INSTITUTO DE FÍSICA

preprint

IFUSP/P-215

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* Paper to be presented at the Eight International Liquid Crystal Conference to be held in Kyoto, Japan, from 30 June to 4 July 1980, and afterwards published in the Conference Proceedings, in a special volume of Molecular Crystals and Liquid Crystals.

APRIL/1980

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ABSTRACT

A type I lyomesophase LK formed by a ternary system (K laurate/KCl/water) was studied by small angle X-ray diffraction in the temperature interval $20^{o}C$ to $65^{o}C$ and a phase transition was detected at $50-55^{o}C$. The diffraction pattern consists of two bands, an inner difuse at 190-90 Å and an outer less difuse at 43 Å in the lower temperature phase P1. In the higher temperature phase P2 the characteristic distance of the outer ring decreases, the ring is sharpened and Bragg points appear on it; the inner halo is transformed into strikes in the directions of the Bragg points. P2 has therefore long range order; macroscopically this phase transition is associated with an increase in the viscosity. Diffraction results are interpreted in terms of formation of large clusters of finite cylindrical micelles of amphiphile closely packed with seggregation of water.

I. INTRODUCTION

Lyomesophases that orient in presence of magnetic fields $\vec{H}$ have been classified as type I and II[1,2] depending on whether the phase director orients parallel or perpendicular to $\vec{H}$. Small angle X-ray diffraction (SAX) on these lyomesophases show tipically[3-6] an inner difuse halo in the region at 100 Å and an outer ring corresponding roughly to the amphiphilic bilayer thickness, at 40 Å. The relative intensity of the two bands depends on the sample thickness and on the degree of orientation[4-6]. SAX results on samples with residual magnetic orientation are consistent with models based on finite planar micelles (platelets) for type II[4] and finite cylindrical micelles for type I[2,6] lyomesophases. Studies of surface orientation and orientation under applied magnetic and electric fields have been performed on both types of lyomesophases[5-7]. The outer ring has been associated with the formation of macromicelles made of aggregates of amphiphilic micelles, probably with solvatation water between them, but with seggregation of disordered water; these macromicelles would be made up of several amphiphilic bilayers[5,7] in type II and of packed cylinders[6] in type I mesophases.

This paper presents the study by SAX of the temperature variation of a type I lyomesophase LK (K laurate/ KCl/water); this same lyomesophase has been already studied under the influence of magnetic and electric fields and of surface orientation at room temperature[6], with results consistent with a model of finite cylindrical micelles.

II. EXPERIMENTAL

The sample composition was 33.6 wt% K laurate/ 2.3 wt% KCl/64.1 wt% water and it was prepared by the NMR laboratory of the Instituto de Química da USP according to procedures already described[1,2,4].

Samples were sealed in lindemann glass capillaries with 0.7mm diameter, placed in vertical position; with their axe perpendicular to the X-ray beam, in a transmission geometry. A small angle Rigaku-Denki diffractometer with CuK_α radiation (Ni filtered) with point focus was used and X-ray diffraction detected by photographing technique.

The capillary with the sample stays in a furnace (Figure 1) with a temperature controlling system. The device, projected and constructed in our laboratory[8], is attached to a goniometer head in a goniometer, allowing the sample position to be freely adjusted. The hot source at the basis of the furnace is thermically insulated from the capillary over it; hot air circulates around the capillary which is then homogeneously heated. Temperature gradients superior to 2^oC along the capillary axis are therefore avoided, since they would be particularly inconvenient in the case of liquid crystals. The furnace has a thin mylar pellicle around it, to keep the hot air around the sample, allowing the whole furnace to be freely adjusted by the goniometer head. The electrical temperature controlling system is switched by a thermocouple and the temperature is controlled within 1^oC, in the temperature interval between ambient and 70^oC.

III. RESULTS AND DISCUSSION

The X-ray diffraction pattern obtained at 20°C (Figure 2a) presents the two bands already mentioned, an inner difuse initiating at 190 Å and extending to 88 Å and an outer less difuse at 43 Å, oriented preferentially on the equator. This result, as discussed in another papers[5-7], is typical of a sample with a moderate effect of surface orientation, due probably to an electrical interaction between the charged micelles and ions on the capillary walls.

As the temperature increases, in the interval from 30°C to 45°C, both bands lose the equatorial orientation and become isotropic (Figure 2b); band positions did not change but they are somewhat narrower. At 50°C there is a changement in the outer band, which moves to a smaller characteristic distance of 38 Å and becomes sharper; some Bragg points appear on it, indicating defined directions of crystallization, while the inner band did not change (Figure 2c). At 55°C the Bragg points on the outer ring increased in number and intensity and the inner band is transformed into radial strikes, oriented in the directions where the Bragg points appear (Figure 2d).

These results indicate a transition to a phase with long range order among micelles; this transition shows also an increase in the viscosity, which we could notice only qualitatively.

No other transition has been observed for temperatures higher than 55°C untill the limit of 65°C imposed by the conditions of stability of the system, which may be destroyed for higher temperatures.

The reversibility of the process has been observed, although the phase transition depends rather strongly on the thermal treatment of the sample. Slow and quick temperature changes resulted in different diffraction patterns, specially regarding the number of Bragg points appearing on the outer ring. However, whatever the thermal treatment, Bragg points always appear in the higher temperature phase.

As has been discussed previously[5-7] and mentioned in the introduction, the external band would be connected to the distance between micelles closely packed (finite cylinders in this case) while there occurs seggregation of water.

Whithin this picture the phase transition can be explained qualitatively by a three steps process:

1 - There are already some groups of cylinders packed togheter through surface effects while others are surrounded by water. The cylindrical micelles, initially oriented through surface effects with their axe preferentially along the capillary axis lose their preferred orientation with the increase in temperature. This could probably be connected to the increase in thermal agitation and the breaking of the electrical interaction between the charged polar heads and ions in the container walls.

2 - At the phase transition the phenomenon of clustering is intensifyed, with further exclusion of water, so that the cylinders become even more closely packed and compact clusters of large size are formed. This would explain the decrease in characteristic distance and the appearence of real Bragg points as these clusters behave as mono-crystallites. However, there are still some cylinders embedded in water, responsible for the difuse inner band.

3 - Finally there is coalescence of the individual cylinders in the clusters and the difuse inner band disappears. The change from the difuse inner band to the radial strikes is probably connected to a transformation from a continuous medium to defined crystallites, so that the directors, initially with continuously varying directions, freeze on discrete directions. This phenomenon was observed[6] also for a thicker sample subjected to the action of an electric field of 12 KV/cm perpendicular to the capillary axis.

In the final situation the cylinders seem to orient with their axe perpendicular to the container walls. Some results evidenced the formation of hexagonally packed arrandjements of cylinders within the large clusters. In one case (Figure 3a) a weak ring was observed with characteristic distance $1/\sqrt{3}$ of the distance of the outer ring, indicating hexagonal packing without correlation between the clusters. In another case (Figure 3b) six Bragg points in an hexagonal configuration appeared in the outer ring. This result would indicate strong correlation among the clusters, with possible formation of networks between them.

The occurence of long range order in the higher temperature phase gives a further weight to the hypothesis of seggregation of water, postulated to explain the strengthtening of the outer ring at approximately the bilayer thickness due to surface orientational effects[5-7]. The increase of the degree of order among micelles probably minimizes the electrostatic energy among charged particles while there may be an increase in the entropy of the seggregated water.

ACKNOWLEDGEMENTS

We thank V.R. Paoli for the skillful preparation of the lyomesophases and to her and Dr. J.A. Vanin for many helpful discussions. The incentive of Prof. L.W. Reeves is also aknowledeged. FINEP and CNPq foundations gave us imprescindible financial support.

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FIGURE CAPTIONS

Figure 1 - Furnace coupled to a goniometer head in a goniometer.

Figure 2 - SAX results in LK with temperature variation:

(a) $20^{o}C$

(b) $45^{o}C$

(c) $50^{o}C$

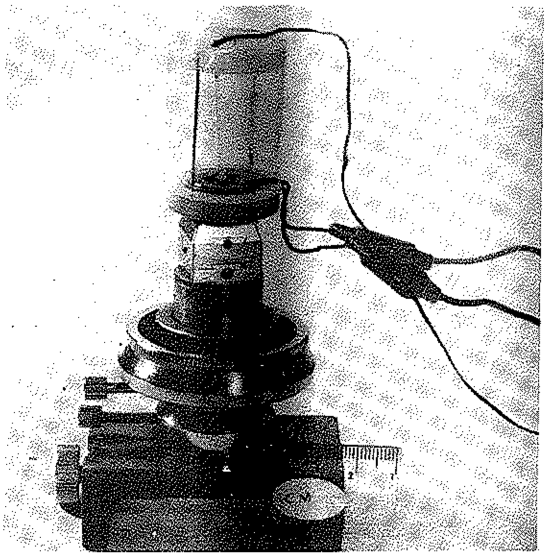
(d) $55^{o}C$.

Figure 3 - SAX results in LK at $55^{o}C$:

(a) with a weak extra ring at $1/\sqrt{3}$ distance from the outer ring;

(b) with a 6-fold hexagonal axis in the direction of the X-ray beam.

FIGURES



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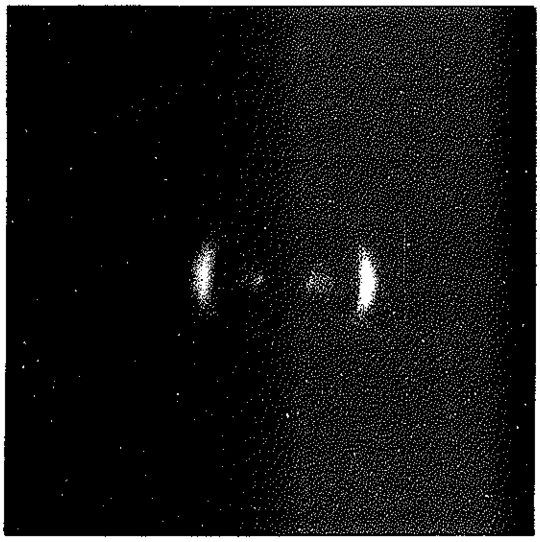

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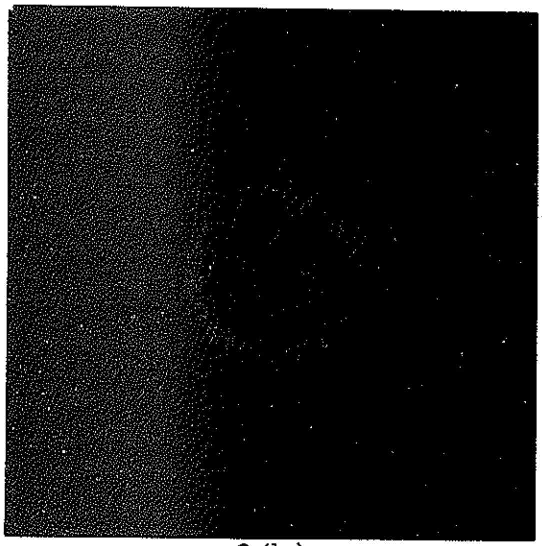

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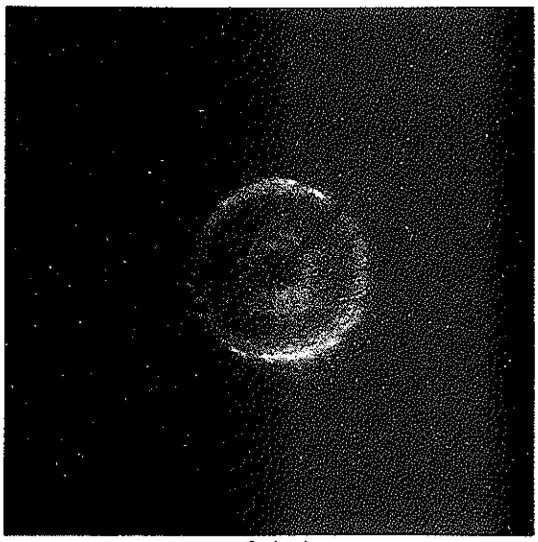

2(c)

2(d)

3(a)

3(b)

ERRATUM

1. Pag.2 Line 17 instead of "solvatation": solvation

2. Pag.5 step 2 change: "At the ... crystallites." for "At the phase transition the phenomenon of clustering is intensifyed: the cylinders become even more closely packed and compact clusters of large size are formed. These clusters behave as monocrystallites and lead to the appearence of Bragg points. The decrease in the characteristic distance could be due either to further exclusion of water or to a decrease in the diameter of the cylinders connected to an increase in the degree of disorder of the paraffin chains inside the cylindrical micelles. However ...."