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Inducer Chemical Nature and the Helical Twist Sense of Cholesteric Lyotropic Mesophases

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In the present work, helical twist senses for induced cholesteric lyotropic liquid crystals are determined. Several chiral inducers able to locate at different mesophase environments were added to lyomesophases based on the amphiphiles decylammonium chloride, potassium laurate, sodium and cesium decylsulphate, sodium dodecylsulphate and potassium decanoate. Polarizing microscopy techniques used for thermotropic cholesteric twist sense determination were extended to lyotropic systems. Only when the inducer remains predominantly in the bulk water its structure plays an important role to establish the cholesteric twist sense. Hydrophobic inducers added to different systems lead to the same helical twist sense, since the paraffinic intra-micellar environment is essentially the same. By the other hand, hydrophilic inducers or hydrophobic solutes with ionizable groups subjected to strong interactions with the electrical double layer will originate cholesteric mesophases whose helical twist sense can be inverted by changes on the charge distribution of the micellar surface.

Keywords: lyotropic mesophases, cholesteric mesophases, cholesteric inducers, optical activity in lyomesophases, optically active amphiphiles, lyotropic cholesteric twist sense

I. INTRODUCTION

Cholesteric mesophases can be prepared by adding chiral solutes to nematic lyomesophases. These are the so called induced lyotropic cholesteric systems. They are characterized by the existence of a helical micellar array with a particular twist sense and a repetition distance, usually referred to as cholesteric pitch. A general review on these systems was published recently.[1]

The relation between the helical twist sense and the nature of the inducer solute is well understood for thermotropic cholesteric liquid crystals.[2] For these mesophases systematic attempts have succeeded in correlating the solute's absolute configuration to the helical sense.[2–4] Therefore, for thermotropic systems it is well known that the same optically active solute will induce the same twist sense in almost all mesogens. Only the presence of bulk groups, such as phenyl or benzyl-groups, in the chiral solute or in the nematic molecules are able to cause changes on twist sense by means of steric effects.[2,4]

A lyotropic system is an association colloid and offers a complex medium for the inducer interaction since several solubilization sites are present. Therefore, it is not clear "a priori" if the same solute, in different lyotropic materials, is able to induce the same twist sense, especially taking into account the variation of amphiphile headgroup nature and charge.

The analysis of the helical twist sense, its correlation with the chiral inducer structure and its chemical properties can play an important role in clarifying the complex cholesterization process in lyotropic systems.

In the present paper we report induced Ch_D lyotropic mesophases prepared from several amphiphiles. The chiral solutes studied were either hydrophobic and hydrophilic molecules; thus we could study the effects of these interactions on the resulting chiral lyomesophases. The twist sense was determined by polarizing microscopy techniques, which allow cholesteric characterization even when a detectable pitch is absent.[5]

II. EXPERIMENTAL

Three different lyotropic systems were studied based on decylammonium chloride (DAC), potassium laurate (KL) and sodium decylsulphate (SDS). In some cases sodium dodecylsulphate (sodium laurylsulphate, SLS), cesium decylsulphate (CsDS) and potassium decanoate (KDeC) lyomesophases were investigated to corroborate some particular results.

Decylammonium chloride was prepared by neutralizing decylamine with hydrochloric acid. The crude product was recrystallized from ethanol/petroleum ether and dried under vacuum.

Sodium decylsulphate was prepared by sulphation of *n*-decanol with either sulfuric acid in the manner previously described by Radley *et al.*[6] or with chlorosulphuric acid.[7] It was recrystallized from 90% ethanol/water mixture. Cesium decylsulphate was synthesized as previously reported[6] with posterior recrystallization from ethanol/ethyl acetate mixture.

Potassium laurate and potassium decanoate were prepared by neutralizing the respective carboxilic acids (from Riedel) with potassium hydroxide. The products were recrystallized from ethanol.

Sodium laurylsulphate was obtained by purification of commercial crude product. It was washed several times with diethyl ether and recrystallized from ethanol.

Additionally, various other materials were used to prepare the solutions studied. These include *n*-decanol (Merck) and analytical grade electrolytes (KCl, NH_4Cl, Na_2SO_4 and Cs_2SO_4 of various sources).

The following inducers were used:

(i) two carbohydrates: D-glucose (Fluka) and L-sorbose (United States Biochemical Co.);

(ii) carbohydrate derivatives: sodium D-gluconate (D-SG, Fluka); diacetone-L-sorbose (L-DAS, 2,3:4,6-di-O-isopropylidene-alpha-L-sorbofuranose) and potassium diacetone-2-keto-L-gulonate (L-KDG);

(iii) potassium or sodium salts of N-lauroyl derivatives from resolved amino-acids:

potassium or sodium N-lauroyl-L-alaninate (L-KNLA or L-SNLA);
sodium N-lauroyl-L-aspartate (L-SNLAsp);
potassium or sodium N-lauroyl-L-valinate (L-KNLV or L-SNLV);
potassium or sodium N-lauroyl-D-serinate (D-KNLS or D-SNLS);
potassium or sodium N-lauroyl-L-glutamate (L-KNLG or L-SNLG);

(iv) The coordination compound D-tris(ethylene-diamine) cobalt (III) iodide (D-Coen);

(v) Cholesterol (Merck).

Each of these substances has a preferential location at one particular mesophase environment, such as the hydrocarbon micellar core, the electrical double layer (edl) or the bulk water.

The carbohydrates, the cholesterol and the sodium gluconate were used without further purification. DAS was prepared by reacting sorbose with acetone according the classical Reichstein Method.[8] The product was recrystallized from petroleum ether. KDG was obtained by potassium hydroxide neutralization of the corresponding acid commercially available from Fluka, afterly recrystallized from ethanol.

The N-lauroyl derivatives of the amino acids were prepared according the synthesis described by Takehara *et al.*,[9] a modified procedure from Jungermann *et al.*[10] It was verified that lauric acid and its corresponding alkaline salt are the main impurities in the resulting chiral amphiphile. Consequently, careful recrystallization from ethanol/hexane mixtures and purity determination by thin layer chromatography were adopted in order to assure high quality standards.

The mesophase composition for the different cholesteric systems are shown in Tables I and III. For clarity sake Table I is divided in four blocks corresponding to the amphiphile used in the nematic matrix.

All Ch_D cholesteric mesophases were characterized by their textures as observed using a Zeiss Universal Polarizing Microscope.

The twist sense can be determined using the polarizing microscope by measuring the optical rotatory power dependence on the sample thickness or on the illuminating wavelength. Monochromatic light was obtained from a continuous interference-filter monochromator Zeiss model 47 43 10 with a passing band of 13 nm. The first method is a modification of the wedge method[2,11] originally applied to thermotropic cholesteric mesophase. The second method is essentially an optical rotatory dispersion method. It is based on the theory developed by De Vries[12–15] to explain the rotatory power and other optical properties of cholesteric liquid crystals. Details of both methods applied to cholesteric lyomesophases were described previously.[16]

III. RESULTS AND DISCUSSIONS

Table II reports the experimental helical twist sense for 51 cholesteric lyomesophases investigated.

TABLE I - Mesophase compositions (% molar fraction).

A) KL Mesophases.

Chiral inducer	% molar fraction				
	KL	KCl	n-Decanol	Water	Inducer
D-Glucose	3.50	3.48	0.92	90.75	1.34
L-Sorbose	3.08	1.49	0.78	94.47	0.18
D-SG	2.16	2.45	0.38	94.34	0.66
L-DAS	3.19	1.49	0.79	94.41	0.12
L-KDG	3.25	1.73	0.80	94.07	0.15
L-CHOLESTEROL	3.07	—	1.03	95.80	0.10
D-Coen	3.71	3.57	0.54	92.00	0.17
L-KNLA *	1.80	2.08	0.59	94.54	0.20
L-SNLA *	1.80	2.08	0.54	94.59	0.20
L-KNLG *	1.80	2.08	0.65	94.48	0.20
L-SNLG *	1.80	2.08	0.65	94.48	0.20
D-KNLS *	1.80	2.08	0.55	94.58	0.20
D-SNLS *	1.80	2.08	0.55	94.58	0.20
L-SNLAsp *	1.80	2.08	0.55	94.58	0.20
L-KNLV *	1.80	2.08	0.55	94.58	0.20
L-SNLV *	1.80	2.08	0.54	94.59	0.20

* In these phases, KOH was added in order to provide a convenient pH for amphiphile solubilization. The KOH concentration in all samples is 0.79 % (molar fraction).

For thermotropic liquid crystals a correlation involving the chirality of the induced helix and that of the inducing compound was observed, despite the different chemical groups around the asymmetric centers.[4] Exceptions were verified when the inducing optically active molecule or the mesogen compound have bulk side-groups.[2,3] In this case, the same chiral solute induces different helical twisting senses in different systems depending on the final molecular packing.

The results on Table II show that arguments valid for thermotropic cholesteric systems can not be applied directly to lyotropic mesophases. For example, in two

TABLE I cont.

B) DAC Mesophases.

Chiral Inducer	% molar fraction DAC	NH_4Cl	Water	Inducer
D-GLUCOSE	6.28	2.90	87.50	3.29
L-SORBOSE	6.51	1.80	90.12	1.57
D-SG	6.53	1.83	90.69	0.93
L-DAS	6.69	1.83	91.41	0.07
L-KDG	6.64	1.96	91.26	0.14
L-CHOLESTEROL	5.11	1.87	92.81	0.21
L-KNLA	5.68	2.23	91.91	0.18
D-Coen	6.68	1.85	91.42	0.06

C) SLS Mesophases.

Chiral Inducer	% molar fraction SLS	n-Decanol	Water	Inducer
L-KNLA	2.02	0.71	97.13	0.13
L-SNLA	2.02	0.72	97.12	0.14
L-KNLG	2.02	0.72	97.13	0.14
L-SNLG	2.02	0.72	97.12	0.14
D-KNLS	2.02	0.72	97.13	0.14
D-SNLS	2.02	0.72	97.12	0.14
L-SNLAsp	2.02	0.72	97.13	0.14
L-KNLV	2.02	0.72	97.12	0.14
L-SNLV	2.02	0.72	97.12	0.14

cases reported on the Table (L-KDG and L-KNLA) simple changes in the nature of the host amphiphile (without great stereochemical changes in any compound) lead to mesophases of different helical twist senses.

It should be noted that lyotropic systems are more complex than thermotropic ones, since there are several possible solubilization sites. The inducer chemical properties determine its interaction with the micelle.

TABLE I Cont.

D) SDS Mesophases.

Chiral Inducer	% molar fraction SDS	Na_2SO_4	n-Decanol	Water	Inducer
D-GLUCOSE	3.96	0.91	1.12	93.69	0.33
L-SORBOSE	4.38	1.09	1.13	92.38	1.02
D-SG	3.27	1.02	0.97	94.51	0.24
L-DAS	4.37	1.05	1.08	93.39	0.11
L-KDG	4.02	1.07	1.14	93.59	0.18
L-CHOLESTEROL	4.36	0.99	1.08	93.46	0.11
D-Coen	4.09	0.84	1.14	93.87	0.07
L-KNLA *	3.05	0.83	1.07	94.68	0.14
L-SNLA *	3.05	0.83	1.07	94.69	0.14
L-KNLG *	3.05	0.83	1.06	94.69	0.14
L-SNLG *	3.05	0.83	1.06	94.69	0.14
D-KNLS *	3.05	0.83	1.07	94.69	0.13
D-SNLS *	3.05	0.83	0.88	94.86	0.14
L-SNLAsp *	3.05	0.83	1.06	94.69	0.14
L-KNLV *	3.05	0.83	1.06	94.69	0.14
L-SNLV *	3.05	0.83	1.06	94.69	0.14

* In these phases, NaOH was added in order to provide a convenient pH for amphiphile solubilization. The NaOH concentration in all samples is 0.23 % (molar fraction).

The experimental results here reported can be grouped in two classes. The chiral solutes of the first class lead to cholesteric mesophases with the same handedness in all systems studied. In the second class the same inducer can give mesophases of different helical twist senses in different systems.

The first class includes solutes which are hydrophobic (cholesterol) or hydrophilic (sorbose, glucose, sodium gluconate or tris(ethylenediamine)cobalt (III) iodide). Coincidentally, all these inducers produce left-twisted mesophases in any system. These results imply weak interaction of the quoted inducers with the micellar edl.

TABLE II - Helical Twist Sense Determinated for Cholesteric Systems.

	DAC	KL	SDS	SLS
D-GLUCOSE	L	L	L	-
L-SORBOSE	L	L	L	-
D-SG	L	L	L	-
D-Coen	L	L	L	-
L-DAS	D	D	D	-
L-KDG	D	L	D	-
L-CHOLESTEROL	L (a)	L	L	-
L-KNLA	D	L	L	L
L-SNLA	-	L	L	-
L-KNLG	-	D	D	D
L-SNLG	-	D	D	D
D-KNLS	-	D	D	D
D-SNLS	-	D	D	D
L-SNLAsp	-	D	D	D
L-KNLV	-	L	L	L
L-SNLV	-	L	L	L

D = Right (or dextro) twisted systems.
L = Left (or laevo) twisted systems.
The empty entries on the table are due to experimental difficulties in the respective mesophase preparation.
(a) The same result was also reported in Ref. 20.

These solutes are respectively located predominantly in the micellar paraffinic interior or in the bulk water, which are compartments that do not alter extensively for the different lyotropic systems here reported.

The interaction of sugars with the micellar systems has not been fully investigated in the literature. Nevertheless, it is reasonable to assume that the solvent medium, especially in a high ionic strength medium such as a lyomesophase, could alter in an unpredictable way their conformational equilibria. Anyway, considering the sugar high hydrophilic character, it is also reasonable to assume similar behaviour in different lyomesophases, inasmuch as the hydrophilic portion is essentially the same. These conclusions can be extended for sodium gluconate ion, since it is a sugar's derivative and its properties are similar to carbohydrates.

TABLE III - Mesophase Compositions (% molar fraction).

	1	2	3
CsDS	5.30	4.35	--
KDeC	--	--	5.28
Na_2SO_4	1.04	--	--
Cs_2SO_4	--	1.00	--
KCl	--	--	1.98
n-Decanol	0.54	1.09	1.53
Water	92.90	93.43	91.06
L-DAS	0.22	0.13	--
L-KDG	--	--	0.15
TWIST SENSE	L	D	L

For metal ions we could expect, at first glance, strong interaction with micellar edl through electrostatic forces. This interaction involves the remotion of a solvent molecule (usually water) from the ion's first coordination sphere producing a site which is able to interact with the charged micelle. Nevertheless, in the present case, we have the $[Co(en)_3]^{3+}$ ion, i.e., a very stable chelate ion, in which all positions of the first sphere of coordination are occupied by the ethylenediamine ligands. Therefore the only possibility of interaction is through the second coordination sphere ("outer-sphere"), leading to a much more weaker interaction.[17] Furthermore, $[Co(en)_3]^{3+}$ is a large complex ion, with a very low charge density, decreasing its interaction with the micellar edl. Therefore, we can assume that $[Co(en)_3]^{3+}$ is located predominantly in bulk water.

The second class of inducers—DAS, KDG and the N-acyl-amino acids derivatives—can give different twist senses for different nematical matrices.

For DAS, the acetone aduct with sorbose increases the hydrophobic character of the resulting compound. DAS is able to induce right-handed cholesteric mesophases in most matrices investigated. A helicity inversion was observed for CsDS mesophases when the cesium sulphate electrolyte (sample 2, Table III) was replaced for sodium sulphate (sample 1, Table III). This finding shows the existence of a counter ion specific interaction in the micellar electric double layer, changing fundamental parameters like surface charge density or surface potential, determining alteration in the inducer/edl interactions.

For KDG the table shows a helicity apparently associated with the nature of the mesophase amphiphile ionic headgroup. When this headgroup corresponds to an

ionic carboxilate group like KL (Table I.A) or potassium decanoate systems (sample 3, Table III), the cholesteric mesophase is left twisted. For the SDS and DAC detergents, the associated cholesteric mesophases are right-twisted. These results can be rationalized considering that KDG, in aqueous media, undergoes ionization process giving an anionic specie that interacts with the micellar edl. This interaction is strongly affected by the edl variations caused by changing the host amphiphile matrix.

The N-acyl-amino acid derivative amphiphiles must be stacked in the micellar palisade with the ionic headgroup anchored at the edl. For a chiral amphiphile solute in different anionic mesophases (KL, SDS and SLS phases) the observed helical sense is the same. This experimental fact shows that the micellar hydrocarbon interior should be essentially comparable in all quoted lyomesophases. Consequently, the twisting ability of a given chiral amphiphile inducer is the same in different media. Nevertheless, the helical twist sense inversion experimentally observed for L-KNLA/DAC systems is evidence that the existence of the inducer ionic headgroup should imply changes in the host chiral amphiphile anchoring process, especially when passing from anionic to cationic mesophases.

DAS, KDG and N-acyl-amino acids derivatives are chemical species that interact strongly with the micellar edl. This solute/edl interaction depends on the factors that alter the edl constitution, such as charge density, surface potential, nature of the amphiphile ionic headgroup and of the counter ions.

All experimental data show that the sense of twist does not exclusively depend on the absolute configuration of the chiral molecule. In order to generalize, we can propose three distinct cases. In the first, the inducer solute is located predominantly in the aqueous portion and its structure (that comprises constitution, configuration and conformation[18,19]) is solely responsible for the helical twist sense.

In the second case, hydrophobic inducer solutes, even submitted to structural changes due to strong interactions in the hydrocarbon core, should induce the same helical twist sense for different lyomesophases, since the environment afforded by the paraffinic chains is essentially comparable.

In the third case, the inducer solute is submitted to strong edl interactions, and two situations deserve attention:

(i) a hydrophilic inducer anchored at the micellar surface;
(ii) a hydrophobic inducer, located at the micellar hydrocarbon core, with an ionic group able to anchor itself in the edl.

In both situations, the helical twist sense should be determined by an inducer/micelle interaction. Therefore, any change in the inducer structure or in the micellar electrical properties could modify the cholesteric pitch length or even the helical twist sense.

The results here reported show a complex cholesterization process that can be attributed to intricate competition mechanisms at the level of electrostatic and hydrophobic interactions. As a global effect, it will cause the transference of the inducer stereochemical information to build the lyotropic cholesteric edifice in a nontrivial way. Hydrophilic or hydrophobic inducers subjected to strong interactions with the edl will originate cholesteric lyomesophases whose helical twist sense

can be modified by charge distribution on the micellar surface. It is evident in this case, more than the inducer chemical nature, the edl drives the chiralization effects.

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