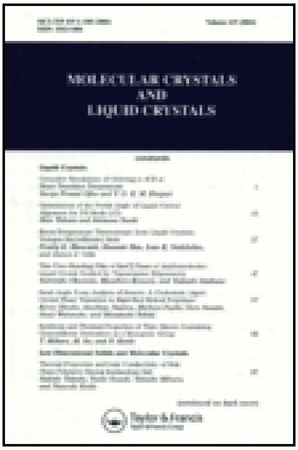


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Study of Type I Lyomesophases by X-ray Diffraction

A. M. Figueiredo Neto [a] & L. Q. Amaral [a]
[a] Instituto de Física, Universidade de São Paulo, CP 20516, São Paulo, CEP 05508, Brazil

To cite this article: A. M. Figueiredo Neto & L. Q. Amaral (1981): Study of Type I Lyomesophases by X-ray Diffraction, Molecular Crystals and Liquid Crystals, 74:1, 109-119

To link to this article: http://dx.doi.org/10.1080/00268948108073697

Mol. Cryst. Liq. Cryst., 1981, Vol. 74, pp. 109–119
0026-8941/81/7404-0109 $06.50/0

Study of Type I Lyomesophases by X-ray Diffraction†

A. M. FIGUEIREDO NETO and L. Q. AMARAL
Instituto de Física, Universidade de São Paulo, CP 20516, São Paulo, CEP 05508, Brazil

(*Received July 25, 1980; in final form January 20, 1981*)

Type I lyomesophase LK (K laureate/KCl/water) and CDS (Cs decyl sulfate/$CsNO_3$/water) were studied by small angle X-ray diffraction and polarized optical microscopy. Different containers were used and samples studied under the influence of applied magnetic and electric fields. Residual magnetic orientation, obtained in thicker LK samples, gave diffraction results compatible with a model of finite cylinders for the amphiphilic micelles; only an inner band in the region of 140 Å is presented in this case. The same sample in presence of an electric field of 14 kV/cm presents a weak outer band at 43 Å. Surface effects in thinner samples correspond to the strengthening of the outer band, which has been associated with clustering of the cylinders and segregation of water. Surface effects are stronger in LK than in CDS. These results indicate that the interaction with the surface is of electrostatic origin.

I INTRODUCTION

Lyotropic liquid crystals formed by binary lipid-water systems[1] and multicomponent systems[2-4] studied by X-ray diffraction revealed several types of uni, bi and even tridimensional structures. The most common lyomesophases are the neat soap (lamelar) and the middle soap (cylindrical micelles with hexagonal order in two dimensions).

Specific lyomesophases that orient in presence of magnetic fields **H** have been known for more than a decade.[5,6] These magnetically oriented lyomesophases have been classified[7,8] as types I and II depending on whether the phase director orients parallel or perpendicular to **H**. The two types can be identified by the NMR spectra obtained with sample spinning about an axis perpendicular to **H**,[7] since type I mesophases do not preserve their orientation in this condition while type II do perserve it. Type I phases are slow to respond to orient-

---

† Paper presented at the Eighth International Liquid Crystal Conference (Kyoto, Japan, 1980)—Abstracts H-16P.

ing forces in a magnetic field while type II phases are more mobile and orient much more rapidly in a magnet.

Amaral *et al.*[9-11] studied a type II lyomesophase formed by a quaternary system SDS (Na decyl sulfate/decanol/Na sulfate/water) by small angle X-ray diffraction (SAX). The diffraction patterns showed a diffuse inner halo at 80–140 Å and a sharp outer ring at 38 Å. From results obtained in samples previously oriented in a magnetic field, which kept residual magnetic orientation in the absence of the field, a model of finite micelles surrounded by water was proposed. These planar micelles consist of an amphiphilic bilayer, in the form of platelets, probably disk-shaped, that align in presence of magnetic fields, with their plane parallel to **H**. Further orientational restrictions are imposed by the container and the platelets tend to remain in a plane that contains **H** and the capillary axis.

In analogy with this model and from considerations of the orientation of carbon chains in magnetic fields, it was proposed[8] that the type I lyomesophases might correspond to finite cylindrical micelles surrounded by water. The names of type I CM (cylindrical micelles) and type II DM (disk micelles) were proposed[8] for these lyomesophases.

This paper presents the study of type I lyomesophases formed by two ternary systems, LK (K laureate/KCl/water) and CDS (Cs decyl sulfate/$CsNO_3$/water), by SAX and optical microscopy (OM). Unoriented samples and samples under the influence of applied magnetic and electric field were studied.

The X-ray results for the SDS type II lyomesophase[9-11] as well as NMR results for both types[12] presented evidence of orientational effects due to the container walls. Recently[13] it was shown that X-ray diffraction results for SDS type II lyomesophases are strongly dependent on the container; the sharper outer band at approximately the bilayer thickness is strengthened by surface effects, becoming a real Bragg reflection. These results have been explained[13] with the hypothesis that under the influence of orientational forces the platelets aggregate forming macromicelles composed of several amphiphilic bilayers slightly swollen while the water is segregated. Since surface effects are so important they have also been investigated in the study of type I lyomesophases here reported by employing several types of containers.

II EXPERIMENTAL

The ternary lyomesophases were prepared by the NMR laboratory of the Instituto de Química da USP according to procedures already described[7,8,11] and with the following compositions: LK (K laurate 33.6 wt %/KCl 2.3 wt %/H_2O 64.1 wt %) and CDS (Cs decyl sulfate 46.5 wt %/$CsNO_3$ 3.7 wt %/H_2O 49.8 wt %).

Samples were sealed in several types of containers:

C1—quartz capillary with 0.3 mm diameter;
C2—quartz capillary with 0.7 mm diameter;
C3—lindemann glass capillary with 0.7 mm diameter;
C4—pyrex glass capillary with 2 mm diameter;
C5—container with very thin parallel walls of mica
(5 mm × 15 mm) and 0.7 mm sample thickness.

Samples in capillaries were magnetically oriented in permanent magnets of 14 KG and 2 KG and afterwards analyzed by SAX and OM.

X-ray diffraction patterns were obtained by photographing technique using a small angle Rigaku-Denki diffractometer with Cuk$_\alpha$ radiation (Ni filtered) in a transmission geometry with point focus.

The capillary was always in the vertical direction. At the sample position the X-ray beam had a diameter of 0.3 mm. Only capillary C1 is therefore embraced by the beam, while the other sample holders received the beam in their central part. Exposure times varied between 24 and 48 hours depending on sample holder.

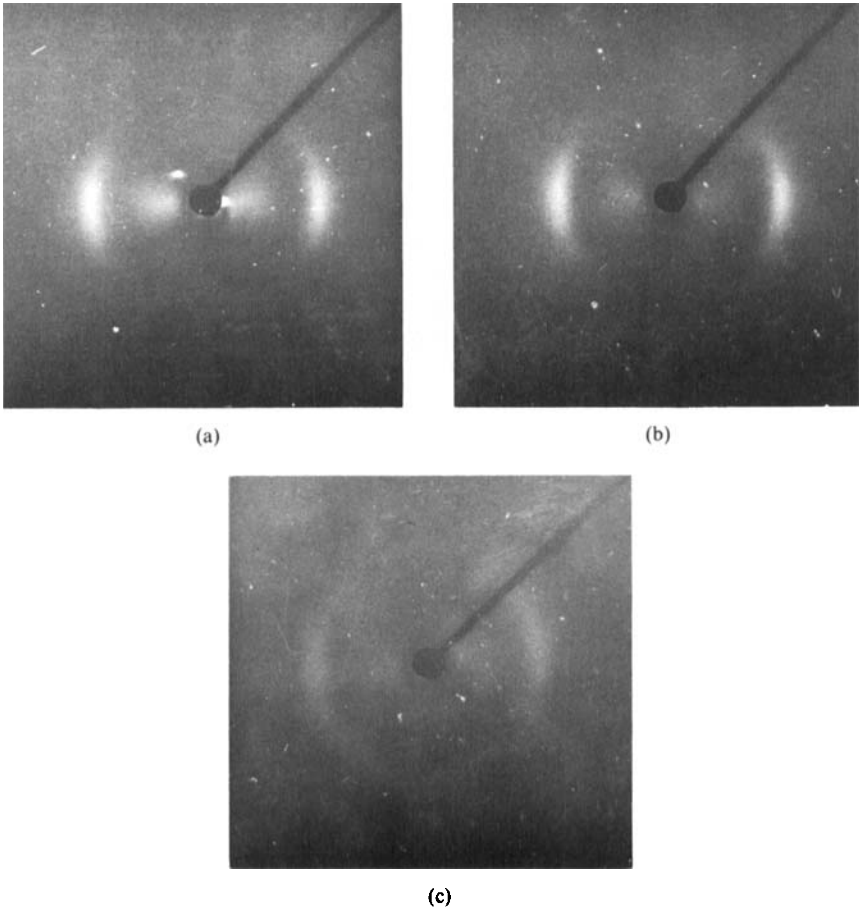
The effect of orientation by an external electric field **E** up to 12 kV/cm in a direction perpendicular to the capillary axis was studied employing an insulated capacitor designed and constructed in our laboratory. The device allows obtaining diffractograms with **E** perpendicular to the X-ray beam. In the geometry **E** parallel to the X-ray beam, in the absence of the electric field, only residual orientational effects are observed.

The samples were also analyzed by OM, using a Wild microscope with crossed polarizers. All results were obtained at room temperature.

III RESULTS AND DISCUSSION

A) Effect of container walls (without any applied fields)

Sample LK hold in all containers with 0.7 mm thickness (C2, C3 and C5) presented similar diffration patterns, shown in Figure 1 (a, b, c). Two bands are present: an inner diffuse from 190 to 88 Å and an outer, less diffuse, at 43 Å. Both bands presented a preferred orientation along the horizontal equator when in capillary holders. The degree of orientation changed slightly with the container, being stronger with C2 and smaller with C5. When LK is in the thicker capillary C4 only the inner band is observed, also with a preferred orientation along the equator (Figure 2). These results are analogous to those obtained for type II lyomesophases[9-11,13] and from these diffraction results it is not possible to establish the structure of the type I lyomesophase. Type I results here reported are less affected by the sample holder material than type II but the sample thickness is a critical parameter for both. The strengthening of



(a) (b)

(c)

FIGURE 1 SAX results for LK samples 0.7 mm thick; capillary in vertical direction in the plane of the figure. (a) quartz capillary C2; (b) lindemann glass capillary C3; (c) parallel walls container C5.

the outer band always occurs for thinner samples and seems to be associated with surface effects, that seem to be felt up to distances of a few tenths of millimeters.

When the outer band is strong it is possible that a contribution due to white radiation occurs in the position of the inner band. However the white radiation contribution must be small since varying the thickness of the Ni filter did not change the intensity ratio between the two bands. The fact that the intensity of the inner band decreases when the outer band increases shows clearly that the inner band is not due mainly to white radiation. Results with C4 show clearly the existence of the inner band.

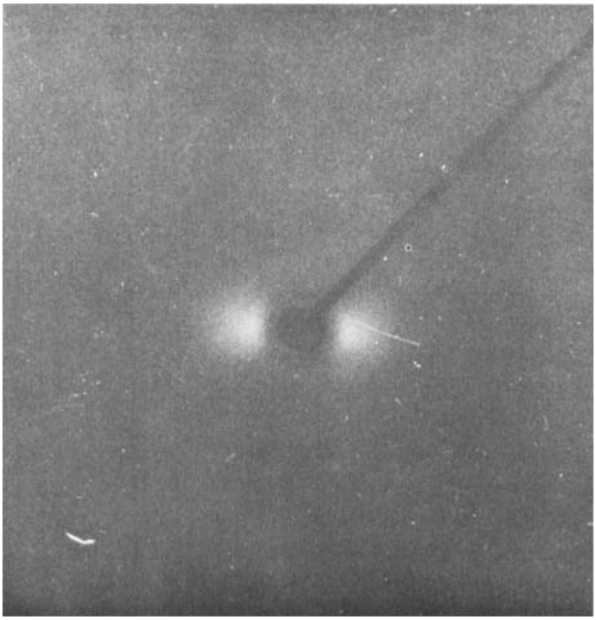


FIGURE 2 SAX result for LK sample held in the thicker capillary C4, in the vertical direction.

Sample CDS presented only the inner diffuse band, with a degree of orientation along the equator smaller than for LK, when held in all containers with 0.7 mm thickness (C2, C3 and C5). The outer band appeared only for CDS hold in the thinner capillary C1 (Figure 3). The two bands correspond to characteristic distances approximately equal to those of LK.

These results show that surface effects responsible for the appearance of the outer band are more intense for LK than for CDS, and therefore more intense for smaller polar heads.

This surface effect may be due to interactions between charged polar heads of the micelles and ions present in the sample holder surface or to interactions of the surface with water molecules (hydrophobic or hydrophilic surface).

With the model of finite cylinders[8] the preferred orientation along the equator indicates that the phase director and the cylinder axis orient parallel to the capillary axis.

The characteristic distances corresponding to the two bands would be related to distances between cylinder axis or between cylinder aggregates.

B) Effect of magnetic orientation

Samples LK and CDS in capillaries of 0.7 mm (C2 and C3) have been exposed to magnetic fields of 14 kG for several days with **H** both parallel and perpen-

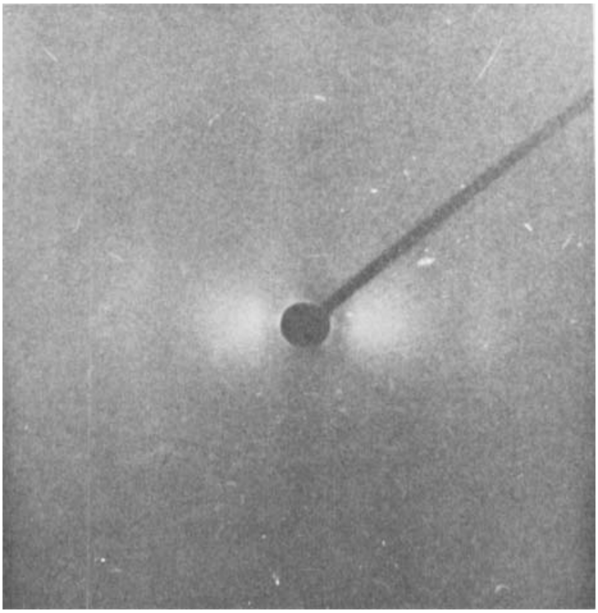


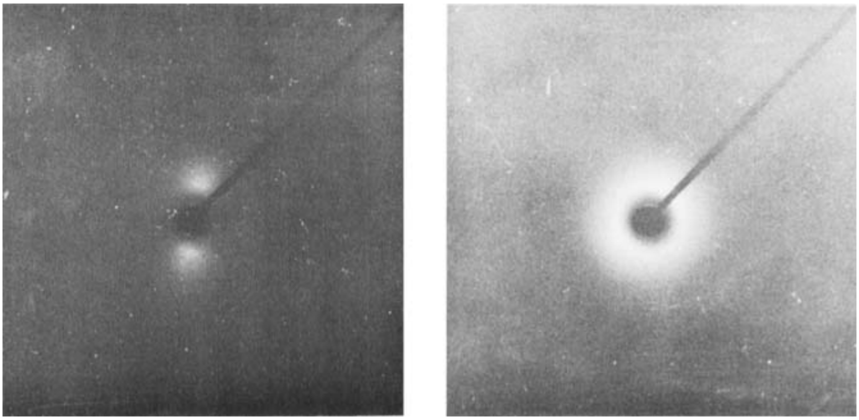
FIGURE 3 SAX result for CDS sample held in the thinner capillary C1, in the vertical direction.

dicular to the capillary axis. Observations of the capillaries by OM showed that the magnetic orientation was quickly lost, after a few hours, so that no SAX measurements on residual magnetic orientation could be obtained in these cases.

LK samples in the thicker capillary C4, exposed to magnetic fields of 2 kG and 14 kG for several days, with **H** perpendicular to the capillary axis, kept residual magnetic orientation for several days in the absence of the field. That is because for C4 surface effects are not so strong, as has been seen in the previous item. X-ray diffraction patterns in these samples with residual magnetic orientation have been obtained with the X-ray beam parallel ($S_{\parallel}$) and perpendicular ($S_{\perp}$) to **H**. $S_{\perp}$ showed only the diffuse inner band, rather oriented along the vertical meridian, perpendicular to the equator (Figure 4a). For $S_{\parallel}$ the diffuse inner band became isotropic (Figure 4b). No difference was observed between samples oriented in the weaker and stronger magnets; more important in the degree of magnetic orientation is the time the sample stays in the magnet.

These diffraction results indicate a cylindrical diffraction unit with the axis parallel to **H** and are therefore consistent with the model of finite cylinders for the amphiphilic micelles previously proposed.[8]

Diffraction patterns don't give the distance between cylinders along their axis which means that the cylinders are longer than 500 Å.



(a) (b)

FIGURE 4 SAX results on LK samples held in C4 (in vertical direction) with residual magnetic orientation: (a) $S_\perp$ configuration, with X-ray beam perpendicular to **H**; (b) $S_\parallel$ configuration, with X-ray parallel to **H**.

There seems to be a strong correlation between these micelles. Diffraction for $S_\perp$ measured in consecutive time intervals showed that the phase director changed collectively and slowly from the direction parallel to **H** to the direction parallel to the capillary axis. An intermediary position is shown in Figure 5.

The diffraction unit has an average diameter of about 140 Å in the plane perpendicular to the magnetic field. The calculated[14] length of a K laurate molecule in its extended configuration is about 20 Å, what would give a maximum value of about 40 Å for the cylinder diameter. Therefore the inner band cannot correspond to the average distance between cylinders in water, which could not be bigger than about 60 Å in view of the phase concentrations.

The observed large distances related to the inner band could correspond to a complex cylinder, with a curved bilayer forming a cylinder filled with water inside. However, such a model would lead to a narrower inner band and would not explain the outer band.

Our results together with X-ray evidence obtained by other authors[15] suggest another interpretation. Charvolin *et al.*[15] studied lyomesophases of types I and II of Na decyl sulfate (SDS). Their experiment, obtained with a conventional Laue camera could detect only the outer band; the inner band occurs in the small angle region which is under the direct beam in the Laue camera. Their perpendicular configuration (analogous to our $S_\perp$) is obtained in presence of a high magnetic field $\mathbf{H}_0$, while their parallel configuration (similar to our $S_\parallel$) is obtained in the absence of $\mathbf{H}_0$ (residual magnetic orientation).

Their results[15] for type I SDS are qualitatively similar to ours, but refer to the outer band (characteristic distance of the order of 40 Å) while our results are obtained in the inner band (190–90 Å). In our case the outer band is absent

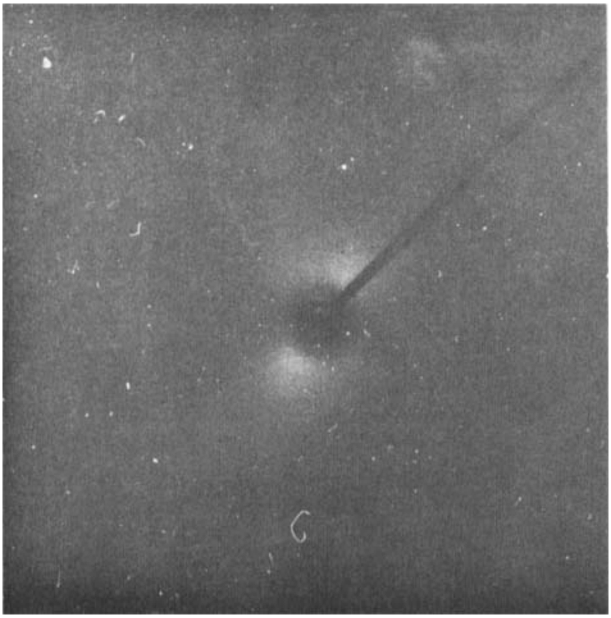


FIGURE 5 SAX result for LK sample held in C4 (in vertical direction) while losing the residual magnetic orientation.

due to the use of capillary C4, which allowed residual magnetic orientation to remain for several days. Charvolin[15] does not discuss the problem of surface effects (the capillary thickness is not mentioned) nor the difficulty in obtaining residual magnetic orientation. We believe that they observed their results in the outer band because they measured $S_{\perp}$ with a strong $\mathbf{H}_0$ present. Their $S_{\parallel}$ refers to residual magnetic orientation and from our experience it is doubtful whether it can be stated, as they do, that in this case the X-ray beam is parallel to the phase director; they could have a disoriented sample as well, and this should have been checked by observing the sample after X-ray exposition on a polarizing microscope.

From our results and Charvolin's results we can conclude that depending on sample thickness the cylindrical diffraction unit varies from a more or less well defined value of 40 Å to a range of values between 80–190 Å (inner and outer bands).

Charvolin, ignoring the inner band, interpreted the outer band as the distance between cylindrical micelles homogenously distributed in water. The hypothesis of homogeneous distribution is implicit in all determinations of amphiphilic bilayer thickness from X-ray data, but it can be wrong and misleading in lyomesophases with excess water.

In the case of K laurate X-ray diffraction results on the middle phase at

86° C and weight concentration 0.42 wt % give[16] a distance between cylinder axes of 42.9 Å, from which a cylinder radius of about 15 Å has been deduced. This represents a value 25% smaller than that expected for the extended configuration, what is on the right order of contraction for a liquid like conformation. Since the hydrocarbon chains have a negative expansion coefficient, one would expect this figure to be a lower limit for the radius at room temperature.

A radius of 15 Å could explain the outer band as associated with the distance between cylinders homogeneously distributed in water, on the same line as Charvolin's interpretation, but would leave the inner band unexplained.

However, if the hypothesis of homogeneous distribution is abandoned, it is possible to build a model of aggregates of cylinders having the cylinder radius as parameter. Interpreting the outer band as a d_{100} interplanar spacing there exists a relationship between the cylinder radius and the amphiphilic concentration within the aggregates. These aggregates would then be separated by the excess water and the average distance between such aggregates originates the inner band. Calculations have been performed for several values of the cylinder radius until a unique value was found that could explain several sizes of aggregates. Such a value gives a radius of 16.5 Å, corresponding to a concentration of 42% in volume within the aggregates, higher than the overall concentration (35% in volume).

Large aggregates, with about a hundred cylinders, would be responsible for the outer band, whose broadness indicates the existence of about 10 reflecting planes; the distance between such large aggregates would be too large to be detected by X-ray.

Smaller aggregates, containing from 2 to 19 cylinders would not contribute significantly to the outer band but the characteristic distances between such aggregates would build up the inner band *B*. The diffusiness of *B* could then be explained by a large distribution of aggregate size. It seems however that aggregates of intermediate size are not energetically favoured, probably due to thermal agitation.

This model of aggregates adequately describes the observed diffraction pattern. The presence of the outer band in thinner capillaries indicates that surface effects correspond to the formation of large aggregates near the walls.

C) Effect of electrical orientation

LK samples in capillaries of 0.7 mm (C2 and C3) did not show effects of orientation in presence of an electric field of 12 kV/cm perpendicular to the capillary axis and to the X-ray; their diffraction patterns remained similar to those obtained without **E**.

LK sample in the thicker capillary C4 stayed in an electric field of 12 kV/cm perpendicular to the capillary axis for 16 days and afterwards was measured by SAX with the X-ray beam perpendicular to **E**. The diffraction pattern

(Figure 6a) presented, in the position of the inner band, many radial lines. The diffraction pattern obtained with residual orientation for E parallel to the X-ray beam (Figure 6b) presented the same radial lines and a very weak but sharp outer ring at the same position observed in thinner samples. This result shows also that the inner band, and the radial streaks, cannot be due mainly to white radiation, since the outer band is very weak. White radiation could be responsible for the inner band or radial streaks only with very strong outer band or Bragg peak.

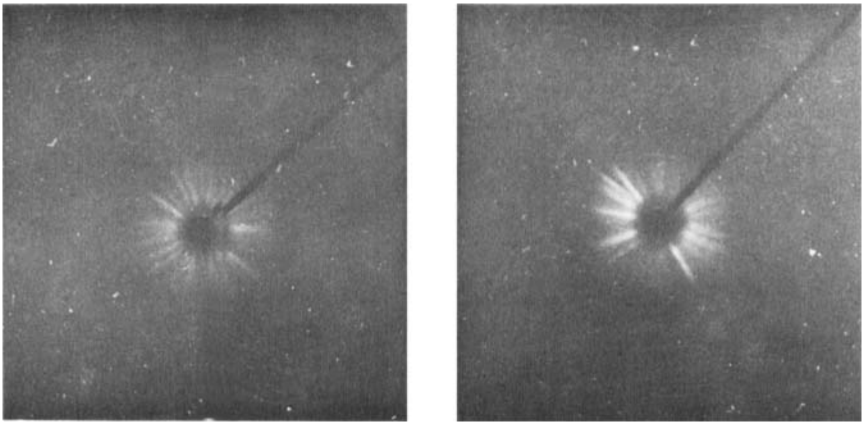
It seems that the electric field transforms the continuously varying directions of the director, typical of a continuous medium, into monocrystallites with discrete directions of the director.

After about 5 days without electric field the diffraction pattern changed, with an increase of intensity of streaks in some directions and decrease of others.

The fact that under influence of an electric field a weak outer ring appears seems to confirm that the interaction with the container walls, responsible for the strengthening of this outer ring, is also essentially of an electrostatic origin.

IV CONCLUSIONS

Diffraction results for magnetically oriented samples are consistent with the model of finite cylindrical micelles previously proposed.[8] The existence of two bands can be explained by the formation of aggregates. The appearance of the



(a) (b)

FIGURE 6 SAX result for LK sample held in C4, in vertical direction: (a) in presence of an electric field E perpendicular to the X-ray beam; (b) with residual orientation for E parallel to the X-ray beam. A weak outer ring is seen in the negative.

outer ring in presence of electric fields and surface orientation suggests the latter to be of an electrostatic nature.

The formation of aggregates of amphiphilic micelles, probably with solvation water between them, but with segregation of disordered water, is considered to be a basic mechanism for both types I and II lyomesophases.

Acknowledgments

We thank V. R. Paoli for the skillful preparation of the lyomesophases and her and Dr. J. A. Vanin for many helpful discussions. The incentive of Prof. L. W. Reeves as well as our discussions are also acknowledged. FINEP, CNPq and FAPESP foundations are acknowledged for financial support.

References

1. V. Luzzati, in *Biological Membranes*, ed. D. Chapman (Academic, London, 1968), pp. 71-123.
2. P. Ekwall, in *Advances in Liquid Crystals*, ed. G. H. Brown (Academic, New York, 1975), **1**, pp. 1-142.
3. P. A. Winsor, *Chem. Rev.*, **68**, 1-40 (1968).
4. G. J. T. Tiddy and B. A. Wheeler, *J. Colloid Interface Sci.*, **47**, 59 (1974).
5. K. D. Lawson and T. J. Flautt, *J. Am. Chem. Soc.*, **89**, 5489 (1967).
6. P. J. Black, K. D. Lawson and T. J. Flautt, *J. Chem. Phys.*, **50**, 542 (1969).
7. K. Radley, L. W. Reeves and A. S. Tracey, *J. Phys. Chem.*, **80**, 174 (1976).
8. F. Fujiwara, L. W. Reeves, M. Suzuki and J. A. Vanin, in *Solution Chemistry of Surfactants*, ed. K. L. Mittal (Plenum, New York, 1979), **1**, pp. 63-77.
9. L. Q. Amaral, C. A. Pimentel and M. R. Tavares, *Acta Crystallog.*, **A34**, (S4) S188 (1978).
10. M. R. Tavares, Master Dissertation (University of São Paulo, Brazil, 1978).
11. L. Q. Amaral, C. A. Pimentel, M. R. Tavares and J. A. Vanin, *J. Chem. Phys.*, **71**, 2940 (1979).
12. F. Y. Fujiwara and L. W. Reeves, *Can. J. Chem.*, **56**, 2178 (1978).
13. L. Q. Amaral and M. R. Tavares, *Mol. Cryst. Liq. Cryst. Lett.*, **56**, 203 (1980).
14. J. E. Leibner and J. Jacobus, *J. Phys. Chem.*, **81**, 130 (1977).
15. J. Charvolin, A. M. Levelut and E. T. Samulski, *J. Phys. Lett.*, **40**, L-587 (1979).
16. B. Gallot et A. Skoulios, *Kolloid Z. Z. Polym.*, **208**, 37 (1966).