Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Amphiphilic cholesteric liquid crystals prepared from the quaternary ammonium surfactant *S*-(-)-1-hexadecyl-1-methyl-2-pyrrolidinemethanol bromide

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To cite this Article Radley, K. and Cattey, H.(1992) 'Amphiphilic cholesteric liquid crystals prepared from the quaternary ammonium surfactant *S*-(-)-1-hexadecyl-1-methyl-2-pyrrolidinemethanol bromide', Liquid Crystals, 12: 5, 875 — 878
To link to this Article: DOI: 10.1080/02678299208029131
URL: http://dx.doi.org/10.1080/02678299208029131

LIQUID CRYSTALS, 1992, VOL. 12, NO. 5, 875–878

Amphiphilic cholesteric liquid crystals prepared from the quaternary ammonium surfactant *S*-(–)-1-hexadecyl-1-methyl-2-pyrrolidinemethanol bromide

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(*Received 29 April 1992; accepted 19 June 1992*)

We describe the first successful attempt to produce amphiphilic cholesteric liquid crystals using a chiral quaternary ammonium surfactant, namely *S*-(–)-1-hexadecyl-1-methyl-2-pyrrolidinemethanol bromide. Only amphiphilic cholesteric liquid crystal samples were made where the micelle structure is related to disc shaped micelles in the achiral N_D phase. The surfactant concentration dependence of the twist and the temperature dependence of the twist were made using laser diffraction. The twist in the amphiphilic cholesteric liquid crystal samples was too small to produce total iridescence.

Amphiphilic cholesteric liquid crystals were first obtained by introducing chiral dopants into amphiphilic nematics [1]. In this early study brucine, which was absorbed on the surface of the micelle was found to be the best chiral dopant. The use of a chiral surfactant with a chiral headgroup for the preparation of amphiphilic cholesterics was found to be a far better way for placing chiral centres on the surface of micelles [2]. Such samples have been prepared using the potassium salts of acylated amino acids as the chiral surfactant, where potassium dodecanoyl-*e*-alaninate (L-KDDA) was found to produce the shortest pitches with a twist of up to 10 000 cm^{-1} [3, 4]. Potassium dodecanoyl-L-serinate (L-KDDS) [5], and potassium dodecanoyl-L-threoninate (L-KDDT) [6] were found to be less effective. Total iridescence exhibited by cholesteric esters, where the twist must be approximately 50 000 cm^{-1} has not been reported in amphiphilic cholesterics. Surfactants based on the chlorides of amino acid esters and primary amines with achiral branched chain gave rise to even smaller twists [7, 8]. Only amphiphilic cholesterics where the micelle structure is related to a chiral N_D have been reported and no achiral N_{BX} or N_C have been reported when a chiral host detergent is involved [9, 10] in the sample preparation. In this preliminary communication we report, that amphiphilic cholesterics can be obtained by using the chiral quaternary ammonium surfactant *S*-(–)-1-hexadecyl-1-methyl-2-pyrrolidinemethanol bromide (*S*-(–)-HDMPMBr). A reversal of the sign of the birefringence and diamagnetic anisotropy, corresponding to the nematic–cholesteric transition has been observed in previous studies [4].

S-(–)-HDMPMBr was prepared by alkylating *S*-(–)-methyl-2-pyrrolidinemethanol (MPM). A mixture of MPM and hexadecyl iodide were refluxed on a water bath for several hours and then let stand overnight. The solid was dissolved in ethanol and AgOH added. AgI was filtered off and the solution was neutralized with concentrated HBr. The solid surfactant obtained by evaporating the surfactant solution to dryness

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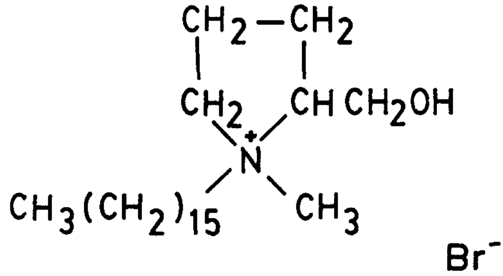

S-(−)-1-Hexadecyl-1-methyl-2-pyrrolidinemethanol bromide.

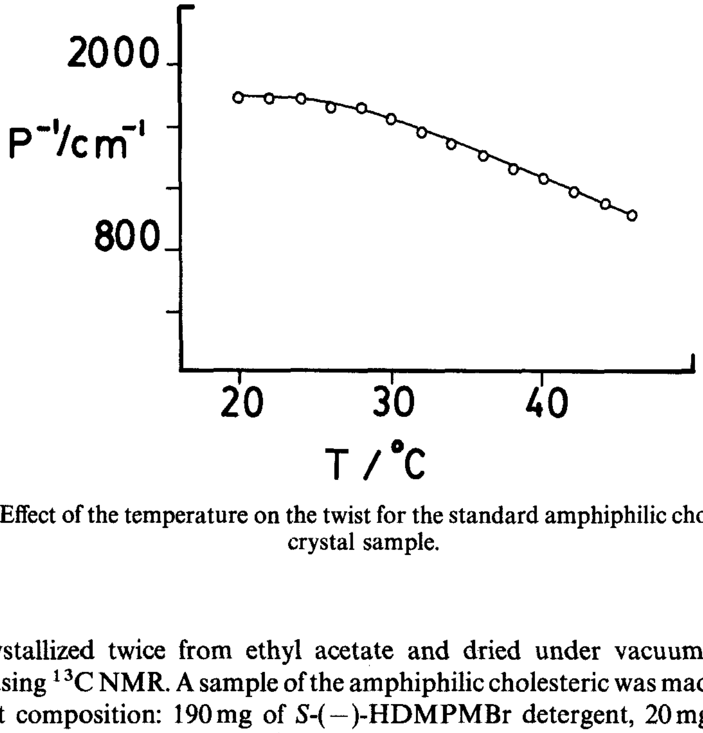

Figure 1. Effect of the temperature on the twist for the standard amphiphilic cholesteric liquid crystal sample.

was recrystallized twice from ethyl acetate and dried under vacuum. Purity was checked using ^{13}C NMR. A sample of the amphiphilic cholesteric was made up with the ingredient composition: 190 mg of *S*-(−)-HDMPMBr detergent, 20 mg of specially purified decanol and 230 mg of double distilled water containing 4 per cent by wt of CsCl which corresponds to wt% 43·2, 4·5 and 52·3, respectively. The ingredients were weighed out into an NMR tube, which was then heat sealed. The components were homogeneously mixed by careful heating and centrifuging. The sample was introduced into a 270 MHz Bruker NMR spectrometer, where the axis of the magnetic field corresponds to the spinning axis in order to align the sample to produce sharp laser diffraction patterns. The temperature dependence of the pitch between 20°C and 45°C was measured using laser diffraction (see figure 1). The twist gradient in the present study, where the twist decreases with increasing temperature, was less pronounced than the corresponding results with L-KDDA and L-KDDS [5] but more pronounced than in L-KDDT [6]. The temperature dependence of the twist, which in amphiphilic cholesterics is opposite to that in thermotropic cholesterics, has been explained for these, by two proposed mechanisms, which involve variations in the molar volume resulting from corresponding variations in the thermal motion [11]. The first process varies the intermolecular distance along the helix axis and the second process involves

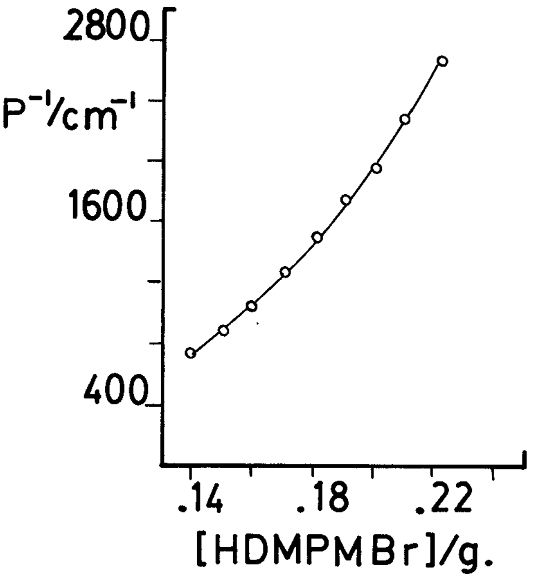

Figure 2. Behaviour of the twist as a function of the surfactant concentration in amphiphilic cholesteric liquid crystal samples whose compositions are discussed in the text. Measurements at 25°C.

the variation of the average displacement angle of the director of one molecule with respect to the adjacent cholesterogenic molecule. The twist temperature dependence in a cholesteric liquid crystal can become very complicated if the cholesterogen has two or more chiral centres or chiral micelles. In chiral micelles, it is thought, the twist is determined by the chiral density on the micelle surface. When a cholesterogen has two chiral centres, where four isomers produce two pairs of diastereoisomers, the twist of one of the pair of diastereoisomers would more than likely move through zero [12].

The lines in the laser diffraction pattern were found to be perpendicular to the spinning axis of the tube. Hence the director axis or optic axis of the amphiphilic cholesteric sample, which corresponds to the helix axis, is aligned parallel to the magnetic field indicating positive diamagnetic anisotropy [4]. The sign of the diamagnetic anisotropy in the corresponding achiral amphiphilic nematic sample would be negative. The ingredients of the cholesteric samples did not include aromatic or fluorocarbon ions, therefore the positive sign of the diamagnetic anisotropy in the cholesteric indicates that the corresponding achiral nematic (not prepared here) [13, 14] is made up of disc shaped micelles. If the diamagnetic anisotropy of the amphiphilic cholesteric sample had been negative the helix would have partially or totally unwound in the magnetic field of the NMR spectrometer, depending on the magnitude of the negative diamagnetic anisotropy.

The pitch was measured using laser diffraction at 25°C on a series of amphiphilic cholesteric samples using the first sample as a standard, where the surfactant concentration was varied between 160 and 220 mg corresponding to 39·0 and 46·8 wt%. The results are presented in figure 2. The twist–surfactant concentration dependence in the present studies, where the twist increases with concentration, is similar to previous studies [5, 6]. An increase in the surfactant concentration induces a change in the head-group orientation with a concurrent increase in the twist of the amphiphilic cholesteric, where the twist is a measure of the distortion induced in the micelle by the chiral centre. Twist in an amphiphilic cholesteric is a consequence of the chiral density in the micelle surface.

When thin films of the amphiphilic cholesteric were observed under a polarizing microscope the fingerprint texture in most of the samples was unresolved. When the same samples were observed conoscopically via a full wave plate and a Bertram lens, interference figures were produced, which are consistent with negative birefringence [5, 6]. The negative sign for the birefringence of the amphiphilic cholesteric corresponds to positive birefringence in the achiral amphiphilic nematic (not prepared here) confirms the disc shaped micellar structure in the mesophase samples. Disc shaped micellar structures in the samples were again confirmed by concentration gradients, where pseudo-isotropic and oily streak textures were observed next to the chiral nematic phases. No amphiphilic cholesterics were prepared where the corresponding achiral nematic had a cylindrical shaped micellar structure [13].

In this preliminary communication the preparation of amphiphilic cholesteric liquid crystals, where the micellar structure is related to disc-shapes, using the chiral quaternary ammonium surfactant *S*-(−)-HDMPMBr has been presented. The twists measured using laser diffraction were between 700–2700 cm^{-1} and so total iridescence was not observed. This is the first report of the preparation of an amphiphilic cholesteric using a quarternary ammonium chiral surfactant.

Dr K. Radley, would like to thank Professor M. I. Page in the Department of Chemical Sciences at the University of Huddersfield for facilitating a self-supporting Visiting Research Fellowship beginning in January 1991. The authors would also like to thank the University of Huddersfield for providing a small research grant to buy chemicals for the present studies. The authors would also like to thank Dr J. E. Lydon at the University of Leeds for the use of the polarizing microscope.

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