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Microscopy and Deuterium NMR Studies on Induced Cholesteric Lyotropic Mesophases of Potassium Laurate

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Induced cholesteric lyotropic mesophases can be formed by the addition of cholesterol to "nematic" phases of potassium laurate/*n*–decanol/water and electrolyte. The resulting mesophases are oriented by magnetic fields, the helicoidal axes being collinear with the field (type II) or perpendicular to it (type I). In the present work, the textures of oriented cholesteric samples were examined under the polarizing microscope. The associated patterns depended on the mesophase type and on the applied field direction. The usual chevron and focal-conic textures were seen in type II cholesteric mesophases. More complex disclinations were exhibited by type I cholesteric phases. The comparison between the relative order profiles for type I and type II mesophases, nematic and cholesteric, obtained by deuterium NMR, shows that great distortions are not present in the micelles of the cholesteric systems. The overall picture suggests that mainly electrostatic interactions are responsible for the cholesteric properties in induced mesophases.

INTRODUCTION

Micellar lyotropic mesophases are multicomponent systems. They are prepared from an amphiphile, an electrolyte and water, usually with a small addition of a long chain alcohol.[1-2] The magnetic behavior and micelle shape are strongly dependent on the phase composition. When samples are placed in a magnet, type I lyomesophases orient with their director parallel to the applied magnetic field ($\mathbf{B}_0$) while type II lyomesophases orient perpendicularly to $\mathbf{B}_0$.[2-4] The different signs of the diamagnetic anisotropy are

responsible for these different orientations.[3] Disk-like or cylindrical micelles were identified by low angle X-ray diffraction studies[5–10] and have been associated, respectively, with type II and type I mesophases[4] when the hydrophobic part of the amphiphile is essentially a hydrocarbon chain.[11]

An induced cholesteric lyotropic mesophase is obtained if a chiral solute is added to a nematic phase. This procedure has been known since the early works on thermotropic liquid crystals but only recently it was extended to lyomesophases.[12,13] Similarly to the nematic micellar phases, there are two kinds of cholesteric lyotropic phases. The inclusion of the chiral solute (the inductor) in a nematic type II phase yields a type II cholesteric mesophase, which is up to orient its helicoidal axis parallel to the magnetic field direction.[12] The addition of the inductor to a type I lyomesophase yields a cholesteric type I phase; in this case, the helicoidal array is untwisted by a sufficiently strong magnetic field.[12,14]

In the present work we report the textures seen under the polarizing microscope for magnetically oriented samples of potassium laurate cholesteric mesophases in which cholesterol was used as inductor. The relative order profiles for perdeuterated amphiphile chains are shown and the predominance of distortions in micelles or electrostatic interactions for cholestericity induction is discussed.

EXPERIMENTAL

Mesophases were prepared according to the usual procedures. Potassium laurate (KL) was recrystallized from ethanol and special care was taken with the purity of all components. Cholestericity was induced by cholesterol addition. The magnetic behavior of the mesophases (compositions shown in Table 1) was verified by deuterium NMR, at 15.3 MHz, using a

TABLE I

Composition of the cholesteric lyomesophases (molar fraction %)

Sample	1	2	3	4	5
KL	3.98	3.92	3.02	4.03	4.43
KCl	0.92	0.93	1.41	2.65	2.61
DeOH*	—	—	0.74	0.70	0.70
H_2O	66.02	94.61	88.04	92.25	91.91
D_2O	28.95	0.09	6.63	0.09	0.09
KOH	—	0.32	—	—	—
Cholesterol	0.13	0.13	0.16	0.28	0.26
Magnetic type	I	I	II	II	II

*DeOH = *n*-decanol

Varian–XL–100–12–FT spectrometer operating with the Gyrocode Option. The angular dependence of the ^2H quadrupole splitting of HDO yields the orientation of the mesophase director relative to the magnetic field.[4]

A Zeiss polarizing microscope, model Universal, with attached camera, has been used to photograph the textures of the samples placed in 500 μm high quality flat capillar cells. The samples were previously oriented, subjecting them to a magnetic field, $\mathbf{B}_0$, of 1.4 tesla parallel (parallel orientation) or normal (perpendicular orientation) to the cell surface. Photomicrographs were taken immediately after the removal of the samples from the magnetic field.

RESULTS

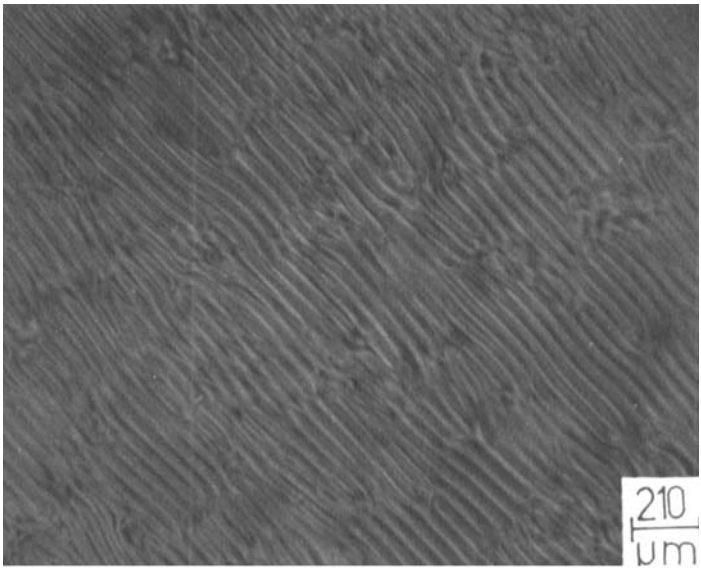
1 Textures observed with the polarizing microscope

The textures observed under the polarizing microscope for a cholesteric lyotropic type II mesophase in parallel orientation are shown in Figure 1a. The usual chevron pattern is exhibited and the helicoidal axes are coincident with the $\mathbf{B}_0$ direction. For the same sample, perpendicularly oriented (Figure 1b), a focal-conic texture[14,15] is clearly seen.

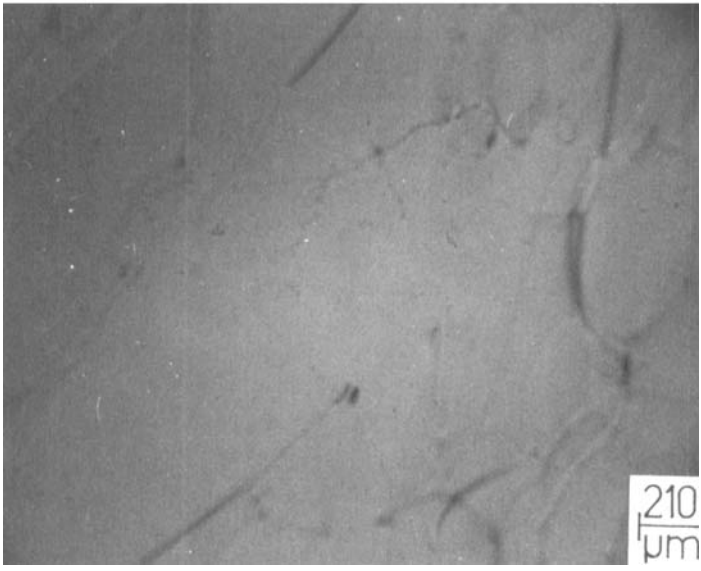
The pattern associated with a cholesteric type I lyomesophase in parallel orientation is shown in Figure 2a. The magnetic field was applied along the largest edge of the picture for a period of 18 h. The general appearance of this texture is different from that reported for normal type I mesophases in perpendicular orientation,[9,10,12,14] associated with a hydrodynamic back flow effect. This kind of cholesteric sample, after two days in the magnetic field, develops a new texture of the mosaic[15] or marble type. The pattern of Figure 2a is attributable to an ordering of the helicoidal array perpendicularly to the field. The untwisting of the cholesteric structure by a prolonged action of the magnetic field justifies the final mosaic texture.

Figure 2b corresponds to the pattern associated with a type I phase in perpendicular orientation. This texture corresponds to helicoidal pairs resulting from τ^+ and λ^+ disclinations[16] and is usually seen in type I cholesteric lyotropic mesophases when in perpendicular orientation.[14] This pattern corresponds to helicoidal axes perpendicular to $\mathbf{B}_0$, and parallel to the cell surfaces. This "spaghetti-like" texture,[14] after five days of magnetic field action, changes to a pseudo-isotropic pattern, corresponding again to the untwisting of the cholesteric array.

Based on the evidences shown in Figure 2a, and especially in Figure 2b, we propose two different orientational times for a cholesteric type I mesophase in a magnetic field: one for the alignment of the helicoidal axes

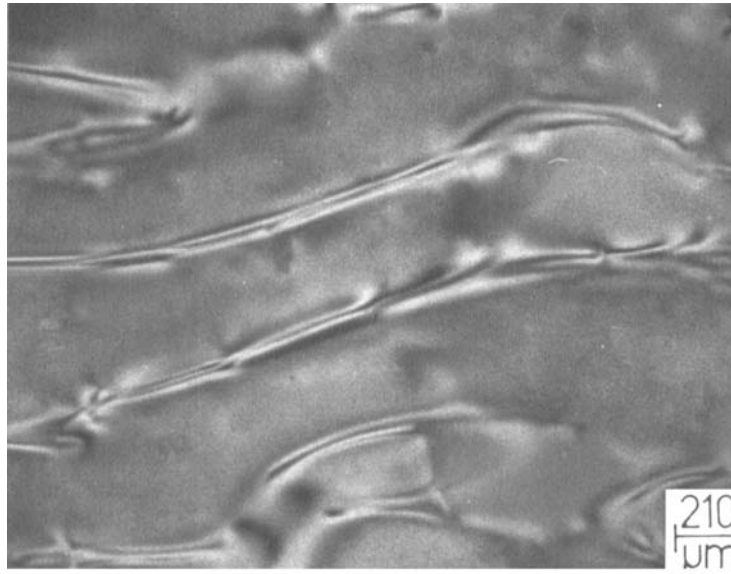


(*a*)

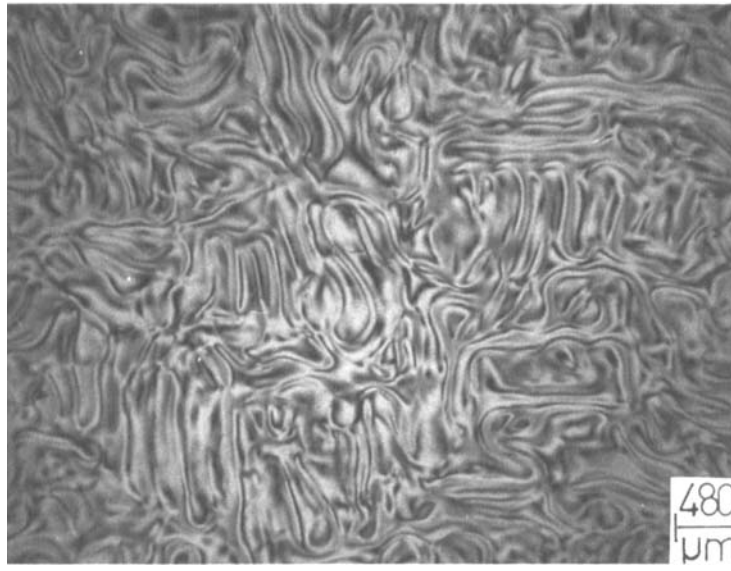


(*b*)

FIGURE 1 Microscopic textures of magnetically oriented type II cholesteric lyomesophases (crossed polarizers). (a) Parallel orientation. The lines of the chevron pattern are approximately perpendicular to the applied field direction. (b) Perpendicular orientation.



(*a*)



(*b*)

FIGURE 2 Microscopic textures of magnetically oriented type I cholesteric lyomesophases (crossed polarizers). (a) Parallel orientation. The magnetic field was applied along the largest edge of the picture. (b) Perpendicular orientation.

perpendicular to $\mathbf{B}_0$ and another for the untwisting process. The required time for each process is different and we have found in our laboratory studying other cholesteric systems,[14,17] that the chemical nature of the mesophase and sometimes wall effects decide whether alignment of the helicoidal axes or untwisting of the helicoids predominates in the magnetic field.

2 Deuteron NMR results

We have reported in a previous note[18] the deuterium NMR order profiles of the perdeuterated laurate chain in cholesteric lyotropic mesophases. Taking these related values for deuterium quadrupole splittings and dividing each one by the value corresponding to the plateau segments, we get the "relative order profiles"[19] shown in Figure 3. These relative values contain only the trans-gauche contributions to the order degree of each hydrocarbon chain segment.[4] For type II mesophases, the relative order profiles are almost the same for cholesteric and nematic lyomesophases except for the eighth and ninth segments. For type I mesophases the largest deviations are observed at the first methylene segment directly attached to the polar head; the general shape of the relative order profile for cholesteric and normal mesophases is preserved, unless for the seventh, eighth and ninth segments.

It is well established from micellar solution studies[20–24] that cholesterol does solubilize in the micelle interior. Besides, it is well known that the

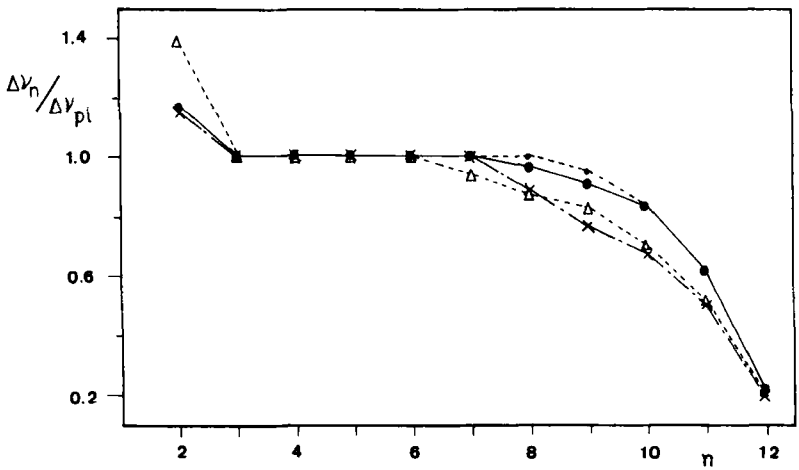


FIGURE 3 $\Delta\nu_n/\Delta\nu_{pl}$ versus corresponding CD_2 segment number, n. $\Delta\nu_{pl}$ is the ^2H quadrupole splitting of the plateau segments: Δ type I (cylindrical micelles—from Ref. 34); X cholesteric type I; • type II (disk-like micelles, from Ref. 35); ● cholesteric type II.

steroidal rings of cholesterol are about 10.5 Å in length and its aliphatic chain is about 6.5 Å long.[25] The length, l, of an extended hydrocarbon chain can be calculated[20] from the formula $l = 1.5 + 1.265n_C$, where n_C is the number of carbons. If on the other hand we ask at which segment of the amphiphile host chain the length $l = 10.5$ Å is attained we obtain, using the previous expression, an n_C value of approximately 7. So, in both cholesteric mesophases the perturbation in the host laurate order profile can be explained as a packing effect of the steroidal rings. The same conclusion can be reached by constructing framework scale models of an amphiphile chain and a cholesterol molecule, and packing them side by side.

The great discrepancy of the first CD_2 segment when comparing type I cholesteric and nematic phases can be rationalized as follows. The area occupied by the cholesterol OH head groups is approximately 37 to 39 $Å^2$.[26] The area occupied by the laurate polar head in type I mesophases is known to be 56 $Å^2$.[10] The introduction of a cholesterol molecule in a type I micelle, cylinder-shaped, would change the packing of the amphiphile polar heads, affecting the ordering of the CD_2 segment directly attached to it. This effect is not seen in type II mesophases where the laurate polar head area is nearly the same as that of the cholesterol OH group.[27]

The similarity of the relative order profiles is evidence that no appreciable distortions of disk-like or cylindrical micelles are brought about by the cholesterol addition or that only small geometric distortions are present in the induced "cholesteric" micelles. This conclusion is supported by well established evidence that ^2H NMR order profiles are very sensitive to microenvironmental changes.[19,28]

CONCLUSIONS

According to Saupe[12] two possibilities should be considered for induction of cholestericity in a lyotropic mesophase in the presence of a chiral solute:

(a) the inclusion of the optically active solute in the micelle interior distorts it to a chiral shape.

(b) the twisting may be caused by the interaction between the micelles through dispersion forces.

The microscopic textures here reported for laurate/cholesterol mesophases show, beyond any doubt, that helicoidal organization is present. The relative order profiles from ^2H NMR spectra show that great distortions should not be present in the micelles of both type I or type II mesophases. So, we can think that if any distortions are present, they should be very small.

An interaction mechanism for a cholesteric micellar phase can be proposed after a survey of the literature concerning lyotropic cholesteric nonaqueous mesophases based on polypeptides.[29–33] In these systems the long chain molecule is itself arranged in an α-helix; the permanent dipoles of this macromolecule are, therefore, in an asymmetric array. The consequent interaction between different α-helices imposes a unidirectional twist, leading to the macroscopic cholesteric helicoidal array.

This basic idea can be transposed to the laurate/cholesterol system. Each cholesterol molecule solubilizes in the lyotropic mesophase without micellar distortions, but creates points of charge asymmetry on the micellar surface. The twist has its origin in the intermicellar forces resulting from the asymmetric distribution of charges. This kind of interaction in induced cholesteric lyotropic mesophases seems to be more effective in creating a pitch than small micellar distortions.

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