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ERRATUM

1. Pag.9 Line 8 instead of "solvatation": solvation.
2. The Figures 1a and 1c are 90^{o} rotated from the right position.

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ABSTRACT

Type I lyomesophase LK (K laureate/KCl/water) and CS (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 present 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 orientation in thinner samples correspond to the strenghtening of the outer band, which has been associated with clustering of the cylinders and seggregation of water. Surface effects are stronger in LK than in CS. These results indicate that the interaction with the surface is of electrical origin.

I. INTRODUCTION

Lyotropic liquid crystals formed by binary lipid-water systems[1] and multicomponent systems[2,3,4] studied by X-ray diffraction revealed several types of uni, bi and even tridimensional structures. The most common lyomesophases are the neat soap (lamellar) and the middle soap (cylindrical micelles with hexagonal order in two dimensions).

Specific lyomesophases that orient in presence of magnetic fields $\vec{H}$ 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 $\vec{H}$. The two types can be identifyed by the NMR spectra obtained with sample spinning about an axis perpendicular to $\vec{H}$[7], since type I mesophases do not preserve their orientation in this condition while type II 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 much more rapidly in a magnet.

Amaral et al[9,10,11] 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 pattern showed a difuse inner halo at 80-140 $\mathring{A}$ and a sharp outer ring at 38 $\mathring{A}$. From results obtained in samples with residual magnetic orientation a model of finite planar 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 $\vec{H}$.

Further orientational restrictions are imposed by the container and the platelets tend to remain in a plane that contains $\vec{H}$ 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 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[9,10,11] 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 strenghtened by surface orientation, 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 swoolen while the water is segregated. Since the effect of surface orientation is so important it has 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 0.3mm diameter;

C2 - quartz capillary with 0.7mm diameter;

C3 - lindemann glass capillary with 0.7mm diameter;

C4 - pyrex glass capillary with 2mm diameter;

C5 - container with very thin parallel walls of mica and 0.7mm sample thickness.

Samples conditioned 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_α radiation (Ni filtered) in a transmission geometry with point focus.

The effect of orientation by an external electric field $\vec{E}$ up to 12 KV/cm in the direction perpendicular to the capillary axis was studied employing an insulated capacitor projected and constructed in our laboratory. The device allows the obtention of diffractograms with $\vec{E}$ perpendicular to the X-ray beam. In the geometry $\vec{E}$ parallel to the X-ray beam only residual orientational effects are observed.

The samples were also analyzed by OM, using a Wild microscope with crossed polaryzers. All results were

obtained at room temperature.

III. RESULTS AND DISCUSSION

A) Effect of container walls

Sample LK conditioned in all containers with 0.7mm thickness (C2, C3 and C5) presented similar diffraction patterns, shown in figure 1 (a,b,c). Two bands are present: an inner difuse from 190 to 88 Å and an outer, less difuse, at 43 Å. Both bands presented a preferred orientation along the horizontal equator. The degree of orientation changed slightly with the container, being stronger with C2 and smaller with C5. When LK is conditioned 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[9,10,11,13] and indicate that the sample thickness is a critical parameter.

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

These results show that orientational effects are more intense for LK than for CDS. The surface orientation responsible for the appearence of the outer band seems to be more intense for smaller polar heads. This would be consistent with that has been observed for SDS type II lyomesophases[13],

with the smallest polar head and the strongest surface orientation, although it may be misleading the comparison between types I and II for this purpose. Suface orientation could due to the interaction between the charged polar heads and ions present in the container walls.

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

The inner band is then associated with the average distance between cylinders in the water. The outer band corresponds roughly to the expected diameter of the cylinders, which does not differ much from a bilayer thickness; the calculated lenght (according to reference [14]) of a K laurate molecule is about 21 Å. The existence of this band is therefore associated with clustering of the charged cylinders and seggregation of water, as it was proposed also for the platelets in the SDS type II lyomesophase[13]. Therefore, also in the case of type I lyomesophases, the appearence of the outer band would correspond to the formation of macromicelles, in this case made up of packed cylinders.

B) Effect of magnetic orientation

Samples LK and CDS conditioned in capillaries of 0.7mm (C2 and C3) have been exposed to magnetic fields of 14 KG for several days with $\vec{H}$ both parallel and perpendicular 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 otained in these cases.

LK samples conditionned in the thicker capillary C4, exposed to magnetic fields of 2 Kg and 14 KG for several days, with $\vec{H}$ perpendicular to the capillary axis, kept residual magnetic orientation for several days. That is because for C4 the effect of surface orientation is 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 $\vec{H}$. $S_{\perp}$ showed only the difuse inner band, rather oriented along the vertical meridian, perpendicular to the equator (figure 4a). For $S_{\parallel}$ the difuse 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 results are 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 axe, what means that the cylinders are longer than 500 $\mathring{A}$. These cylindrical micelles orient with their axe parallel to the magnetic field.

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 $\vec{H}$ to the direction parallel to the capillary axis. An intermediary position is shown in figure 5.

C) Effect of electrical orientation

LK samples conditioned in capillaries of 0.7mm

(C2 and C3) did not evidence effects of orientation in presence of an electric field of 12 KV/cm perpendicular to the capillary axis and to the X-ray beam; their diffraction patterns remained similar to those obtained without $\vec{E}$.

LK sample conditioned 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 $\vec{E}$. The diffraction pattern (figure 6a) presented, in the position of the inner band, many radial lines. The diffraction pattern obtained with residual orientation for $\vec{E}$ parallel to the X-ray beam (figure 6b) presented the same radial lines a very weak but sharp outer ring at the same position observed in thinner samples. In about 5 days the electrically induced orientation was lost and the radial lines gave place to the inner difuse band oriented prefentially in the equator.

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.

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 fo the strenghtening of this outer ring, is also essentially of an electrical origin.

IV. CONCLUSIONS

Diffraction results for magnetically oriented samples are consistent with the model of finite cylindrical

micelles previously proposed[8]. The existence of the outer ring corresponding approximately to the cylinder diameter suggests that in certain circunstances these cylinders are closely packed with seggregation of water. The appearence of this ring in presence of electric fields and surface orientation suggests the latter to be of an electrical nature.

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

Our results are therefore in disagreement with those recently reported by Charvolin et al[15], that sutudied lyomesophases of types I and II of Na decyl sulfate. 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. They concluded that the outer band corresponds to the distance between micelles homogeneously distributed in water and therefore attributed to the bilayer thickness a value of only 20 $\mathring{A}$, what could be possible only if the micelles consisted of stiff interdigitating paraffin chains[1]. That this seems not to be the case has been already discussed for type II lyomesophases[13], and the same arguments are valid for type I phases: chain order profiles obtained from NMR[16,17,18] do not favour this hypothesis neither does it the existence of the inner band observed by SAX and the inexistence of sharp lines in the higher angle region.

Their paper[15] also does not discuss the problem of surface orientation (the capillary thickness is not even

mentioned) neither the difficulty in obtaining residual magnetic orientation. Regarding type I lyomesophases, their parallel configuration refors 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 due precautions to avoid this are not mentioned.

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FIGURE CAPTIONS

Fig. 1 - SAX results for LK samples 0.7mm thick:

(a) - quartz capillary C2

(b) - lindemann glass capillary C3

(c) - parallel walls container C5 .

Fig. 2 - SAX result for LK sample conditioned in the thicker capillary C4.

Fig. 3 - SAX result for CDS sample conditioned in the thinner capillary C1.

Fig. 4 - SAX results on LK samples conditioned in C4 with residual magnetic orientation:

(a) - $S_{\perp}$ configuration, with X-ray beam perpendicular to $\vec{H}$

(b) - $S_{\parallel}$ configurattion, with X-ray beam parallel to $\vec{H}$.

Fig. 5 - SAX result for LK sample conditioned in C4 while losing the residual magnetic orientation.

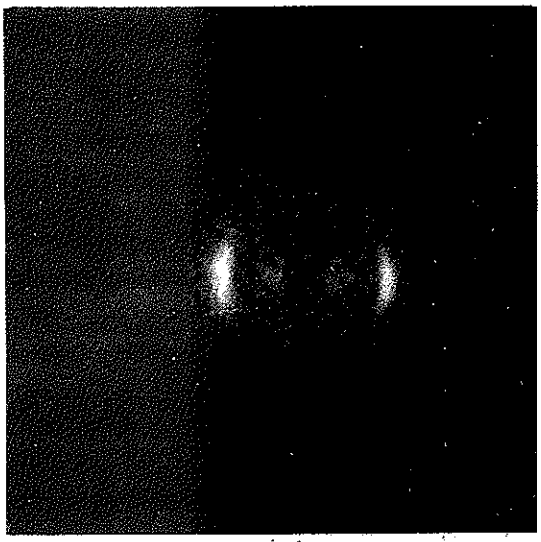
Fig. 6 - SAX result for LK sample conditioned in C4:

(a) - in presence of an electric field $\vec{E}$ perpendicular to the X-ray beam

(b) - with residual orientation for $\vec{E}$ parallel to the X-ray beam. A weak outer ring is seen in the negative.

FIGURES

1(a)



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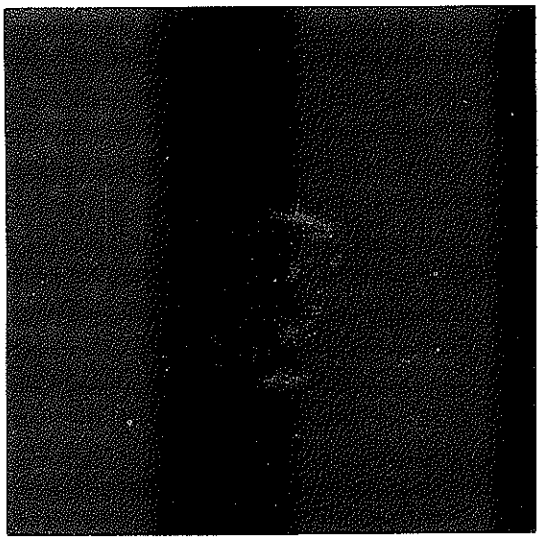

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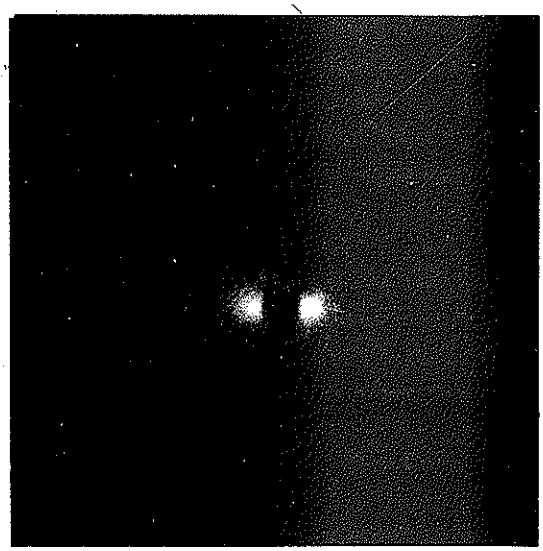

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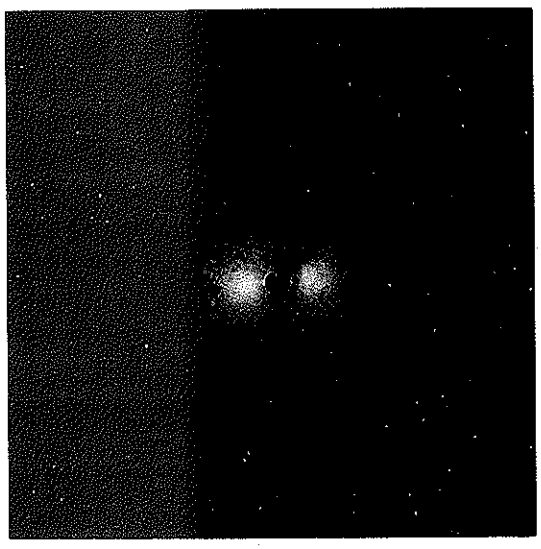

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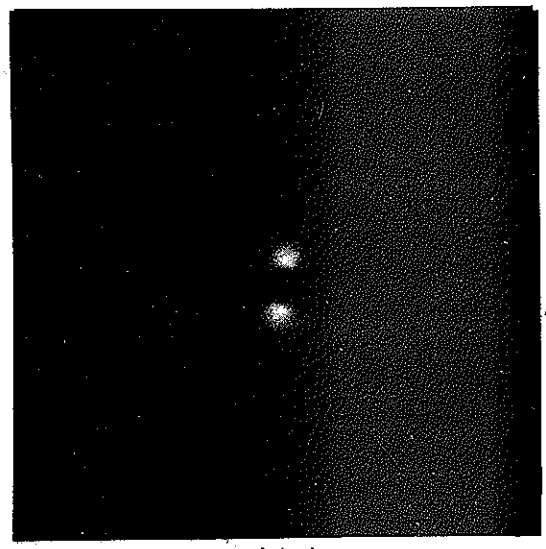

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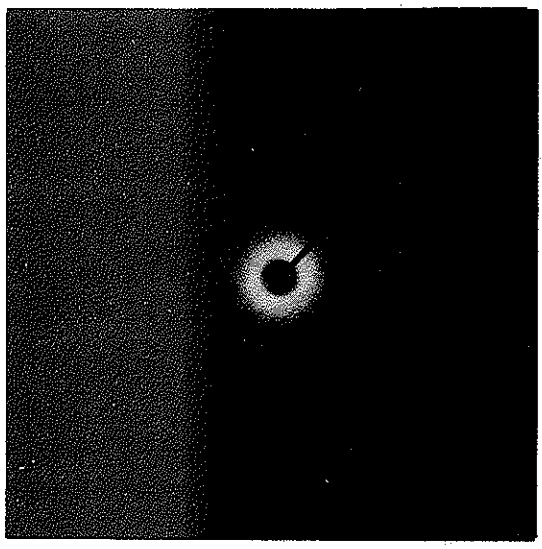

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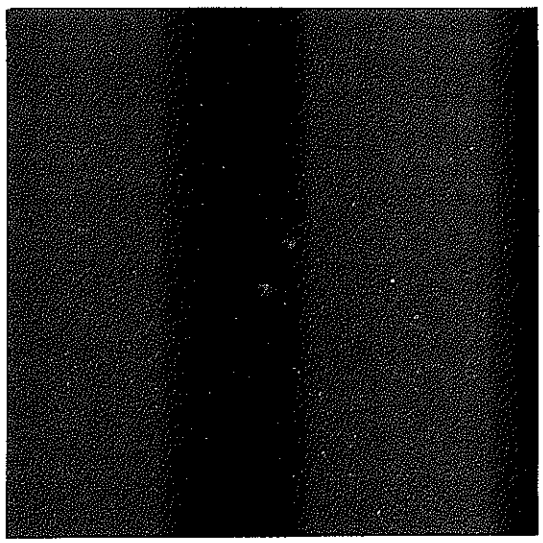

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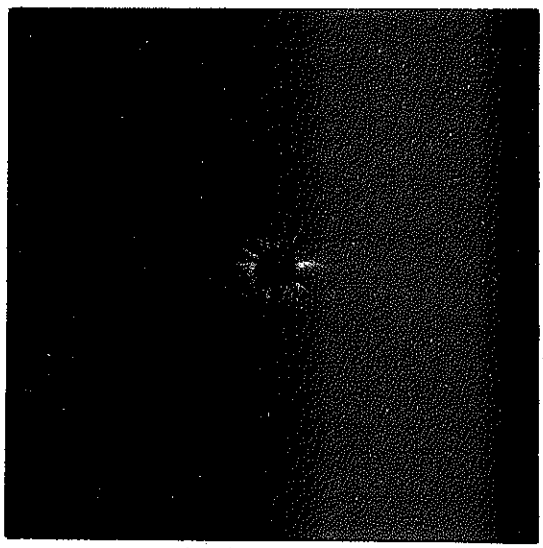

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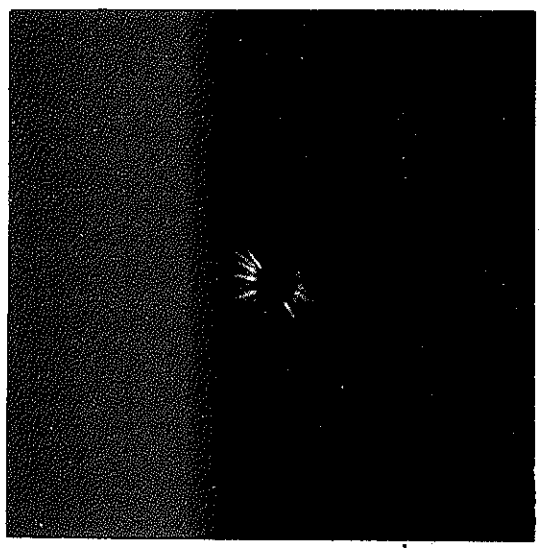

6 (b)