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Liquid Crystals

Publication details, including instructions for authors and subscription information:

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To cite this Article Radley, Keith(1992) 'A laser diffraction study of amphiphilic cholesteric liquid crystals prepared from potassium dodecanoyl *L*-serinate', *Liquid Crystals*, 11: 5, 753 – 760

To link to this Article: DOI: 10.1080/02678299208029026

URL: <http://dx.doi.org/10.1080/02678299208029026>

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A laser diffraction study of amphiphilic cholesteric liquid crystals prepared from potassium dodecanoyl *l*-serinate

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(Received 18 September 1991; accepted 7 December 1991)

Amphiphilic cholesteric liquid crystal samples have been prepared using potassium dodecanoyl *l*-serinate (KDDS). Laser diffraction was used to determine the twist of the helix in these samples. Detergent concentration and the temperature dependence of the twist have been investigated. The results were found to be similar to those using the detergent potassium dodecanoyl *l*-alaninate (KDDA). A binary cholesterol study has been made using both the detergents KDDS and KDDA. The twist was not enhanced and the inter-cholesterol (detergent) interaction was shown not to be present in these micellar mixtures.

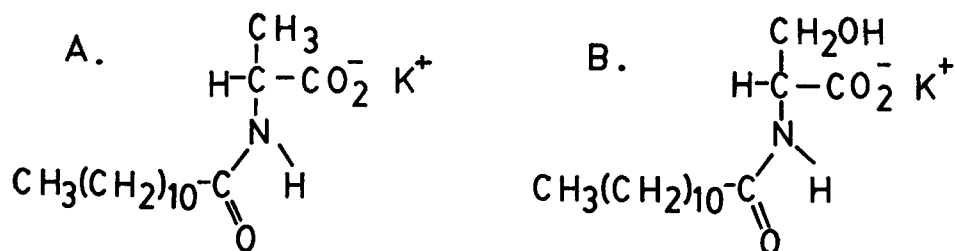
1. Introduction

Cholesteric liquid crystals are formed when chiral centres are introduced into nematic liquid crystals. Cholesterol esters which were the first examples of these so-called cholesteric or twisted nematic liquid crystals are characterized by strong iridescent colours, arising from the spontaneously twisted structures [1]. In thermotropic liquid crystals the formation of nematic liquid crystals is determined by the occurrence of orientational order derived from molecular interactions. In amphiphilic nematic liquid crystals this orientational order is derived from inter-micelle interactions. Cholesteric states are thus nematic states, where a chiral centre creates asymmetric orientational order, which facilitates a spontaneously twisted structure. In amphiphilic cholesteric liquid crystals unlike their thermotropic analogues the asymmetric orientational order could be created via two possible mechanisms. The first involves pairwise interactions between chiral molecules of adjacent micelles. The second model involves specific interactions between the chiral centres of the molecules within the individual micelles. The asymmetry in such interactions could produce a chiral shaped micelle. The present evidence does not favour either model.

The first amphiphilic cholesteric liquid crystals were prepared by adding chiral dopants to amphiphilic nematic liquid crystals [2]. Brucine, which was thought to be located in the micelle surface, was found in this investigation to produce the largest twists, when compared with cholesterol sitting in the chains and tartaric acid sitting in the aqueous layer. The twist produced by adding the dopant brucine was measured using a polarizing microscope, by observing the fingerprint texture, and was found to be several orders of magnitude less than what would be needed for total iridescence. It would seem that to make samples with larger twists more chiral centres would have to be introduced into the surface of the micelle. This has been achieved successfully by using chiral detergents such as the optically active salts of acylated amino acids [3-5]. In acylated amino acids the chiral centre is part of the head group, which facilitates the incorporation of the chiral centres in the micelle surface. For larger twists the

fingerprint texture is not visible under a polarizing microscope, but the twist was easily measured using laser diffraction. So far *l*KDDA has produced the largest twists, but these twists are still an order of magnitude away from total iridescence [6, 7]. Only Ch_D type systems (disc-shaped micelles) were produced in *l*KDDA systems. A reversal of the sign of the birefringence and diamagnetic anisotropy, corresponding to the nematic-cholesteric transition was also observed [7].

Studies with a chiral dopant have produced amphiphilic cholesteric liquid crystals related to both N_D and N_C phases and a third intermediate phase, the so-called biaxial phase [8–11]. When a second chiral centre was introduced into the detergent head group, using potassium dodecanoyl *l*-threoninate, larger twists in the corresponding amphiphilic cholesteric liquid crystals were not produced. In thermotropic cholesteric liquid crystal systems the twist has been enhanced by mixing two cholesterogens [2, 3]. The accompanying theory would have to be modified somewhat for systems formed from two chiral detergents. In the present investigation amphiphilic cholesteric liquid crystal samples will be prepared using the chiral and racemized detergents *l*KDDS, *l*KDDA, *dl*KDDS and *dl*KDDA (see the structures, where A is potassium dodecanoyl *dl* alaninate and B is potassium dodecanoyl *dl* serinate). The theory involves at least three interactions. The first two will be the intra-cholesterogen (detergent) and the third will be the inter-cholesterogen (detergent). In order to separate out these interactions clearly and to define clearly the inter-cholesterogen interaction racemized detergents were used in the investigation. In amphiphilic cholesteric liquid crystals made with chiral detergents the twist is produced by the interaction of the chiral head group with the surface of the micelle. When the alaninate head group is exchanged for the serinate head group the surface of the micelle will be modified as well as the twist. The thermotropic work did not use racemized cholesterogens [12, 13].



In this section and elsewhere N_C and N_D refer to amphiphilic nematic liquid crystal phase samples where the subscripts refer to the micelle structure, i.e. cylindrical and disc-shaped micelles, respectively. Ch_C and Ch_D refer to amphiphilic nematic liquid crystal phase samples where the subscripts refer to the achiral equivalent sample's micelle structure, i.e. cylindrical and disc-shaped micelles, respectively.

2. Experimental

KDDS, *dl*KDDS, *l*KDDA and *dl*KDDA were prepared by acylating the appropriate amino acid with dodecanoyl chloride as described previously [14]. The acids after purification, were neutralized using potassium hydroxide. The resulting potassium salts were recrystallized three times from hexane and alcohol and their purity was checked using proton decoupled ^{13}C NMR.

Samples of amphiphilic cholesteric liquid crystals were prepared as described previously [6, 7, 15]. The compositions for the KDDS/KDDA binary detergent system

are presented in the table. All of the mixed KDDS and KDDA samples have the same molar ratio 36:1:0.44 water/detergent/decanol. The weights used in sample preparation are found in the table, this includes 420 mg of water and 45 mg of decanol. The twist dependence on the detergent concentration was studied for a series of samples starting with 160 mg of *l*KDDS and finishing with 280 mg of *l*KDDS, together with 450 mg of water solution and 45 mg of decanol, where the molar ratio of the first sample is 50:8:1:0.58 and the last sample is 29:1:0.33. Specially purified decanol and double distilled water were used throughout. The composition of the water solution was 8 per cent CsCl and 2 per cent K_2CO_3 . These salts were less than 1 per cent in mole terms of the aqueous solution. The molar ratios were only calculated to two significant figures so the small salt concentrations were ignored. It was found that previously although achiral salts were important in phase formation, only the addition of chiral salts have a dramatic effect on the twist in amphiphilic cholesteric liquid crystals.

Various samples were investigated using a polarizing microscope. The samples were held in unsealed CAMLAB microslides or between a microscope slide and a cover slip. Conoscopic observations were made through a Bertrand lens and a full wave retardation plate at 294 K in order to determine the sign of the birefringence. Textures were also observed in order to recognize the phases, as well as to infer the structure of the micelles in the samples. A cholesteric phase gives rise to fingerprint textures, the N_D phase gives oily streaks and pseudo-isotropic textures and the N_C phase gives planar textures under the polarizing microscope.

The twist of the helix axis of the amphiphilic cholesteric liquid crystal samples was measured using laser diffraction. The wavelength of light from the laser was 6.328×10^{-5} cm. The temperature of the samples were controlled to within $0.1^\circ C$ by placing them in a brass block suitably drilled for water flow, sample placement and optical path. The temperature was controlled by circulating water from a thermostated water bath. Except for variable temperature studies all measurements were made at

The composition of amphiphilic cholesteric liquid crystals prepared from mixed chiral and racemized cholesterol (detergents) KDDA/KDDS together with laser diffraction twist measurements.

Composition†			Twist of helix P^{-1}/cm^{-1}			
mol %‡	KDDA/mg	KDDS/mg	A	B	A + B	C
0	0	210	3550	0	3550	3550
10	20	189	2950	800	3750	3600
20	40	168	2500	1350	3850	3850
30	60	147	2100	1900	4000	3900
40	80	126	1900	2350	4250	4100
50	100	105	1350	2850	4200	4250
60	120	84	950	3400	4350	4400
70	140	63	600	4100	4700	4750
80	160	42	— §	4750	—	4900
90	180	21	— §	5100	—	5150
100	200	0	0	5400	5400	5400

† Weight of KDDA and KDDS plus 45 mg decanol and 420 mg water solution.

‡ mol % = $([KDDA]/[KDDA] + [KDDS]) \times 100$.

§ Could not be measured under the present set-up.

A, *dl*KDDA/*l*KDDS; B, *l*KDDA/*dl*KDDS; C, *l*KDDA/*l*KDDS.

302 K. Variable temperature measurements were made on two samples, these were made from individual chiral detergents. The first *IKDDS* and the second *IKDDA* sample have the same compositions as in the table; at the top and the bottom of column C, respectively.

3. Results and discussion

When some of the amphiphilic cholesteric liquid crystal samples were viewed under a polarizing microscope fingerprint textures were produced if the twist was less than about 1000 cm^{-1} . When mixtures with higher twists were observed under a polarizing microscope the lines of the fingerprint texture could not be observed. When these unresolved textures were viewed via a Bertrand lens and a full wave retardation plate an interference figure which indicated negative birefringence, was produced. Samples prepared from racemized detergents gave rise to pseudo-isotropic textures with positive birefringence when observed under a polarizing microscope in a similar fashion. This indicated that the racemized cholesteric liquid crystal samples have a disc-shaped micelle structure. The reversal of the sign of the birefringence corresponding to the nematic-cholesteric transition has been observed before both in thermotropic and amphiphilic cholesteric liquid crystals [7, 15, 16]. In the cholesteric phases the optic axis is parallel to the helix axis, whereas in the nematic phases the optic axis is parallel to the unique axis of the micelle. In the cholesteric phases the unique axis of the micelle is perpendicular to the helix axis of the phases.

The temperature dependence of the twist was measured between 20°C and 47°C in two amphiphilic cholesteric liquid crystal samples. One was made with 100 mol% *IKDDA* and the second contained 100 mol% *IKDDS*. The first sample reached the two phase cholesteric/isotropic region at 48°C while the second sample reached the corresponding transition at 50°C . The results are presented in figure 1. In both cases the twist decreases with increasing temperature, while samples derived from *IKDDT* in a previous study had a twist which was nearly temperature independent [15]. For the first sample containing *IKDDA* the twist changed by a factor of three over the temperature range while for the second sample containing *IKDDS* it changed by a factor of two over the temperature range. In thermotropic cholesteric phases two mechanisms have been proposed to explain the temperature dependence of the twist, where usually in thermotropics the twist increases with increasing temperature. Both mechanisms involve a variation in the molar volume resulting from a corresponding variation in the thermal motion. Each of these two processes, which affect the molar volume, have opposite effects on the twist. The first process varies the intermolecular distance along the helix axis and the second involves the variation of the average displacement angle of the director of one molecule (or micelle) with respect to the adjacent cholesterogenic molecule. If these processes, which are opposite, were both as important, they would effectively cancel each other out, as is the case for the amphiphilic cholesteric liquid crystal samples derived from *IKDDT*. In micelles the second mechanism operates at two levels. At the most fundamental level it applies to the interaction of chiral centres leading to a chiral micelle (as with thermotropics). At a higher level the mechanism involves the interaction between adjacent micelles. For the cholesteric phase samples derived from *IKDDA* and *IKDDS* the first mechanism would seem to dominate and to an even greater extent with *IKDDA*.

The twist dependence on concentration of the detergent was measured and the results are presented in figure 2. The twist increased by a factor of five when the *IKDDS* concentration was increased from 0.16 g to 0.28 g. The present results are very similar to

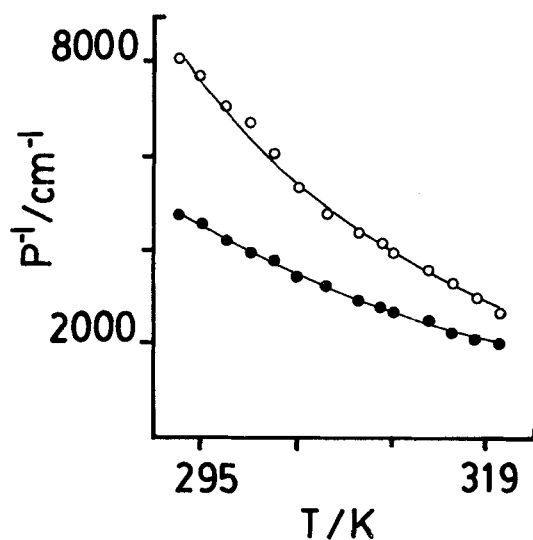


Figure 1. The effect of temperature on the twist ($1/P$) for sected samples of amphiphilic cholesteric liquid crystals. (○) /KDDA and (●) /KDDS.

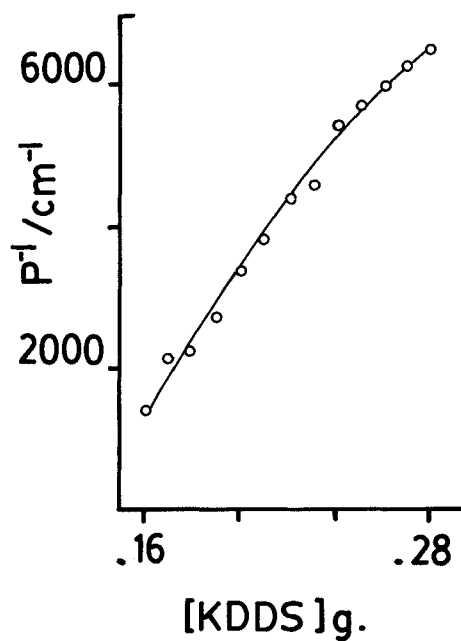


Figure 2. The behaviour of the twist ($1/P$) as a function of the detergent concentration in amphiphilic cholesteric liquid crystal samples whose compositions are discussed in the text. Measurements were made at 302 K.

those previously observed for *l*KDDA in both absolute and relative magnitude [6]. An increase in the detergent concentration will induce a change in the head group orientation with a concurrent increase in the twisting of the amphiphilic cholesteric liquid crystal. The increase of the twist with increasing amounts of detergent, results from changes in the orientation of the head group, where the twist is a measure of the distortion induced in the micelle by the chiral centre. On the other hand these results could be looked upon as a variation in the decanol concentration. The presence of decanol in the micelles dilutes the amphiphile head groups and pushes the chiral centres apart and lowers the twist. Twist in an amphiphilic cholesteric liquid crystal is a consequence of the chiral centre density in the micelle surface. Studies with amphiphilic cholesteric liquid crystal samples prepared by mixing chiral and racemized detergents show that the twist is directly proportional to the chiral detergent excess under compatible chemical situations [6, 15].

In a thermotropic cholesteric involving two chiral components the twist dependence on the concentration has been treated theoretically [12, 13]. Here the pitch equation is written as

$$\frac{(n_A + n_B)l}{2P} = n_A^2\alpha + n_B^2\beta + n_A n_B \gamma;$$

n_A and n_B are the number of chiral centres, α and β are the intra-cholesterogen interactions and γ is the inter-cholesterogen interaction. If a study is made where A is an optically active cholesterogen and B is a racemized cholesterogen $\gamma=0$, $\beta=0$, hence $1/P=n_A\alpha$, and vice versa if $\gamma=0$, $\alpha=0$, then $1/P=n_B\beta$. In the present study with amphiphilic cholesteric liquid crystals this procedure has been followed and the results are presented in columns A and B in the table. The results have been transferred to figure 3. The results for *l*KDDA/*d*lKDDA have a positive divergence from a straight

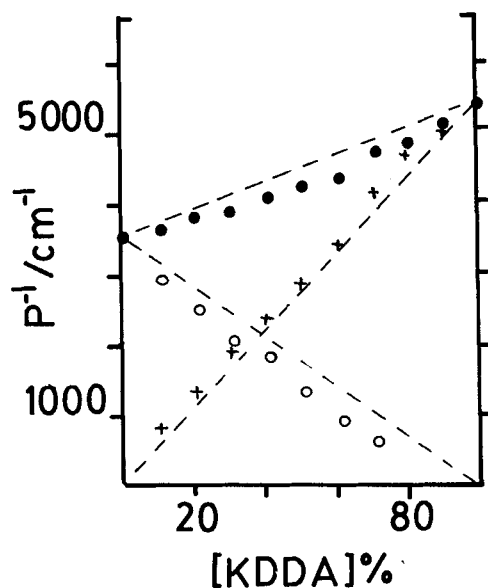


Figure 3. The magnitude of the twist ($1/P$) induced in a binary cholesterogen (detergent) amphiphilic cholesteric liquid crystal system. *l*KDDA/*i*KDDA (●), *d*lKDDA/*i*KDDA (+), *l*KDDA/*d*lKDDA (○). Measurements were made at 302 K.

line, while the results for *IKDDS/dIKDDA* have a negative divergence from a straight line. These divergences from the straight lines are not due to intra-cholesterogen (detergents) interaction, but due to modifications in the surface of the micelle resulting from changes in the chemistry of the head group. The hydrogen of the alaninate methyl is substituted for the hydroxyl of the serinate and vice versa. If the study involved amphiphilic cholesteric liquid crystal samples using two optically active cholesterogens (detergent), i.e. *IKDDA* and *IKDDS*, it is possible to estimate γ the inter-cholesterogen interaction and so make allowances for the chemical changes in the micelle surface. The results are presented in column C of the table and in figure 3. The results were non-linear as would be expected. If the results in columns A and B are added together the contribution to the twist due to the changes in the chemistry of the micelle can be estimated. It was found that the sum of the results in columns A and B within experimental error were equal to the results in column C of the table. The significance of this result is $\gamma=0$ and consequently the inter-cholesterogen (detergent) interaction in this micelle system does not make a contribution to the twist. Previous studies of thermotropic cholesterics on a binary cholesterogen system were incomplete because racemized cholesterogens were not investigated. In these thermotropic studies it was not possible to separate chemical modification of the components from the inter-cholesterogen interaction and say how much each contributes to the divergence from linearity in the results.

4. Conclusion

In the binary cholesterogen (detergents) amphiphilic cholesteric liquid crystal system prepared from *IKDDA* and *IKDDS* the magnitude of the twist is not enhanced. There is, in fact, a small negative divergence from linearity. When experiments were made using a racemized and a second optically active detergent this divergence from linearity was shown to be due to chemical changes in the micelle surface and not due to the intra-cholesterogen (detergent) interaction. Amphiphilic cholesteric liquid crystal samples made with pure *IKDDS* and a molar composition comparable to samples with pure *IKDDA* give rise to twists which for *IKDDS* are approximately 60 per cent those for *IKDDA*.

The author would like to thank Professor M. I. Page in the Department of Chemical and Physical Sciences at Huddersfield Polytechnic for facilitating a self-supporting visiting Research Fellowship beginning in January 1991.

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