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Optical Sign Determinations on Cholesteric Lyotropic Mesophases

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Optical signs of type I and II micellar cholesteric lyotropic mesophases were for the first time determined. Lyomesophases were prepared from the following amphiphiles: potassium *l-N*-lauroyl-serinate, potassium laurate, sodium decylsulfate, cesium decylsulfate and decyl-ammonium chloride. Cholesterol was added to all mesophases in order to obtain the chevron pattern for magnetically oriented samples. The method involves the direct observation of the textures at the polarizing microscope. Using a quartz-wedge retardation plate the directions of the slow and fast light vibration components are determined. This method is simpler than the usual observation, under conoscopic illumination, of the basal interference figure which is hardly obtained in micellar lyotropic cholesteric mesophases. All type I cholesteric lyotropic mesophases here investigated exhibited a positive optical sign, whereas all type II cholesteric lyomesophases showed a negative birefringence.

1. INTRODUCTION

Optical signs of thermotropic liquid crystals have been known since the classical essay by Friedel.[1] In that work a negative optical sign for cholesteric mesophases and a positive one for nematic and smectic phases was reported.

The birefringence of lyotropic liquid crystals based on amphiphiles has been also investigated. The optical signs have been reported as follows:

(i) *Positive*:

(a) for "neat" or "lamellar" mesophases.[2] When prepared from branched-chain amphiphiles, in certain circumstances, the neat phase may show a negative optical sign[3–6];

(b) for type II lyomesophases[7–8] formed by disk-like micelles.[9–10].

(ii) *Negative*:

(a) for "middle" or "hexagonal" phases[4,5];

(b) for type I lyomesophases[8] based on cylindrical micelles.[10-12]

The origins of birefringence in lyotropic phases[6] are more complex than those found in thermotropic liquid crystals. Several factors should be considered: form birefringence associated with micellar shape; anisotropic polarizabilities of oriented C—H bonds; bond systems of the polar groups (even from the additives); anisotropic distribution of water molecules.[5,6]

The usual technique for characterization of the birefringence sign involves the determination of the direction of the slow and fast light vibration components by observation of the basal interference figure under conoscopic illumination on a polarizing microscope.[12]

In the present work, optical signs were determined for aqueous micellar cholesteric lyotropic systems, which until now have not been reported.

The method here described is based on the determination of the fast and slow vibration directions, observing the interference colour variation when a quartz wedge is inserted in the microscope optical path. A necessary condition to apply this method is the previous knowledge of the sample optical axis direction.

When working with a magnetically oriented cholesteric lyomesophase, exhibiting the "chevron" pattern, the optical axis corresponds to the direction perpendicular to the lines of this texture. This procedure is convenient for micellar cholesteric lyotropic liquid crystals where the basal interference figure for planar orientation[12] is hard to obtain.

2. EXPERIMENTAL

Several amphiphiles were investigated. Four of them were anionic, namely, sodium decylsulfate (NaDS), cesium decylsulfate (CsDS), potassium laurate (LK) and potassium *l*-*N*-lauroyl-serinate (*l*-KNLS). The only cationic detergent used was decyl-ammonium chloride (CDA). It should be noted that the levo enantiomer *l*-KNLS has a complex polar head.[13,14] Type II intrinsic cholesteric mesophases based on this amphiphile exhibit a large helical pitch[14], and do not show the "chevron" texture. Therefore, it was necessary to prepare a new mesophase, with small amounts of cholesterol added in order to induce a chevron texture (Sample I in Table I).

TABLE I

Mesophases Composition (% molar fraction)

	NaDS^{a}	LK^{b}	CsDS^{c}	CDA^{d}	*l*-KNLS^{e}	Na_2SO_4	KCl	NH_4Cl	H_2O	KOH	2, *d*, 2-undecanol	*n*-decanol	cholesterol	tartaric acid	glycine d_5	Magnetic type
A	4.59	—	—	—	—	0.81	—	—	94.43^{f}	—	—	—	0.11	—	0.06	I
B	5.08	—	—	—	—	0.95	—	—	93.75^{f}	—	—	—	0.11	—	0.11	I
C	—	3.69	—	—	—	—	0.97	—	95.13^{g}	—	—	—	0.21	—	—	I
D	—	3.79	—	—	—	—	1.06	—	94.11	0.44	—	—	0.08	—	0.52	I
E	—	3.69	—	—	—	—	1.47	—	94.00	0.26	0.47	—	0.11	—	—	II
F	—	—	6.00	—	—	0.66	—	—	92.33^{f}	—	—	—	—	0.56	0.45	I
G	—	—	5.98	—	—	0.63	—	—	92.47	—	—	—	—	0.67	0.25	I
H	—	—	—	5.05	—	—	—	1.86	92.88^{h}	—	—	—	0.21	—	—	II
I^{j}	—	—	—	—	2.71	—	1.52	—	92.55^{i}	2.40	—	0.47	0.35	—	—	II

[a] NaDS—sodium decylsulfate

[b] LK—potassium laurate

[c] CsDS—cesium decylsulfate

[d] CDA—decyl-ammonium chloride

[e] *l*-KNLS—potassium-*l*-*N*-lauroyl-serinate;

[f] 0, 1NH$_2$SO$_4$

[g] 32% D_2O

[h] 5% D_2O

[i] 18% D_2O

[j] Ref. 17

All mesophases were prepared by the usual mixing and homogenization procedure, their compositions are reported in Table I.

The magnetic type was characterized by deuterium NMR of the HDO present in the lyomesophase.[15-18]

A Zeiss polarizing microscope, model Universal, with attached camera was used. Samples were contained in flat capillar cells of 0.3 mm thickness. The textures of all mesophases were photomicrographed with and without quartz wedge. To achieve orientation, a magnetic field of 1.4 tesla was applied parallel to the cell surface for a time long enough for the development of the chevron texture.

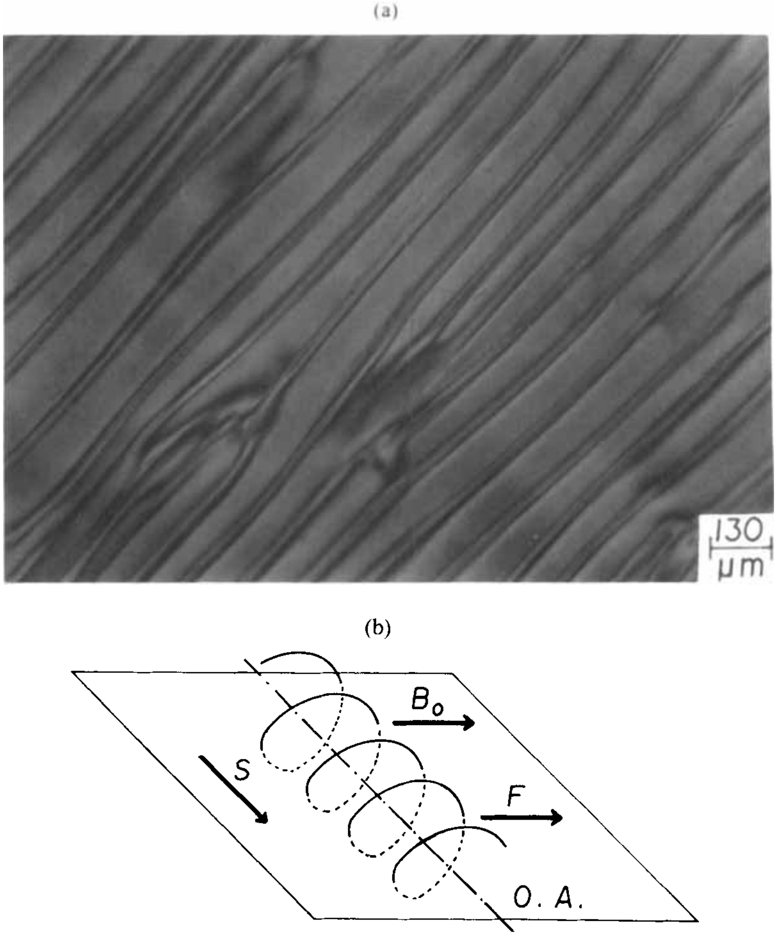

FIGURE 1 Type I cholesteric lyotropic mesophase. (a) Typical chevron texture. (b) Schematic representation of the relative positions among the helical array, optical axis (O.A.) and magnetic field (B_0). The slow (S) and fast (F) vibration directions were determined by the quartz wedge method. See Color Plate IV, Vol. 111.

For type I and type II cholesteric samples the lines of this texture appear, respectively, parallel (Figure 1) and perpendicular (Figure 2) to the magnetic field direction. Special care should be taken with type I cholesteric mesophases since these systems are untwisted by a prolonged exposure to the magnetic field.[15,16]

For optical sign determination, the oriented sample is placed on the rotating stage of the polarizing microscope in an extinction position (orthoscopic illumination). With crossed polarizers, this situation is obtained when the sample optical axis is parallel or perpendicular to the polarizer. The stage is turned 45° and the quartz wedge is inserted.[19,20] If the direction of the light's slow component in the quartz wedge matches the slow vibration direction in the sample, the

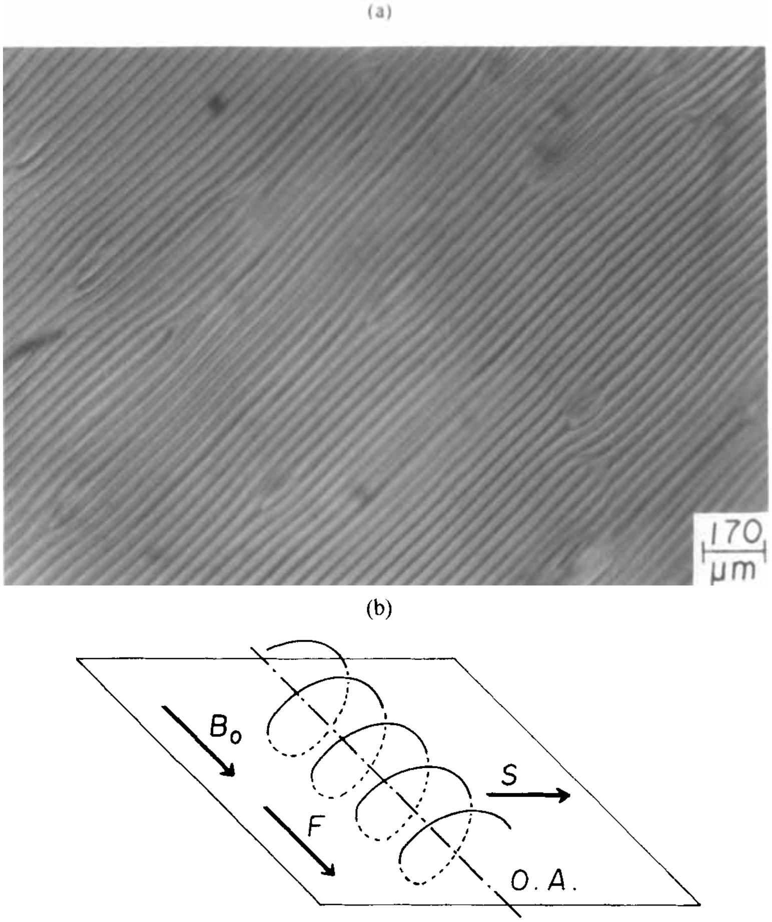

FIGURE 2 Type II cholesteric lyotropic mesophase. (a) Typical chevron texture. (b) Schematic representation similar to Figure 1.b. See Color Plate V, Vol. 111.

interference colours will increase on the Newton scale. If the slow component of the quartz wedge is parallel to the sample's fast component, a resulting decrease in the interference colours will be seen. In this way, the fast and slow directions in the sample can be determined.

As it was stated before, when the sample presents the chevron texture, its optical axis is oriented in the plane of the sample cell, perpendicularly to the lines of this pattern. If the slow component direction in the sample is parallel to its optical axis, the birefringence sign will be positive.[12,19,20] Obviously, if the fast component is parallel to the quoted axis, the birefringence will be negative.[12,19,20]

3. RESULTS AND DISCUSSIONS

The measured optical signs and cholesteric half-pitches (distance for a 180° change of director) are shown in Table II.

For type I mesophases, the half-pitches, measured directly with the microscope eyepiece micrometer, are in the range from 80 to 100 μm for phases B, C, D, F, G and about 250 μm for phase A. As can be seen in Table II these distances are greater than that correspondent to type II lyomesophases, in which values between 20 and 40 μm were found. It should be mentioned that for type I cholesteric lyomesophases the half-pitch values are affected by the partial untwisting process of the helical array. Nevertheless, the reported values are typical, for types I and II cholesteric lyomesophases of amphiphiles, as we have found in previous studies in our laboratory.[13-18]

TABLE II

Optical signs and half pitches obtained for cholesteric lyotropic mesophases

phase	A	B	C	D	E	F	G	H	I[c]
Magnetic type	I	I	I	I	II	I	I	II	II
half pitch (μm)	240	96	80	105	42	84	90	32	21
optical sign	(+)[a]	(+)	(+)	(+)	(−)[b]	(+)	(+)	(−)	(−)

[a] (+) = positive optical sign
[b] (−) = negative optical sign
[c] Ref. 17

Figure 1.b shows a scheme of the relative positions between applied magnetic field and helical array, as it was observed for cholesteric type I systems. The arrows *S* and *F* indicate the relative positions of the slow and fast vibration planes, as determined by the quartz wedge method. Since the slow component is parallel to the optical axis, a positive optical sign is implied.

The analogous scheme corresponding to cholesteric type II mesophases is shown in Figure 2.b. The fast vibration direction for these systems is determined as being parallel to the optical axis. This situation is compatible with a negative birefringence.

The positive and negative signs were reproducible, respectively, for all type I and type II cholesteric systems.

It should be remembered that Friedel[1] had pointed out that the negative optical sign for cholesteric thermotropic phases is a consequence of the strong twisting around the normal to the elementar optical axis (molecular optical axis) to which a positive birefringence[12] is associated. Therefore, applying the same reasoning to lyotropic type I cholesteric systems, their birefringence should be expected to be positive, as indeed it is experimentally detected. For a type I nematic phase, the elementar optical axis corresponds to the axis of the cylindrical micelles, which are known to have negative character.[8]

By comparing type II cholesteric and nematic systems, the same argument would lead, "mutatis mutandis", to the expectation of the observed negative optical sign.

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