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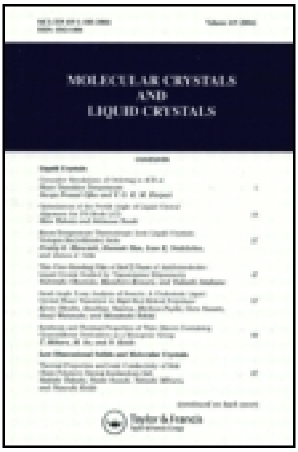

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Study of the Cholesteric-to-Cholesteric Phase Transitions on the Lyotropic Mixture of KL/K_2SO_4/1-Undecanol/Water/Brucine Presenting the Cholesteric Biaxial Phase

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Study of the Cholesteric-to-Cholesteric Phase Transitions on the Lyotropic Mixture of KL/K_2SO_4/1-Undecanol/Water/Brucine Presenting the Cholesteric Biaxial Phase

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Lyotropic cholesteric liquid crystalline phases were prepared by doping the quaternary mixture of potassium laurate (KL)/potassium sulfate (K_2SO_4)/1-undecanol (UndeOH)/water with brucine. The phase diagram was constructed as a function of the brucine concentration. Three cholesteric phases were identified: cholesteric biaxial, calamitic uniaxial, and discotic uniaxial. It was observed that there is a critical brucine concentration (X_b^*) to cholesterize the nematic host phase when the mixture is confined in a thin sample holder, below which the cholesteric helical arrangement is not achieved. The helical twisting power of brucine was calculated as 12.12 ± 0.40 μm^{-1}.

Keywords Lyotropic liquid crystal; cholesteric phases; phase transition; brucine; helical twisting power; intrinsically biaxial micelles model

Introduction

Lyotropic biaxial nematic phase (N_B) is known as an intermediate phase between uniaxial discotic (N_D) and uniaxial calamitic (N_C) nematic phases. The N_B phase has two optical axes [1–3], while both uniaxials (N_D and N_C) have only one optical axis. If an external magnetic field is applied to these nematic phases (mixtures made of amphiphiles with carbonic chains), they behave differently: the optical axis or director of the N_D (N_C) phase aligns perpendicular (parallel) to the magnetic field direction [4,5] and, in the case of the N_B phase, the two optical axes and the magnetic field lie in the same plane [6].

Similar to the lyotropic N_B phase, lyotropic cholesteric or chiral nematic phase (Ch_B) exists between two uniaxial cholesteric discotic (Ch_D) and calamitic (Ch_C) phases. These cholesteric phases may be prepared by either doping a chiral dopant molecule such as R-hexahydromandelic acid into an achiral nematic host phase [7–11] or directly using L- or D-enantiomer of a racemic (DL-form) amphiphilic molecule, for example L-serinehydrochloride dodecylester [12–14]. The cholesteric phases obtained by the former and latter ways are known as "induced" and "intrinsic" cholesteric phases, respectively. In

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addition, a third way was reported which indicated that chiral solvents might induced the cholesteric phases [15].

The most important behavior of the cholesteric phases, which differs them from nematic counterparts, is that the micelles form the structure, so called "helix" in the cholesteric phases. This structure arises from the 2π rotation of the micelles around the helical axis to gain their initial orientations [16, 17]. In other words, the helix axis is now the optical axis of the phase. For the cholesteric phases, the distance between three similar orientations of the local director is called pitch length (P), which is related to the helical twisting power (htp) of the chiral dopant molecule or L-enantiomer via the following equation [18]:

$$P^{-1} = \pm\,(\text{htp}).X_i, \tag{1}$$

where P^{-1} is the reciprocal of the pitch and also known as twist, X_i is the mole fraction of the chiral dopant or L-enantiomer in the lyotropic mixture and $+$ ($-$) sign indicates the right (left) handed helix. It can be seen from Equation 1, htp is calculated from the slope of P^{-1} versus X_i plot, which gives a straight line.

In the case of the addition of small amount of chiral dopant to the nematic mixture, as it can be seen from Equation 1, P is inversely proportional to X_i [18–20], i.e. the more the chiral dopant concentration increases, the smaller the pitch. This situation was reported by Neto et al. in 1987 investigating the effect of the chiral molecule brucine sulphate heptahydrate (BS) in the KL/1-decanol(DeOH)/D_2O lyotropic nematic mixture [21]. It was observed that at low concentration limit of the BS the pitch was shortened as a function of increasing BS concentration. Moreover, in another study in 1988, Neto et al. also investigated the relation between the micelles shape anisotropy and the pitch via X-ray diffraction and birefringences of the similar cholesteric phases prepared by the dissolution of the BS in the KL/DeOH/water mixture [22]. They showed that, when the BS concentration was relatively kept constant and the KL and DeOH concentrations were relatively varied, the greater the shape anisotropy of the micelles, the smaller the pitch (Ch_D phase).

In the present study, we investigated the effect of the brucine molecule on the KL/K_2SO_4/UndeOH/H_2O lyotropic quaternary mixture. This mixture had birefringence ($\sim 4 \times 10^{-3}$, [23]) about two times greater than the conventional KL/decanol/water ($\sim 2 \times 10^{-3}$, [24]). Since brucine molecule has less polar regions than brucine sulphate, important differences between the cholesterization processes of both systems are expected.

Experimental

Lauric acid was commercially available (Merck) and potassium laurate (KL) was prepared by its neutralization with potassium hydroxide (Merck). The pure KL was obtained after its recrystallization from absolute ethanol several times. The salt K_2SO_4 and water-based ferrofluid were obtained from Fischer and Ferrotec, respectively.

The sample preparation of the lyotropic quaternary mixture of KL/K_2SO_4/Unde OH/H_2O, which gave the nematic host phase, was discussed in [23] and [25]. The concentration of brucine in mole fraction was varied keeping the others constant. After the weigh all constituents into a well-closed test tube, homogeneous mixtures were obtained by centrifugation and mixing with a vortex mixer periodically until no precipitate was seen at the bottom of the test tube. Sometimes the test tubes were put into a water bath of 40–50°C for some seconds.

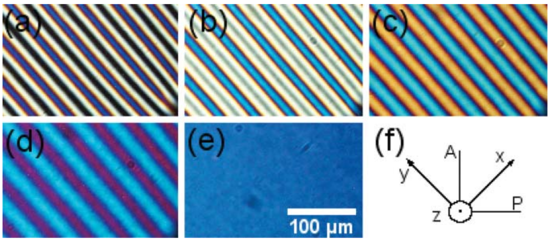

Figure 1. Cholesteric textures of the mixture *b*7: (a) Ch_D at 35.0°C; (b) just after Ch_D-to-Ch_B transition at 30.5°C; (c) Ch_B at 28.0°C; (d) just before Ch_B-to-Ch_C transition at 27.0°C; and (e) unwounded Ch_C at 26.8°C. In (f) the laboratory frame of reference was drawn, where A and P stand for the analyzer and polarizer directions. The magnetic field was applied along the x-axis at 45° from the P direction.

For texture investigation and pitch measurements with a Leitz orthoplan-pol polarized light microscope the samples were doped with ferrofluid ($\sim$1 μL in 1 g of lyotropic mixture) to help the alignment in the magnetic field, and then transferred into 0.2 mm thick microslides, which were sealed to prevent water loss. Then, the microslides were put into an INSTEC HS1 hot stage system, which allowed controlling the temperature with accuracy of 0.01°C, and was positioned in the microscope.

After, a uniform magnetic field of 0.9 kG was applied to the sample in the x direction of the laboratory frame of reference, Fig. 1(f), where the x-axis is parallel to the magnetic field direction, the z-axis is parallel to the light beam, y-axis is parallel to the long side of the microslide, and the A and P axis refer to the analyzer and polarizer directions, respectively.

Initially, well-aligned cholesteric stripes (Ch_D phase) were obtained after keeping the samples in the magnetic field for about 6 hours. Starting from these Ch_D phases, whose helical axis is parallel to the magnetic field direction, the temperature was varied step by step. At each temperature, photographs of the aligned textures were taken, of which the lyotropic phases were identified and the pitches were measured.

Results and Discussion

Texture Analysis and Phase Diagram

The textures of each lyotropic mixture presenting cholesteric phases were identified with polarized light microscopy. The quaternary brucine-undoped mixtures of $KL/K_2SO_4/UndeOH/H_2O$ were investigated in our previous study [23,25]. In the case of brucine-doped mixtures, the samples were kept in the magnetic field until well-aligned cholesteric stripes were observed in the Ch_D phases, i.e. stripes mostly perfectly aligned parallel to each other. Then, the cholesteric uniaxial-to-cholesteric biaxial phase transition temperatures were determined precisely. In the Ch_D phase, the dark regions were observed between the bright cholesteric stripes, Fig. 1a, and, by decreasing temperature, these dark regions turned to be first white, Fig. 1b, and then further decreasing the temperature caused the appearance of yellow/orange and purple colors, Fig. 1c–d. This means that in the dark regions of the Ch_D phase, the local director is parallel to the incident light and perpendicular to the magnetic field direction (homeotropic alignment). However, when the phase transition from Ch_D to Ch_B occurs, two optical axes are present, and the homeotropic alignment is no more obtained. On further decreasing temperature the system approaches the Ch_B

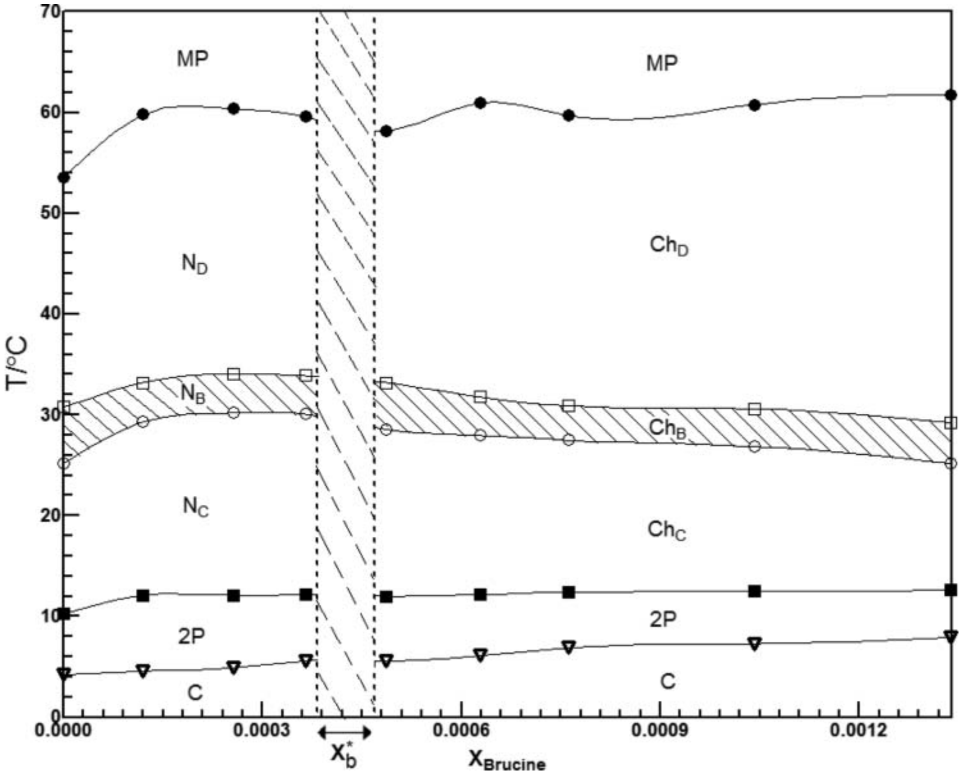

Figure 2. Phase diagram of KL/K_2SO_4/UndeOH/H_2O/brucine lyotropic mixture. The vertical region bordered with dashed lines corresponds to the region where the critical brucine concentration exists.

to Ch_C transition. Then, in the Ch_C phase, since the helical structure is unwounded by the effect of the external magnetic field, the local director orients parallel to the magnetic field direction. The texture of the Ch_C phase is given in Fig. 1e. Other observed phases are multi-phase (MP) at temperatures above Ch_D phase, two-phase region (2P) and crystalline phase (C) in regions at low temperatures, Fig. 2.

As can be seen from the phase diagram, it presents two different parts: above and below some particular brucine concentration, X_b^*. This brucine concentration X_b^* is in the region between two dashed lines parallel to the temperature axis of the phase diagram and it is around ~0.00045 in mole fraction. Below this concentration, the phase remained in the nematic phases (N_D, N_B and N_C). This indicates that brucine molecule cannot achieve to transfer its chirality to the whole phase with the microslide thickness used in this experiment. AboveX_b^*, the cholesteric Ch_D, Ch_B and Ch_C phases were observed instead of the nematic phases. In addition, if the phase diagram is compared with the phase diagram of brucine undoped mixtures of KL/K_2SO_4/UndeOH/H_2O [23], the biaxial domain in the cholesteric is a little bit smaller than the nematic one.

In the phase diagram of Fig. 2, we may interpret what happens below and above X_b^* via the threshold pitch [26,27], defined as $p_{th} = 2.d.K_{22}/K_{33}$, where d is sample thickness, K_{22} and K_{33} are the Frank elastic constants for twist and bend deformations [28, 29]. If $p < p_{th}$, the chiral torque will be strong enough to overcome the anchoring energy of the aligning surfaces, which leads to the observation of the twisted cholesteric phase [26, 27].

Table 1. Molar fractions (X) of each components in the lyotropic cholesteric mixtures KL/K_2SO_4/UndeOH/H_2O/Brucine. P and C_R are pitch and confinement ratio, respectively.

Mixture	X_{KL}	$X_{K_2SO_4}$	X_{UndeOH}	X_{H_2O}	$X_{brucine}$	P/μm	C_R	Phase type
*b0**	0.0383	0.0060	0.0114	0.9443	0.0000	—	0.00	N_C,N_B,N_D
b1	0.0383	0.0060	0.0114	0.9442	0.0001	—	0.00	N_C,N_B,N_D
b2	0.0382	0.0060	0.0114	0.9441	0.0003	—	0.00	N_C,N_B,N_D
b3	0.0383	0.0060	0.0114	0.9440	0.0004	—	0.00	N_C,N_B,N_D
b4	0.0383	0.0060	0.0114	0.9439	0.0005	162.5	1.23	Ch_C,Ch_B,Ch_D
b5	0.0382	0.0060	0.0114	0.9437	0.0006	120.0	1.67	Ch_C,Ch_B,Ch_D
b6	0.0382	0.0060	0.0114	0.9436	0.0008	99.0	2.02	Ch_C,Ch_B,Ch_D
b7**	0.0382	0.0060	0.0114	0.9433	0.0010	78.5	2.55	Ch_C,Ch_B,Ch_D
b8	0.0382	0.0060	0.0114	0.9430	0.0013	61.5	3.25	Ch_C,Ch_B,Ch_D

*From Ref. [30], **From Refs. [23, 25, 31].

In the latter case, $p > p_{th}$, the chiral torque is not enough and the cholesteric structure is not achieved [26, 27]. It is known that there are two control parameters for the N-Ch transformation, or unwinding the helix: temperature and external magnetic or electric field [32]. If the temperature is kept constant, the external magnetic field is the control parameter for the unwinding of the helix. In the case of the external magnetic field acting as an additional control parameter, the confinement ratio is more precisely a control parameter, which is given by $C_R = d/P$. In the literature, two different values of C_R were identified [32]: (a) C_c is the critical confinement ratio and (b) C^* is the "spinodal limit" of confinement ratio [32]. For $C_R \leq C_c \approx 1.2$, the helix structure of the cholesteric phase is unwound, which leads to the formation of homeotropically aligned nematic phase. If C_R is between Cc and C^*, $C_c \leq C_R \leq C^*$, a "fingerprint" texture of cholesteric phase forms separated by homeotropic nematic. In the case of $C_R \geq C^* \approx 1.6$, a fingerprint texture is still observed, but the fingers adhere together.

If these general rules are used to analyse our values of C_R (Table 1), they are in very good agreement with those rules. We calculated the C_R value for the mixture b4, which was the first observed cholesteric phase in the phase diagram, and found 1.23, which is just over the minimum value to observe the cholesteric phase. In Table 1, the confinement ratios for the mixtures from b0 to b3 were "zero," because the pitch in the nematic state is set as infinite. If the C_R values are plotted versus the brucine concentration, Fig. 3, a linear dependence is obtained and it is observed that the N-Ch transition is discontinuous or first-order as predicted by Dequidt [33].

The Pitch Measurements

The pitch measurements of KL/K_2SO_4/UndeOH/H_2O/brucine system were made using polarized light microscopy. The pitch values, P, at 35°C (Ch_D) are given in Table 1. The dependence of P^{-1}, or twist, with the brucine concentration (Fig. 3), was very similar to that of the brucine sulfate in the KL/DeOH/D_2O system, at low brucine sulfate concentration [21], except that the brucine has higher htp than brucine sulfate, as discussed in the following. The htp value of the brucine at 35°C in our work was calculated as 12.12 ± 0.40 μm^{-1} from the slope of the straight line in Fig. 3, according to Eq. 1. The BS in the KL/DeOH/D_2O/BS mixture had htp value of about 1.88 μm^{-1} at 12–14°C (read from

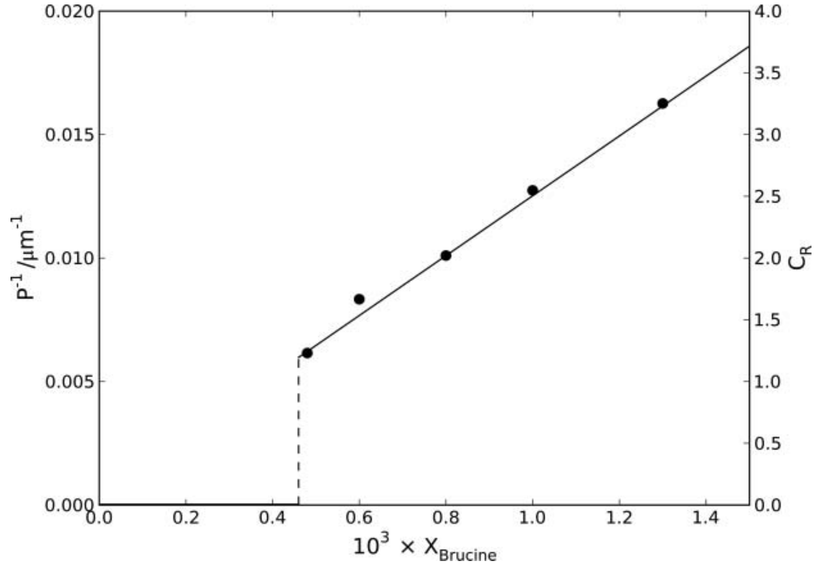

Figure 3. Reciprocal pitch or twist as a function of brucine concentration in molar fractions for the samples at 35°C (Ch_D phase). The vertical scale to the right is the confinement ratio C_R.

Fig. 4 of Ref. [21]). It is known that htp depends on the temperature [34–37] and it was stated that the htp decreases with increasing temperature, as a result of the inversion of the sign of the htp. In other words, the BS would have had smaller htp than 1.88 μm^{-1} at 35°C and the brucine may have about at least 10 times higher htp than the BS. This conclusion may be drawn if the micelles in both systems investigated were the same. However, this is not the case since this depends on the particular compounds used to prepare the mixture. Another important fact that must be taken into account is the effect of the chiral molecule on the micelles themselves. Since the brucine has more nonpolar regions in their structure with respect to the BS, the brucine may distort the micelles more efficiently than the BS molecules. Although there is little information in the literature about the solubilities of brucine and brucine sulfate in water, we check from the producers that they are about

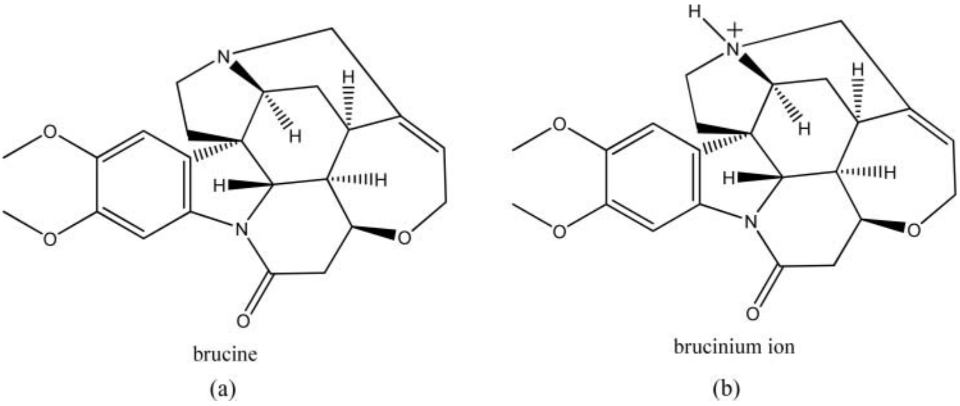

Figure 4. Molecular structures of (a) brucine and (b) brucinium ion of brucine sulfate.

0.48 mg/mL and 14 mg/mL, respectively, i.e. brucine solubility is approximately 29 times less than brucine sulfate solubility. If we compare their molecular structures, Fig. 4, it may be seen that the brucine molecule, Fig. 4(a), is electrically neutral, with an essentially nonpolar structure. However, brucine sulfate consists of two brucinium ions and this ion has positive charge on the –NH... group. So, since brucinium ion has to be near the micelle surfaces, brucine molecule should prefer to pack in the micelles bilayer.

Before we discuss the results in more details let us to summarize the fundamentals of the "intrinsically biaxial micelles model, IBM" that will be used in the following. This model was proposed for the first time by Neto et al. [38] and Galerne et al. [39]. It is our conviction that the IBM model is the best model in the literature to explain the existence of the lyotropic biaxial nematic phases, N_B, with respect to the other models published in the literature. In the early studies after the biaxial nematic phase was discovered by Yu and Saupe [40], it was thought that the biaxial phase is a mixture of two uniaxial calamitic, N_C, and discotic, N_D, nematic phases based on the model of "mixtures of calamitic and discotic nematic phases, MCD" [41]. However, from the experimental and theoretical points of view, it was shown that the discotic and cylindrical objects cannot coexist and demixing occurs [42], i.e. a mixture of discotic and cylindrical objects is not stable. Because of this, we should reject the MCD type models. If we come back to the IBM model, the micelles in the three discotic, biaxial and calamitic nematic phases have orthorhombic symmetry [3]. When a chiral dopant is added to a nematic phase, the orthorhombic micelle may be deformed, depending on the packing of the chiral molecule added. However, similar to the nematic phases, the occurrence of three different cholesteric phases, Ch_D, Ch_B and Ch_C, are still based on the orientational fluctuations of correlation volumes. When the chiral dopant brucine is added to our quaternary mixtures of $KL/K_2SO_4/UndeOH/H_2O$, due to the nonpolar characteristic of the molecule, it is expected that they pack in the main amphiphile bilayer. This packing increases the thickness of the bilayer, favoring the calamitic-type orientations fluctuations (according to the IBM).

Conclusions

The chiral agent brucine was added in different concentrations to the lyotropic mixture of $KL/K_2SO_4/UndeOH/H_2O$, giving rise to the three cholesteric phases. The phase diagram of the brucine doped mixtures was constructed, and it was shown the existence of a critical brucine concentration to cholesterize the quaternary nematic host phase. The brucine addition in the former mixture with the nematic phases imposes a decreasing of the biaxial region in the phase diagram. This situation was interpreted via the packing of the brucine in the bilayer of the micelles. This packing favors the orientational fluctuations responsible for the formation of the Ch_C phase. Furthermore, the pitch measurements were performed and the htp value was calculated. It was observed that the htp value was higher than that of brucine sulfate previously reported in the literature. This showed that even small differences exists between similar molecules (in our case, the difference is only that the brucine sulfate has positive ionic charge), it may affect the pitch and also htp values.

Acknowledgments

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