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Study of a Phase Transition in a Lyotropic Liquid Crystal of Potassium Laurate/KCl/ Water by X-ray Diffraction and Optical Microscopy

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Type I lyomesophase of potassium laurate was studied by X-ray diffraction and optical microscopy techniques with temperature variation. For increasing temperatures from 22°C to about 54°C only a nematic phase (N) was observed. For temperatures between 60°C and 74°C it was observed coexistence of an isotropic (I) and hexagonal (H_α) phase with lattice parameter (47 ±1) Å. For temperatures between 54°C and 60°C, in some experiments, it was observed the coexistence of phases N and H_α. A binary system of potassium laurate/water (H_α phase) was also studied by both techniques at room temperature; the lattice parameter is (44.9 ±0.5) Å. Possible models for the N phase are discussed and compared with the obtained lattice parameters and associated micellar radius.

I. INTRODUCTION

Nematic lyomesophases that spontaneously orient in presence of magnetic fields $\vec{H}$ have been classified as types I and II,[1,2] depending on whether the phase director orients parallel or perpendicular to $\vec{H}$. The characterization of these mesophases as nematics was made by observation of its optical textures in a polarized microscope,[3–6] which resemble nematic ones. When the diamagnetism comes from the hydrocarbon portion of the amphiphile, this classification corresponds to a structure of finite planar micelles for type II[2,3,7–11] and finite cylindrical micelles for type I.[2,3,12]

Amaral and co-workers[7–11] studied a type II lyomesophase by small angle X-ray scattering, proposing a model of finite planar micelles, in the

form of platelets, not homogeneously distributed in water, forming lamellar aggregates.

Type I lyomesophases of potassium laurate (K laurate/KCl/water) called LK and cesium decylsulfate (Cs decylsulfate/Cs NO_3/water) called CDS were studied[12] by X-ray diffraction and optical microscopy in several experimental conditions: different sample holders and samples in electric and magnetic fields at room temperature. The results obtained with magnetically oriented samples[12] confirm the previously proposed[2,3] model of cylindrical symmetry for the scatterers, with micellar length larger than 500 Å.

In a previous paper[13] we discuss the interpretation of X-ray diffraction results of mesophase LK in terms of a pure nematic structure and its difficulties, specifically because the width of the diffraction peak observed at $s^{-1} = 43.3$ Å (absolute value of the scattering vector) is very narrow in comparison with the predictions of the usual nematic theories. Assuming for LK mesophase an homogeneous distribution of micelles in water the characteristic parameters are:[13] micellar radius R = (14.2 ±0.5) Å and mean distance between neighboring micelles d = (47.0 ±0.5) Å. The analysis of the diffraction patterns of LK samples,[13,14] however, could be done assuming nonhomogeneous distribution of amphiphilic in water with the formation of aggregates of cylindrical micelles. In this model,[13] the micelles have R = (17 ±1) Å and are packed in an hexagonal lattice of parameter a = (47.5 ±0.5) Å. The diffraction peak is associated to the 100 diffraction of the hexagonal array, for aggregates of about 25 micelles. So, the nematic type I phase could be thought as composed by microdomains of the middle soap phase order (called H_α).

Fujiwara and Reeves[15] studied by nuclear magnetic resonance (NMR) the LK lyomesophase (with deuterium instead of water) in the range of temperatures from 10 to 70°C. The analysis of the temperature dependence of D_2O deuterium quadrupole splittings evidences the coexistence of H_α and nematic phases ($21 \leq T \leq 59$°C) and H_α in coexistence with an isotropic phase for temperatures above 59°C.

Preliminary X-ray diffraction studies with temperature variation were made[16] in mesophase LK, whose diffraction patterns present bands (characteristic of a nematic phase) and Bragg's points (characteristic of H_α phase). In this paper, mesophase LK is studied by X-ray diffraction and optical microscopy in the range of temperatures of 22°C to about 75°C. The binary mixture K laurate/water (called LKb), which forms a lyomesophase in the middle soap phase, is also studied.

II. EXPERIMENTAL

The mesophases LK and LKb were prepared according to usual procedures,[1,2] with the compositions given in Table I:

TABLE I
Composition in wt.% of the mesophases LK and Lkb

Sample	K laurate (wt.%)	H_2O (wt.%)	KCl (wt.%)
LK	33.19 ± 0.06	65.5 ± 0.1	1.35 ± 0.01
LKb	38.00 ± 0.06	62.0 ± 0.1	—

For the X-ray diffraction experiments the samples were sealed in lindemann, quartz and sodium glass capillaries with 0.7 mm diameter, placed in vertical position, with their axes perpendicular to the X-ray beam in a transmission geometry. A small angle Rigaku-Denki diffractometer and a Laue camera, both with Cu K_α monochromatic (LiF asymmetric crystal) and Cu Ni filtered radiation with point focus were used. The X-ray diffraction patterns were obtained by photographing technique.

The capillary with the sample stays in a furnace with a temperature controlling system. The device, designed and constructed in our laboratory, is attached to a goniometer head in a goniometer, allowing the sample position to be freely adjusted. The sample is heated by a flux of hot air. The hot source consists of a stainless steel box, where there is a 44Ω resistor composed by Ni-Cr wires. At the exit of the box there is a thermocouple connected to the electrical temperature controlling system. The hot air leaving the box reaches two Cu capillaries positioned parallel to the sample, with small holes in their surfaces, pointing to it. The hot atmosphere is kept by a thin cylindrical mylar film with radius of 15 mm and height of 40 mm. Another thermocouple is positioned inside the mylar cylinder for the temperature reading. The air flux is maintained by a conventional compressor and the temperature could be controlled by it and by the voltage at the resistor. This device prevents the contact between the hot source and the sample and promotes a homogeneous heating along the capillary. Temperature gradients greater than 0.5°C along the capillary axis are therefore avoided, since they would be particularly inconvenient in the case of liquid crystals. The temperature is controlled within 1°C in the range between room temperature to about 75°C.

At the sample position the X-ray beam has a diameter of 0.3 mm in small angle measurements and about 0.5 mm in Laue camera measurements. All

sample holders in both conditions received the beam in their central part. Exposure times varied between 24 and 48 hours (in small angle measurements) and between 1 and 24 hours (in Laue measurements).

For the optical microscopy experiments it was used a Zeiss crossed polarized light microscope with a heating platinum stage, placed in a temperature controlled room. The temperature is read by means of a thermometer coupled to the hot stage with an evaluated error of about 0.5°C. The samples were sealed in precision rectangle borosilicate glass capillaries tubing with inside dimension: path length 0.4 mm × width 8 mm. Microphotographs were obtained with a colored 135 mm film, ASA 100.

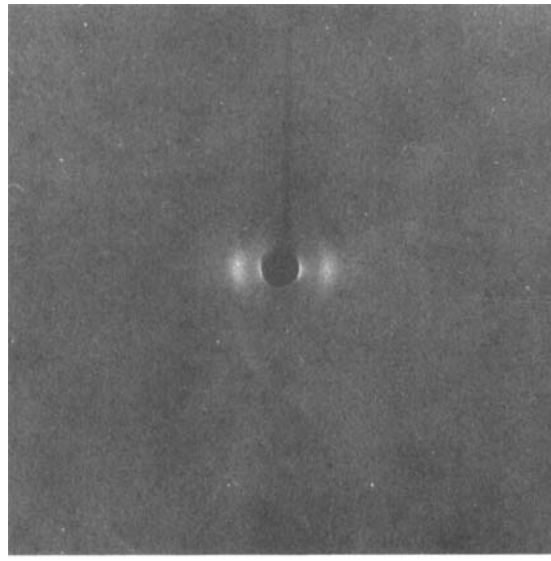
The rate of heating of all the experiment was about 5°C per hour (different rates are specified in the text).

III. RESULTS AND DISCUSSION

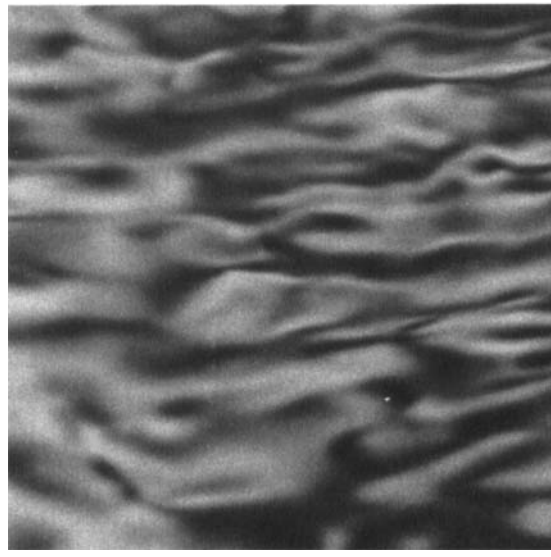
The photographing diffraction pattern obtained with sample LK at room temperature (~22°C) shows a diffraction band OB at $s^{-1} = (43.3 \pm 0.5)$ Å (when 0.7 mm capillaries were used) with preferred orientation along the horizontal equator[12] (Figure 1a). This result, as previously discussed,[12] is characteristic of a sample with moderate degree of orientation of the micelles, caused by the glass surface. The inner band present in the patterns obtained without monochromatic radiation are due to white radiation.[13] The observed texture is shown in Figure 1b, which resemble a nematic one.[3-6] This diffraction band has been studied by counter method[13] and the cylindrical Patterson function obtained from the experimental scattered intensity indicate a mean distance between axes of neighboring parallel micelles $d = (47.0 \pm 0.5)$ Å. Assuming homogeneous distribution of micelles in water, the value $R = (14.2 \pm 0.5)$ Å for the micellar radius is obtained.

For increasing temperatures in the range from 22°C to about 54°C only the nematic phase was observed with both experimental techniques, without significant variation of the angular position of OB.

For temperatures between 60°C and 74°C the diffraction pattern is totally modified: some Bragg points appear at $s_1^{-1} = (40.7 \pm 0.6)$ Å and $s_2^{-1} = (22 \pm 1)$ Å (average values of various experiments), whose relation s_2/s_1 is about $\sqrt{3}$, indicating an hexagonal array of cylindrical micelles where the diffractions at s_1 and s_2 are respectively identified to the 100 and 110 ones. The lattice parameter obtained from them is (47 ± 1) Å. Besides the Bragg's points characteristic of the H_α phase, the diffraction patterns present at the OB region a diffuse halo at $s^{-1} = (43 \pm 2)$ Å without any preferred orientation, indicating the existence of an isotropic phase (I) in coexistence with H_α. Figure 2a presents a superexposed pattern at which

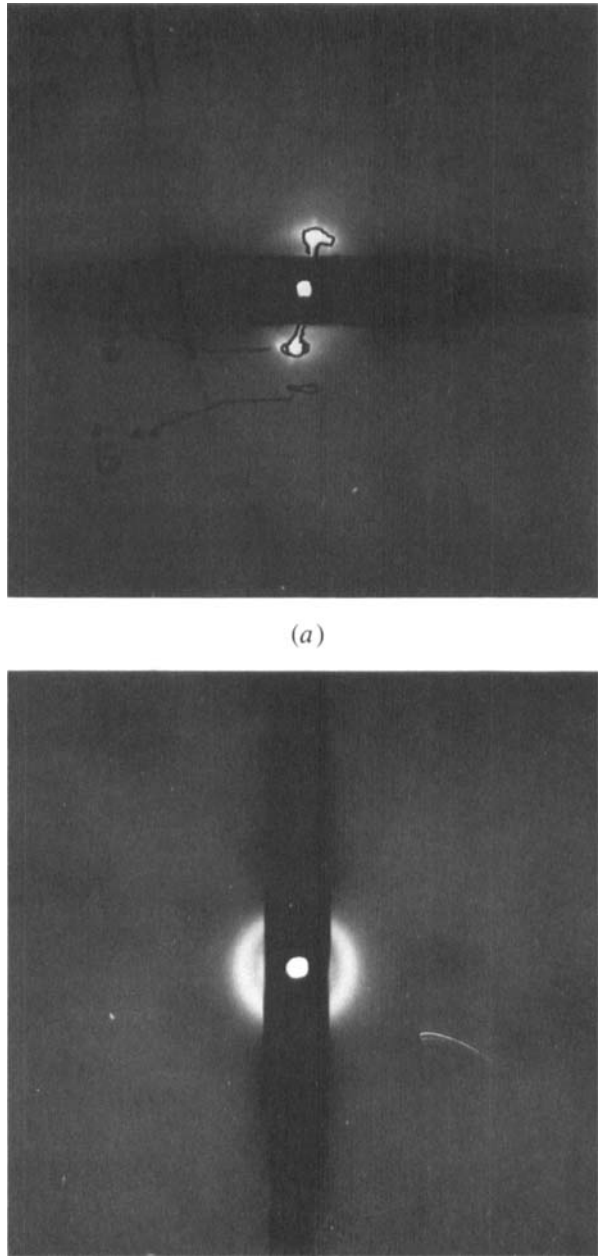


(*a*)



(*b*)

FIGURE 1 (a) X-ray diffraction result with sample LK in 0.7 mm thick capillary (placed in vertical direction in the plane of the figure). Temperature of about 22°C, Laue camera (Cu Ni filtered radiation). Nematic phase (N). (b) Optical texture of mesophase LK temperature of about 22°C, nematic phase-N (1 cm = 0.12×10^3 μm).



(a)

(b)

FIGURE 2 X-ray diffraction result with sample LK in 0.7 mm thick capillary (placed in vertical direction in the plane of the figure). Laue camera (Cu Ni filtered radiation), temperature of 62°C, (a) predominance of the hexagonal phase H_α; (b) predominance of the isotropic phase I.

it is observed a predominance of the H_α phase, and Figure 2b the predominance of the isotropic phase.

The coexistence of phases H_α and I was also observed by optical microscopy. Figure 3a shows a region of the sample with a fan-like texture

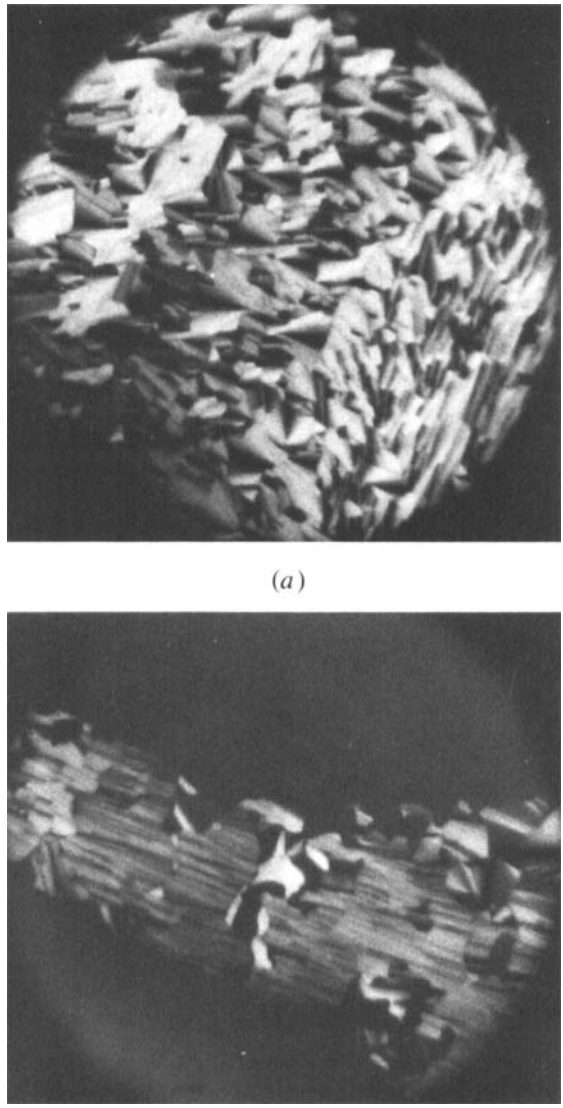


FIGURE 3 Optical textures of mesophase LK (1 cm = 0.46 × $10^3\mu$m). (a) hexagonal H_α phase, temperature of 61°C; (b) hexagonal (H_α) and isotropic (I) coexistent phases, temperature of 69°C.

characteristic of an H_α phase[17] and Figure 3b a region where the fan-like texture is observed beside an isotropic one, indicating the coexistence I and H_α phases. For temperatures above 75°C, only phase I was observed by optical microscopy.

Our results for temperatures above 60°C agrees with the obtained by Fujiwara and Reeves[15] by means of the NMR technique measurements.

Macroscopically, there is an observable decrease in the fluidity of LK samples in 15 mm diameter tubes (where the sample is prepared) with the temperature rise, which must be connected to the higher viscosity of H_α phase.

The reversibility of the process was verified and no thermal hysteresis effect was observed with both experimental techniques.

For temperatures between 54°C and 60°C it was observed in some experiments, especially with a quick rise of the temperature, the coexistence of the H_α phase with a nematic one. Figure 4 shows the Bragg's points characteristic of the H_α phase, with the oriented band, now appearing at $s^{-1} = (41 \pm 1)$ Å, of the nematic phase.

Optical microscopy observation of mesophase LK in this range of temperature have not a trivial interpretation. Figure 5a shows the observed

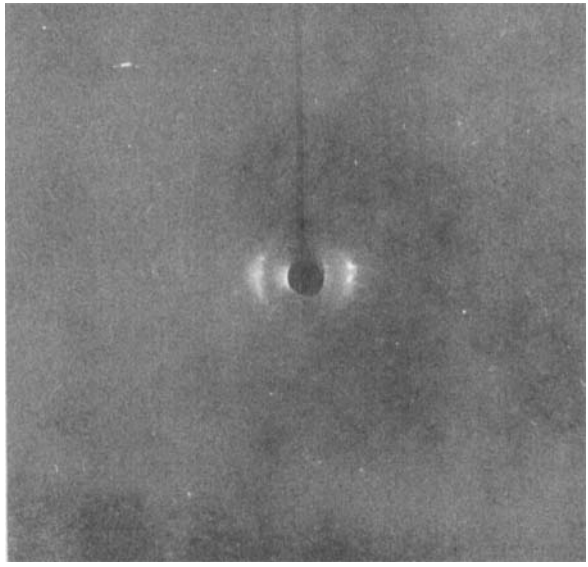
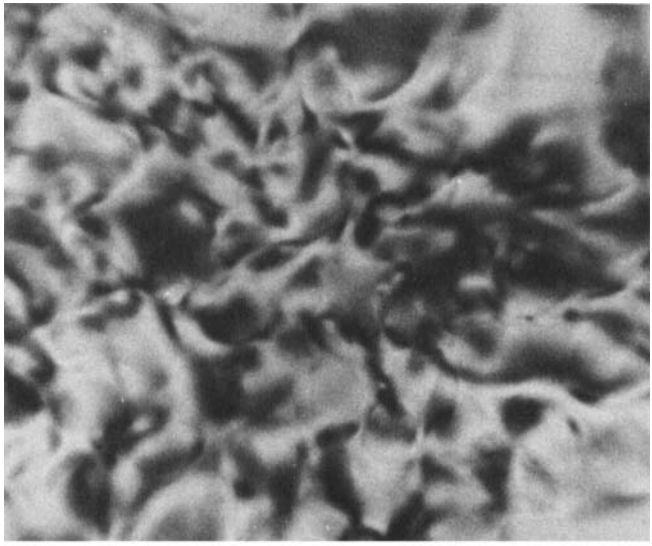
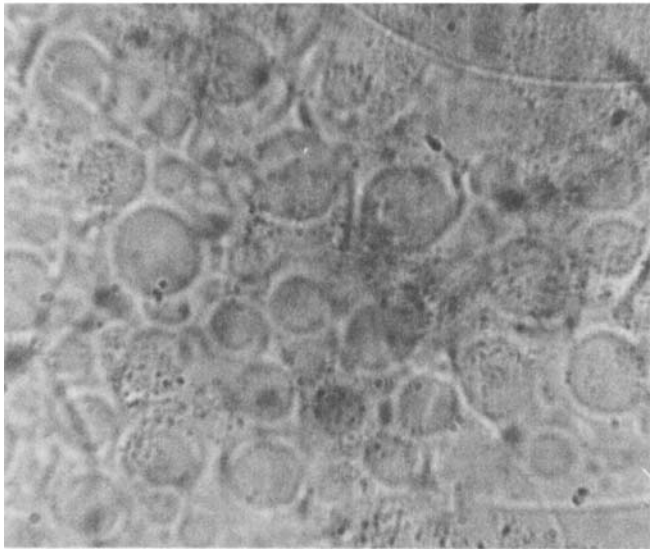


FIGURE 4 X-ray diffraction result with sample LK in 0.7 mm thick capillary (placed in vertical direction in the plane of the figure). Laue camera (Cu Ni filtered radiation), temperature of 55°C. Coexistence of hexagonal (H_α) and nematic (N) phases.



(*a*)



(*b*)

FIGURE 5 Optical textures of mesophase LK (1 cm = 0.12×10^4 μm), temperature of 55°C. Coexistence of hexagonal (H_α) and nematic (N) phases. (a) observation with the analyzer; (b) observation without the analyzer.

texture at 55°C. It could be interpreted as a nematic texture but there is also some circular regions that could be characteristic of the beginning of the formation of H_α phase. In Figure 5b, the same region of the sample was observed without the analyzer and it is possible to identify two regions of different refractive index. Out of this temperature interval it was not observed the coexistence of H_α and N phases as discussed by Fujiwara and Reeves.[15] However, the comparison between our and his experiment must take into account that the NMR measurements need a strong magnetic field which could influence the appearance of the H_α phase at lower temperatures.

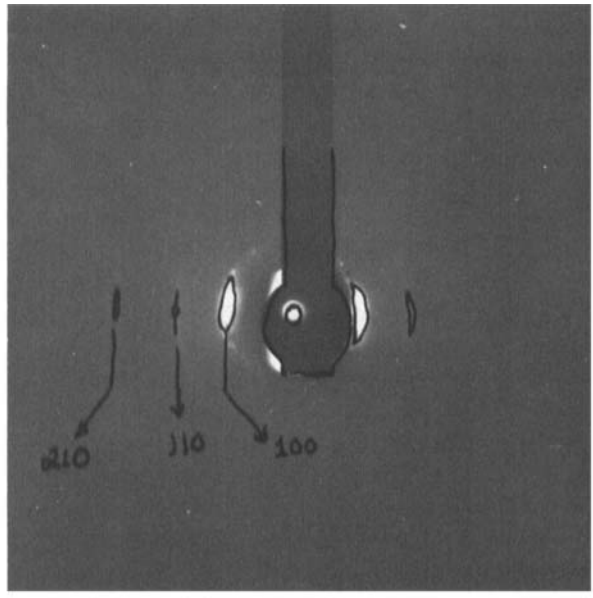
The modification of the nematic band position of about 2.3 Å (from $s^{-1} = 43.3$ Å to $s^{-1} = 41$ Å) could be explained in terms of the decreasing of the micellar radius for increasing temperatures, essentially caused by the carbon chain contraction.[18,19] The expected modification[19] (decrease) of the micellar radius from 22°C to about 55°C is 1.2 Å which, in terms of the distance between micellar axes corresponds to a decrease of 2.4 Å.

The coincidence of the nematic band position with the 100 diffraction of the H_α phase could indicate that the band is a broad 100 diffraction of aggregates of micelles which are going to constitute an extended hexagonal array of scatterers (phase H_α).

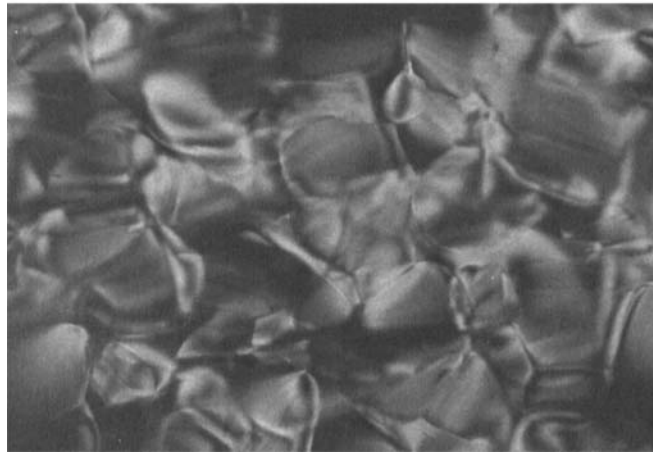
As the expected average distance between neighboring micelles in the nematic phase at $T \simeq 60$°C is about 45 Å (2.4 Å smaller than the obtained at room temperature), if these micelles lose their orientational correlation to form phase I at high temperatures, we would expect an average distance between neighboring micelles greater than the nematic one. This average distance (phase I) is about 43 Å (interpreting the position of the scattering halo directly as the average distance). So, phase I could be composed by anisotropic micelles different from the nematic ones without orientational correlation or by isotropic micelles.

To compare the coexistent H_α phase with the conventional middle soap phase, the binary system LKb was studied. Figure 6a shows a super-exposed diffraction pattern (monochromatic CuK_α radiation) of mesophase LKb at room temperature where it is possible to identify the 100, 110 and a very weak 210 reflections. Figure 6b shows the observed fan-like texture in a polarizer microscope. The lattice parameter of the hexagonal array of micelles obtained from X-ray diffraction data is (44.9 ±0.5) Å.

Husson and co-workers[18,19] studied LKb phase in the range of amphiphilic concentration of 60 wt.% to 50 wt.%, observing an increase of the lattice parameter as concentration decreases and for the micellar radius a value practically constant (of about 17 A° at 22°C — taking into account the dependence with temperature).[13] Our value of the lattice parameter (at 38 wt.%) is comparable to the one extrapolated from their results.



(*a*)



(*b*)

FIGURE 6 (a) X-ray diffraction result of mesophase LKb in 0.7 mm thick capillary (placed in vertical direction in the plane of the figure). Laue camera (monochromatic CuK_α radiation). Temperature of about 22°C. (b) Optical texture of mesophase LKb (1 cm = $0.12 \times 10^3 \mu m$). Temperature of about 22°C, Hexagonal H_α phase.

The measured specific partial volume of the potassium laurate in LKb (by means of a calibrated micropicnometer) is (0.93 ±0.01) cm^3/g, which gives a volume concentration for the amphiphilic of (0.362 ±0.001). Assuming homogeneous distribution of long micelles in water,[18,19] the obtained cylinder radius is (14.2 ±0.1) Å.

The value of the micellar radius obtained for mesophase LKb (H_α phase) is the same previously obtained for mesophase LK (nematic phase) admitting homogeneous distribution of micelles in water.[13] The length of an extended carbon chain of K laurate[20] at room temperature is 14.2 Å and the polar head (COO^-K^+) has a diameter of about 3 Å[21] so, an extended K laurate molecule has a length of about 17 Å. Our value of the cylinder radius (mesophase LKb) is about 3 Å smaller than the length of an extended K laurate molecule and the observations of Husson and co-workers[19] in another range of amphiphilic concentration. At this point there are two possibilities: (i) the micellar radius presents a small variation as a function of the amphiphilic concentration most accentuate at high water concentrations; (ii) the procedure used for the calculation of the radius assuming the micelles of infinite extent hexagonally packed[18] are not totally correct for high water concentrations. It would be possible to obtain a micellar radius greater than the obtained for mesophase LKb considering that we have water among the cylinders along their long axes.

In a first approach, we will consider hypothesis (i) and its micellar radius a good one (mesophase LKb). The thermal linear dilatation coefficient[19] for the carbon chains is $-1.3 \times 10^{-3}\,°C^{-1}$ so, the micellar radius (mesophase LKb) at 60°C is expected to be (13.5 ±0.1) Å and the lattice parameter (42.7 ±0.1) Å.

The lattice parameter of the coexistent H_α phase (T = 60°C, amphiphilic concentration of about 33 wt.%) is about 4 Å bigger than the obtained for LKb middle soap phase (T = 60°C, amphiphilic concentration of about 38 wt.%). This result is consistent with Husson and co-workers[18] observations which foresees an increase of the lattice parameter for decreasing amphiphilic concentrations.

To compare the micellar radius of the H_α coexistent phase with the LKb phase it is necessary to consider the two possible descriptions of the type I mesophase structure[13] presented in section I. The micellar radii at 60°C obtained from the two models described in section I, taken into account the thermal linear dilatation coefficient are: 13.5 Å for the nematic structure model and 16.2 Å for the aggregates of micelles model. The radius obtained from the nematic structure model is consistent with the LKb H_α phase one at 60°C (hypothesis (i)). So, the H_α coexistent phase (ternary system) could have approximately the same parameters (a and R) of the LKb H_α phase according to the nematic model.

Considering now the second hypothesis, the cylinder radius of mesophases LKb and LK have a constant value, the formation of the coexistent

H_α phase could be thought as a flocculation of cylindrical micelles around the small seed aggregates (the lattice parameter of the model of the aggregates is about the same obtained for the coexistent H_α phase).

As an end point it is necessary to take into account another parameter that was not discussed in the comparison among the different phases: the length of the micelles. In all cases it was assumed that the micelles are long; however, important differences could exist between the phases in terms of this parameter, specifically for the coexistent H_α and I phases. The determination of micellar length and radius by means of an independent experiment of H_α and I coexistent phases is necessary to give a complete description of the system.

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References

1. K. Radley, L. W. Reeves and A. S. Tracey, *J. Phys. Chem.*, **80**, 174 (1976).
2. F. Fujiwara, L. W. Reeves, M. Suzuki and J. A. Vanin, in *Solution Chemistry of Surfactants*, ed. K. Mittal (Plenum Press, New York, 1979), vol. 1, pp. 63–77.
3. J. Charvolin, A. M. Levelut and E. T. Samulski, *J. Physique Lett.*, **40**, L587 (1979).
4. K. Radley and A. Saupe, *Mol. Cryst.*, **44**, 227 (1978).
5. K. Radley and A. Saupe, *Mol. Phys.*, **35**, 1405 (1978).
6. J. Charvolin and Y. Hendrikx, *J. Physique Lett.*, **41**, L597 (1980).
7. L. Q. Amaral, C. A. Pimentel and M. R. Tavares, *Acta Cryst.*, **A34** (S4) S188 (1978).
8. L. Q. Amaral, C. A. Pimentel and M. R. Tavares, Collected Abstracts of the IX Hungarian Diffraction Conference (Pecs, 1978) p. 1.
9. L. Q. Amaral, C. A. Pimentel, M. R. Tavares and J. A. Vanin, *J. Phys. Chem.*, **71**, 2940 (1979).
10. L. Q. Amaral, M. R. Tavares, *Mol. Cryst. Liq. Cryst. Lett*, **56**, 203 (1980).
11. L. Q. Amaral, *Acta Cryst.*, **A37** (Suppl.), C-364 (1981).
12. A. M. Figueiredo Neto and L. Q. Amaral, *Mol. Cryst. Liq. Cryst.*, **74**, 109 (1981).
13. A. M. Figueiredo Neto and L. Q. Amaral, *Acta Cryst. A* (in the press) (1983).
14. A. M. Figueiredo Neto, "Formation of Aggregates of Micelles in Type I Lyotropic Liquid Crystals — A study by X-ray Diffraction and Other Techniques". Doctoral thesis. Univ. of São Paulo, São Paulo, Brazil (1981).
15. F. Y. Fujiwara and L. W. Reeves, *J. Phys. Chem.*, **84**, 653 (1980).
16. A. M. Figueiredo Neto and L. Q. Amaral, 8th International Liquid Crystal Conference, Kyoto, Japan, 1980, Abstracts H-15P, p. 313.
17. F. B. Rosevear, *J. Am. Chem. Soc.*, **31**, 628 (1954); *J. Soc. Cosmetic. Chem.*, **19**, 581 (1968).
18. V. Luzzati, H. Mustacchi, A. Skoulios et F. R. Husson, *Acta Cryst.*, **13**, 660 (1960).
19. F. R. Husson, H. Mustacchi and V. Luzzati, *Acta Cryst.*, **13**, 668 (1960).
20. J. E. Leibner and J. Jacobus, *J. Phys. Chem.*, **81**, 130 (1977).
21. T. C. Waddington, Advances in Inorganic Chemistry and Radio-Chemistry, Edited by H. J. Emeléus and A. J. Sharpe, vol. 1, pp. 157–221. New York: Acad. Press.