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Potassium Salts of Acylated Amino Acids as Chiral Dopants and Hosts in the Formation of Amphiphilic Cholesteric Liquid Crystals

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Several potassium salts of acylated amino acids have been synthesized. These chiral detergents have been used in the preparation of Amphiphilic Cholesteric Liquid Crystals (ACLC), both as chiral dopants and as chiral hosts. These ACLC samples have been characterised by laser diffraction twist measurements as well as by polar microscopy. L-KDDA (C_{12} alaninate) was found to be the optimum chiral dopant. L-KDDA and L-KTDA (C_{14} alaninate) were found to be the most efficient chiral hosts. Where L-KTDA was much more effective at low decanol concentrations. Using polar microscopy, the optical rotation along the helix axis was found to be positive in all cases.

Keywords: acylated amino acids, chiral, cholesteric, laser diffraction

INTRODUCTION

The formation of a Cholesteric Liquid Crystal (CLC) can be achieved by the inclusion of chiral centres in a Nematic Liquid Crystal (NLC), either as a chiral dopant or as a chiral host. Cholesteric states are nematic states, where the chiral centres create asymmetry in the orientational order, facilitating spontaneously twisted structures. The formation of Thermotropic Nematic Liquid Crystals (TNLC) is determined by the occurrence of orientational order derived from molecular interactions, whereas in Amphiphilic Nematic Liquid Crystals (ANLC) the orientational order is derived from micellar interactions. The first examples of CLC were cholesterol esters, which were characterised by strong iridescent colours whose wavelengths corresponded to the spontaneously twisted structure. The first samples of Amphiphilic Cholesteric Liquid Crystals (ACLC) were prepared by using chiral dopants.[1] Brucine which was thought to be located in the surface of the micelle was found in this study to be the most effective chiral dopant in terms of inducing twist. A host detergent with a chiral head group was later found to be a much more effective way of introducing a chiral centre into the micelle surface of a ACLC

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sample. The acylated amino acid potassium salts L-KDDA,[2] L-KDDS[3] and L-KDDT[4] have been found to be very effective chiral hosts, while the chiral cationic detergents were found to be less successful as chiral hosts.[5,6,7,8] Only L-KDDA has been studied previously as a chiral dopant, where the inclusion of L-KDDA in a host potassium laurate (KDD) ANLC sample, as well as facilitating ACLC formation, induced phase changes to give in sequence Ch_D, Ch_{BX} and Ch_C phases.[9] ANLC samples can have phases with both disk and cylindrical shaped micelles with a biaxial intermediate N_D, N_C and N_{BX}, respectively. When the ACLC sample host is a chiral detergent only Ch_D phase samples have been prepared.[2,3,4,10]

In this study it is proposed to investigate the effectiveness of the potassium salts of several acylated amino acids as chiral dopants. Laser diffraction twist measurements will be made together with polar microscope observations, in order to investigate the micelle structure of the achiral equivalent sample and to determine the sign of the optical rotation along the helix axis. Three chiral precursors L-alanine, L-serine and L-threonine will be used. Alanine is to be acylated with the carboxylic acid chlorides of four different chain lengths. The results will be compared to the chiral host situation and new chiral host investigations, will be made where the acylated L-alaninate has not been previously studied.

EXPERIMENTAL

The chiral detergents, which were the potassium salts of acylated amino- acids; potassium decanoyl L-alaninate L-KDeDA; potassium dodecanoyl L-alaninate L-KDDA; potassium tetradecanoyl L-alaninate L-KTDA; potassium hexadecanoyl L-alaninate L-KHDA; potassium dodecanoyl L-threoninate L-KDDT and potassium dodecanoyl L-serinate L-KDDS; were prepared via the acids by acylating the amino acids with the appropriate acid chloride in an aqueous medium kept neutral with NaOH[11] below 4°C. When the reaction was completed, the acylated amino acids were liberated by excess H_2SO_4 and extracted with ether. After rotavaping to dryness the acids were recrystallised from hexane followed by neutralisation with KOH. The resulting chiral detergents were twice recrystallised from ethanol and ethyl acetate followed by drying under vacuum. The purity of the final product was checked using proton decoupled ^{13}C NMR of S/N of about 100:1 which allowed the estimation of impurities to within 1%. The presence of the potassium carboxylate derived from the untreated acid chloride was the most likely impurity. If it was detected, the product was recycled to the acid form and the pure carboxylic acid was prepared by recrystallization with hexane as above.

Samples were made up by weighing out the materials into test tubes, to which a constriction had been made in the middle. Afterwards the test tubes were flame sealed. Homogeneously mixing was achieved by repeated heating and centrifuging the materials through the constriction in the test tube. In the chiral dopant studies, which involved the six of the above mentioned detergents, the host sample of ANLC was KDD 300 mg (31.25%); decanol 30 mg (6.25%) and H_2O (containing 5% CsCl) 600 mg (62.5%). A series of sets of doped ACLC samples were made by adding 10, 20, 30, 40, 50 and 60 mg to the host ANLC with the exception of

L-KHDA where 15, 30, 45 and 60 mg were added. The chiral host studies involved four chiral detergents where the head group was alanine and the chain length was varied from C_{10} to C_{16}. The sample compositions were: a) L-KDDA; decanol; water between 130 mg (20.8%); 45 mg (7.2%); 450 mg (72%) and 290 mg (36.9%); 45 mg (5.73%); 450 mg (57.32%), respectively. b) L-KTDA; decanol; water between 110 mg (18.6%); 30 mg (5.08%); 450 mg (76.2%) and 210 mg (30.4%); 30 mg (4.3%); 450 mg (65%), respectively. c) L-KDeDA; decanol; water between 240 mg (34.5%); 55 mg (7.9%); 400 mg (57.6%) and 270 mg (37.2%); 55 mg (7.6%); 400 mg (55.2%), respectively. Attempts were made to prepare ACLC samples from L-KHDA but at 30°C the detergent crystallized out. The ascending and descending compositions of the ACLC samples in each chiral host set differed by 10 mg. The water in the chiral host samples was double distilled and contained 10% CsCl. The decanol was specially purified by fractional crystallization.

Information concerning the micelle structure of the achiral equivalent phase sample to each ACLC sample was inferred from the observation of concentration gradients under the polarising microscope. If the neighbouring dimensionally ordered phase under a concentration gradient has pseudo-isotropic or contained oily streaks polar microscopic textures, the micelle structure would be inferred to be disk shaped Ch_D and similarly if the polar microscopic textures were planar, cylindrical micelle structure would be inferred to be Ch_C.[12] Nematic phase samples give rise to pseudoisotropic and schlieren textures when observed under the polarising microscope, where cholesteric phase samples can give rise to fingerprint textures, which can be used to determine the twist of the helix, through counting the lines. Cholesteric phase samples can also give rise to Grandjean planes under a polarising microscope which can be used to determine the sign of the optical rotation along the helix axis.[13]

The helix twist in the ACLC samples was measured non-destructively using laser diffraction. The wavelength of the laser beam was 6.328×10^{-5} cm. The temperature of the ACLC sample used in the laser diffraction was controlled to within 0.1°C by placing the sample in a brass block, suitably drilled for waterflow, sample placement and optical path. The temperature was controlled by circulating water from a thermostated water bath. The accuracy of the twist measurement was about 10%. The twist and optical rotation along the helix axis have opposite signs.

RESULTS AND DISCUSSION

The composition of the host ANLC sample which in the present chiral dopant study induced cholesteric states, was selected so that the phase changes encountered in a previous study where KDD was the host and L-KDDA was the dopant, did not interfere with the present results.[9] The micelle structure of disks in the achiral nematic was confirmed in a number of ACLC samples using the polarising microscope. Selected chiral dopant ACLC samples were mixed after the twist had been determined by laser diffraction, and the twist was again determined after mixing. This data is set out in Table I. It is easily seen that the twists in the final mixtures were approximately the sum of the twists in the individual mixture and not the

TABLE I

The effects on the magnitude of the twist (l/p) when individual chiral dopant ACLC samples are mixed to form new ACLC samples

Detergent A			Detergent B			Calculated		Exp.
	Mol %	$\frac{1}{P_A}$ *		Mol %	$\frac{1}{P_B}$ *	$\frac{\frac{1}{P_A}+\frac{1}{P_B}}{2}$ *	$\frac{\frac{1}{P_A}-\frac{1}{P_B}}{2}$ *	$\frac{1}{P}$ *
L-KDDA	8.98	2840	L-KDeDA	9.79	1920	2380	460	2190
L-KHDA	4.77	870	L-KDDA	5.15	1340	1100	240	1100
L-KDDA	7.15	2310	L-KTDA	8.30	2270	2290	20	2300
L-KDDS	10.12	1420	L-KDDT	8.25	1570	1490	80	1420
L-KTDA	7.79	2610	L-KDDT	9.74	1340	1970	640	1960
L-KDDA	10.59	3320	L-KDDS	8.58	1070	2190	1130	1840

(* : cm^{-1})

difference in the twists. These results indicate the sign of the twists induced by each individual acylated amino- acid salt and hence the optical rotation have the same sign. The absolute sign of the optical rotation along the helix axis in several ACLC samples was determined by observing Grandjean textures under a polarising microscope. In each individual case the sign of the optical rotation was found to be positive. Consistently useful information is difficult to obtain from the optical rotation measurements in isotropic chiral solutions. L-Alanine, L-threonine and L-serine all have the same absolute molecular configuration, S, but in an isotropic chiral solution, L-threonine and L-serine have the same sign of optical rotation, negative, and alanine has the opposite sign, positive. Optical rotations in anisotropic chiral solutions are usually made in a well defined direction, i.e. along the helix axis, and have been found to be in some cases 10,000 times larger than in isotropic chiral solutions. In isotropic chiral solution the chirality (optical rotation) arises from the interaction energy between two chiral tetrahedral molecules.[14] Discriminating interactions between chiral tetrahedral molecules arise when six centered forces play an important role. Chirality is ensured by the different natures (e.g. charge, electronegativity, etc.) of the four substituents. In an isotropic environment the asymmetrical part of the interaction field unlike the symmetrical part fails to average to zero. In an ACLC sample the hydrocarbon chain is well defined in respect to the micelles surface. Chirality and hence the optical rotation along the helix axis is defined by the micelle surface.[15] When ACLC are prepared using several salts of acylated amino acids with the same S configuration, if the micelle surface has an important role to play in defining the chirality, the sign of the optical rotation should be the same in each individual case, as was observed in the present experiments. In a recent study where two chiral quaternary ammonium detergent precursors were S- 1,2 and S- 2,1 amino propanol, the sign of the optical rotation in the ACLC samples prepared from the first chiral detergent was opposite to that in the second chiral detergent.[8] The molecular configurations of the chiral detergents were unchanged during the synthesis. The hydrocarbon chain attached via

the quaternary ammonium was coupled to the opposite sides of the head group in the first case in respect to the second case and vice versa. This results in the configuration of the first detergent being opposite to the second detergent in respect to the micelle surface, hence the optical rotation in the ACLC sample for the first chiral detergent should be opposite to that of the second chiral detergent, as was observed experimentally.

In Figure 1 the twist of the helix was plotted as a function of molar % of each chiral dopant respect to the total amphiphile (chiral dopant + KDD + decanol) L-KDDA (C_{12} alaninate) was found to be the most effective for inducing twist in the host potassium laurate ANLC sample. In similar circumstances L-KTDA (C_{14} alaninate), L-KDeDA (C_{10} alaninate) and L-KHDA (C_{16} alaninate) are in descending order of effectiveness. L-KDDS and L-KDDT were even less effective chiral dopants. As a chiral dopant L-KDDT was more effective than L-KDDS but this is the reverse of that found in a previous study where L-KDDS and L-KDDT were the chiral hosts. L-KDDT has two chiral centres due to the extra CH_3 group on the chiral precursor, which could be more important for chiral dopants, whereas the size of the head group could be more important for chiral hosts.

The data from Figure 1 was transformed so that in Figure 2 the chain length of the carboxylic acid used in the synthesis of the acylated alaninate could then be plotted as a function of the twist for several molar % (2, 4, 6, 8 and 10). From Figure 2 it is obvious there is an optimum chain length associated with chiral dopancy in respect to the alaninate and the KDD host. This optimum chain length is C_{12}. If in the present case in the micelle surface, the charge part of the host and

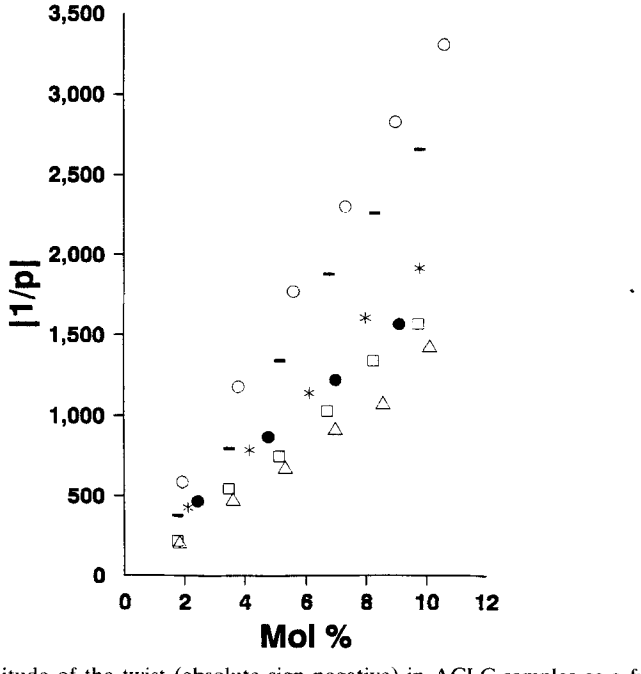

FIGURE 1 The magnitude of the twist (absolute sign negative) in ACLC samples as a function of the chiral dopant Mol %: ○ L-KDDA, ━ L-KTDA, * L-KDeDA, ● L-KHDA, □ L-KDDT and △ L-KDDS at 303°K.

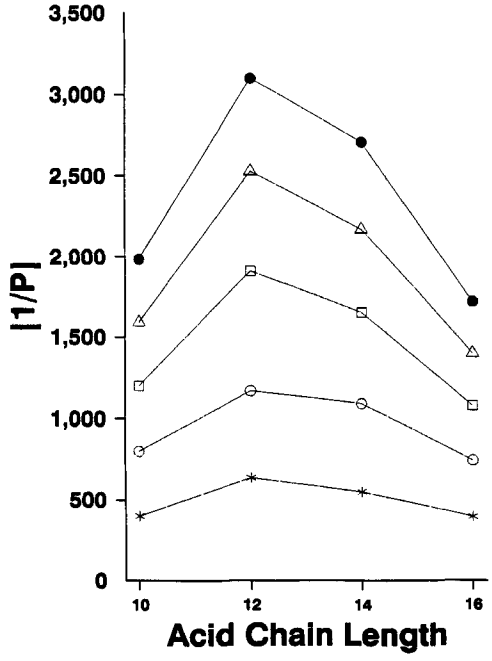

FIGURE 2 The magnitude of the twist (absolute sign negative) in ACLC samples as a function of the chiral dopant Mol %: * 2, ○ 4, □ 6, △ 8 and ● 10 at 303°K.

the chiral dopant coincided, L-KDDA would not necessarily be the optimum chiral dopant, on pure packing considerations. It was suggested in a previous study the correspondence of the dopant and the host in the micelle surface was the carbon chain carbonyl groups and not the charge of the amphiphiles. The effectiveness of L-KDeDA (C_{10} alaninate) would be reduced due to the extra space for the chain motion i.e. the waggle of the shorter hydrocarbon chains, as was experimentally observed. The longer hydrocarbon chains C_{14} and C_{16} in terms of packing consideration will tend to increase the size of the micelles and undermine the micelle surface as long as the KDD amphiphile dominates the micelle surface and remains the host. L-KTDA (C_{14} alaninate) has an intermediate effectiveness whereas L-KHDA (C_{16} alaninate) has a lesser effectiveness as a chiral dopant.

Attempts to use L-KHDA (C_{16} alaninate) as the chiral host for the preparation of ACLC samples are fairly limited because the detergent crystallizes out below 30°C. L-KDDA (C_{12} alaninate) and L-KTDA (C_{14} alaninate) were found to be very effective chiral hosts but L-KDeDA (C_{10} alaninate) was disappointing with only four samples in the range covered by Figure 3. In Figure 3 the ACLC sample helix twist is plotted against the double molar quotient M_Q where M_Q = moles of detergent/(moles of water × moles of decanol). In several amphiphilic systems the formation of ANLC in respect to sample composition has been found to be chain length dependent, where an increase in the chain length of the amphiphile by two carbons involves a doubling of the water content or an halving of the decanol

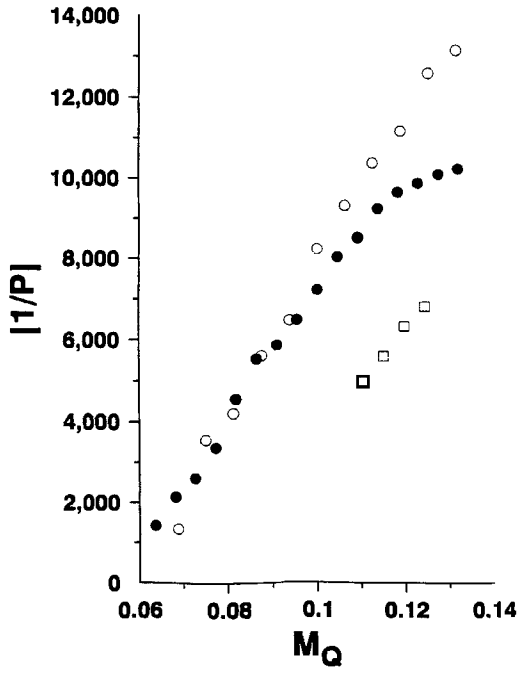

FIGURE 3 The magnitude of the twist (absolute sign negative) in ACLC samples as a function of the chiral host Mol %: ○ L-KTDA, ● L-KDDA and □ L-KDeDA at 298°K.

content in order to maintain the formation of ANLC samples.[16,17] The formation of orientational ordered micelles involves the fine balancing of the hydrophobic and hydrophilic forces, where the head group faces towards the water and the hydrocarbon chain faces away. These processes are thought to be usually driven by the interactions of the head group of the detergents with the aqueous region, where the hydrocarbon chain, which is not in contact with the aqueous region, is thought to be rather passive. In the present study the twist produced by L-KTDA as a chiral host is sometimes a third higher than in the corresponding L-KDDA ACLC samples. The relative effectiveness of L-KTDA and L-KDDA as chiral hosts is the reverse that of these chiral detergents as chiral dopants. The relationship of chiral dopants to packing has already been discussed. In the host situation the inactive hydrocarbon chain is increased by two carbons resulting in rather large increases in twist. When the amphiphile acyl chain increases from C_{12} to C_{14} the chain length increases physically by approximately 10% but the corresponding increase in the volume of the simple micelle could be at least 30%. Absolute micelle size could have a profound effect in the effectiveness of chiral hosts in inducing twist in ACLC samples. In the present study when the decanol concentration was high the L-KTDA and the L-KDDA twist (M_Q) results in Figure 3 converged. When the decanol concentration was low, i.e. when the host has almost total control of the formation of the micelles, the results diverged.

CONCLUSIONS

The acylated amino acids as chiral dopants produced ACLC samples where the sign of the optical rotations for each chiral detergent were identical and positive. The optimum chiral dopant in respect to the acyl chain was found to be L-KDDA (C_{12} alaninate). L-KDDA and L-KTDA (C_{14} alaninate) were found to be the best chiral hosts. L-KTDA in respect to L-KDDA was found to be the best chiral host at low decanol concentrations, the reverse that of the chiral dopant situation. L-KDDS and L-KDDT have been found to be less effective chiral dopants than the alaninates but in the reverse order to the previous chiral host studies.

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