Effect of Alkyl Chain Length of Alcohols on Cholesteric Uniaxial to Cholesteric Biaxial Phase Transitions in a Potassium Laurate/Alcohol/ Potassium Sulfate/Water/Brucine Lyotropic Mixture: Evidence of a First-Order Phase Transition

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ABSTRACT: Lyotropic cholesteric liquid crystalline phases were prepared by doping the quaternary mixture of potassium laurate (KL)/potassium sulfate $(K_2SO_4)/alcohol (n-OH)/$ water with the chiral agent brucine. Different long-chain alcohols whose alkyl chains (*n*) vary from 8 (1-octanol) to 16 (1-hexadecanol) were used. The cholesteric uniaxial to



cholesteric biaxial phase transitions were investigated by measuring the birefringences via polarizing optical microscopy, and the phase diagram was constructed as a function of the alkyl chain length of the alcohols. Alcohols with $9 \le n \le 12$ presented the three cholesteric phases (cholesteric discotic—Ch_D, cholesteric biaxial—Ch_B, and cholesteric calamitic—Ch_C). The Ch_D-to-Ch_B transition was shown to be continuous, with a bare correlation length bigger than the typical micellar dimensions. Mixtures with n = 8 and n = 13 showed a first-order phase transition between the Ch_D and the Ch_C phases, without the presence of the Ch_B phase in between. These results are interpreted in terms of the nanosegregation of the alcohol molecules in the micelles with respect to the main amphiphiles molecules.

INTRODUCTION

Lyotropic biaxial nematic phase (N_B) is an intermediate phase between uniaxial discotic (N_D) and uniaxial calamitic (N_C) nematic phases.^{1–3} The phase transitions between the uniaxial and biaxial phases are of second order, well-described within a mean-field approach.²

Cholesteric lyotropic phases (also named lyocholesterics) can be obtained by doping the lyotropic mixture, presenting the nematic phase, with chiral agents.⁴⁻⁶ Similarly to the nematic phases, three types of cholesteric lyotropics were identified:6 cholesteric biaxial (Ch_B) , cholesteric discotic (Ch_D) , and cholesteric calamitic (Ch_C). The labels refer to the original nematic phase cholesterized by the addition of the chiral agent. These phases can be produced by three ways: (i) addition of chiral dopant molecule such as brucine sulfate to the achiral nematic phase composed of amphiphilic molecules, e.g., potassium laurate (KL) and other additives (salt, water, and/ or cosurfactant like another amphiphilic molecule or 1alcohol),^{7–11} (ii) directly using L- or D-enantiomer of a racemic (DL-form) amphiphilic molecule, for example, L-alaninehydro-chloride dodecylester,^{12–14} and (iii) using chiral solvents.¹⁵ The first two ways are widely used to produce lyotropic cholesteric phases by several research groups, and the last one is not so common.

The structure of lyocholesterics was shown to be formed by micelles organized in a helical arrangement keeping, locally, the pseudolamellar ordering observed in lyotropic nematics.¹⁶ The pitch of the cholesteric structure (P) depends on the relative molar concentration of the chiral agent (c_m), with respect to the

concentration of the main amphiphile¹⁷ and on the shape anisotropy of the micelles.¹⁸ The bigger the concentration of the chiral agent and/or the shape anisotropy of the micelles, the smaller the cholesteric pitch.

Cholesteric-to-cholesteric phase transitions in the lyotropic mixture of sodium decyl sulfate/decanol/water/brucine sulfate heptahydrate were discussed by Yu and Saupe.¹⁹ The phase diagrams of lyotropic mixtures with the three cholesteric phases present some features that differ from those of mixtures with the three nematic phases. Examples of phase diagrams, where the three cholesteric phases are present, are given in refs 6, 20, and 21. In all these phase diagrams, the Ch_B phase domain is located in between the Ch_D and the Ch_C domains. To the best of our knowledge, a direct transition between the Ch_D and the Ch_C was not experimentally reported.

Experimentally, the $Ch_D - Ch_B$ phase transition was shown to be continuous,²² differently from the $N_D - N_B$ transition, with correlation length $\xi \approx 12$ nm, which coincides with the typical dimensions of the micelles in lyocholesterics. This modification on the behavior of the phase transition was attributed to the *chiral elastic field* present in cholesteric phases.

From the theoretical point of view, Brand and Pleiner²³ invoked symmetry reasons to conclude that the $Ch_{D/C}$ - Ch_B transitions should be of first order or continuous, discarding the second-order phase transition. However, there is not in the

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Table	1. Molar	Fractions	(X)	of Each	Component	in the	Lyotropic	Cho	lesteric	Mixtures
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mixture	alcohol	$X_{ m KL}$	$X_{\mathrm{K_2SO_4}}$	$X_{ m alcohol}$	$X_{ m H_2O}$	$X_{ m brucine}$	cholesteric phase ^a	$\Delta T_{\rm B} \ (^{\circ}{\rm C})^b$
n_8	OcOH	0.0382	0.0060	0.0114	0.9434	0.0010	Ch _C , Ch _D	
n_9	NonOH	0.0382	0.0060	0.0114	0.9434	0.0010	Ch _B , Ch _D	>9.4
<i>n</i> ₁₀	DeOH	0.0382	0.0060	0.0114	0.9434	0.0010	Ch _C , Ch _B , Ch _D	5.2
n_{11}	UnDeOH	0.0382	0.0060	0.0114	0.9433	0.0010	Ch _C , Ch _B , Ch _D	3.7
n_{12}	DDeOH	0.0382	0.0060	0.0114	0.9433	0.0010	Ch _C , Ch _B , Ch _D	2.5
<i>n</i> ₁₃	TDeOH	0.0382	0.0060	0.0114	0.9434	0.0010	Ch _C , Ch _D	
n_{14}	TeDeOH	0.0382	0.0060	0.0114	0.9433	0.0010	Ch _C	
n ₁₅	PDeOH	0.0382	0.0060	0.0114	0.9433	0.0010	Ch _C	
<i>n</i> ₁₆	HDeOH	0.0382	0.0060	0.0114	0.9434	0.0010	Ch_C	
^a The lowest working temperature was 5.0 °C. ${}^{b}\Delta T_{\rm B}$ corresponds to the cholesteric biaxial temperature range.								

literature an experimental report of a first-order phase transition between cholesteric phases. As pointed out before, lyotropic cholesterics have two degrees of freedom which may be worked out to explore the behavior of the phase transition: the intensity of the chiral elastic field, controlled by the amount of chiral agent present in the mixture, and the shape anisotropy of the micelles which will be organized in the helical structure, controlled by the types of the surfactant and cosurfactant in the mixture. Usually, experimentalists employ the first approach, keeping the same basic mixture and increasing the amount of chiral dopant, giving rise to the phase diagrams already referred. Less frequent is the investigation of the effect of the micellar shape anisotropy in the phase transition behavior, keeping constant the amount of chiral dopant and changing the type and relative concentration of surfactant and cosurfactant. Recently, we discussed the effect of different cosurfactants in the uniaxial-to-biaxial phase transition in lyotropic mixtures presenting the N_B phase. 24,25 Some of these mixtures presented high values of the optical birefringence that could indicate the existence of more anisometric micelles and/or a nanosegregation of the cosurfactant in the micelles. These effects could be explored to investigate the nature of lyocholesteric mixtures obtained by adding chiral dopants to those lyotropic mixtures presenting the uniaxial and biaxial nematic phases.

In this study, we investigated the effect of the alkyl chain length of the long-chain 1-alcohols (n-OH) on the phase diagram and phase transitions of lyocholesterics mixtures. For this purpose, we used the quaternary lyotropic mixtures of potassium laurate $(KL)/K_2SO_4/n-OH/H_2O_7^{24,25}$ which present the three nematic phases, and introduced brucine as the chiral agent. Different cholesteric mixtures were prepared with the cosurfactant varying from 1-octanol to 1-hexadecanol, keeping all the components concentrations (in mole fractions) constant. Polarizing optical microscopy and measurements of the optical birefringences were used to identify the mesophases and study the phase transitions.²²

EXPERIMENTAL SECTION

Potassium laurate was synthesized in our laboratory by neutralization of lauric acid (Merck) with potassium hydroxide (Merck). Following the neutralization, it was recrystallized several times from absolute ethanol. Long-chain alcohols, 1octanol (OcOH), 1-nonanol (NonOH), 1-decanol (DeOH), 1undecanol (UndeOH), 1-dodecanol (DDeOH), 1-tridecanol (TDeOH), 1-tetradecanol (TeDeOH), 1-pentadecanol (PDeOH), and 1-hexadecanol (HDeOH), and brucine were commercially available from Merck and Sigma with purity >99%. The salt K_2SO_4 and water-based ferrofluid were obtained from Fischer and Ferrotec, respectively. A small amount of ferrofluid (less than 1 μ L in about 2.5 mL of the mixture) was used to improve the alignment of the mixture subjected to an external magnetic field of about 0.9 kG. We have checked that, at this small concentration, no detectable changes in the transition temperatures and birefringences were observed, within our accuracy. With the ferrofluid doping, the time necessary to obtain a well-oriented sample decreases from days to hours.

The details of the preparation of the lyotropic quaternary mixtures of $KL/K_2SO_4/alcohol/H_2O$, which presented the nematic phases, were discussed elsewhere.^{24,25} The alcohols in the mixtures were changed from octanol (OcOH) to hexadecanol (HDeOH), keeping the mole fractions of all constituents constant (Table 1).

For texture investigation, pitch, and birefringences measurements, lyotropic samples were encapsulated in 0.2 mm thick microslides. A Leitz Ortoplan-Pol microscope (with monochromatic light, $\lambda = 546$ nm) and a temperature-controlled device for the sample were employed in the experiments. To prevent water loss, both ends of the microslides were closed with special glue on which UV-light was applied to polymerize it. Microslides were put into a heating stage (Instec) to identify the phases and determine the transition temperatures. The stage was thermally insulated in such a way that the temperature was controlled with an accuracy of 0.01 °C.

The birefringences of the Ch_D and Ch_B phases were measured following a procedure similar to the one described in ref 22. Shortly, the microslide filled with the sample was put in the heating stage and a magnetic field $(|\vec{B}| = 0.9 \text{ kG})$ was applied to the sample, in the plane of the microscope stage. The laboratory frame of reference is defined as follows: the x-axis is parallel to the magnetic field direction; the z-axis is parallel to the light beam; the y-axis is the third orthogonal axis of the frame. The Ch_D and Ch_B orient with the helical axis parallel to \vec{B} . The well-aligned cholesteric fingerprint texture with stripes (Ch_D) was obtained after keeping the samples in the magnetic field for about 6 h. Starting from the Ch_D phase, the temperature was changed step by step until the next phase $(Ch_B \text{ or } Ch_C)$. At each stabilized temperature, pictures were taken with a digital CCD camera keeping constant the light intensity of the microscope illuminator as well as all the parameters of the camera (zoom, focal length, f-number, and shutter speed). The light intensity was measured from the intensities of the pixels in different positions along the stripes of the fingerprint texture in the Ch_B or Ch_D phases using the software ImageJ from NIH Image. It is important to notice that the Ch_C has the helical structure unwound in the presence of the magnetic field.

RESULTS AND DISCUSSION

Phase Diagram. The textures were identified under polarizing optical microscope. Samples in the Ch_D phase were kept in the magnetic field until well-aligned cholesteric stripes were observed, i.e., stripes mostly perfectly aligned parallel to each other and perpendicular to the magnetic field. In all the mixtures investigated, when the three cholesteric phases are present, the Ch_D phase domain is located at higher temperatures with respect to the Ch_B and Ch_C phase domains. Then, the cholesteric uniaxial to cholesteric biaxial phase transition temperatures were determined precisely by carefully changing the temperature of the samples. As a working example, let us analyze the case of a mixture that presented the three cholesteric phases. In the Ch_D phase, dark regions were observed between the bright cholesteric stripes, Figure 1a.



Figure 1. Textures from the mixture n_9 . (a) Ch_D phase, T = 20.00 °C; (b) Ch_B phase, T = 12.50 °C. The labels P and A refer to the polarizer and analyzer, respectively. The magnetic field is oriented along the *x*-axis at 45° from the polarizer.

These regions correspond to the director oriented parallel to the light propagation direction, perpendicular to the plane of the analyzer and polarizer of the microscope. They correspond to the cholesteric planes homeotropically oriented. Decreasing the temperature, near the vicinity of the Ch_D-to-Ch_B transition, light starts to be transmitted by the sample at these previously black regions (Figure 1b). This means that, at the Ch_B phase, the two optical axes that spin around the helical axis are not in a homeotropic orientation. Details about the determination of this transition temperature will be given in the following. Further decreasing the temperature sample transits to the Ch_C phase, and as the magnetic field is present, the helical axis is unwound and a planar texture (with the director oriented parallel to the magnetic field) is observed. Pleiner and Brand predicted the existence of defects with singular cores in the Ch_B phase.26

After all phase transition temperatures were obtained, they were used to construct the surface of the phase diagram shown in Figure 2, as a function of the alkyl chain length of the alcohol. Two important results can be seen in Figure 2, as the alkyl chain length of the alcohols increases: (i) the cholesteric uniaxial to cholesteric biaxial phase transition is shifted to the higher temperatures; (ii) the cholesteric biaxial domain got smaller. These results are similar to our previous observations with the mixtures of KL/K₂SO₄/alcohol/H₂O, presenting the three nematic phases, with different long-chain alcohols.²⁵

A remarkable aspect of this phase diagram is the direct Ch_D to- Ch_C phase transition without passing through the Ch_B phase, observed in mixtures with n_8 (the shortest) and n_{13} (the longest) alcohols. Figure 3 shows the textures of the mixture Article



Figure 2. Phase diagram of $KL/K_2SO_4/alcohol/H_2O/brucine mixtures, which was constructed by plotting the phase transition temperatures vs the alkyl chain length of the alcohols. The labels 2P, MP, I, and C correspond to two-phase (one of them is isotropic) and multiphase (one of them is isotropic) regions, isotropic, and crystalline phase, respectively. Solid and dashed lines are only guides for the eyes.$



Figure 3. Textures from the mixture n_{13} . (a) Ch_D phase, T = 46.70 °C; (b) coexistence between Ch_D and Ch_C phases, T = 45.35 °C; (c) coexistence between Ch_D and Ch_C phases, T = 43.50 °C. The labels P and A refer to the polarizer and analyzer. The magnetic field is oriented along the *x*-axis.

with n_{13} , observed under the microscope in three different temperatures. Figure 3a corresponds to the Ch_D phase with the homeotropic black stripes. Decreasing the temperature, coexistence between the Ch_D and the Ch_C is observed. Figure 3b shows the original Ch_D texture, now with droplets of the Ch_C being formed on it. Decreasing more the temperature, still in the coexistence phase domain, some homeotropic regions (from the Ch_D) are present, together with planar regions (from the unwound Ch_C)—Figure 3c. Decreasing more the temperature the entire sample transits to the Ch_C phase, showing a homogeneous planar texture. As pointed out in the Introduction section, this direct transition was not experimentally reported before, although theoretically predicted.²³

These aspects will be discussed in the following. Mixtures whose composition had alcohol with more than 13 carbons in the chain provided only Ch_C phase.

Scalar Order Parameter and the Landau Coefficients. The free-energy density (F) of the cholesteric phase, in the vicinity of the uniaxial-to-biaxial transition, may be written as^{21,22}

$$F = \frac{1}{2}a(T)\varsigma^{2} + \frac{1}{4}b\varsigma^{4} - cq^{2}\varsigma$$
(1)

where ς is the scalar order parameter of the biaxial phase, q = $2\pi/P$, $a(T) = a_0(T - T_c)$, a_0 , b, c are the Landau coefficients, and T_c is the cholesteric uniaxial-to-biaxial transition temperature. Minimization of eq 1 with respect to ς gives an expression that relates the scalar biaxial order parameter with Tand *q*: $cq^2 = a_0(T - T_c)\zeta + b\zeta^3$. The asymptotic behaviors of ζ^2 as a function of T are $\zeta = 0$ in the Ch_D phase and $\zeta^2 = -(a_0/2)$ $b(T - T_c)$ in the Ch_B phase. From the experimental point of view, the scalar order parameter may be obtained by measuring the optical birefringences of the sample. We define the optical birefringences as $\Delta n = n_3 - n_2$ and $\delta n = n_2 - n_1$, where the labels 1, 2, and 3 refer to a frame which spins along the helical structure, with the 1-axis parallel to the x-axis. In the homeotropic regions of the oriented Ch_D texture, the 3-axis (representing the director direction) is parallel to the z-axis of the laboratory frame. In this condition $\delta n = 0$ and $\Delta n \neq 0$. When the sample transits to the Ch_B phase, both birefringences are different from zero. In a first-order approach, the biaxial scalar order parameter may be written as $\zeta \sim \delta n / \Delta n$.²² To measure Δn we took pictures of a well-oriented sample in the Ch_D phase close to the Ch_D - Ch_B phase transition temperature, plotted the light intensity (I) along the x-axis, and compared with the equation²²

$$I = I_0 \sin^2[(\pi D/\lambda)\Delta n \sin^2(qx)]$$
⁽²⁾

where I_0 is the maximum intensity of the stripes, D is the sample thickness, and the homeotropic regions were set as the background of the pattern. Figure 4 shows a typical result of I as a function of x in the Ch_D phase. The values Δn of each sample are given in Table 2.

To obtain we measured the light intensity in the homeotropic regions of the pattern as a function of the



Figure 4. Normalized light intensity measured as a function of the distance *x* from a homeotropic stripe, along the magnetic field direction. Sample n_{11} in the Ch_D phase, T = 31.00 °C. The solid line is the plot of eq 3.

Table 2. Birefringence (Δn) , Pitch (P), Ratios between Landau Coefficients, and Bare Correlation Length (ξ_0) of the Cholesteric Mixtures

mixture	$\begin{array}{c} 10^3 \\ (\Delta n \pm 0.2) \end{array}$	$P \pm 2.0 \; (\mu \mathrm{m})$	b/a_0 (K)	$10^9 c/a_0 (cm^2 K)$	$\xi_0 \ (nm)$
n_8	1.3	84.2			
n_9	3.4	62.2	8.1 ± 0.7	1.2 ± 0.2	20 ± 2
n_{10}	3.2	67.3	2.9 ± 0.2	1.2 ± 0.3	20 ± 3
n_{11}	3.6	65.6	3.6 ± 0.3	0.7 ± 0.5	15 ± 5
n_{12}	3.4	93.1	5.1 ± 0.4	2.7 ± 1.2	30 ± 6
n_{13}	2.0	186.2			

temperature, around the $\rm Ch_D-\rm Ch_B$ transition temperature, for each sample, and the values were substituted into the equation^{22}

$$I = I_0 \sin^2[(\pi D/\lambda)\delta n]$$
(3)

Figure 5 shows the plots of ς^2 as a function of the temperature for all the samples investigated and the fits of the equation



Figure 5. Squared biaxial order parameter as a function of the temperature for the different mixtures with the different alcohols. Solid lines are fits of the equation obtained by the minimization of the free-energy density F with respect to ς , taking into account the asymptotic behaviors, to the experimental data.

obtained by the minimization of the free-energy density F with respect to ς , taking into account the asymptotic behaviors. The parameters obtained from these fits are presented in Table 2.

Assuming that the Landau coefficient *c* has the same order of magnitude of the typical Frank elastic constant (*K*) of the cholesteric phase,²² we can write the bare correlation length of the biaxial order parameter as $\xi_0 \sim [c/(|a_0|T_c)]^{1/2}$. The values of ξ_0 for the mixtures are given in Table 2.

Samples n_9 , n_{10} , n_{11} , and n_{12} presented an interesting behavior of ζ^2 as a function of the temperature in the vicinity of T_{cv} where a rounding off connects the two asymptotic behaviors. This characteristic is due to the presence of the *elastic chiral field* that imposes a chirality-induced biaxiality in the Ch_D phase. The rounding off is more pronounced in samples n_9 and n_{12} .

The ratio c/a_0 informs about the chirality-induced biaxiality in the Ch_D phase and, in our experiment, has the order of magnitude of ~10⁻⁹ cm² K. This order of magnitude agrees with the estimations of $K/a_0 \sim 3 \times 10^{-9}$ cm² K from data available in the literature for the magnetically induced biaxiality in the uniaxial discotic nematic to biaxial nematic phase

transition.^{27,28} Comparing this ratio with other cholesteric mixtures, our values are about 1 order of magnitude bigger than that obtained with the mixtures of KL/DeOH/H₂O, with the chiral agents brucine sulfate heptahydrate (BSH), 1-N-lauroyl potassium alaninate, and d-octanol,²² and 2 orders of magnitude smaller than that obtained with the mixture of KL/decylammonium chloride/water/BSH.²¹ The bare correlation length (ξ_0) calculated in our experiment also agrees with that evaluated by light-scattering measurements in lyotropic nematics,²⁹ being larger than the typical micellar dimensions (of the order of 10 nm). This result suggests that the structural changes responsible for the transition occurs in a length scale bigger than the micellar dimensions, supporting the intrinsically biaxial micelle (IBM) model.^{30,31} The IBM assumes that in lyotropic mixtures with a surfactant and a cosurfactant, presenting the uniaxial and biaxial phases, micelles are intrinsically biaxial (orthorhombic symmetry) and orientational fluctuations are responsible for the phase transitions. In the case of the cholesteric phases, obtained by the doping of originally nematic phases with chiral molecules, no drastic modifications of the micelles are expected. The elastic chiral field arranges the correlation volumes in a helical structure in length scales of the order of $10^2 \mu m$. This elastic field, however, changes the character of the transition, from the second order, in the case of the nematics, to continuous in the case of some of the cholesterics investigated in the present work. The other theoretically predicted possibility, the first-order transition, was observed in mixtures n_8 and n_{13} .

Role of the Alcohol Chain Length. In order to understand the role of the alkyl chain length of the alcohol in the cholesteric phases and phase transitions, we have to consider how alcohol molecules are located in the micelles. The neutron contrast studies with the mixture KL/DeOH/H2O indicated that the DeOH molecules are preferentially located in the flattest surface of the micelle, rather than in their rims.³³ This result tells us that the surfactant and alcohol molecules are not homogeneously distributed in the micelle, implying a molecular segregation. However, this segregation may be more or less pronounced, depending on the alcohol (or cosurfactant) chain length. This aspect was already discussed in the case of lyotropic mixtures with the three nematic phases, with different alcohols.²⁵ Let us summarize the main conclusions of this study where the main surfactant was the KL ($n_{\rm KL} = 11$ carbons in the chain³³) and different alcohols, with number of carbons in the alkyl chain (n) varying from 8 to 16, were used to prepare the lyotropic mixtures. According to the IBM model, the orthorhombic local symmetry of the micelles is the same in the three nematic phases, and orientational fluctuations of them lead to the macroscopic nature of the two uniaxial and the biaxial nematic phase. These orientational fluctuations depend on the shape anisotropy of the micelles, which change as a function of the temperature, relative concentration of the different compounds of the mixture, and the relation between the chain length of the main amphiphile and that of the alcohol. The chain length of the main amphiphile defines the micellar double layer and the pseudolamellar ordering observed in lyonematics (and on lyocholesterics). Just to help the understanding, let us assume that the micelle may be (instantly) sketched as a parallelepiped of dimensions A', B', C', with A' >B' > C', where the dimensions A', B' form the largest micellar flat surface, and C' represents the bilayer. Our results lead to the conclusion that alcohol molecules segregate in different ways, depending on the value of *n* with respect to n_{KL} . For $n > n_{\text{KL}}$

 $n_{\rm KL}$ alcohol molecules accumulate more in the flattest surface of the micelles (favoring the discotic nematic phase—A', B' plane), whereas for $n > n_{\rm KL}$ alcohol molecules accumulate preferentially in the curved surfaces of the micelle (favoring the calamitic nematic phase). The same behavior is observed in our present experimental phase diagram with the cholesteric phases (Figure 2). Taking into account only the mixtures that present the three cholesteric phases, increasing the alcohol chain length leads to an increase of the Ch_C phase domain and a decrease of the Ch_B and Ch_D domains (Figure 6). This result suggests that



Figure 6. Temperature ranges of the (a) Ch_{D} , (b) Ch_{B} , and (c) Ch_{C} phases as a function of the number of carbons on the alcohol alkyl chain.

long-chain alcohols ($n > n_{\text{KL}}$) tend to pack preferentially in the rims, probably due to steric reasons since it is easy to accommodate longer molecules on this part of micelles, increasing the shape anisotropy of the micelles in the sense that they become more elongated (for instance, increasing more A' with respect to B'). This shape anisotropy favors the orientational fluctuations which gives rise to the N_C and, consequently, the Ch_C phase (Figure 2). On the other hand, small-chain alcohols may be more easily incorporated in the flattest surface of micelles, favoring the cholesteric discotic phase (Figure 2).

In the case of the cholesteric phases, it can be expected that, depending on the nature of the chiral dopant, they can be placed in the micelle differently. For instance, a small chiral dopant, like L-mandelic acid, may be located between the head groups of the surfactant molecules existing on the large micelle surfaces and/or in the rims of the micelles. However, relatively large chiral dopants, like brucine, should be located differently. The brucine molecule has two different parts: one (part 1) consists of the planar benzene ring to which two ether groups $(-OCH_3)$ are bound; the other (part 2) is a little bit complex part which is not as planar as part 1 (Figure 7).



Figure 7. Molecular structure of brucine.

If we consider it in 3D in space, part 2 is bulkier than part 1. When this chiral dopant is added to our quaternary mixtures of $KL/K_2SO_4/alcohol/H_2O$, the nonpolar part of the brucine is expected to pack inside the micelle, in the KL double layer. This packing leads to an increase of this typical micellar dimension (*C'*), which, according to the IBM model, favors the orientational fluctuations that give rise to the Ch_C phase. In the present experiment, as the molar fraction of brucine is the same in all the mixtures investigated, we may consider that the

amplitude of the chiral elastic field remains the same for all the samples investigated. What changes with the different alcohols used is the elastic medium that will be cholesterized by the dopant. The value of the pitch of the cholesteric structure may be seen as a measurement of the efficiency of the elastic chiral field to establish the helical arrangement. The smaller the pitch, more efficient is the elastic chiral field. It was previously shown that 1/P is proportional to the concentration of the chiral agent and to the micellar shape anisotropy.^{17,18}

Our results indicate that as the number of carbon atoms in the alcohol chain differs more with respect to that of the main amphiphile $(n_{\rm KL} = 11)$, the bigger the pitch. In the IBM framework, this indicates less anisometric micelles and, consequently, for the same chiral agent concentration, a higher value of the pitch (Figure 8).



Figure 8. Pitch of the Ch_D phase as a function of the number of carbons in the alcohol alkyl chain. The molar fraction of brucine is kept constant. The dashed line is only a guide for the eyes.

As pointed out before, the existence of a first-order transition between the Ch_D and Ch_C phases is remarkable. The temperature ranges of the phase coexistence domains are about 5 and 3 °C for mixtures n_8 and n_{13} , respectively. The existence of the Ch_B phase between the two uniaxial phases seems to be strongly dependent on the shape anisotropy of the micelles. In the case of the mixture n_{13} , due to that the length of the alcohol molecule is bigger than that of the KL, it seems reasonable to assume that the alcohol molecules preferentially accumulate in the micellar rims. This segregation should increase one of the micellar dimensions, for instance, A'. Changes in the temperature may modify the nanosegregation of the alcohol molecules in the rims. Increasing the temperature may promote a more homogeneous distribution of the alcohol in the rims, implying in a more symmetric micelle $(A' \approx B')$. This new geometry favors the orientational fluctuations characteristics of the discotic phase. The micellar shape anisotropy that allows the existence of the biaxial phase is not achieved. A similar process may occur in the case of mixtures with n_{8} , now with the alcohol molecules accumulating preferentially in the flattest surface of the micelles. This picture certainly must be investigated in more details by using complementary techniques as, e.g., NMR and contrast neutron scattering experiments.

CONCLUSION

Article

of the alkyl chain length of the alcohol, keeping constant the mole fraction of all the mixture constituents. The mixtures with $n_{\rm KL}$ < 12, where $n_{\rm KL}$ is the number of carbons of the KL, presented the three cholesteric phases. As the alkyl chain length of the alcohols increases the cholesteric uniaxial to cholesteric biaxial phase transitions is shifted to the higher temperatures, and the cholesteric biaxial domain got smaller. Measurements of the biaxial order parameter in the vicinity of the transition Ch_D-to-Ch_B revealed that this transition is continuous. The chiral elastic field imposes a chirality-induced biaxiality in the Ch_D phase. The order of magnitude of this chirality-induced biaxiality in the Ch_D phase agrees with the estimations for the magnetically induced biaxiality in the uniaxial discotic nematic to biaxial nematic phase transition. The bare correlation length calculated agrees with that evaluated by light-scattering measurements in lyotropic nematics, being larger than the typical micellar dimensions. This result suggests that the structural changes responsible for the transitions occur in a length scale bigger than the micellar dimensions, supporting the IBM model. Mixtures with alcohols of n = 8 and n = 13 carbon atoms presented a first-order phase transition between the Ch_Dto-Ch_C. This result was interpreted as a consequence of the nanosegregation of the alcohol molecules in the micelles with respect to the main amphiphile molecules (KL).

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Notes

The authors declare no competing financial interest.

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