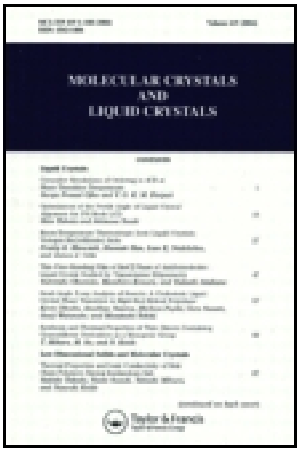

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Microscopic Textures of Micellar Cholesteric Liquid Crystals

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Microscopic Textures of Micellar Cholesteric Liquid Crystals

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Cholesteric Phases of Micellar solutions consisting of potassium laurate (KL), 1-decanol and D_2O were studied as a function of the concentration of a chiral additive, brucine sulfate (BS). The molar ratio of decanol to KL was kept constant at 0.36:1, while the molar ratio of BS to KL was varied from zero to 0.016:1. The D_2O concentration was kept near 67% by weight. Microscopic observations of the textures and phase transitions were made on thin films. The phase diagram shows three different cholesteric phases, including a biaxial cholesteric phase. Reentrant cholesteric phases occur in a small concentration range. The transitions between the different cholesteric phases appear sharp but continuous. A new type of a cholesteric texture was found in the biaxial range. The texture seems to have a multiple twist and a three dimensional periodicity in the micellar alignment.

Keywords: miceller cholesterics, microscopic textures

INTRODUCTION

Micellar solutions show several types of nematic phases.[1-3] There are two uniaxial phases, which differ by the signs of their anisotropies, and a biaxial nematic phase. The three nematic phases can occur in the same mixture separated by well defined phase transitions.

The biaxial phase is a new type of nematic state that was first observed in the potassium laurate (KL)/1-decanol/D_2O system[4] and in a similar system with sodium decylsulfate as the surfactant.[4,5] In the KL system it forms in concentration and temperature ranges that separate two uniaxial nematics which we denote as N_L and N_C. The N_L phase has a negative diamagnetic anisotropy while that of the N_C is positive. The signs of the optical anisotropies are opposite to the

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magnetic anisotropies. In thin films the N_L phase aligns homeotropically while the N_C and biaxial phase, N_{bx}, relax to typical schlieren textures.[6] The schlieren texture of the N_{bx} phase becomes colorless and fades out as the transition to the N_L phase is approached. The transitions between nematic phases are second order.[7,8] Entering N_{bx} from either uniaxial nematic phase on heating or cooling results in a spotty and irregular texture. It is due to the appearance of biaxiality with secondary axes of the index ellipsoid under random orientation in a plane perpendicular to the original optical axis. This irregular texture gradually relaxes into a smooth schlieren texture.

Cholesteric states, can in first approximation, be considered as nematics which, because the presence of molecules with a chiral symmetry, assume a spontaneously twisted structure. The addition of a chiral compound to a micellar nematic induces the transition to a cholesteric state.[9,10] It was found that the twist power of brucine sulfate (BS) is relatively strong. We use it as a chiral additive in the present experimental studies made on the KL system.

The equilibrium structures of micellar cholesterics obtained by chiralizing uniaxial nematics are uniformly twisted. In thin films the twist axis tends to align perpendicular to the film and an optically active texture is formed which is known as a Grandjean texture. The twist induces some biaxiality and we cannot strictly differentiate between uniaxial and biaxial cholesteric phases. In other words there is no difference in the symmetry classes of the two cholesterics obtained from biaxial and from uniaxial nematic phases provided that both are in a Grandjean texture. Correspondingly, there can be no second order phase transitions between cholesterics in Grandjean textures.[12] First order transitions between cholesteric phases with a discontinuous change in pitch can occur and have been observed experimentally.[10,11] Any second order transitions that may occur between cholesterics must be connected with a change in the symmetry of the equilibrium texture, i.e. a transition where the simple Grandjean texture changes continuously to a more complicated texture of different translational symmetry.

As there is always twist induced biaxiality it might be expected that the uniaxial-biaxial transition disappears in chiralized materials analogous to the smoothing out of the N_L-N_{bx} transition in the presence of a magnetic field.[7]

Inspite of the discussed difficulties in differentiating between uniaxial and biaxial symmetry we will classify the cholesteric phases of the chiralized KL system as Ch_L, Ch_C, and Ch_{bx} by analogy to their corresponding nematic phases. A fairly clear distinction can be made in practice between these three phases when the twist is weak.

The application of a magnetic field can be useful to differentiate between these three cholesteric phases. The Ch_L phase in the chiralized KL system has a molecular order which is practically uniaxial and of negative diamagnetic anisotropy. It aligns with the twist axis parallel to sufficiently strong magnetic fields. The Ch_C phase is also practically uniaxial but has a positive diamagnetic anisotropy. It can be untwisted by applying a magnetic field, that is it makes a field induced transition to a uniaxial nematic phase. The Ch_{bx} phase aligns in magnetic fields similar to the Ch_L phase. It assumes a uniformly twisted texture with the twist axis parallel to the field. We can by definition assign to Ch_C the range where the field induces a transition to a uniaxial nematic phase. Similarly, we can assign to Ch_L the range where untwisting by some other external field (e.g. a rotating magnetic field) leads again to a uniaxial nematic phase while Ch_{bx} is the range where a twisted structure is retained in any external field. In practice we determined the phase ranges, however, by monitoring the change of texture as a function of temperature.

We report here microscopic observations on the textures of the micellar cholesteric phases formed in thin films filled between glass plates. We observed a new cholesteric texture in the Ch_{bx} range. The texture seems to correspond to a structure with a multiple twist and with a 3-dimensional periodicity in the order parameter.

SAMPLE PREPARATION AND PHASE DIAGRAM

The samples were prepared in the concentrations shown in Table I. A nearly constant weight ratio KL:1-decanol:D_2O = 1:0.238:2.560 was used in most of the samples to which various amounts of brucine sulfate (BS) were added. The weight ratio corresponds to a molar ratio of KL:1-decanol = 1:0.36 and a molar ratio of KL:D_2O = 1:30.4. The temperatures of the isotropic-cholesteric transitions were first determined in the freshly mixed bulk samples. Subsequently, small quantities were sealed in flat capillaries of 0.3 mm thickness (Vitro Dynamics Inc.) for microscopic observations. We also filled capillaries with two mixtures in contact with each other to obtain a qualitative overview of the concentration dependence of the phase transitions. Microslide samples with isotropic-cholesteric transition

TABLE I

Sample Compositions and Transition Temperatures

Sample No.	Weight Ratio KL:Dec:D_2O:BS	Transition Temperatures (°C)						
		Ch_{L}[2]	Ch_{bx}	Ch_{C}	Ch_{bx}	Ch_{L}	I	Two Phase Region[3]
BSO[1]	1:0.238:2.562:0	13.8	15.3	15.4			44.5	
BS6	1:0.238:2.559:0.021	12	20.3	20.8			42.4	
BS10	1:0.239:2.561:0.022	13	20.1	20.4			41.5	
BS15	1:0.239:2.560:0.022	12.5	20.5	20.8			42	
BS21	1:0.239:2.560:0.027	12.5	21.7	23.1	39.7	39.8	42.4	
BS13	1:0.239:2.559:0.028	12.5	22.5	24.5	39	39.1	42.5	43
BS12	1:0.239:2.559:0.033	12	27			32.2		42.5
BS14	1:0.238:2.559:0.042	11						42
BS11	1:0.239:2.561:0.043	11.5						42.5
BS17	1:0.239:2.560:0.066	10.8						41
BS15A	1:0.239:2.546:0.022	12.5	21.4	23	40.4	40.5	42.7	43.5
BS16	1:0.238:2.584:0.022	15.3					38.2	

[1] No brucine sulfate forms nematics.

[2] Transitions from lower temperature isotropic phase.

[3] Ch_{L} or I plus lamellar smectic (batonnets).

temperatures which deviated more than ±1.5°C from the bulk measurements were usually discarded. The deviations were due to leaky seals or due to water losses during the filling process. In addition, the KL system is not completely stable chemically. Probably a slow esterification takes place between the potassium laurate and the decanol which results in a time dependant shift of the phase transitions. Samples containing BS are even less stable but the reaction is still slow and it had no significant effect on our observations.

The graph in Figure 1 shows the general dependance of the transition temperatures on the concentration of BS. The effect of BS on the phase transitions is similar to that of 1-decanol.[4] It increases the range of Ch_L and decreases the Ch_C range. The Ch_C and the Ch_{bx} ranges disappear completely when sufficient BS is added (BS/KL > 0.034). Similar observations have been made with the sodium decylsulfate system.[10] When more than 0.75 weight % of BS is added

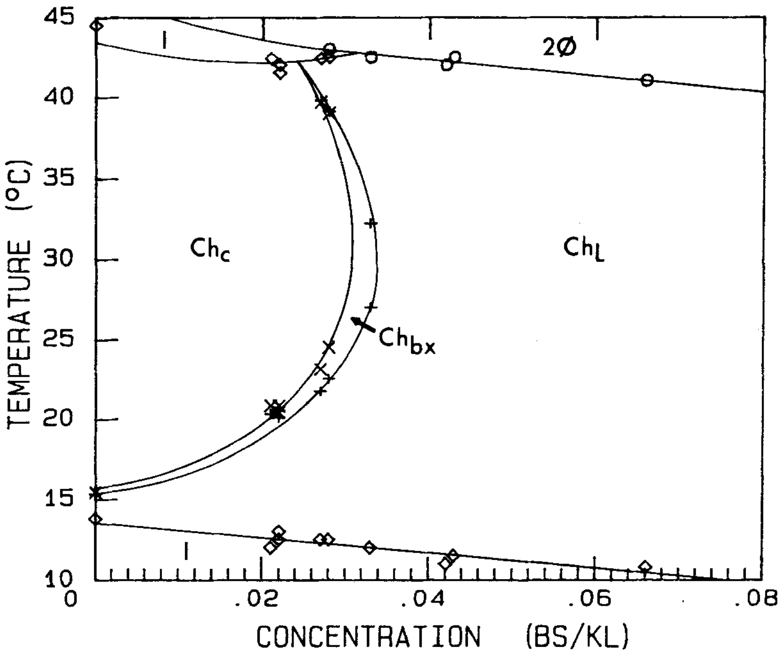

FIGURE 1 Phase diagram for the dependance of the weight ratio of brucine sulfate to potassium laurate. Constant weight ratio of KL:1-decanol:D_2O = 1:0.238:2.560. 2ϕ is a two phase region of the lamellar smectic phase (batonnets) and either the Ch_L phase, at higher BS concentrations, or the isotropic phase at lower BS concentrations.

(BS/KL > 0.030 bt wt.) the upper temperature Ch_L-isotropic transition is replaced by a transition of the Ch_L to a two phase region of lamellar smectic (batonnets) plus the Ch_L.

Figure 2 shows the induced twist, the inverse of the pitch, as a function of the BS concentration. Within error limits the induced twist is proportional to the BS concentration. Of course the added amounts are still relatively small and at higher concentrations deviations from the linearity can be expected. The twist power of a chiral compound is defined by $1/PM_a$ where M_a is the mol fraction of BS in 1 mol of KL, 1-decanol, and BS, and P is the pitch. The twist power of BS in the KL system in N_L at about 20°C is $14 \times 10^3 \text{cm}^{-1}$. It is smaller than the twist power of BS in the ammonium decylsulfate system which is about $30 \times 10^3 \text{cm}^{-1}$ [9] at low concentrations and also smaller than that observed in the sodium decylsulfate system, about $25 \times 10^3 \text{cm}^{-1}$ in the N_C phase and about $55 \times 10^3 \text{cm}^{-1}$ in the N_L phase.[10]

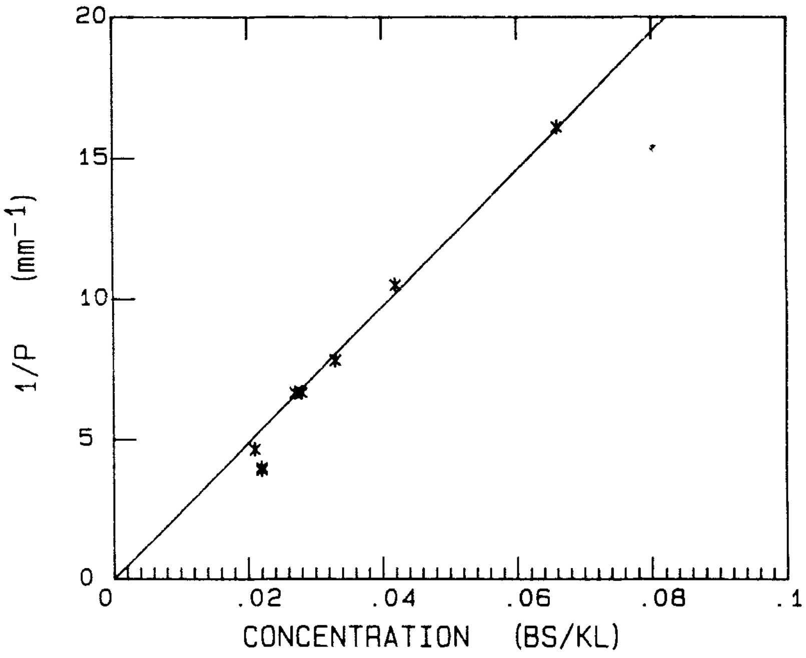

FIGURE 2 The induced twist (inverse pitch) is a linear function of the BS concentration for the samples of Table I. The brucine sulfate ratio is varied as shown. Pitch measurements were made on magnetic field aligned Ch_L phases between 18°C and 20°C.

MICROSCOPIC OBSERVATIONS

The relaxed textures of the Ch_L and Ch_C phases are smooth, optically active, Grandjean textures. Examples are shown in Figures 3 and 5. The micrographs show the same sample at 18 and 25.1°C respectively. Between crossed polarizers the Ch_L phase appears darker then the Ch_C phase although both phases have about the same optical anisotropy.[8] The probable reason is that the surface alignment of Ch_L induces homeotropic surface layers which reduce the thickness of the birefringent part of the film by about the length of half the pitch.

At the transitions from the Ch_L or from Ch_C to the Ch_{bx} the smooth Grandjean textures "break up" into irregular patterns, see Figures 4 and 6. The change in the textures is similar to that observed at the corresponding nematic phase transitions. The irregular textures relax gradually into equilibrium textures with patterns which will be discussed later. No broken textures are formed at the reverse transitions from Ch_{bx} to Ch_L or Ch_C. The transitions appear to be continuous and there is no indication that the transitions have turned first order. They remain about as well defined as in the transitions between the nematic states.

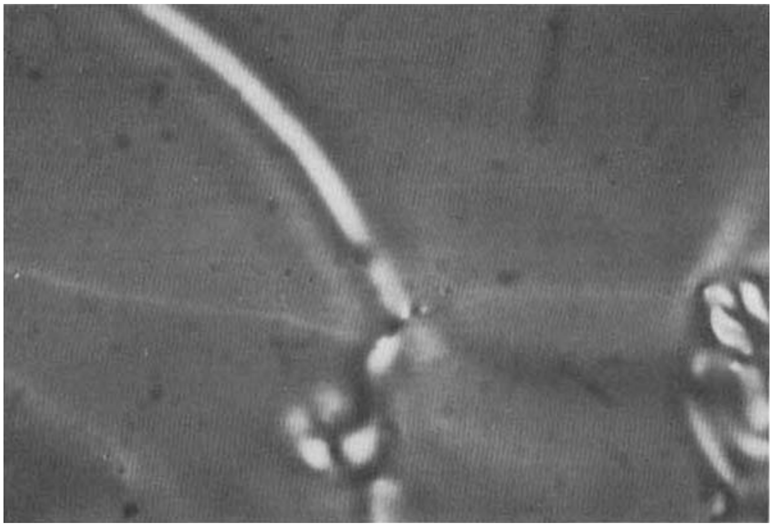

FIGURE 3 Grandjean texture of Ch_L at 18°C. Magnification 80X, crossed polarizers, sample BS21. See Color Plate V

FIGURE 4 Texture at the Ch_L-Ch_{bx} transition at 21.9°C on heating with a rate of about 0.2°C/min. Same region and settings as in Figure 3. See Color Plate VI

FIGURE 5 Grandjean texture of Ch_C at 25.1°C under parallel polarizers. Same sample and magnification as in Figure 3. See Color Plate VI

FIGURE 6 Texture at the Ch_C-Ch_{bx} transition at 22.9°C on cooling with a rate of about 0.2°C/minute. Same region and magnification as in Figure 5. Polarizers are under 45° to each other for better contrast. See Color Plate VII

Figures 7 and 8 shows cholesteric samples that were aligned in a magnetic field of 10 kG applied in the plane of the film. The Ch_L phase produces a striped texture (Figure 7 and Figure 8 lower left corner) with the stripes normal to the field. Between crossed polarizers, with the polarizations parallel and perpendicular to the stripes, the texture appears dark. This shows the twist axis is parallel to the film. The persistance of this texture after removal of the field depends on the chirality of the sample. At short pitchs ($<$100 μm) the textures remain practically unchanged for over a week and take more than one month to reorient to the smooth Grandjean texture. Textures with weak twists (pitch $>$250 μm) completely realign to a Grandjean texture in less than two days.

Figure 8 shows a sample with a concentration gradient due to water losses at the right end of the capillary. In the lower left corner is the well developed pattern of the Ch_L phase with alternating black and reddish brown stripes. Next follows a range of Ch_{bx} which also has a striped pattern but the black is replaced by a yellowish color that becomes increasingly brighter and deeper with the distance from the N_L phase. The Ch_C phase, on the right, is uniform and of a deep yellow color. It is untwisted due to a magnetic field induced cholesteric-nematic transition. In the Ch_{bx} range the contrast of the stripe

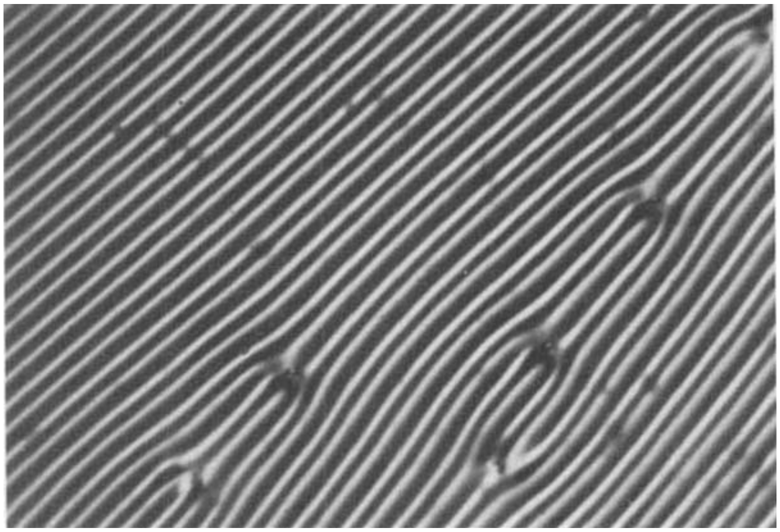

FIGURE 7 Magnetic field aligned Ch_L phase at 18.5°C, pitch 150 μm. Same sample and settings as in Figure 3, polarization directions under 45° to stripes. See Color Plate VIII

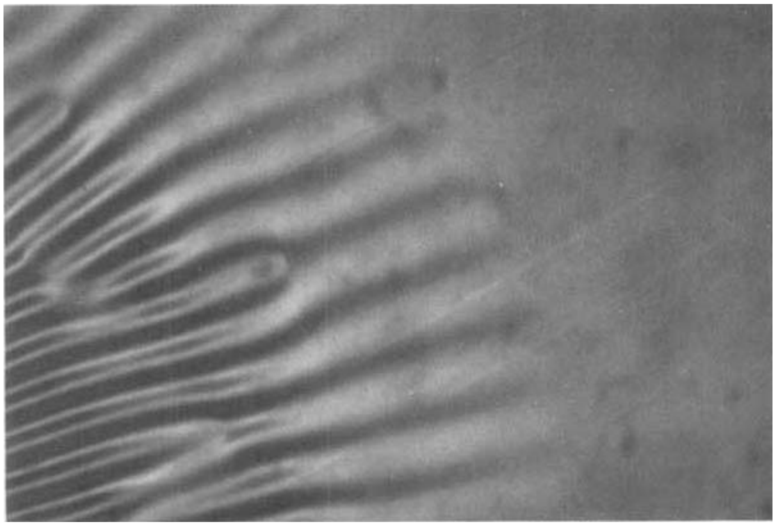

FIGURE 8 Magnetic field aligned sample with D_2O concentration gradient at 23°C, shows Ch_L, Ch_{bx}, and Ch_C ranges. Sample BS6, the gradient is due to water evaporation at the right end of the capillary. Crossed polarizers under 45° to stripes, magnification 80X. See Color Plate VIII

pattern varies continuously from Ch_L to Ch_C. The pattern fades out completely at the transition to the untwisted Ch_C phase.

Figure 9 shows a sample that has been aligned in the Ch_L phase and then heated so that part of the sample makes a transition to the Ch_{bx} phase. The change in the texture is analogous to that observed in the unaligned phase.

Figure 10 shows a novel equilibrium texture that was observed in the Ch_{bx} range after a long relaxation period (24 hours). The texture shows a double periodicity and appears to be formed by two crossing striped patterns. Obviously the Grandjean texture is not stable in the Ch_{bx} range. Magnetic fields cause a transition that leads back to the simple stripe pattern of the biaxial range shown in Figure 8. Presumably the new texture has a primary axis, which corresponds to the twist axis of the Ch_C phase and is aligned normal to the surface, and two secondary (local) twist axes perpendicular to each other and to the primary axis. The secondary twist is linked to the biaxiality and the pattern simply fades out at the Ch_{bx}-Ch_C transition (see Figure 14). As the Ch_{bx}-Ch_L transition is approached, one of the secondary twist axes becomes the primary axis and the twist in the other direction disappears. The transformation requires significant realignment and is very slow as is illustrated in Figure 11. The cross pattern gradually

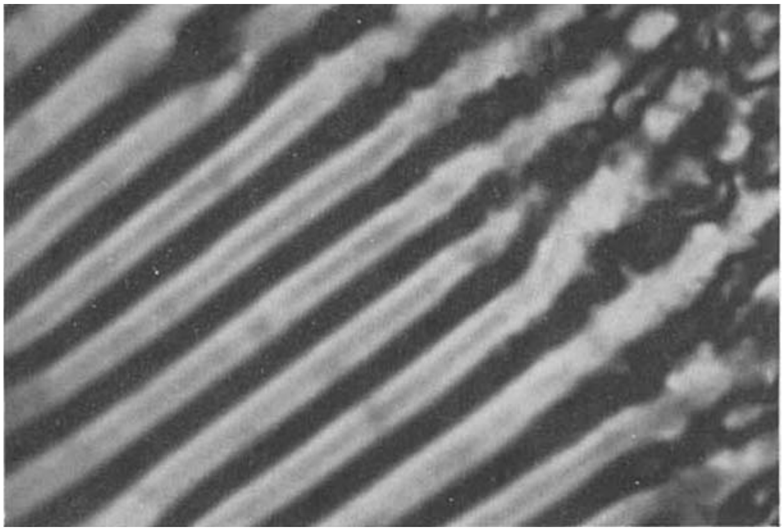

FIGURE 9 Contact sample (BS15/BS16) at 23.1°C on heating. Magnetic field aligned in Ch_L at 18°C. Pitch = 255 μm, settings as in Figure 8. See Color Plate IX

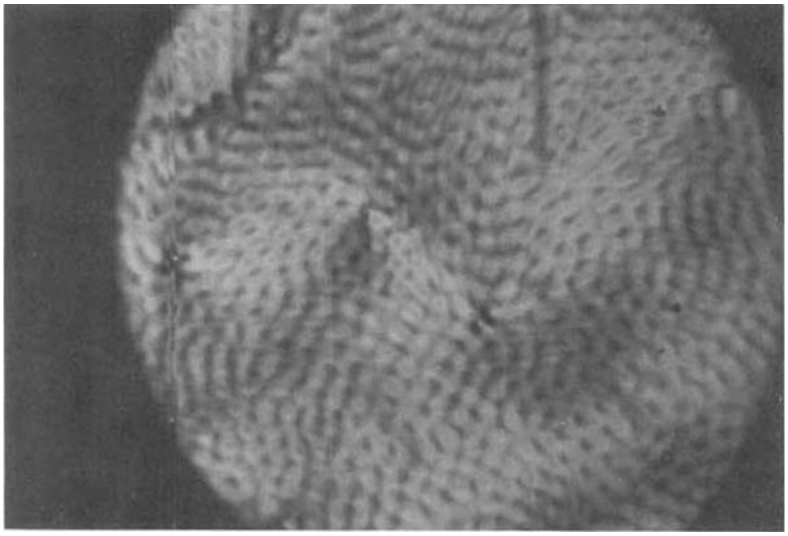

FIGURE 10 Relaxed Ch_{bx} phase at 22.7°C after 24 hours. The texture shows a double periodicity (cross texture). Magnification 35X, crossed polarizers, same sample as in Figure 3. See Color Plate X

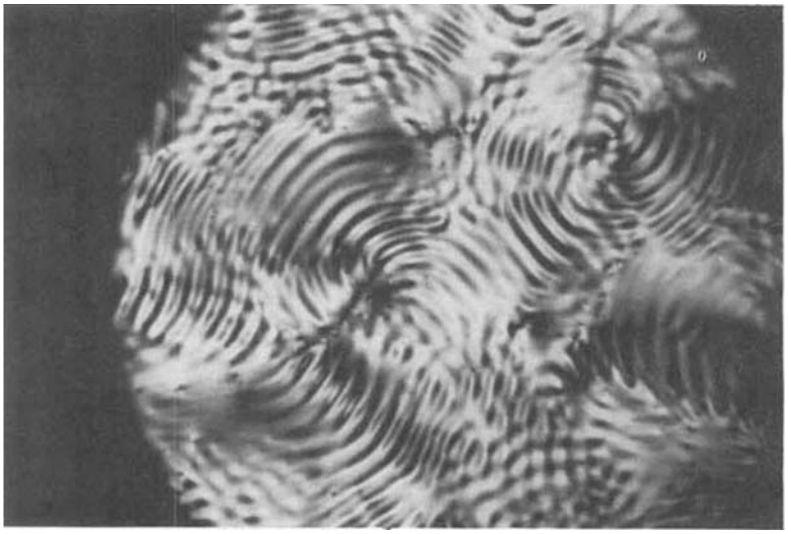

FIGURE 11 Ch_L texture observed 24 hours after cooling from the Ch_{bx} texture of Figure 10 to 21.1°C. Magnification 35X, crossed polarizers, same sample as in Figure 3. See Color Plate X changes to a simple stripe texture before the smooth Grandjean texture of the relaxed Ch_L phase is formed as shown in Figure 3.

The textures formed at the phase transitions depend on the rate of heating. An example of a phase transition boundary in a contact sample (BS14/BS15A) under fairly rapid heating is shown in Figure 12. The sample was aligned in the Ch_L phase at 18°C with a magnetic field in the plane of the film. The whole sample assumed a striped texture that is still present in the upper right corner of Figure 12. The corresponding pitch is near 100 μm. After alignment the sample was removed from the field and heated at a rate of 2°C/min. The transition started in the BS15A region and progressed with a sharp boundary towards the BS14 end. It has the appearance of a first order transition. The dark homeotropic stripes of the Ch_L phase (upper right corner) turn blue near the transition to the Ch_{bx} phase, probably because the twist axis tilts slightly out of the plane of the surface as the transition is approached.

When the sample is kept at the same temperature for some time the sharp boundary changes and smoothes out. Figure 13 shows the sample after one hour at the same temperature. After 48 hours, three ranges can be recognized (Figure 14), the Ch_L range with the striped

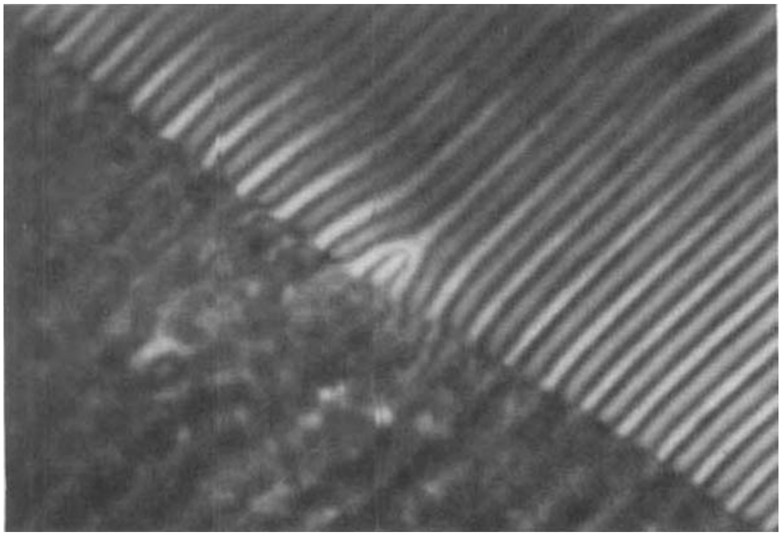

FIGURE 12 Transition boundary in a contact sample (BS14/BS15A) at 24°C on heating at a rate of about 2°C/minute. Pitch 100μm, magnification 80X, stripes under 45° to crossed polarizers. Sample was previously aligned in a magnetic field while entirely in the Ch_L phase. See Color Plate XI

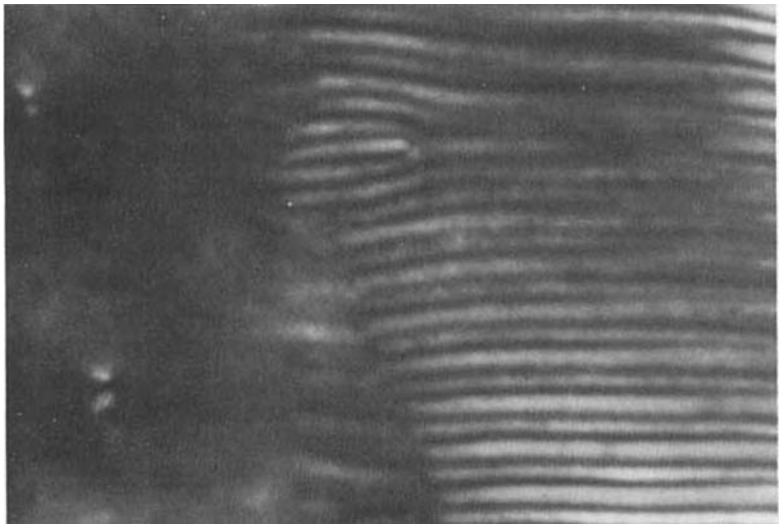

FIGURE 13 Transition boundary of Figure 12 at 24°C after 1 hour. The polarizers are under 28°. See Color Plate XII

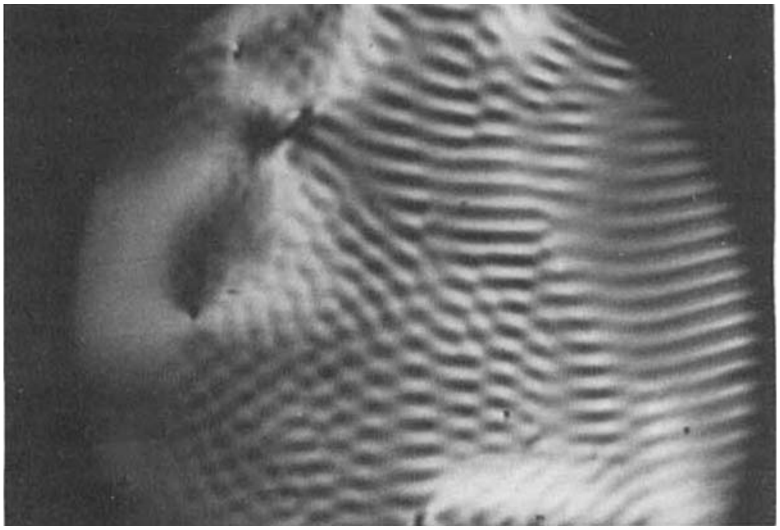

FIGURE 14 Contact sample of Figure 12 at 24°C after 48 hours. Magnification 35X, crossed polarizers. See Color Plate XII

texture, the Ch_{bx} range with the cross texture, and a Ch_C range with a smooth Grandjean texture. The change from the stripe to the cross texture appears to progress with a formation of screw dislocations. The Ch_L stripe texture eventually also realigns to a Grandjean texture but, as mentioned, the change takes more than a month for samples with a pitch of about 100μm.

CONCLUSIONS

The microscopic observations allow us to differentiate between three cholesteric phases in the KL/1-decanol/BS/D_2O system. The transitions between the cholesteric phases, when observed with slow rates of temperature changes, appear to be very similar to the transitions between nematic phases. There is no indication that the transitions smooth out, as might be expected on the basis of symmetry considerations. There is also no indication that the transitions turn first order. It should be kept in mind, however, that the chiral properties of the mixtures were weak and the twist accordingly small so that the twist induced effects on the transitions are also small and difficult to observe.

The new equilibrium texture observed in the biaxial range needs further investigation. It may correspond to a new phase which, analogous to the blue phase, has a three dimensional periodicity due to the spatial variation of the molecular order. It will be of particular interest to study the nature of the transitions to the Grandjean textures that correspond to the equilibrium in the adjacent uniaxial cholesteric phases.

The appearance of a first order transition at higher heating rates is, at least in the chiralized KL system, a non-equilibrium process. Similar first order transitions have been observed with the chiralized sodium decylsulfate system.[10,11] However, it needs to be verified whether the transitions are indeed transitions between equilibrium states.

The transitions between the various cholesteric states of the chiralized systems change significantly in presence of magnetic fields. Specifically, the transition $Ch_C - Ch_{bx}$ becomes a transition between a nematic and a biaxial cholesteric state. According to our observations the transition appears to be continuous but it remains a sharp transition since there is a change in symmetry. It may be analogous to the transition between smectic A and C* in chiralized systems but in contrast to smectic C* the biaxial cholesteric is not ferroelectric (the local order has D_2 symmetry). In sum the chiralized micellar systems show interesting cholesteric phase properties and phase transitions which need further theoretical and experimental studies.

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