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An amphiphile system forming a lyotropic blue phase

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A partial phase diagram of the potassium *N*-tetradecanoyl-L-alaninate/decanol/water (+ 10 per cent CsCl) system has been charted using polarizing microscopy, laser diffraction, and NMR spectroscopy. At low amphiphile concentrations, a chiral nematic $\mathrm{Ch_D}$ phase with disc-like micelles occurs and at higher concentrations there occur a chiral nematic, $\mathrm{Ch_C}$ phase with cylindrical micelles and a chiral version of a dimensionally-ordered (probably rectangular or hexagonal) phase. Between the $\mathrm{Ch_C}$ phase and the genuine isotropic liquid there is a chiral isotropic phase which appears to be a micellar analogue of a thermotropic blue phase. This isotropic chiral $\mathrm{I_C}$ phase showed flow birefringence.

The first chiral liquid crystalline systems to be recognized were the twisted nematic (cholesteric) phases of the cholesteryl esters [1]. Shortly afterwards, the so-called ‘blue phases’—the optically-isotropic cubic phases—which occur at the upper temperature limit of the cholesteric phase—were recognized as being distinct. Their structures appear to be purely a consequence of the molecular chirality—and there are no comparable non-chiral systems. The colours observed for blue phases are not always blue, and arise from periodicities in the structures which are of dimensions comparable to visible wavelengths [2–7].

Chiral thermotropic dimensionally-ordered phases were predicted in 1973 by Meyer [8] and the $\mathrm{S_C^*}$ phase was characterized in 1978 [9]. More recently, the chiral analogue of the smectic A phase—the twist grain boundary phase was reported by Goodby *et al.*, in 1988 [10].

Chiral mesophases of helical polymer solutions (of DNA, RNA and synthetic polypeptides) have been known for many years, but reports of chiral mesophases of amphiphilic micellar systems are relatively recent. They can be created from non-chiral systems either by modifying the molecules with chiral groups [11, 12] or by adding chiral dopants [13, 14]. Until recently, the only chiral nematic phases to have been found in host micellar systems of the first type contained disc-shaped micelles, whereas dopant micellar systems containing chiral nematic phases with both disc-like and rod-like micelles have been found (together with chiral biaxial phases).

This paper, describes the mesomorphic properties of the recently discovered chiral lyotropic system formed by potassium *N*-tetradecanoyl-L-alaninate/decanol/water containing 10 per cent CsCl—L-KTDA mixtures [15]. The system was investigated by optical microscopy, laser diffraction and NMR spectroscopy. At least four chiral phases are present; a chiral nematic phase with disc-like micelles ($\mathrm{Ch_D}$), a chiral nematic phase with rod-like micelles ($\mathrm{Ch_C}$), a chiral viscous isotropic phase ($\mathrm{I_C}$) and, at high concentrations, a chiral dimensionally-ordered phase (R) (probably rectangular or hexagonal) [16]. In order to throw some light on the nature of the $\mathrm{I_C}$ phase, the form of the phase diagram and the structures and properties of the neighbouring phases were examined.

The classical tool for mapping out the phase diagram of a new mesophase system is hot-stage polarizing microscopy, but for chiral systems the twist of the phase is generally very sensitive to phase structure, varying noticeably from one phase to another (and within a single phase region, with composition and temperature). Laser diffraction is therefore an effective tool for establishing the positions of phase boundaries of such systems.

Laser diffraction was used to determine the way in which the twist of a range of L-KTDA samples varied with temperature. Fifteen samples were examined with amphiphile compositions ranging from 0·13 g to 0·25 g in 0·01 g increments, together with 0·03 g of decanol, and 0·45 g of water containing 10 per cent CsCl. If CsCl is not present in the samples, the chiral liquid crystal phases do not appear on the phase diagram. Consequently there are nearly as many $\mathrm{Cs^+}$ ions as $\mathrm{K^+}$ ions in each phase of the sample. The observed twist values were used to map out the partial phase diagram shown in figure 1 (*a*) and a typical plot of twist against temperature is shown in figure 1 (*b*). The $\mathrm{Ch_C}$ and $\mathrm{Ch_D}$ phases show different patterns of variation of twist with temperature. For the $\mathrm{Ch_C}$ phase, the twist decreased as the temperature rose, but for

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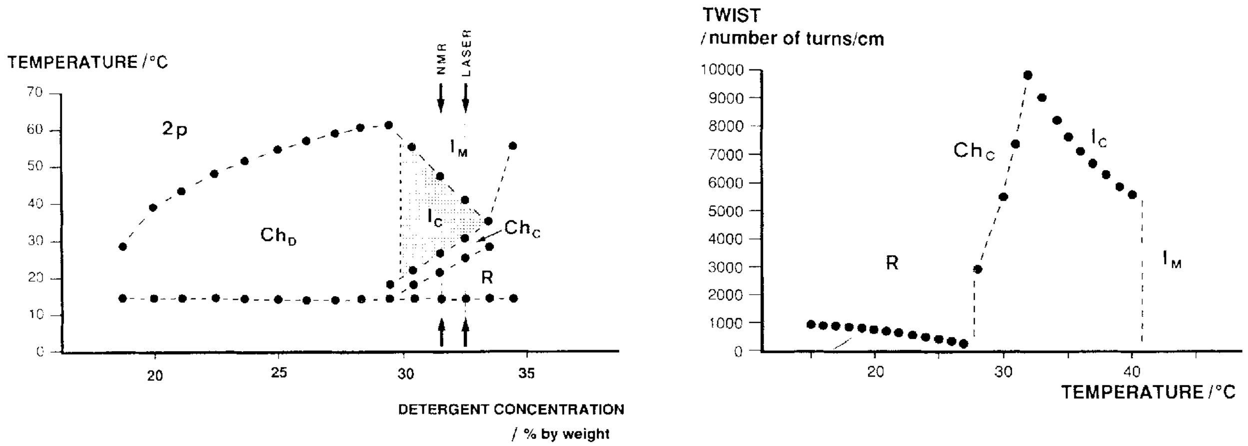

(*a*) (*b*)

Figure 1. (*a*) A partial phase diagram of the L-KTDA system. Ch$_{\mathrm{D}}$: Chiral nematic phase with disc-like micelles. Ch$_{\mathrm{C}}$: Chiral nematic phase with rod-like micelles. I$_{\mathrm{C}}$: Chiral isotropic phase (considered to be a lyotropic blue phase with a cubic array of helical rod micelles). R: A dimensionally-ordered phase considered to be a chiral version of the hexagonal middle phase. I$_{\mathrm{M}}$: Isotropic liquid phase containing cylindrical micelles. 2p: Two-phase region of Ch$_{\mathrm{D}}$ and isotropic micellar solution. The experimental points shown here were determined by laser diffraction studies of 15 samples of L-KTDA rising in 0·01 g increments from 0·11 g to 0·25 g, with 0·03 g of decanol and 0·45 g of water containing 10 per cent of CsCl). The dashed line in this figure corresponds to the laser diffraction study shown in (*b*). The detergent composition only includes L-KTDA and excludes the decanol concentration. This system was also studied by hot-stage optical microscopy and ^{2}D NMR. Within the Experimental errors, there was no incompatibility in the positions of the phase boundaries indicated by these different techniques. (*b*) Variation of twist with temperature for a 32·5 wt % sample of L-KTDA as shown by laser diffraction. The twist of the sample (i.e. the reciprocal of the wavelength of maximum scattering) in plotted against temperature for a sample of fixed composition. Fifteen similar graphs were used in establishing the phase diagram. This particular graph corresponds to the dashed line shown in (*a*). Note the way in which the R and I$_{\mathrm{C}}$ phases show negative twist/temperature gradients, whereas the Ch$_{\mathrm{C}}$ phase shows a positive gradient like that usually observed for thermotropic cholesteric phases.

the Ch$_{\mathrm{D}}$ phase the opposite occurred. Two distinct mechanisms have been proposed for the change of twist with temperature in micellar phases [17]. The first involves the unwinding of the bulk structure—and this appears to be the situation for the Ch$_{\mathrm{C}}$ phase. The second mechanism involves changes in the micelle spacing—and this appears to be the dominant effect in the Ch$_{\mathrm{D}}$ phase.

The general form of the phase diagram is shown in figure 1 (*a*). It appears to be the result of two distinct factors: one concerned with change of concentration and the other with change of temperature. From left to right, as the amphiphile concentration increases, there is a change of micelle type from disc-like micelles to rod-like cylindrical micelles, which first pack in a twisted nematic array and then, at higher concentrations, form a chiral dimensionally-ordered array. From the bottom to the top of the phase diagram in the high amphiphile region, the pattern is similar to that of a thermotropic cholesteric system, where a chiral cubic phase, I$_{\mathrm{C}}$, lies between the twisted nematic phase and isotropic liquid. The I$_{\mathrm{C}}$ phase sample flowed in the NMR tube and exhibited birefringence, when viewed between crossed polarizers. The birefringence disappeared overnight and the I$_{\mathrm{C}}$ phase became optically isotropic.

^{2}D NMR data were taken of a sample which was cooled through the I$_{\mathrm{C}}$ phase into the Ch$_{\mathrm{C}}$ phase (down the dotted line shown in figure 1)—see figure 2. The spectra of the I$_{\mathrm{C}}$ phase showed a quadrupolar splitting not equal to zero. In the achiral system, the isotropic phase next to the N$_{\mathrm{C}}$ phase, the ^{2}D NMR spectra gave rise to zero quadrupolar splitting and hence no anisotropy. The N$_{\mathrm{C}}$ phase was also shown to have positive diamagnetic anisotropy through

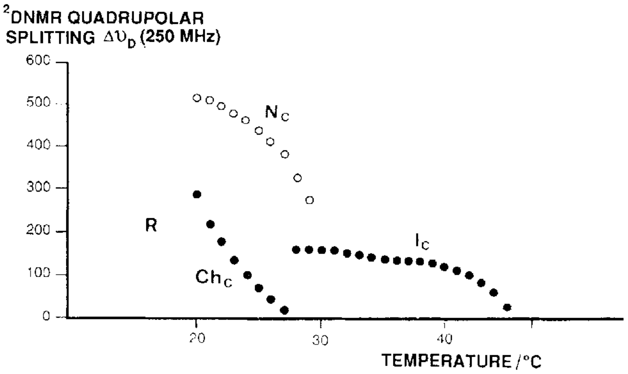

Figure 2. 2D NMR quadrupolar splittings for 31·5 wt % samples of KTDA plotted as a function of temperature. The open circles refer to a chiral racemic DL system and the closed circles refer to a chiral L sample.

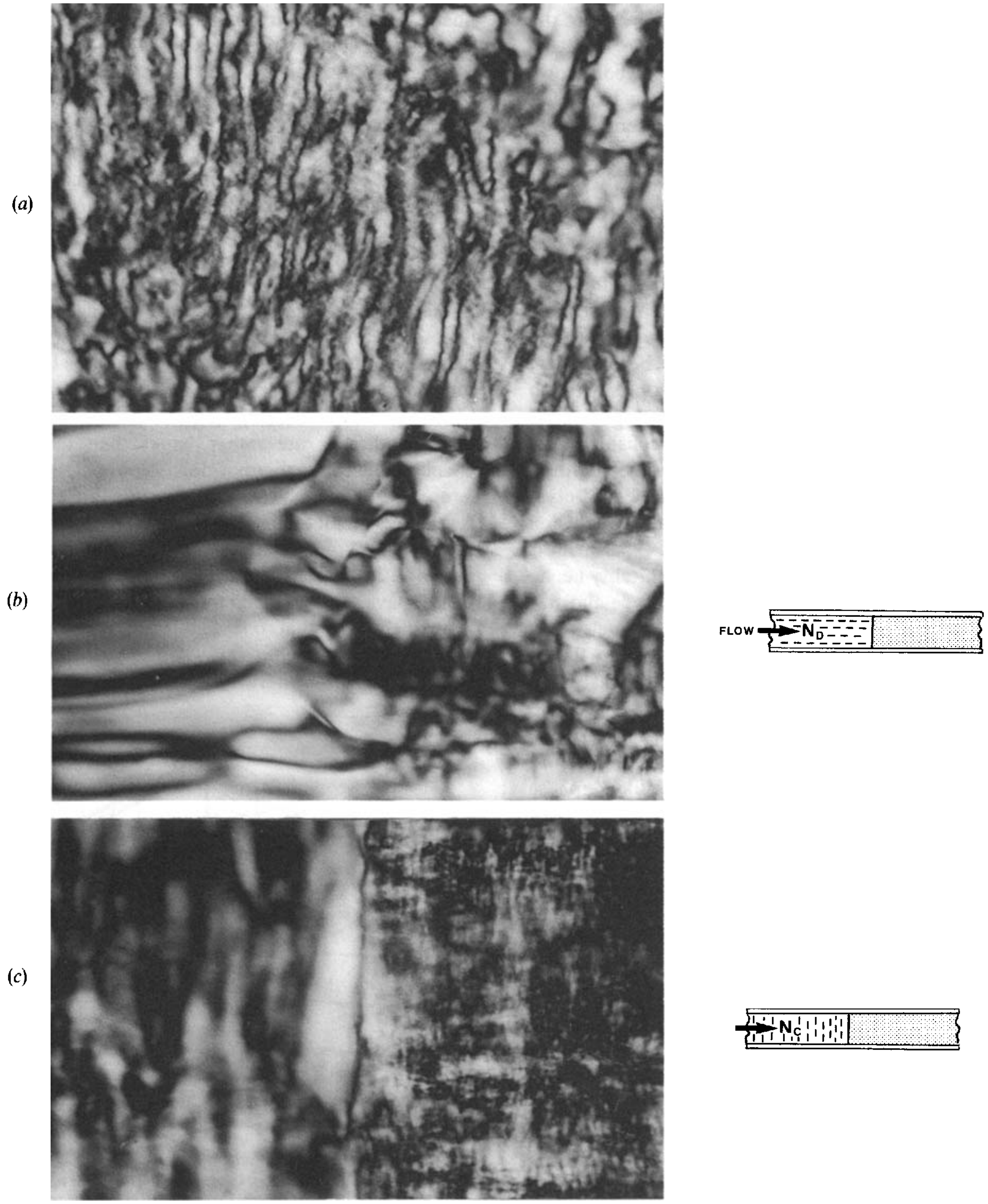

Figure 3. Optical textures of the KTDA system. (*a*) A non-racemic sample of L-KTDA in the Ch_C phase shortly after being introduced into the microslide tube. The larger scale pattern of transverse striations results from flow-alignment. The small scale detail results from the helicoidal twist of the phase and will eventually develop into a characteristic fingerprint texture. (*b*) A racemic sample of DL-KTDA—with a concentration gradient (concentration decreasing from left to right) produced by allowing a sample in the N_C phase to evaporate—partially showing the boundary between the R phase on the right and the N_C phase on the left. The transverse striations in the N_C phase are a relic of the flow-alignment caused when the sample was introduced into the microslide tube. (*c*) A racemic example of DL-DTDA—with a concentration gradient (concentration decreasing from left to right) produced by allowing a sample in the N_D phase to evaporate partially—showing the boundary between a lamellar phase on the right and the N_D phase on the left. (Note the pattern of longitudinal striations in the N_D phase resulting from flow-alignment when the sample was introduced into the microslide tube.)

the time evolution of D_2O ^{2}D NMR. Therefore the anisotropy in the I_C phase is present as the result of chirality. At first sight this would appear to be incompatible with the cubic symmetry of the I_C phase. However, a probable explanation lies in terms of the extremely large unit cell of this structure. Each amphiphile molecule would 'see itself' as being in the disymmetric environment of a helical rod, and the self diffusion would not be sufficiently rapid to give a zero quadrupolar splitting.

If the Ch_C phase has the structure proposed (i.e. helical cylindrical micelles lying in a helicoidal array), then one would expect a positive micellar diamagnetic anisotropy and a negative bulk diamagnetic anisotropy. The time evolution NMR data were complex (and will be the subject of further paper), but they appeared to be consistent with this picture. Time evolution NMR studies, both theoretical and experimental, have not previously been considered for cholesteric liquid crystals. These should not be confused with similar NMR observations for nematic liquid crystals, which are well established. The main conclusion relevant to this paper concerning the NMR experiment is that the I_C phase anisotropy is the result of chirality i.e. no chirality, no anisotropy. Micelle and lattice type and size are as yet unknown. Any conclusions and estimates of a quantitative nature concerning self-diffusion in the I_C phase based on the NMR data are questionable.

The structures proposed for the Ch_C and Ch_D phases and the general form of the phase diagram shown in figure 1 (*a*) appear to be confirmed by the observed optical textures. When viewed between crossed polarizers, the I_C phase gave virtually perfect extinction—but it did show flow birefringence when the sample was mechanically disturbed. The observed optical textures of this system are often complicated by the flow-alignment of the sample as it is introduced into the microslide tube [18, 19]. The optical micrograph shown in figure 3 (*c*), is of a sample in the Ch_C phase taken shortly after the sample tube had been filled. The broad striations (which lie transversely in the tube) arise from the flow-alignment—and they gradually disappear. The finer detail arises from the helicoidal pitch of the sample and this gradually becomes better defined, ultimately giving a fingerprint texture.

A racemic mixture of DL-KTDA was also examined. This forms non-chiral nematic analogues of the Ch_C and Ch_D phases (N_D and N_C, respectively). Samples of these phases also show flow alignment when they are introduced into the microslide tubes. For N_D samples, the striations were parallel to the flow direction, as shown in figure 3 (*b*), whereas for the N_C samples, the striations were perpendicular, as shown in figure 3 (*a*). Presumably this difference in pattern of flow alignment can be explained in terms of the Leslie–Erickson theory [20]. For the N_D phase, the flow striations gradually reverted via a schlieren texture, to a texture indicating a homeotropic state. For the N_C phase, the striations gradually reverted to a planar texture (again via a schlieren texture).

The I_C phase of L-KTDA is optically isotropic. It selectively reflects circularly polarized light in the near-visible range, showing that it has repeat distances of the order of micrometers. In the phase diagram, it occupies a region between the chiral nematic phase and the genuine isotropic liquid and, as indicated by the NMR spectra, its anisotropy is derived from the chirality. It therefore appears to have all of the credentials of a micellar analogue of one of the thermotropic blue phases—see figure 4. There are two quantitative rather than qualitative differences between this I_C phase and typical thermotropic blue phases: (i) The reflected wavelength: for this I_C phase, the reflected wavelength is in the infrared region rather than in the visible—indicating (perhaps not surprisingly) that the periodicities are rather larger than those usually encountered with thermotropic blue phases. (ii) The temperature range: The thermotropic blue phases are stable over small temperature ranges, typically about one degree (although an unusual blue phase with a temperature range of 20 degrees has been reported). Lyotropic blue phases have been expected for some years and at one stage it was thought that one had been encountered in a chirally-doped chromonic system [21]. However, this report was later withdrawn [22]. As far as the author is

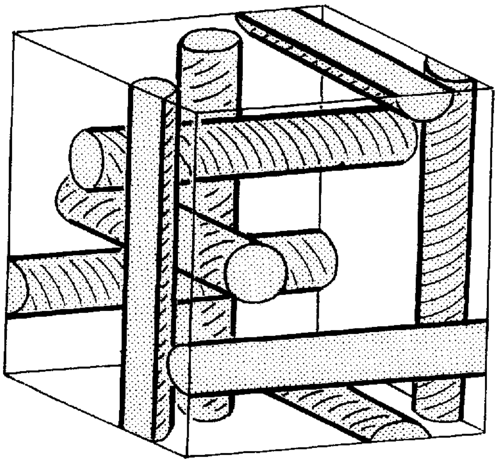

Figure 4. A tentative model for the I_C phase. This model consists of cubic array of helical cylindrical micelles and is based on a model for one of the thermotropic blue phases proposed by Berreman *et al.* [23, 24]. It consists of cylindrical micelles in a water continuum, lying in an array with overall cubic symmetry. Because of the chirality of the amphiphile, the surface patterning of the micelles will also be chiral. In this sketch, this is represented by the helical decoration on the cylinder surfaces. The assembling of the micellar cylinders into this structure can be pictured as the meshing of helical ridges and troughs on the cylinder surfaces. (In the Berreman model, the rods represented lines of helical disclination through the structure.)

aware, the L-KTDA I_C phase is the first micellar blue phase to be characterized.

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