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New Induced Cholesteric Micellar Liquid Crystals. Characterization and Pitch Determination

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Summary. New induced cholesteric micellar liquid crystals have been prepared based on potassium laurate and sodium decyl sulfate. The chiral molecule D-glucose was used as dopant. The inverse pitch length is found to be proportional to the added guest. The twist induced by the dopant strongly depends on the nature of the detergent, the principal component of the mesophases. The mesophases are characterized on the basis of the microscopic textures. Deuterium NMR spectra in D_2O shows positive diamagnetic anisotropy for these cholesteric mesophases.

Keywords. Liquid crystals; Amphiphile; Pitch; D-Glucose; Polarizing microscope; NMR.

Neue induzierte cholesterische micellare Flüssigkristalle. Charakterisierung und Ganghöhenbestimmung

Zusammenfassung. Es wurden neue induzierte cholesterische micellare Flüssigkristalle basierend auf Kaliumlaurat und Natriumdecylsulfat hergestellt. Als chirales Molekül zur Ausbildung der Phasen wurde D-Glucose benutzt. Es wurde festgestellt, daß die inverse Ganghöhe proportional zur zugesetzten Gastkomponente ist. Die induzierte Schraubung hängt stark von der Natur des Detergens, der Hauptkomponente der Mesophase, ab. Die Mesophasen werden auf der Basis der mikroskopischen Textur charakterisiert. Die Deuterium-NMR-Spektren in D_2O zeigen für diese cholesterischen Mesophasen eine positive diamagnetische Anisotropie.

Introduction

The term liquid crystal designates a state of matter that is intermediate betweeen the crystalline solid and the ordinary (isotropic) liquid phase. Liquid crystals flow like ordinary liquids, e.g. they adopt the shape of their container. On the other hand, they exhibit anisotropic properties as do solid crystals. Because of their intermediate nature, they are also called mesophases.

Many thousands of organic compounds form liquid crystals when the solid crystals are heated above their melting points. Such liquid crystals which are formed when the temperature is varied are called thermotropic. Many compounds form a second kind of mesophase when a solvent is added, e.g. a long chain fatty acid in aqueous solutions. Mesophases of this kind are called lyotropic or micellar, and are the subject of this article.

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Lyotropic liquid crystals are the cornerstone of the life processes, namely the biological membrane matrix [1]. The complex integral lipids and lipoproteins of many living cells and tissues exist as lyotropic mesophases within the thermal range 4–42°C. These mesophases also represent a vital physicochemical element in the organization of certain components in protoplasm for organic precursors [2, 3]. It is worthwhile, therefore, to prepare and study micellar liquid crystals to understand the mechanism and function of the membrane matrix.

Thermotropic liquid crystals were classified long before as smectic, nematic and cholesteric mesophases [4]. Lyotropic mesophases were classified almost entirely as lamellar, hexagonal and to a smaller extent, cubic up until the 1960's [5]. In the 1960's lyotropic nematics were characterized [1, 6] and in the late 1970's also lyotropic cholesteric mesophases [7, 8]. These discoveries greatly reduced the gap in analogy between thermotropic and lyotropic liquid crystals. While the building blocks of thermotropic liquid crystals are individual molecules, the analogous components for the lyotropic liquid crystals are molecular aggregates, the micelles.

The concept of the helicoidal arrangement of mesomorphic molecules and the thermotropic cholesteric mesophase as a particular nematic phase with optical activity had been established in the early 1920's [4]. In comparison lyotropic cholesteric mesophases are a relatively new subject. The first aqueous lyotropic cholesteric mesophases were reported by Diehl and Tracey [9] by adding chiral detergent in the anisotropic micelles. Using this same approach Saupe and coworkers [8, 10] induced cholestericity by dissolving optically active substance such as cholesterol in lyomesophases based on sodium decyl sulfate and decyl ammonium chloride. The cholesteric mesophases undergo spontaneous orientation in a magnetic field with either positive or negative diamagnetic susceptibilities [7, 11]. The pitch of the induced cholesteric phase was found to be dependent on the nature as well as on the amount of the guest molecules [8].

Cholesteric micellar liquid crystals have been intensively investigated in recent years [7, 8, 10, 12]. Because of their easy solubility in micellar systems, guest molecules of amphiphilic nature have been mostly used to prepare these phases. In this article new lyotropic induced cholesteric mesophases are reported. The hydrophilic molecules D-glucose was used as guest (dopant). The classification of mesophases follows from the work of Fujiwara and Reeves [13]. The lyomesophases are characterized by ^{2}H NMR and on the basis of their polarizing microscope textures.

Experimental

Lauric acid was obtained from the Aldrich Chemical Company and was made alkaline with alcoholic KOH. The potassium salts were recrystallized at least three times from absolute ethanol and finally dried. Other chemicals were properly dried and used without further purification.

The mesophases were prepared by weighing the appropriate amounts of components into small test tubes. The mixtures were alternately stirred followed by centrifugation until the sample was seen to be homogeneous under crossed polarizers. For microscopic study the samples were sealed in microslides of 3–5 mm wide and of 0.1–0.3 mm internal thickness (Vitrodynamics, New Jersey), when necessary aligned in a 2.3 T magnetic field and examined with a Zeiss standard microscope equiped with crossed polaroids and camera. Pitch measurements were made either by microscopic observation or by laser diffraction using a He—Ne laser, $\lambda = 6\,328$ Å. The pitch measurements were not corrected for the refractive index difference [14]. Deuterium NMR spectrum were obtained by using the Bruker AM 250 and CXP 200 MHz spectrometers. Unless otherwise mentioned, all measurements were done at room temperature. Composition and pitch lengths of the induced cholesteric mesophases are provided in Tables 1–3. Microscopic textures, variation of the inverse pitch lengths against the amounts of guest and the deuterium NMR spectra from D_2O are shown in Figs. 1–3.

Results and Discussion

Both potassium laurate and sodium decyl sulfate in presence of D-glucose (concentration 0.15–0.91% by wt.) was found to form lyomesophases by examination with a crossed polarizer. The initial textures observed in the polarizing microscope were coarse granular but in a few hours the nonaligned fingerprint pattern characteristic of cholesteric mesophases developed [7]. When the sample is aligned in the thin slide in a 2.3T magnetic field with the plane of the slide being parallel to the field, the cholesteric texture shows alternate dark and light stripes perpendicular to the direction of the applied field (Fig. 1). This indicates that the helical axis aligns along the direction of the magnetic field [8, 10]. The pitch of the helix was determined by the perpendicular distance between two dark and two light stripes. When the pitch length became very short the texture was used as a diffraction grating for a He/Ne laser. The angle of the diffraction spots gave a distance of half the pitch length [15].

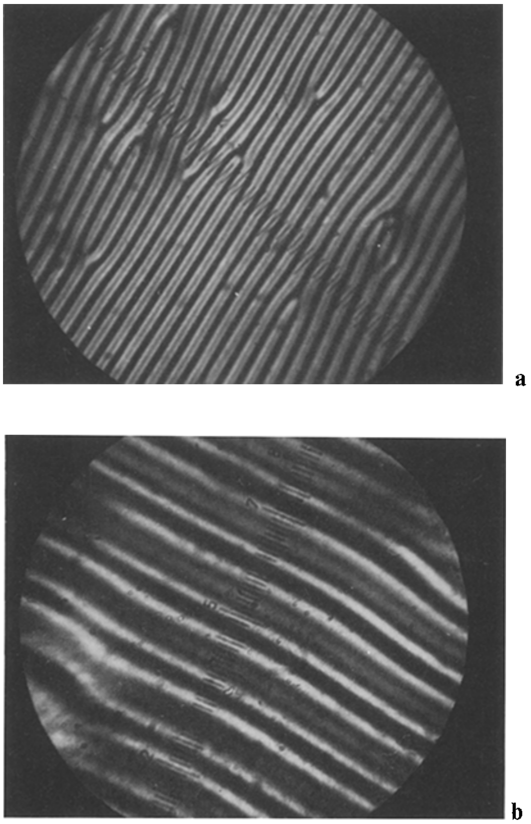

Fig. 1. Aligned induced cholesteric texture based on K-laurate (**a**) and sodium decyl sulfate (**b**) observed microscopically between crossed polaroids at room temperature. Sample thickness was 0.3 mm and the magnification 400 times. The direction of the applied magnetic field (2.3T) is in the plane of the figure and perpendicular to the cholesteric lines

Table 1. Compositions (in gm) of the induced cholesteric micellar liquid crystals based on potassium laurate

Amphiphile	KCl	D_2O	D-Glucose
1.701	0.196	3.366	0.009
1.701	0.196	3.366	0.013
1.701	0.196	3.366	0.018
1.701	0.196	3.366	0.022
1.701	0.196	3.366	0.028
1.701	0.196	3.366	0.035
1.701	0.196	3.366	0.039
1.701	0.196	3.366	0.045
1.701	0.196	3.366	0.048

Table 2. Compositions (in gm) of the induced cholesteric micellar liquid crystals based on sodium decyl sulfate

Amphiphile	Na_2SO_4	D_2O	D-Glucose
1.402	0.142	1.706	0.005
1.402	0.142	1.706	0.008
1.402	0.142	1.706	0.010
1.402	0.142	1.706	0.013
1.402	0.142	1.706	0.016
1.402	0.142	1.706	0.020
1.402	0.142	1.706	0.023
1.402	0.142	1.706	0.026
1.402	0.142	1.706	0.030

The inverse pitch length versus D-glucose content of the mesophases based on potassium laurate and sodium decyl sulfate is plotted in Fig. 2. The inverse pitch is found to be proportional to the added guest. The minimum pitch lengths induced by D-glucose in these phases are of 27.0 and 54.1 μm, respectively. These values are close to the pitch lengths reported previously for sodium decyl sulfate and tartaric acid systems [8]. Longer pitch for induced cholesteric phase based on sodium decyl sulfate than potassium laurate clearly indicates that the twist induced by the chiral molecules is highly dependent on the nature of the detergent, the main component of the mesophases. Remaining in the aqueous phase of the miceller solutions, the hydrophilic guest D-glucose is thus capable of inducing a significant twist in the micelles. This twisting effect by the chiral guest is tentatively described as due to some intermolecular interactions, the exact nature and molecular mechanism of which is yet to be clarified [15]. The twisting power of D-glucose is comparable to those of the tartaric acid [8], both of which being hydrophilic in nature exists in the aqueous phase of the micellar solutions.

Cholesteric liquid crystals of type 11 align in a magnetic field with their helix parallel to the field i.e. the individual director in the nematic planes aligns

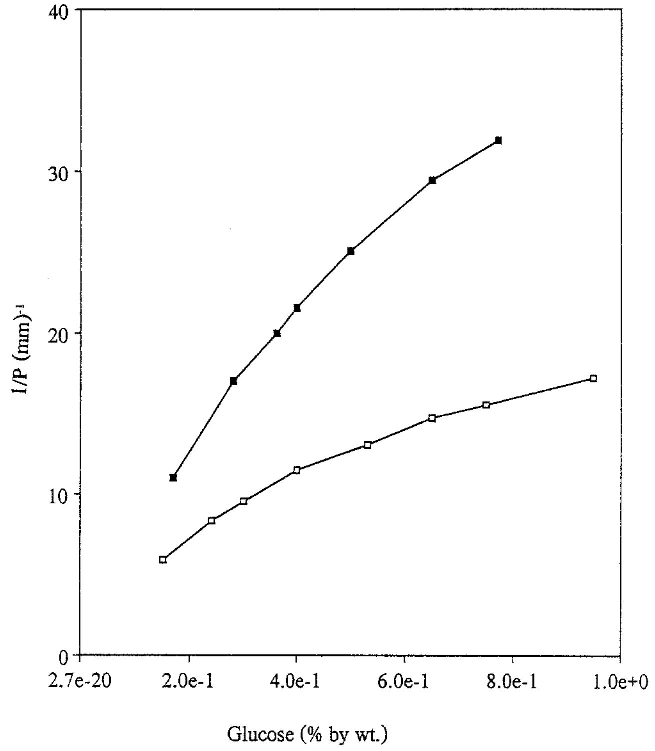

Fig. 2. Plots of inverse pitch lengths $(mm)^{-1}$ versus amounts of D-glucose (% by wt.) added as guest. Dark square points correspond to mesophase based on K-laurate and open square points to mesophase based on sodium decyl sulfate

Table 3. Amounts of D-glucose (guest) and the corresponding pitch lengths (P) induced in the lyomesophase

Amphiphile	D-Glucose (% by wt.)	P (mm)	1/P (mm^{-1})
K-Laurate	0.17	0.0870	11.5
	0.24	0.0625	16.0
	0.34	0.0465	21.5
	0.42	0.0392	25.5
	0.53	0.0333	30.0
	0.66	0.0299	33.5
	0.74	0.0286	35.0
	0.85	0.0274	36.5
	0.90	0.0270	37.0
Na-Decyl sulfate	0.15	0.1818	5.5
	0.25	0.1177	8.5
	0.31	0.0980	10.2
	0.40	0.0807	12.4
	0.49	0.0714	14.0
	0.61	0.0625	16.0
	0.70	0.0588	17.0
	0.79	0.0562	17.8
	0.91	0.0541	18.5

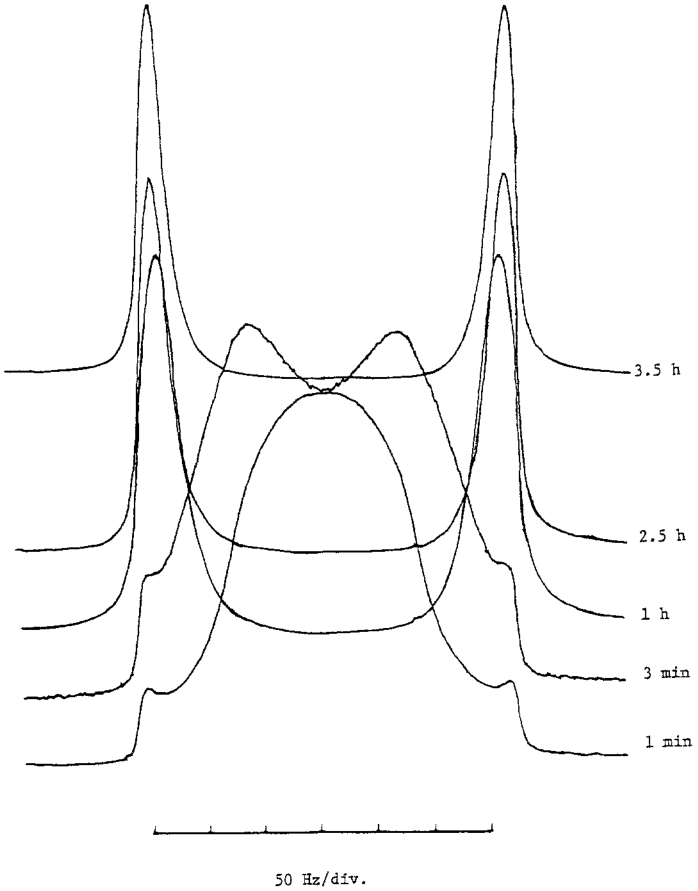

Fig. 3. Deuterium NMR spectra from D_2O as a function of time showing the change in deuterium signal as the mesophase based on sodium decyl sulfate progressively aligns in the magnetic field of the Bruker AM 250 MHz spectrometer. The highest quadrupole splitting is 318 Hz

perpendicular to the field. After complete alignment in the field, it shows characteristic dark and light stripes perpendicular to the field. Type 1 cholesteric liquid crystals, on the other hand, loses their helical arrangement in the magnetic field due to unwinding of the helix [15].

In this study both potassium laurate and sodium decyl sulfate in presence of D-glucose formed cholesteric type 11 lyomesophase having characteristic microscopic texture (Fig. 1, described earlier). Deuterium NMR spectra in D_2O, immediately after placing the sample in the spectrometer and at later time intervals, showed positive diamagnetic anisotropy (Fig. 3). Signal intensity develops at the extremes of the spectrum, a result caused by the spontaneous alignment of the director along the magnetic field. This behaviour is in contrast to the normal behaviour of the micellar liquid crystals of the type 11 nematic. Similar results has also been reported for other cholesteric systems [16]. To explain this unusual deuterium NMR behaviour of the cholesteric system it is proposed [16], "with development of cholesteric behaviour, the individual micelles twisted into chiral shape, then aggregated to form domain like structures. The major axis of these aggregates is the axis along which the helix propagated and this local axis serves as the director axis for the aggregates. The individual aggregates reorient as a unit when placed in the strong magnetic field of an NMR spectrometer. As a consequence of this, the mesophase showed positive diamagnetic anisotropy". The author agrees with the above hypothesis. The positive diamagnetic anisotropy shown by deuterium NMR is reasonable in this model.

Conclusions

This study reveals the following: (1) Guest molecules having aqueous phase solubility can induce cholestericity in a nematic phase. (2) The pitch lengths of the induced cholesteric phase depends on the nature and amounts of the added guest. (3) The induced twist by an added chiral guest is highly dependent on the nature of the detergent, the principal component of a mesophase. (4) Cholestericity induced by the interaction of the host and water soluble chiral guest needs elaborate studies to address the question of the mechanism of this twist induction. (5) A detailed study of the diamagnetic anisotropic behaviour in terms of type 1 and type 11 cholesteric with their nematic analogues is necessary for an unambiguous classification.

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