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Study of ferrocholesteric discotic and calamitic lyotropics by optical microscopy and X-ray diffraction

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Résumé. — Nous avons étudié la cholestérisation des ferronématiques lyotropes discotiques et calamitiques par addition d'un agent chiral, le sulfate de Brucine. Les techniques utilisées ont été l'observation des textures par microscopie optique et la détermination des structures par la diffraction des rayons X. Les résultats concernant le pas et le pouvoir rotatoire d'échantillons orientés, comprenant ou pas des ferrofluides, sont discutés en termes de la théorie de Vries. Nous avons aussi examiné la possibilité de déformation des micelles par la présence de sulfate de brucine. Enfin, nous avons étudié les instabilités hydrodynamiques créées dans des échantillons de cholestérique calamitique au préalable orientés par un champ magnétique.

Abstract. — We have studied the cholesterization of discotic and calamitic lyotropic ferronematics by addition of brucine sulphate. The techniques used are optical microscopy for the textures and X-ray diffraction for the structures. The results concerning the pitch and the rotatory power of oriented samples containing or not ferrofluids are discussed in terms of de Vries theory. We have also examined the possibility of micellar deformation by addition of brucine sulphate. Finally, we have studied the hydrodynamic instabilities created in the sample of calamitic ferrocholesteric initially untwisted in a magnetic filed.

1. Introduction.

The nematic mesophases [1] are of two kinds which differ by the sign of the anisotropy of the diamagnetic susceptibility ($\Delta\chi$). A mesophase of $\Delta\chi > 0$ correspond to a suspension of oriented prolate micelles (calamitic) while nematics with a $\Delta\chi < 0$ are an assembly of oblate micelles (discotic). The process of cholesterization induced by an optically active substance [2-10] is not yet well known. In particular there is no answer to the following question : is the shape of the micelles disturbed by the presence of chiral compounds [7] ? In order to have an insight upon this important problem we have studied the influence of the amount of chiral molecules upon the optical properties of the lyomesophases and we have added an X ray diffraction study of the same samples.

The major difficulty for any optical study is the obtention of oriented samples which need the application of rather high magnetic field since the diamagnetic anisotropies are low. We have escaped this difficulty by adding a small amount of ferrofluid [11-13] to the mesophase. With lyotropic systems one can easily obtain a stable suspension which keeps the same properties of orientation as the corresponding pure mesophase but with very low magnetic fields (10 gauss [4]). At low concentration the addition of ferrofluid does not perturb the optical properties and we will not discuss the problem of the coupling between the magnetic grains and the mesophase.

Therefore in this paper we present results obtained with both calamitic and discotic ferrocholesteric mesophases. For each type we describe the textures which can provide a measure of the pitch of the helicoidal structure, we give measurements of the rotatory power of oriented samples and discuss the data in terms of the theory of de Vries for cholesteric mesophase [14]. The X-Ray diffraction results presented here are the first made in aqueous cholesteric lyomesophases and give an idea of the micellar shapes.

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We discuss the behaviour of the calamitic mesophase in more detail since some textures which were interpreted [7, 10] in terms of helicoidal structure seem to be characteristic of hydrodynamic instabilities. Moreover such textures correspond to an anisotropic repartition of magnetic clusters of ferrofluid grains which act as markers of the texture.

2. Experimental.

The cholesteric mesophases were prepared according to conventional procedures [16] with the compositions given in tables I and II. Sodium decyl sulphate (SdS), 1-decanol (DeOH) and the brucine sulphate (BS) are of commercial origin (Merck p.p.e. > 99 %), (FLUKA p.p.e. > 99 %) and (FLUKA : purum) respectively. Potassium Laurate (KL) was prepared in the laboratory.

After the homogeneization of the samples a small quantity (about 0.05 % in weight) of ferrofluid of commercial origin (Ferrofluidics Corp) was added. The ferrofluid used (water-base ferrofluid) has a magnetization at saturation of 220 G/cm^3, a mean diameter of 154 Å, standard distribution of 94 Å and 1.9×10^{16} grains per cm^3. After the addition of the ferrofluid the homogeneization process [16] was repeated.

For the X-Ray diffraction experiments the samples were introduced into sealed glass capillaries, (diameter : 1,5 mm) placed in the vertical position, with their axes perpendicular to the X-ray beam in a transmission geometry. A monochromatic Laue camera [17] with CuKα radiation and a sample to film distance of 120 mm was used. X-ray diffraction patterns were obtained by photographic method. Samples were oriented by a magnetic field of controlled intensity at the equatorial plane. The exposure times were of about 2 hours each.

For the optical microscopy experiments a Leitz (orthoplan Pol) polarized light microscope with a temperature controlling device was used. The samples were sealed in rectangular glass microslides (thickness = 200 µm, width = 2 mm, length = 2 cm) from Vitro Dynamics Inc.

The measurements of the rotatory power were made using the microscope with monochromatic light (a = 5 460 Å). The samples could be oriented by a magnetic field (about 10 G. from a Helmholtz coil). We define the axes x, y and z according to figure 1.

Table I. — *Composition in weight % of the cholesteric discotic mesophases stable at* 22 °C.

Sample	KL	SdS	DeOH	H_2O	BS
1	—	37.34 ± 0.06	7.40 ± 0.01	54.5 ± 0.1	0.78 ± 0.01
2 (*)	—	38.82	7.29	53.0	0.93
3	—	37.24	7.47	54.2	1.06
4	—	37.22	7.46	54.3	1.06
5	—	38.41	7.23	52.8	1.61
6	—	38.28	7.22	52.3	2.24
7	—	36.85	7.37	53.4	2.39
8	27.13 ± 0.05	—	6.74	64.8	1.38
9	28.81	—	6.41	62.5	2.29
10	26.63	—	6.62	63.6	3.21

(*) 2 presents a cholesteric calamitic mesophase at 24 °C.

Table II. — *Composition in weight % of the cholesteric calamitic mesophase at* 24 °C.

Sample	SdS	DeOH	H_2O	BS
11	38.82 ± 0.06	7.44 ± 0.01	53.2 ± 0.1	0.50 ± 0.01
12	38.77	7.43	53.2	0.61
13	38.87	7.31	53.0	0.87
14 (*)	38.82	7.29	53.0	0.93

(*) 14 is the same as 2 (*) in Table I.

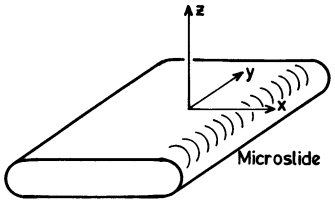


Fig. 1. — Definition of the axes x, y and z at the microslide cell for the optical microscopy observations.

3. Results and discussion.

3.1 Discotic ferrocholesterics.

3.1.1 *Optical observations.* — The characteristic texture observed in samples which were not magnetically oriented is composed of small domains of parallel lines (Chevrons). The magnetic field **H** (of about 10 G) favours the formation of small needles (< 1 μm) of ferrofluid and orients these needles parallel to **H**. The mechanical coupling between these anisotropic magnetic grains and the micellar helicoidal structure [12] promotes the orientation of the cholesteric planes perpendicular to **H** (Fig. 2).

Therefore, the distance between three parallel lines measure the pitch of the helix (P). Our values of the pitch agree with those previously published by Yu and Saupe [7]. Within the experimental error, the addition of the ferrofluid to a discotic cholesteric mesophase does not modify the value of the measured pitch. We call Ma the mole % of BS depending of the total amount of SdS (or KL), DeOH and BS [7].

Mesophases with both SdS and KL presented qualitatively the same dependence of P on Ma, the pitch becoming shorter with increasing quantities of BS. The values of the pitch for the KL mesophases are about 7 times larger (Table III) than those of SdS mesophases (for the same Ma).

We have studied with greater accuracy the case of SdS mixtures for which we have a greater range of BS concentrations : the measured pitch *versus* the amount of the chiral compound is a function of the type $P = \beta(\mathrm{Ma})^{\gamma}$. The fitting to the experimental results gives $\beta = 16.92$ and $\gamma = -1.06$ with P in μm and Ma in mole %.

Fig. 2. — Discotic ferrocholesteric oriented in a magnetic field (**H**) of about 10 G in the x direction. SdS sample, crossed polarizers. Microslide 200 μm thick.

Table III. — *Pitch (P) of the discotic ferrocholesterics and rotatory power (ψ/d) as a function of the quantity of the chiral compound* (Ma). *Temperature* = 22 °C.

Sample	Ma %	P (μm)	$\frac{\psi}{d} \pm 0.2 \times 10^{-2}$ (deg/μm)
1	0.40	51 ± 2	3.8×10^{-2}
2	0.46	38 ± 2	—
3	0.52	30 ± 2	—
4	0.55	32 ± 2	3.0×10^{-2}
5	0.81	20 ± 2	2.1×10^{-2}
6	1.13	15 ± 2	1.8×10^{-2}
7	1.26	14 ± 2	—
8	0.86	151 ± 10	—
9	1.37	82 ± 7	—
10	2.02	86 ± 8	—

For the measurement of the rotatory power of the SdS mesophases, the helical axes were oriented parallel to the direction of propagation of the light (Z axis). The presence of the magnetically oriented needles of ferrofluid in the sample ensured a good orientation of the helicoidal structure. If λ is the wave length of the light used in the experiment ($\lambda = 0.546$ μm), we are in the regime $\lambda \ll P$. The optical rotation per unit length (ψ/d) may be expressed as follows [14, 18] :

$$\frac{\psi}{d} = \frac{\pi}{16\,P}\left(\frac{n_e^2 - n_o^2}{n_e^2 + n_o^2}\right)^2 \frac{1}{\left(\frac{\lambda}{P}\right)^2\left[1 - \left(\frac{\lambda}{P}\right)^2\right]}, \quad (1)$$

where n_e and n_o are the extraordinary and ordinary indexes, respectively. We define the parameter

$$\alpha = \left(\frac{n_e^2 - n_o^2}{n_e^2 + n_o^2}\right)^2$$

The measured values of ψ/d are presented in table III. With these values of ψ/d and P, equation (1) may be used to calculate the values of α. We observed that for increasing values of the pitch, the calculated α tends to the nematic value $\alpha_N = 1.3 \times 10^{-5}$ [19] (Fig. 4). This higher birefringence observed for small values of the pitch cannot be caused by the oriented needles of ferrofluid since its amount is about the same in all the samples. As the pitch decreases for increasing amounts of BS, it is possible that the discrepancy between the calculated values of α and α_N is due to the molecules of BS oriented by the micellar helical structure. Besides this effect, it is also possible that the micelles themselves are deformed

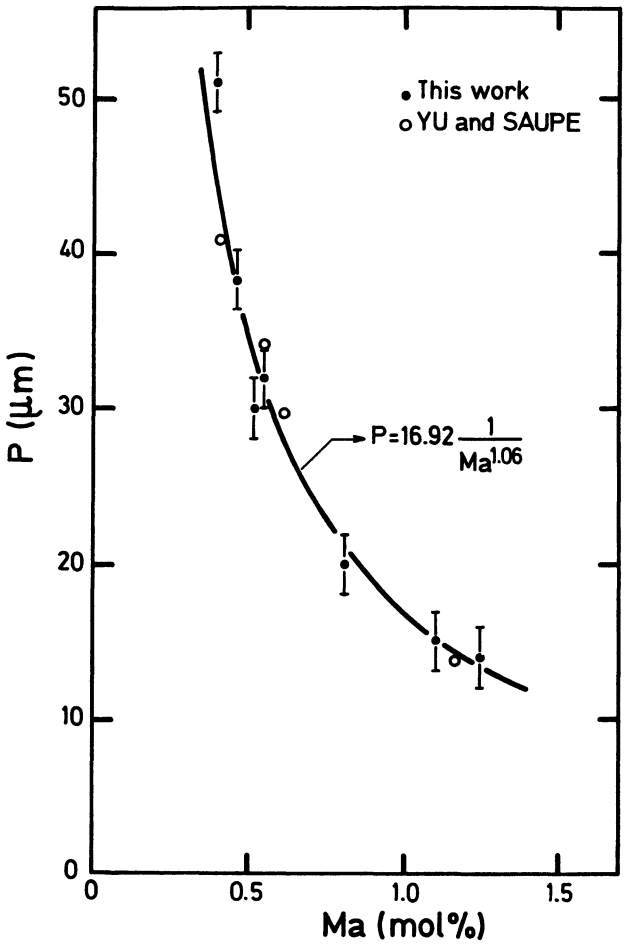


Fig. 3. — Helical pitch (P) as a function of the quantity of brucine sulfate (Ma) for discotic ferrocholesteric SdS mesophases.

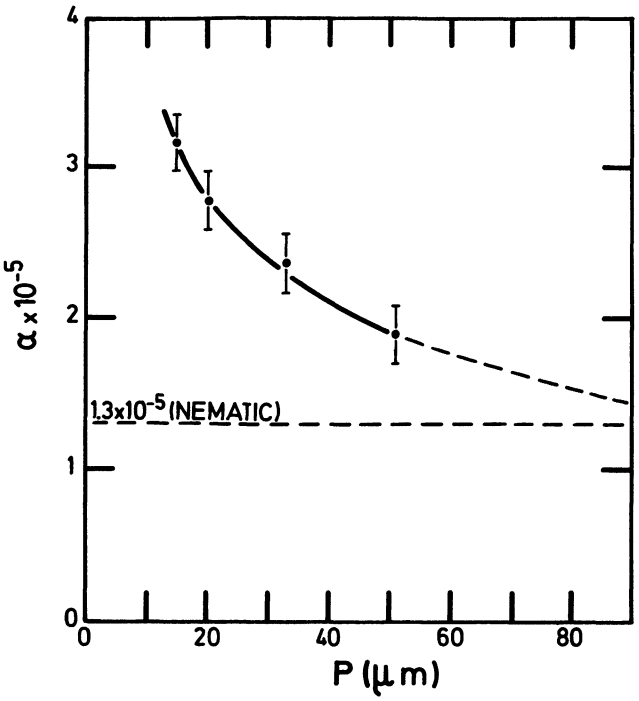


Fig. 4. — Parameter $\alpha = \left(\frac{n_e^2 - n_0^2}{n_e^2 + n_0^2}\right)^2$ where n_e and n_0 are the extraordinary and ordinary indexes respectively as a function of the pitch (P) for discotic ferrocholesteric SdS mesophases.

by the molecules of BS. The BS molecule has six asymmetric carbon and is approximately disc-shaped with a diameter of about 15 Å and a thickness of 6.5 Å. The number of BS molecules per micelle (assuming that each micelle has about 100 molecules of SdS [16] and a diameter of about 65 Å [20]) varies from 1 to 3. If the interaction of the BS molecules with the disk shaped micelles promotes a deformation of the micelles, the birefringence of the mesophase composed of these deformed objects in a helicoidal arrangement is expected to be different from the birefringence of the same structure composed of non-deformed objects.

This micellar deformation could be a function of the quantity of the chiral compound. Thus our results (Fig. 4) could be interpreted as an evidence for the micellar deformation in a discotic cholesteric lyomesophase.

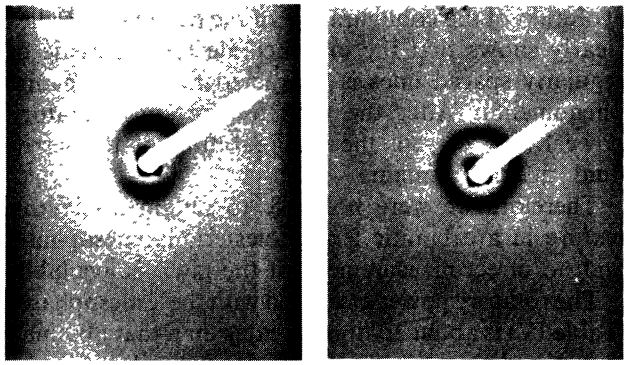
3.1.2 *X-ray diffraction patterns.* — The diffraction patterns were obtained in two different experimental configurations :

H_1 – X-ray beam perpendicular to the magnetic field **H** (for the discotic cholesteric lyomesophases the axis of the helix orients parallel to **H**).

H_2 – X-ray beam parallel to the axis of the cholesteric helix (obtained by rotating the capillary tube by 90° about its axis after switching off the magnetic field).

In the high angle region, the diffraction pattern presents a diffuse ring at $s^{-1} = (4.5 \pm 0.1)$ Å characteristic of the liquid arrangement of the paraffinic chains in the micelles.

The diffraction patterns in the small angle region for the H_1 and H_2 configurations are shown in figure 5. The results will be discussed in terms of the scattering vector $s(2 \sin \theta/\lambda)$. In figure 5a (H_1) there are two intense spots along the meridian (direction perpendicular to the axis of the helix) at $s_m^{-1} = (39 \pm 1)$ Å joined by two weaker arcs at $s_e^{-1} = (47 \pm 1)$ Å. In the H_2 configuration (Fig. 5b) the pattern presents a ring at $s^{-1} = (39 \pm 1)$ Å. These patterns represent sections of the reciprocal space perpendicular and parallel to the axis of the helix, respectively. In this space the structure can be schematized as a hollow oblate elipsoid with the symmetry axis parallel to the axis of the helix. In real space, if we assume that the diffraction is dominated by the interference between objects, the diffracting unit may be oblate ellipsoids organized in a helicoidal structure. The ratio s_m/s_e is about 0.8. The diffraction pattern (H_1 configuration) may be thought as a superposi-



a) b)

Fig. 5. — Small angle X-ray diffraction patterns with SdS discotic ferrocholesteric mesophase in a 1.5 mm thick capillary. The capillary was set up in the vertical direction in the plane of the figure. (a) H_1 configuration; (b) H_2 configuration.

tion of the patterns from the nematic structures where the director (**n**) lies in the meridian plane (plane which contains the X-ray beam and is perpendicular to **H**). The direction of **n** varies continuously in this plane to form the helicoidal structure. The same approach may be used to analyse the H_2 configuration. Our values of s^{-1} are consistent with a helical structure formed by non-deformed oblate ellipsoids (or discs) [20]. However, the hypothesis of deformed objects (as discussed in section 3.1.1) is not excluded from the X-ray diffraction results. Nevertheless within our experimental accuracy, no changes were observed in the X-ray diffraction patterns for different concentrations of BS.

3.2 Calamitic ferrocholesterics.

3.2.1 *Optical observations.* — The basic characteristic of a calamitic ferrocholesteric phase in the presence of a magnetic field (about 10 G in our experiment), is that the helical structure is untwisted. The same result was previously obtained for cholesteric lyomesophases without the ferrofluid, with strong magnetic fields [7, 10].

If the applied magnetic field lies in a plane perpendicular to the direction of propagation of the light in the microscope (x axis), after a few hours a planar texture is obtained.

After removal of the field, beginning from both the edges of the microslide used as sample holder a texture with regular parallel lines develops perpendicular to the direction of the previously applied magnetic field (Fig. 6). The distance between consecutive lines is (95 ± 5) μm.

This kind of texture was previously observed in other cholesteric lyotropic systems [10] and was interpreted as a chevron characteristic of a cholesteric mesophase [7, 10]. The texture with regularly spaced lines spreads all over the sample (Fig. 7). The periodicity however becomes more irregular with time and after some hours only a few lines are visible in a homogeneous texture. After a long time, the texture becomes homogeneous (with some defects), without the lines, and it was observed to have a rotatory power. This evolution of the texture was observed with the mesophases of both KL and SdS.

This final texture is characteristic of a helicoidal structure with the helical axis parallel to the direction of propagation of light (i.e. perpendicular to the largest surface of the sample holder). In this configuration, the axes of the cylindrical micelles remain perpendicular to the axis of the helix and parallel to the glass surface. In a calamitic nematic mesophase the glass surface (without any special treatment) behaves as to orient the micellar axis parallel to the wall [21].

Fig. 6. — Calamitic SdS ferrocholesteric in a microslide 200 μm thick some minutes after removal of the magnetic field (applied at the X direction). Crossed polarizers, observation along the z direction. Hydrodynamic instabilities starting at the edge of the cell.

Fig. 7. — Calamitic SdS ferrocholesteric in a microslide 200 μm thick a few hours after removal of the magnetic field (applied along the X direction). Crossed polarizers, observation along the z direction. Hydrodynamic instabilities, roll structure.

The intermediate texture observed between the planar configuration (**H** present) and the final one with a rotatory power, is characteristic of hydrodynamic instabilities. The BS cholesterization effect gives rise to a somewhat different configuration of the wall. Roll structures were observed in calamitic nematic lyomesophases [15] with the application of a magnetic field and in PBL G samples [22] after shearing. In our case, however, the relaxation process of a previously untwisted sample induces the roll structures.

The formation of these hydrodynamic instabilities can be qualitatively explained as follows :

(i) in the presence of **H**, (along the X axis) the micellar axes are oriented parallel to the field (planar texture) and are also parallel to the largest surface of the microslide. Except at both edges of the microslide the micellar axes are not parallel to the glass surface;

(ii) with the removal of **H** the micelles near the edges are reoriented by the wall effect and create a back flow convective movement of matter, which propagates throughout the sample;

(iii) the convective motion induced by the wall orientational effect is coupled to the BS cholesterization effect and the final micellar arrangement will be such as to minimize the free energy of the system, taking these two different effects into account. So, a helical structure with the cylindrical micelles in the plane xy (Fig. 1) is obtained.

The backflow convective motion could be observed in our experiment by following the modifications of the form of the relatively big ferrofluid needles (> 10 μm). In the presence of **H**, the needles are parallel to the field.

After its removal the needles change their straight shape (Fig. 8) and it was possible to identify a flow along the z direction (characteristic of a roll structure) and also a component along the y direction. The evolution of the configuration of the ferrofluid needles clearly shows that the intermediate texture made of regularly spaced lines is characteristic of a dynamic phenomenon. After the final texture (with rotatory power) is observed, the configuration of the ferrofluid needles remains static.

Therefore we were not able to obtain a chevron texture in a calamitic ferrocholesteric lyomesophase, and no direct measurement of the pitch is available.

The rotatory power measured with these mesophases (Table IV) is about 10 times greater than that obtained with the discotic ferrocholesteric (Table III) for the same BS concentration. Thus, their pitches are expected to be very large, about 10 times those observed with the discotic cholesterics (See Eq. (1)).

We do not have any independent measurement of the pitch associated with the rotatory power to calculate the values of α (as we did for the discotic ferrocholesteric).

Thus, we will assume the value of α of the calamitic nematic ($\alpha_N = 1.2 \times 10^{-5}$ [19]) to calculate the pitch as a function of the measured rotatory power (Eq. (1)). This procedure gives us an order of magnitude for P (Table IV and Fig. 9).

Table IV. — *Pitch of the calamitic cholesteric phase (P) and rotatory power (ψ/d) as a function of the quantity of the chiral compound* (Ma). *Temperature* = 24 °C.

Sample	Ma %	P (μm)	$\frac{\psi}{d}$ (deg/μm)
11	0.24	560 ± 60	(2.8 ± 0.2) × 10^{-1}
12	0.30	417 ± 42	(2.1 ± 0.2) × 10^{-1}
13	0.44	260 ± 30	(1.3 ± 0.1) × 10^{-1}
14	0.46	200 ± 40	(1.0 ± 0.1) × 10^{-1}

Fig. 8. — Calamitic SdS ferrocholesteric in a microslide 200 μm thick a few minutes after removal of the magnetic field (applied along the X direction). Crossed polarizers, observation along the z direction. Needles of ferrofluid deformed by the hydrodynamic instabilities.

A function of the type $P = \beta\,(\mathrm{Ma})^{\gamma}$ was fitted to the experimental results with the following parameters : $\beta = 71.1$ and $\gamma = -1.5$. Our values of P do not agree with those previously published by Yu and Saupe [7]; our values are about 2.5 times larger than theirs. In order to measure P, they first began with an untwisted sample (planar orientation – **H** present). After the removal of the field, domains of parallel lines appear; these domains are oriented by spinning the sample in a magnetic field. Since the hydrodynamic effects are very important for these mesophases (as previously discussed), we believe that in fact they measured the periodicity of a dynamic roll structure.

3.2.2 *X-ray diffraction patterns.* — The diffraction patterns (Fig. 10) were obtained in the same experimental configurations as those described in section 3.1.2.

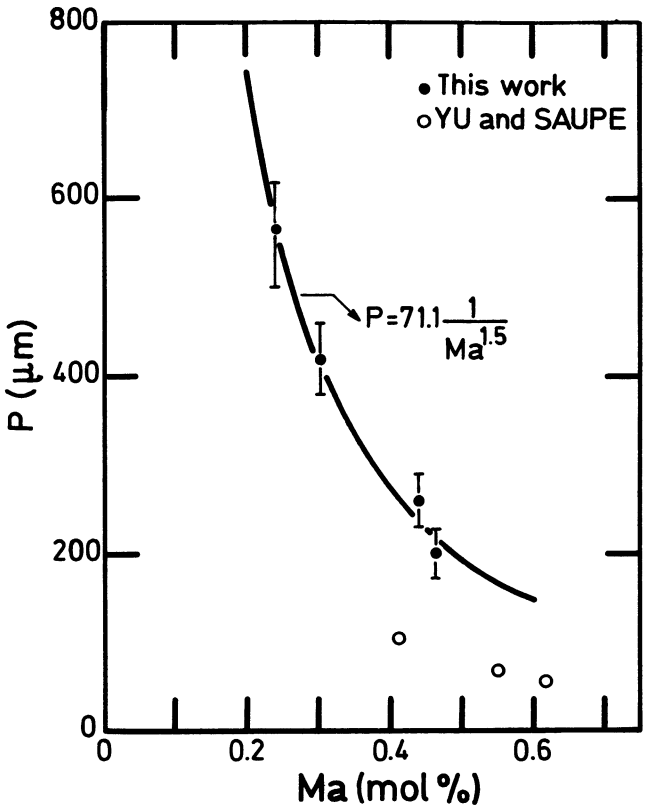


Fig. 9. — Helical pitch (P) as a function of the quantity of brucine sulfate (Ma) for calamitic SdS ferrocholesteric mesophases.

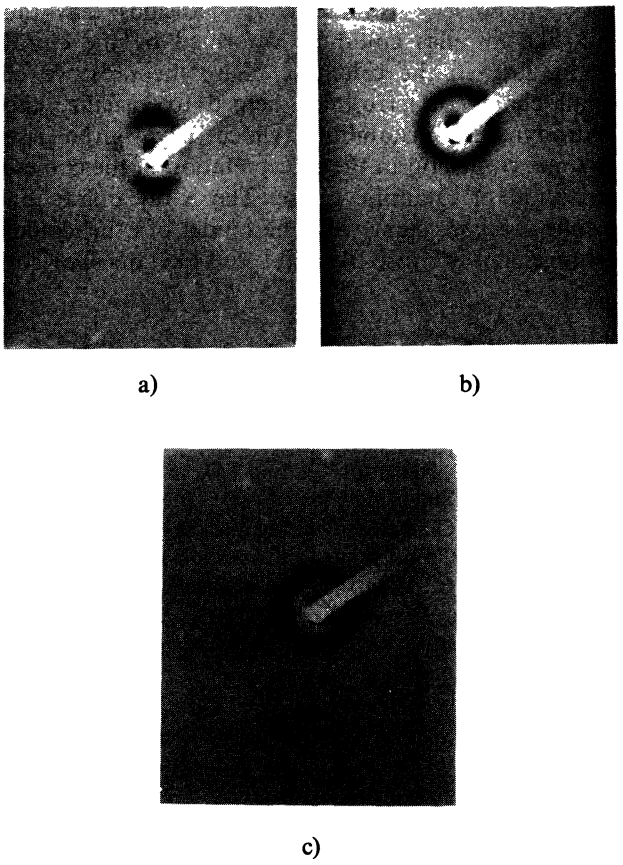


Fig. 10. — Small angle X-ray diffraction patterns with SdS calamitic ferrocholesteric mesophase in a 1.5 mm thick capillary. The capillary was set up in the vertical direction in the plane of the figure. (a) H_1 configuration; (b) H_2 configuration; (c) H_1 and H_2 configurations a few hours after removal of the field.

In figure 10a (H_1) there are two intense spots along the meridian at $s_m^{-1} = (40 \pm 1)$ Å and at the H_2 configuration (Fig. 10b) the pattern presents a ring at $s^{-1} = (40 \pm 1)$ Å. These diffraction patterns in the small angle region are typical of a calamitic nematic lyomesophase [20, 21] : the magnetic field untwists the cholesteric structure.

In the absence of magnetic field both patterns presented an evolution as a function of time to the final pattern shown in figure 10c. This diffraction pattern is composed of a ring at $s^{-1} = (40 \pm 1)$ Å with an increase in its intensity near the equator. A similar result was obtained [4] in solutions of poly-γ-benzyl-L-glutamate (PBLG) which present a cholesteric structure.

The X-ray diffraction pattern of a calamitic nematic mesophase in capillaries, oriented by the glass surface only presents two intense spots at the equator [23]. The spatial configuration of the diffracting units (prolate ellipsoids) in real space which give rise to figure 10c may be understood as follows : near the capillary walls the axes of the cylindrical micelles are approximately parallel to the capillary axis (as in a nematic structure); from the edges to the centre of the capillary the micellar axis turn continuously around an axis perpendicular to it and normal to the glass surface. The intensity increase near the equator indicates that the calamitic ferrocholesteric structure may be thought of as a weakly deformed calamitic nematic structure. This fact is consistent with the large values of the pitch (Table III) discussed in section 3.2.1.

In the high angle region the diffraction pattern is similar to that of the discotic ferrocholesteric with a diffuse ring at $s^{-1} = (4.5 \pm 0.1)$ Å corresponding to the liquid arrangement of paraffinic chains.

4. Concluding remarks.

Using a ferrofluid to prepare ferrocholesterics we have easily followed, by applying a relatively small magnetic field, the formation of good oriented samples in the discotic case and the untwisting of the helicoidal structure in the calamitic case. The addition of brucine sulphate as chiral agent seems to have a large influence on the discotic ferrocholesterics and a very weak one on the calamitic phase. The analysis of the parameter α (related to the refraction indexes) for dis-

cotic cholesteric lyomesophases indicates that the disk-like micelles could be deformed by the chiral compound. In the calamitic phase the presence of small chains of ferrofluids helped to visualize the hydrodynamic instabilities which have given rise to some confusion in the interpretation of the cholesterization of calamitic phase. The X-ray diffraction results are consistent with the model of a helicoidal arrangement of disc-like and rod-like micelles for discotic and calamitic cholesteric lyomesophases, respectively.

Acknowledgments.

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