrer camera and a conventional diffractometer.

Two types of sample holders were employed. One of them consists of a sandwich of three rectangular plates with holes 2 x 1.5 mm in the center; the two outer are metallic plates screwed to an inner spacer of teflon 1.4 mm thick, where the sample is placed between very thin mylar walls. This container has the advantage of almost no interactions with the X-ray beam; however, although a rubber pellicle is used to avoid leakage, the sample is not perfectly sealed, losing water with time, and

it is not possible to keep a constant composition. Besides, the geometry of the sample is not suitable for magnetic orientation studies. In addition to the first sample holder, thin-walled glass capillaries of 1.5-2 mm diameter, held in a metallic block and sealed off, were used to condition the sample; the atenuation was very high and exposure times were of the order of 90 hours for point focus and 30 hours for line focus.

The influence of magnetic orientation was tested in a series of small angle experiments: first, diffraction of the sample not subjected to magnetic field was obtained (S_o). Afterwards, the sample stayed for 48 hours in a magnetic field $\vec{H}$ of ca. 2 kG, perpendicular to the capillary axis; later, diffraction patterns were obtained with the X-ray beam parallel and perpendicular to the direction of $\vec{H}$ (respectively $S_{\parallel}$ and $S_{\perp}$). Such series of mesurements were performed with line and point focus; each series was repeated twice, with new samples, and results were reproduced consistently. Table I shows the various experimental conditions.

The liquid crystalline state of the sample was verified by checking its birefringency under crossed polarizers, before and after the X-ray exposition. The temperature in the surroundings of the sample was controlled, being (26 ± 2) ^{o}C.

This same lyomesophase was observed in a XL-100-12-FT Varian NMR spectrometer, with the gyrocode option, for measuring spectra of protons and other convenient nuclei. Samples were prepared in NMR sample tubes.

III - RESULTS AND DISCUSSION

Lyomesophases with similar compositions were widely studied by NMR[11-19,29,30]. The state of the lyomesophase can be monitored by the broad line of the proton NMR spectra or by the quadrupole splittings of ^{23}Na or ^{2}H [18,19]. For type II phases[19] the broad line under the water signal, of about 2.5 kHz half-width in the proton spectrum, remains unchanged, even with sample spinning about an axis perpendicular to $\vec{H}$. For type I, this broad line disappears with sample spinning and a "super Lorentzian" line[31] is recorded.

Our NMR results indicate that the mesophase is of type II, with the phase director oriented perpendicular to the magnetic field.

The small angle X-ray diffraction pattern obtained with point focus and using the sample holder with mylar parallel walls is shown in figure 1. This figure shows a diffuse inner isotropic halo and a sharper outer ring with a certain degree of orientation, corresponding to 90 $\mathring{A}$ and 37 $\mathring{A}$, respectively. This diffraction pattern differs from reported results on lyomesophases in several points: there are only two diffraction maxima and they differ in broadness and degree of orientation; interplanar spacings obtained on the basis of Bragg's law do not resemble those expected for regular structures.

These facts indicate that no regular superstructure seems to be present and that the two rings cannot be simply interpreted in terms of uni, bi or tridimensional structures. The diffraction pattern resembles more the results obtained by de Vries on thermotropics[32], where a sharper inner ring and a

diffuse outer ring were interpreted in terms of molecular length and intermolecular average distance, in a so-called cybotactic nematic phase. This first diffraction result cannot lead to a model for the superstructure, but shows orientational effects due to the container.

Figures 2 through 5 show small angle X-ray diffraction results obtained with glass capillaries as sample holders under conditions specified in Table I. With point focus, for S_o (Fig.2) there is only a weak diffuse inner halo, with some degree of orientation along the equator, perpendicular to the capillary axis. For $S_{||}$ (Fig.3) there are a diffuse inner spot and a sharp, but weaker, outer spot which appear along the equator; this indicates a strong orientation of the sample. Diffraction patterns obtained with line focus correspond essentially to point focus results superposed for the point beam dislocating along a line. For S_o (Fig.4) a diffuse inner band and a weak outer line can be observed. For $S_{||}$ (Fig.5) the diffuse inner band is very strong and the sharp outer line can be very clearly seen. For $S_{\perp}$ no diffraction pattern is observed neither for point nor for line focus.

From Bragg's law, the sharp outer maximum corresponds to (38 ± 1) Å. The diffuse inner band extends from 70 Å to 160 Å, having sometimes two maxima at (90 ± 4) Å and (135 ± 4) Å and a minimum at (110 ± 2) Å. Higher angle X-ray measurements showed that no other diffraction maxima due to the superstructure are present.

While it is very difficult to determine the structure from so few maxima, it is possible to make an analysis according to the more common models of lamellae and cylindrical micelles. Spherical micelles are ruled out by the optical anisotropy of the

mesophase. Regular uni, bi or tridimensional structures are ruled out for reasons mentioned in the first diffraction pattern analysis.

The volume composition of the system was calculated from tabulated densities and molecular masses and from an estimate of length and volume of hydrocarbon chains[21,33]. An estimate of electronic densities gave 1.2 e/$\mathring{A}^3$ for the polar head, 0.27 e/$\mathring{A}^3$ for the paraffin tail and 0.33 e/$\mathring{A}^3$ for the water. This means that X-ray scattering is due mainly to polar heads and that X-rays almost do not differentiate between paraffin tails and water. This is not unusual for lyomesophases[9]. The estimated length of Na decyl sulfate, including the hydrocarbon chain and the polar head, is 18.75 $\mathring{A}$; thus for a bilayer the estimated thickness is 37.5 $\mathring{A}$.

The results obtained with oriented samples eliminate the possibility of a nematic structure with finite cylindrical micelles; let's analyse why:

a) Cylinder axis parallel to $\vec{H}$ - one could expect two rings for $S_{\parallel}$, one related to the average distance between cylinders and another one related to the distance between polar heads in each cylinder. For $S_{\perp}$ these rings would reduce to spots along the meridian perpendicular to the equator.

b) Cylinder axis perpendicular to $\vec{H}$ - with this only restriction, the cylinder axes could be distributed in any direction in a plane perpendicular to $\vec{H}$, what would give isotropic scattering for $S_{\parallel}$. The observed preferred orientation along the equator would indicate a further restriction, with the cylinder

axis parallel to the capillary axis. However, for such a model, the diffraction pattern obtained when turning the capillary around its axis should remain the same.

c) no angle between the cylinder axis and $\vec{H}$ could explain the observed diffraction results.

However the possibility of lamellae not forming a regular unidimensional superstructure remains. This possibility is the basis for the model for the mesophase presented below.

IV - PROPOSED MODEL

To explain the absence of diffraction for $S_{\perp}$, it is necessary to assume that, in the plane perpendicular to the beam, there is no characteristic distance giving diffraction at small angle. This could correspond to the lamellar plane containing the polar heads. On the other hand, for $S_{\parallel}$ the equatorial maxima indicate the existence of lamellae with the planes of polar heads in the vertical direction, but without formation of a unidimensional lattice.

Based on these X-ray diffraction results, we propose a model of planar micelles of large but finite dimensions, forming platelets of amphiphile surrounded by water; these platelets orient in presence of magnetic fields, as shown in figure 6.

As there are no diffraction maxima for $S_{\perp}$, the average distance between the centers of platelets, in the direction of the polar heads plane, must be very large, over 500 Å, indicating an average radius for the platelets larger than 250 Å. The most probable form for these platelets would be disk-type micelles.

The diffraction results for $S_{\parallel}$ and $S_{\perp}$ indicate that the platelets are parallel and thus the plane of the polar heads is parallel to $\vec{H}$, with a further restriction: this plane is preferentially parallel to a plane defined by the field direction and the capillary axis. This further restriction is probably due to the sample holder, whose orientational effects add to the magnetic orientation.

As there are only two maxima and the interplanar spacings do not correspond to a lamellar structure (d;d/2;d/3; d/4;etc.), one might initially suppose that the diffraction pattern corresponds to a nematic type of structure, with planar micelles. One might then interpret the outer maximum at 38 Å as the bilayer thickness (distance between two polar heads) and the inner band as an average distance between platelets.

However, the width of the sharp outer maximum is too small to be associated with diffraction by one platelet; as these platelets tend to be parallel, it seems that some periodicity appears in the direction perpendicular to the polar heads plane. It seems better therefore to assume diffraction by multiple planes. According to Scherrer's formula, the observed width corresponds to about 20 planes , indicating that some periodicity extends to about 1000 Å. Thus this outer maximum should perhaps be interpreted in terms of a Bragg reflection.

On the other hand, the diffuse inner band corresponds to a few planes, according to Scherrer's equation. This band can therefore be interpreted in terms of diffraction by particles and gives an average distance between micelles in the direction perpendicular to the planes. Accepting this distance

as a rough estimate it is meaningless to correct Bragg's formula by any correction factor[34].

Taking into account the evidence of periodicity given by the sharpness of the outer maximum, it is worthwhile to analyse in more detail the possibility of a regular lamellar model. This is done in the Appendix. The analysis in the Appendix suggests that the 38 Å peak might be a (300) reflection from a bilayered structure of repetition distance (114 ± 3) Å. The (300) reflection would be four times stronger than the first and second order reflections.

It is expected that this (300) reflection appears only when there is enough periodicity, which happens when the platelets remain parallel and with constant water separation. When the planar micelles are not perfectly parallel or when the amount of water separating them varies, there is no long range order any more and one can only talk about an average distance between platelets associated with the diffuse inner band, characteristic of a nematic arrangement. This leads to the conclusion that this lyomesophase falls somewhere in between the lamellar and the nematic mesophases. The mesophase satisfies the definition for nematic taking into account periodicities induced in nematic phases by magnetic fields[35].

V - CONCLUSIONS

It is clear both from the results presented here and from the previous NMR studies that this lyomesophase cannot be classified among the already established structures for lyomesophases and inaugurates a new class of structures.

We believe that this type II lyomesophase cannot be modeled in terms of spherical and cylindrical micelles but rather in terms of finite planar micelles, made of a bilayer (membrane like), in the form of platelets, probably disk-shaped, surrounded by water. These platelets align in presence of magnetic fields, with their plane parallel to $\vec{H}$, and further orientational restrictions are imposed by the container; they tend to be parallel and to have some periodicity, forming a structure with characteristics between the lamellar and the nematic mesophases. Perhaps the idea of cybotactic nematic groups of de Vries[32] could also apply to these lyomesophases.

Another evidence giving credibility to our proposed model is the fact that a binary system (decylammonium chloride/water) known to have a lamellar structure[6,8] produces a type II mesophase by addition of small amounts of electrolyte[16]. Lamellar and type II mesophases co-exist in a small concentration region and appear to form an equilibrium mixture[16]. We suggest the break of extended lamellae into the proposed platelets as a possible mechanism for the lamellar/type II transition.

It is not possible however to exclude more complex models for the studied type II mesophase, involving variable concentrations of planar micelles and water with periodic and aperiodic regions, undulated micelles, or equilibrium among these forms. The inner band has sometimes two maxima and a minimum, and for the detailed interpretation of this band quantitative results using detector are in progress. To ascertain whether the outer maximum is directly related to the bilayer thickness or whether it is a higher order reflection from a semiperiodic structure, it would be necessary to study systems with different

concentrations and different bilayer thicknesses.

Diffraction patterns in a Debye-Scherrer camera do not show the characteristic band of liquid paraffin, indicating that within the micelles the paraffin chains retain a certain degree of order. This result is in agreement with chain order profiles from NMR that indicate a decreasing order from the methylenes near the polar head to the final methyl groups[16,17].

This mesophase has been classifield as type II by NMR (director of the phase perpendicular to $\vec{H}$); this corresponds to a director perpendicular to the platelet which is reasonable. The magnetic orientation observed, with the plane of polar heads parallel to $\vec{H}$, is in agreement with the fact that extended carbon chains tend to be perpendicular to the magnetic field[36].

The study of type II mesophases by NMR during sample spinning perpendicular to the magnetic field suggests that the sample rotation causes the director to take up the unique direction perpendicular to the field and parallel to the spinning axis. The usual NMR practice has shown that this process is not instantaneous but requires a few minutes to several hours, depending on the viscosity of the sample. On the other hand, X-ray diffraction has shown that in static condition the director is in the unique direction perpendicular both to the field and to the capillary axis. We therefore conclude that magnetic orientation induces the director of the mesophase to be perpendicular to the field, but other influences, such as the sample container or dynamical forces of spinning, can add further restrictions to the orientation of the platelets. The influence of sample container on the orientation of this lyomesophase is being studied further by X-ray diffraction in our laboratory.

The reason for the residual magnetic orientation in a sample rather fluid and without a magnetic atom is still an open question.

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APPENDIX

ANALYSIS IN TERMS OF A LAMELLAR STRUCTURE

For this lyomesophase X-rays practically do not differentiate between water an paraffin tails and are scattered mainly by polar heads. Thus the repetition unit (water plus detergent) can be considered in first approximation as three polar head layers in a homogeneous medium, as shown in figure 7. The relative position of the middle layer depends on the sample composition and defines the structure factor for the several reflections; this relative position can be defined by the parameter $u = d_{\ell}/d$, where d is the repetition distance and d_{ℓ} the distance between centers of polar heads in the amphiphile. Table II gives the structure factor for the first four reflections of a unidimensional lattice as a function of u, considering point scattering.

u can be estimated from the volume composition of the sample, assuming homogeneous distribution. The components of the system expected to build the micelles (amphiphile plus alcohol) correspond to 38% of the total volume[31].

For a bilayer model, it is possible to estimate the thickness of the water layer from the calculated length of the detergent bilayer which results in a value of 61.2 Å. The radius of the polar head has been estimated at 2.3 Å[31]; thus the distance between centers of polar heads is d_w=65.8 Å = $d-d_{\ell}$.

For a monolayer model the thickness of the water layer is estimated at 30.6 Å and the distance between centers of polar heads is d_w=35.2 Å.

These are rough estimates, but we can say that one would expect d ~100 Å with u=1/3 for a bilayer model, and d ~50 Å with u=1/3.5 for a monolayer model.

The sharp 38 Å peak cannot be interpreted as a first order reflection, neither for a bilayer nor for a monolayer model. The only possible assignment would be a (300) reflection from a bilayered structure with d = 114 Å and u = 1/3, which gives a third order four times stronger than the first, second and fourth orders.

REFERENCES

1 V.Luzzati, H.Mustacchi and A.Skoulios, Nature 180, 600 (1957); Disc.Faraday Soc. 25, 43 (1958).

2 V.Luzzati, H.Mustacchi, A.Skoulios, F.Husson, Acta Cryst. 13, 660 (1960).

3 F.Husson, H.Mustacchi and V.Luzzati, Acta Cryst. 13, 668 (1960).

4 V.Luzzati in Biological Membranes, p.71-123, ed. D.Chapman (Academic Press, London and N.York, 1968).

5 L.Mandell, K.Fontell and P.Ekwall in Ordered Fluids and Liquid Crystals, ed. R.S.Porter and J.I.Johnson, Adv.Chem.Series 63, 89-124 (1967).

6 P.Ekwall, L.Mandell and K.Fontell, J.Colloid and Interface Sci. 31, 508-539 (1969).

7 P.Ekwall in Advances in Liquid Crystals, vol. 1, pp.1-142, ed. G.H.Brown (Academic Press, New York, San Francisco, London 1975).

8 P.A.Winsor, Chem.Rev. 68, 1-40 (1968).

9 G.J.T.Tiddy and B.A.Wheeler, J.Colloid and Interface Sc. 47, 59 (1974).

10 K.D.Lawson, A.J.Mabis and T.J.Flautt, J.Phys.Chem. 72, 2058 (1968).

11 K.D.Lawson and T.J.Flautt, J.Am.Chem.Soc. 89, 5489 (1967).

12 P.J.Black, K.D.Lawson and T.J.Flautt, J.Chem.Phys. 50, 542 (1969).

13 L.W.Reeves, J.Sanches de Cara, M.Suzuki and A.S.Tracey, Mol. Phys. 25, 1481 (1973).

14 K.Radley and L.W.Reeves, Can.J.Chem. 53, 2998 (1975).

15 L.W.Reeves and A.S.Tracey, J.Am.Chem.Soc. 97, 5729 (1975).

16 D.M.Chen, F.Y.Fujiwara and L.W.Reeves, Can J.Chem. 55, 2396 (1977); 55, 2404 (1977).

17 F.Y.Fujiwara and L.W.Reeves, J.Am.Chem.Soc. 98,6790 (1976).

18 D.M.Chen, K.Radley and L.W.Reeves, J.Am.Chem.Soc. 96, 5251 (1974).

19 K.Radley, L.W.Reeves and A.S.Tracey, J.Phys.Chem. 80, 174 (1976).

20 L.Q.Amaral, C.A.Pimentel and M.R.Tavares, Acta Cryst. A34

(Supplement S4) S 188 (1978).

21 M.R.Tavares, Master Dissertation (Instituto de Física da Universidade de São Paulo, 1978).

22 G.H.Brown, J.W.Doane and V.D.Neff, A Review of the Structure and Physical Properties of Liquid Crystals (CRC Press, Cleveland, 1971).

23 P.G.de Gennes, The Physics of Liquid Crystals (Clarendon Press, Oxford, 1974).

24 H.S.Subramhanyam and D.Krishnamurti, Mol.Cryst. & Liquid Cryst. 22, 239 (1973).

25 C.S.Yannoni, J.Am.Chem.Soc. 91, 4611 (1969).

26 Z.Luz and S.Meiboom, J.Chem.Phys. 59, 275 (1973).

27 S.Meiboom and Z.Luz, Mol.Cryst. & Liquid Cryst. 22, 143 (1973).

28 A.Johansson and T.Drakenberg, Mol.Cryst. & Liquid Crist. 14, 23 (1971).

29 M.Suzuki, Ms.Dissertation (Instituto de Química da Universidade de São Paulo, Brasil, 1974).

30 J.A.Vanin, Ph.D.Thesis (Instituto de Química da Universidade de São Paulo, Brasil, 1974).

31 T.J.Flautt and K.D.Lawson, Adv.Chem.Series 63, 26 (1967).

32 A.de Vries, Mol.Cryst. & Liquid Crystals 10, 219 (1970); 11, 361 (1970); 20, 119 (1973).

33 J.E.Leibner and J.Jacobus, J.Phys.Chem. 81, 130 (1977).

34 A.Guinier and G.Fournet, Small-Angle Scattering of X-Ray (John Willey and Sons, New York, 1955).

35 A.Sakamoto and U.Kubo, Mol.Cryst. & Liquid Cryst. 43, 249 (1977).

36 J.A.Pople, W.G.Schneider and H.J.Bernstein, High Resolution Nuclear Magnetic Resonance (Mc Graw Hill, New York, 1959).

TABLE I

Experimental conditions of series of small angle diffraction measurements: sample not subjected to magnetic field $\vec{H}$ (S_o) and samples previously oriented with $\vec{H}$ parallel and perpendicular to the X-ray beam ($S_{\parallel}$ and $S_{\perp}$).

geometry	sample holder	sample orientation	figure
point focus	parallel mylar walls	S_o	1
point focus	glass capillary	S_o	2
		$S_{\parallel}$	3
		$S_{\perp}$	no diffraction
line focus	glass capillary	S_o	4
		$S_{\parallel}$	5
		$S_{\perp}$	no diffraction

. TABLE II

Structure factor F^2/f^2 as a function of the relative position u of the middle polar head layer for the several reflections h.

h \ u	1/2	1/2.5	1/2.8	1/3	1/4
1	0	.38	.75	1	2
2	4	2.62	1.55	1	0
3	0	2.62	3.80	4	2
4	4	.38	.20	1	4

. FIGURE CAPTIONS

Fig. 1 - Diffraction pattern S_o with point focus; sample container with parallel mylar walls. The outer ring is double because unfiltered Cu radiation was used in this case.

Fig. 2 - Diffraction pattern S_o with point focus; capillary in vertical direction. Only the diffuse inner halo appears, with a certain degree of orientation.

Fig. 3 - Diffraction pattern $S_{||}$ with point focus; capillary in vertical direction. Besides the diffuse inner spot, the negative shows a weak outer arc centered in the equator.

Fig. 4 - Diffraction pattern S_o with line focus; capillary in vertical direction. Besides the diffuse inner band, a weak sharp outer line can be seen in the negative.

Fig. 5 - Diffraction pattern $S_{||}$ with line focus; capillary in the vertical direction. In the part more oriented of the sample, the sharp outer line appears clearly.

Fig. 6 - Proposed model for type II lyomesophase: finite planar micelles, forming platelets of amphiphilic bilayer, probably disk-shaped, surrounded by water. The plane of polar heads aligns in the direction of the magnetic field $\vec{H}$.

Fig. 7 - Schematic representation of a unidimensional lattice in case of lamellar model with repetition distance $d = d_w + d_\ell$.

FIGURA 1

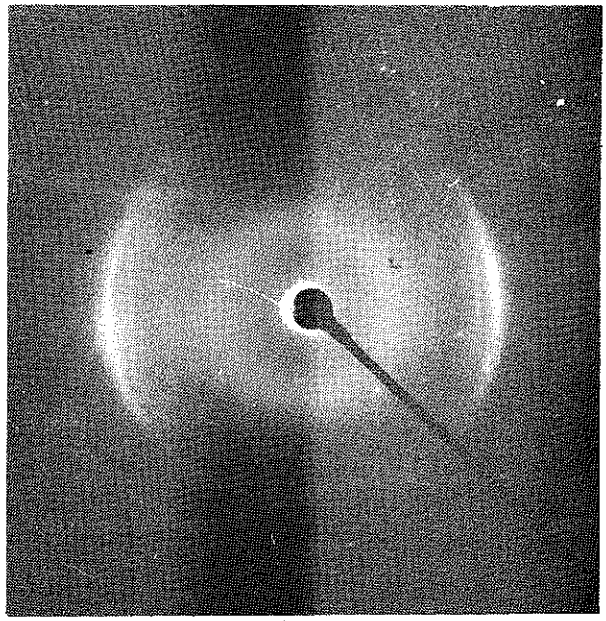

FIGURA 2

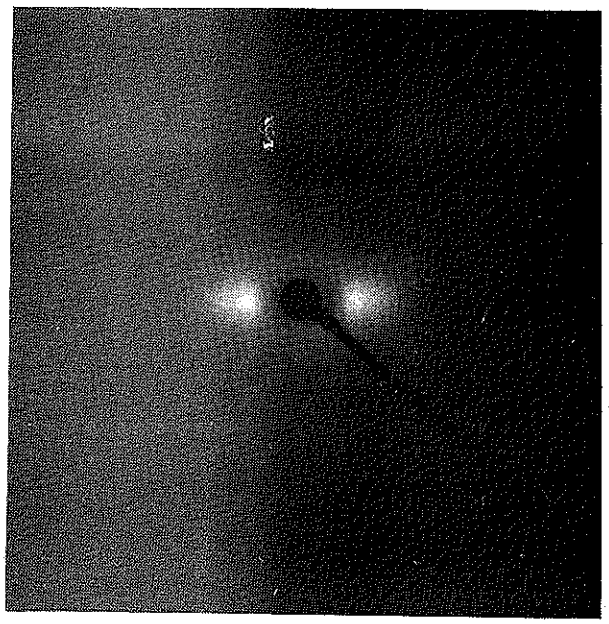

FIGURA 3

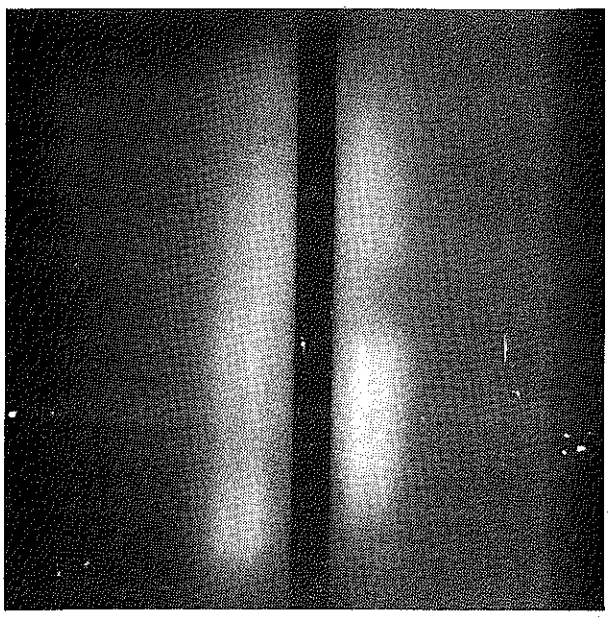

FIGURA 4

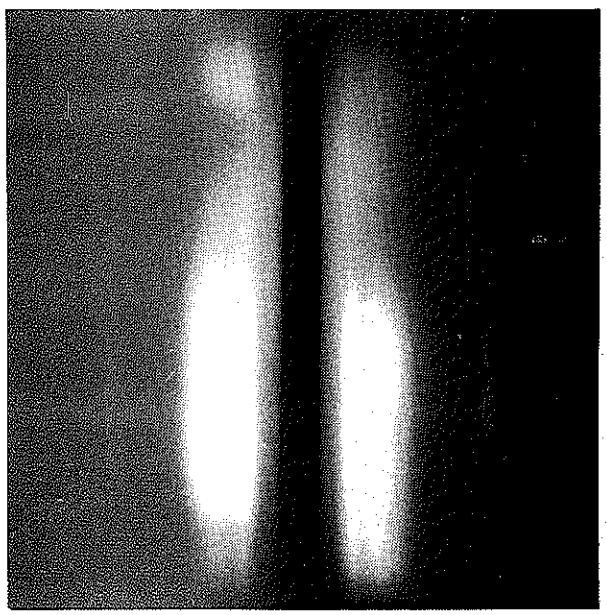

FIGURA 5

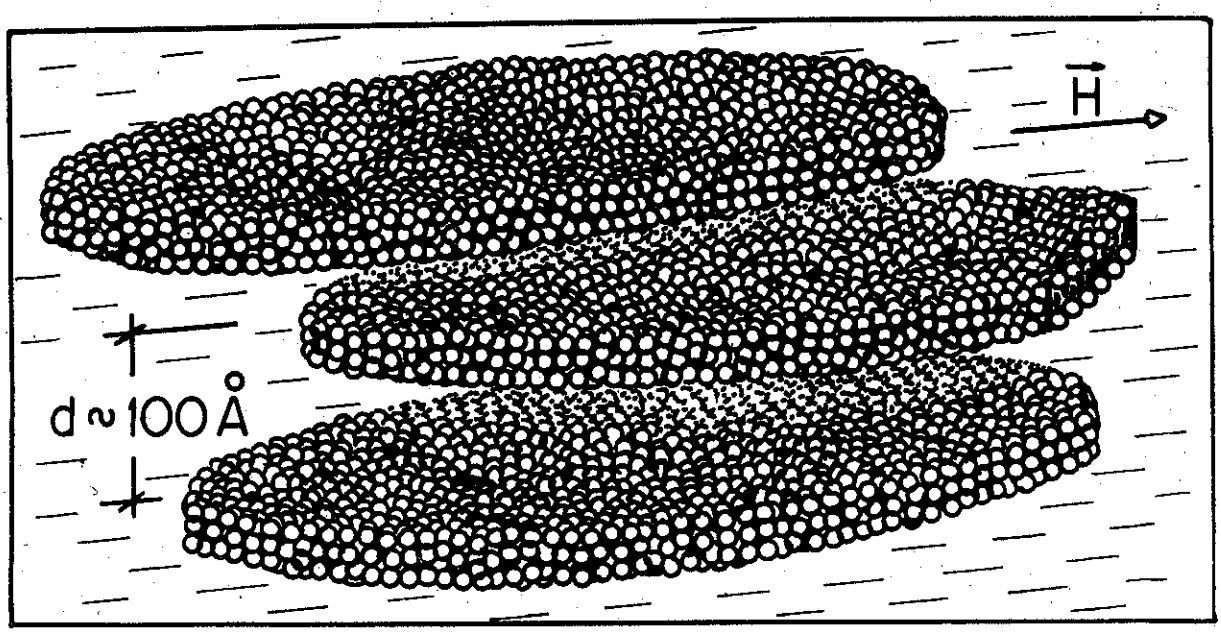

FIGURA 6

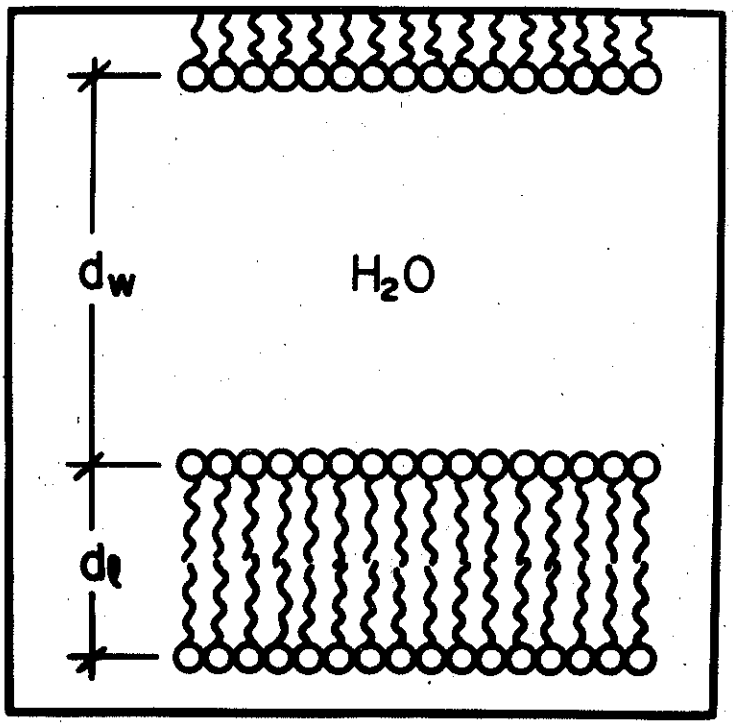

FIGURA 7