Anomalous Behavior in the Crossover between the Negative and Positive Biaxial Nematic Mesophases in a Lyotropic Liquid Crystal

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A novel quaternary lyotropic liquid-crystalline mixture of dodecyltrimethylammonium bromide (DDTMABr)/sodium bromide/1-dodecanol/water, presenting the biaxial nematic phase (N_B) in addition to two uniaxial discotic (N_D) and calamitic (N_C) nematic ones, was synthesized. The partial phase diagram of this new mixture was constructed as a function of the DDTMABr molar-fraction concentration. The phase transitions from uniaxial to biaxial nematic phases were studied by means of the temperature dependence of the optical birefringence. In a particular region of the phase diagram, anomalous behavior was observed in the crossover from N_B^- to N_B^+ : the contrast of the conoscopic fringes, which allows the birefringence measurements, almost vanishes, and the sample loses its alignment. This behavior, which was not observed before in lyotropics, was interpreted as a decrease in the mean diamagnetic susceptibility anisotropy ($\Delta\chi$) of the sample, which was related to the shape anisotropy of the micelles. Small-angle X-ray scattering measurements were performed to evaluate the micellar shape anisotropy; these revealed that this mixture presented a smaller shape anisotropy than those of other lyotropic micellar systems presenting the N_B phase.

1. Introduction

The physics of lyotropic liquid crystals, particularly with regard to phase transitions and critical phenomena,[1] is a fascinating field of research due to the richness of the phase diagrams experimentally found and the variety of phases encountered in these materials.

One of these phases is the nematic.[2] The existence of three nematic phases was predicted from symmetry considerations in the 1970s by Freiser[3] and Alben.[4] Despite the fact that nematic ordering experimentally observed in thermotropics is essentially uniaxial,[5] in lyotropics two uniaxial phases (N_D, discotic; N_C, calamitic) and a biaxial phase (N_B) have been identified.[6] Until 2003, just eight lyotropic mixtures were shown to present the N_B phase; however, in recent years, many others were synthesized.[7] It is important to note that all mixtures presenting the N_B phase have a surfactant and a cosurfactant. Mixtures with only one surfactant present only one of the uniaxial nematic phases.[1]

Let us consider the case of lyotropic mixtures made of a solvent and amphiphilic molecules with hydrocarbon chains, which present three nematic phases. The anisotropy of diamagnetic susceptibility of these mesophases is such that, in the presence of an external magnetic field ($\vec{H}$), the director, $\hat{n}$, in the N_D (N_C) phase orients perpendicular (parallel) to $\vec{H}$.[1] The biaxial phase has three diamagnetic susceptibilities χ_{ii} ($i = 1,2$, and 3), each one along their respective twofold symmetry axes or directors ($\vec{n}$, $\vec{m}$, and $\vec{l} = \vec{n} \times \vec{m}$). The alignment behavior of N_B in the presence of $\vec{H}$ may be used to classify the biaxial phase as being of N_B^+ or N_B^- type.[8] If the anisotropy of diamagnetic susceptibility $\left(\Delta\chi = \chi_{33} - \frac{1}{2}(\chi_{11} + \chi_{22}) \right)$ is positive, the biaxial phase aligns with the axis of the largest diamagnetic susceptibility parallel to the magnetic field (N_B^+); if $\Delta\chi < 0$, the biaxial phase aligns with the axis of the largest diamagnetic susceptibility perpendicular to the magnetic field (N_B^-).[9] However, from symmetry considerations,[3,4] the two classes, N_B^+ and N_B^-, belong to the same and unique biaxial phase, N_B.

The order parameter that characterizes the nematic phases is a second-rank, symmetric, and traceless tensor. It has two and three eigenvalues in the uniaxial and biaxial phases, respectively. The optical dielectric tensor, which is usually chosen as the order parameter,[10] can be obtained by measuring the differences between the refractive indices (i.e. the birefringences $\Delta n = n_2 - n_1$ and $\delta n = n_3 - n_2$) of the sample in the three nematic phases. The subscripts 1, 2, and 3 refer to the three orthogonal axes of the laboratory frame.[11] In the N_D and N_C phase domains, $\Delta n = 0$, $\delta n \neq 0$, and $\Delta n \neq 0$, $\delta n = 0$, respectively. In the N_B phase, $\Delta n \neq 0$, $\delta n \neq 0$, and N_B^- (N_B^+) is characterized simply by $\delta n > \Delta n$ ($\Delta n > \delta n$).

The phase transitions between the uniaxial and biaxial nematic phases were shown to be of second order, from the theoretical[3,4] and experimental[10] points of view. On the other hand, the transition between the nematic and isotropic phase is of first order, with a discontinuity in the order parameter as a function of the temperature and phase-coexistence domains.

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On the nanoscopic scale, the intrinsically biaxial micelles (IBM) model is the most adequate to describe the main characteristics of the nematic phases and phase transitions[1, 12] of mixtures with uniaxial and biaxial phases. It is based on three fundamental concepts: 1) orthorhombic micelle symmetry; 2) continuous modifications of the micellar dimensions as a function of the temperature; and 3) micellar orientational fluctuations. According to the IBM model, the micelles have orthorhombic symmetry, Figure 1 a, in all three nematic phases,
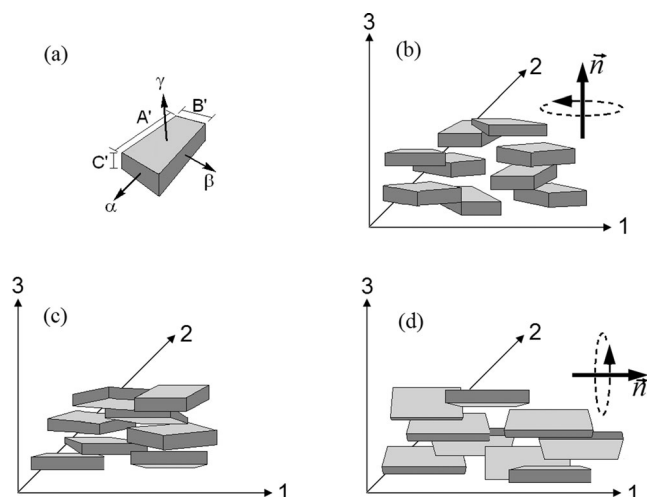
3) lead to the N_B phase (Figure 1 c). Large-amplitude orientational fluctuations around the axis parallel to the largest micelle dimension (along the symmetry axis $\alpha||1$) give rise to the formation of the N_C phase (with the phase director $\vec{n}||1$; Figure 1 d). Different orientational fluctuations are triggered by continuous changes in the micellar dimensions, as measured by means of small-angle X-ray scattering (SAXS).[12]

An adequate experimental technique to measure the birefringences (Δn and δn) as a function of temperature in lyotropic nematics is laser conoscopy.[10] This technique is employed because typical values of the birefringence in lyotropics are of the order of 10^{-3}, which leads to the need for thick samples to achieve a precise measurement. In all experimental measurements of the birefringences in the N_B phase reported to date, the crossover N_B^+-N_B^- happens without any anomalies. Both birefringences are measured from analysis of the conoscopic fringes observed in the experiments. The conoscopic fringes are particularly visible in the pattern and show a strong contrast between bright and dark regions. Herein, we present a new lyotropic mixture that has the three nematic phases, but a complete set of measurements of the birefringences by using classical laser conoscopy in the N_B^+ phase is impossible for some relative concentrations of the mixture of compounds.

2. Results and Discussion

Figure 2 shows the birefringences (Figure 2 a) and the invariants σ_2 (Figure 2 b) and σ_3 (Figure 2 c)[13] of the order parameter as a function of the temperature, and a plot of σ_2 versus σ_3 (Figure 2 d) of sample d1, which presents three nematic phases. These results are similar to those obtained previously with other lyotropic mixtures.[7] This behavior was only ob-
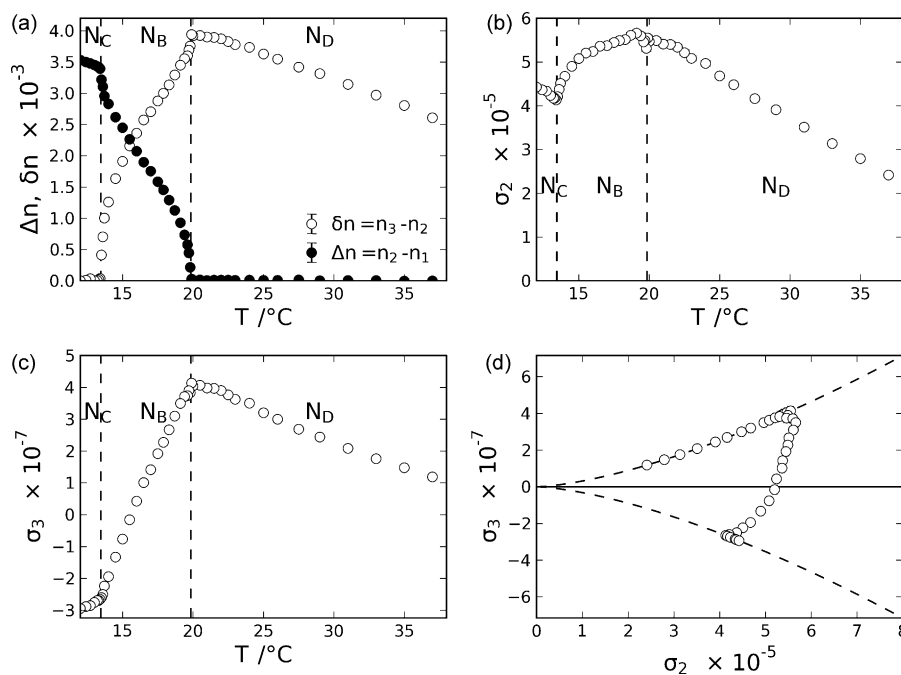

Figure 1. a) Sketch of the orthorhombic micelle and selected laboratory frame axis. According to the IBM model, based on the different orientational fluctuations, the formations of b) N_D, c) N_B, and c) N_C phases. $\vec{n}$ represents the director (optical axis) of the N_D and N_C phases.

and the occurrence of the two uniaxial and biaxial phases is due to orientational fluctuations of micellar correlation volumes. If we sketch micelles as an object of orthorhombic symmetry, as in Figure 1 a, with typical dimensions A', B', and C', we may choose the axes of the coordinate system fixed in the micelles as α, β, and γ. These orthorhombic micelles exhibit different orientational fluctuations along the laboratory frame axes (1, 2, and 3) for the occurrence of the N_D, N_B, or N_C phases. Large-amplitude orientational fluctuations around the axis perpendicular to the largest micelle surface (along the symmetry axis $\gamma||3$) give rise to the formation of the N_D phase (with the phase director $\vec{n}||3$; Figure 1 b). Small-amplitude orientational fluctuations along three axes (1, 2, and

Figure 2. a) Birefringences [Δn (●), δn (○)] and invariants b) σ_2 and c) σ_3 of the order parameter as a function of the temperature, and d) a plot of σ_2 versus σ_3 for sample d1.
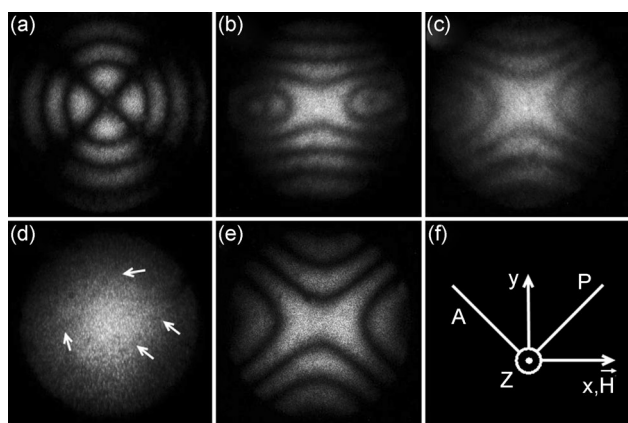
Figure 3. Conoscopic patterns of sample d6 in the nematic phases: a) N_D ($T=32.00\,°C$); b) N_B^- ($T=30.10\,°C$, near the N_D to N_B^- transition); c) N_B^- ($T=29.70\,°C$, near the crossover to N_B^+); d) N_B^+ ($T=29.50\,°C$), e) N_C ($T=26.00\,°C$). f) Geometry of the experiment with the laboratory frame axes, polarizer (P), and analyzer (A) directions, and the direction of the applied magnetic field ($\vec{H}$). Arrows in d) indicate the presence of distorted conoscopic fringes with weak contrast.

served in samples d1 and d2. The conoscopic fringes appear in all nematic domains and allow the precise measurement of the birefringences (see Figure 3 a,b, and e, corresponding to the conoscopic patterns of the N_D, N_B, and N_C phases, respectively). It is worth stressing that a simple visual inspection of the conoscopic patterns does not allow the identification of the nematic phase between the N_C and the N_B because their patterns are too similar. Identification is only possible by measuring both birefringences (Δn and δn). The crossover from N_B^- to N_B^+ corresponds to the point at which the relative biaxiality in the refractive index passes through an extreme.[11,14] The partial phase diagram of the mixture investigated is shown in Figure 4. The temperature domain of the N_B phase is almost in-
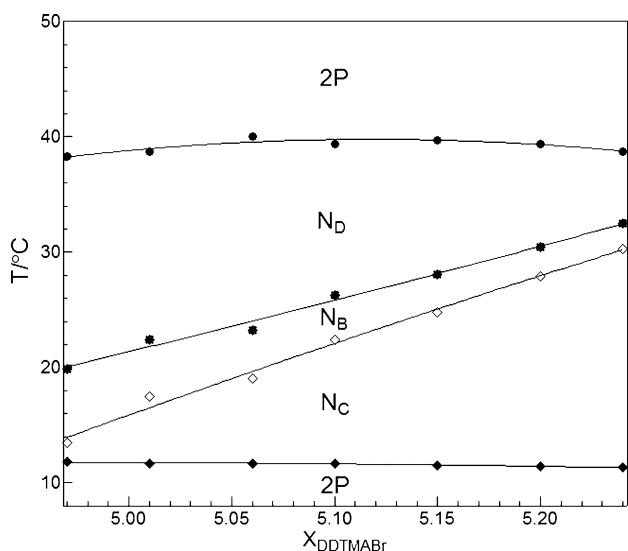

Figure 4. Partial phase diagram of the mixture of dodecyltrimethylammonium bromide (DDTMABr)/NaBr/1-dodecanol (DDeOH)/water. The mole-fraction percentages of NaBr and DDeOH were kept fixed (see Table 1). The label 2P corresponds to two-phase regions.

dependent of the percentage molar fraction of the main amphiphile; nevertheless, at low concentrations, the N_B domain is larger than that at high concentrations. However, upon increasing this molar fraction, the N_D (N_C) phase domain tends to decrease (increase). In addition, in the working temperature range, at high and low temperatures above the N_D and N_C phase domains, respectively; two-phase regions (2P in Figure 4) were observed.

Anomalous behavior occurred in the measurement of the birefringences of samples d3 to d7, in the crossover between N_B^- and N_B^+: the contrast of conoscopic fringes with respect to the background practically vanishes, avoiding measurement of the birefringences (Figure 3 c and d). The pattern shown in Figure 3 d may not be identified directly as that of the N_B^+ phase only by inspection. We return to this point later. When the sample transits to the N_C phase, by decreasing the temperature, the fringes appear again, with typical symmetry of the N_C phase, and measurement of the birefringences is possible again (Figure 3 e). The same behavior occurs when the sample is in the N_C phase and the temperature is increased towards the N_B^+ phase: the fringes practically disappear in the N_B^+ phase domain and reappear when the sample transits to the N_B^- phase. The sequence from Figure 3 a to e was obtained upon decreasing the temperature and corresponded to the phases N_D, N_B, and N_C. It is important to note that, in the N_B^+ phase domain, near the transition to the N_C phase, the pattern observed has some fringes without characteristic symmetry of the biaxial phase (see Figure 3 d), with a poor contrast with respect to the background. The orienting procedure employed to align the N_B phase, effective with samples d1 and d2 and all lyotropic mixtures reported until now,[1] does not help to make the fringes appear again in the N_B^+ phase domain. In the N_B^- phase domain, this orienting procedure works well with samples from mixtures d1 to d7.

The typical textures, observed in the polarized optical microscope, are shown in Figure 5. Figure 5 a–d presents textures of sample d3 in a glass capillary 300 µm thick, corresponding to the mesophases N_D, N_B^-, N_B^+, and N_C, respectively, without the magnetic field. Figure 5 e–g presents textures of the same sample, now with an applied magnetic field of 300 G, corresponding to the phases N_C, N_B^+ (at a temperature just above the phase transition), and N_B^-, respectively. The textures shown in Figures 5 f and g are particularly interesting and different from those observed in typical lyotropic mixtures and samples from mixtures d1 and d2. In the case of samples d1 and d2, just above the N_C to N_B^+ transition temperature, the texture observed in N_B^+ is planar, similar to that of the N_C phase (Figure 5 e). Figure 5 f (N_B^+) presents an almost periodic structure with a typical wavelength (distance between three dark lines) of about 80 µm perpendicular to the applied magnetic field. Inspection of this texture in the polarized microscope indicates that the previous orientation of one of the directors, which was perfectly oriented in the N_C phase, was practically lost (not completely) in the transition. A bend-like undulation of this director is observed in the direction of the applied magnetic field. Moreover, the two other directors are not oriented. After 10 h in the magnetic field, the sample showed a planar tex-
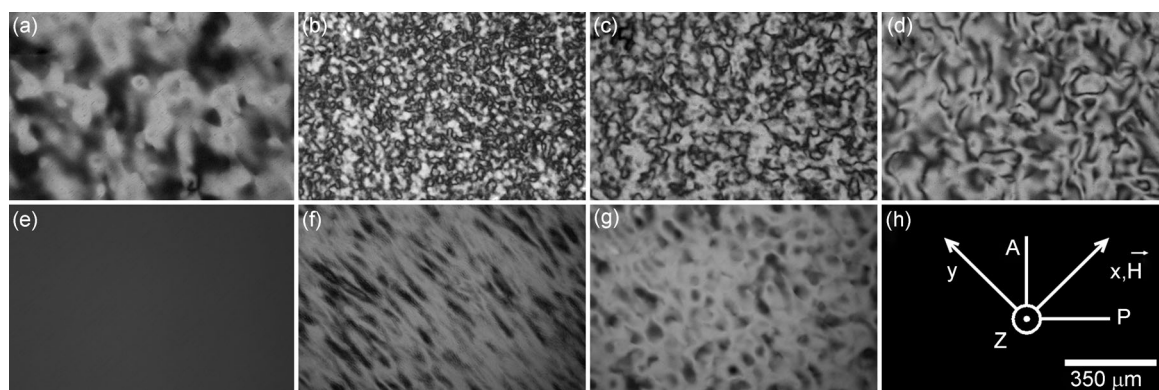
Figure 5. Typical textures observed in the polarized light microscope. Sample d3 without magnetic field: a) N_D, b) N_B^-, c) N_B^+, and d) N_C; with magnetic field: e) N_C, f) N_B^+, g) N_B^-. h) Geometry of the experiment with the laboratory frame axes, polarizer (P), and analyzer (A) directions, and direction of the applied magnetic field ($\vec{H}$).

ture, that is, the walls of the glass capillary orient one of the directors of the biaxial phase and the magnetic field orients the other. This result differs from what we observed in the conoscopic experiment because the sample thickness used in concoscopy was much larger than that in the microslide. In the case of thick samples, the wall effect is not efficient enough to impose the orientation of the second director in the bulk of the sample. To illustrate these statements, Figure 6 includes the measurements of the birefringences in two setups: the laser conoscopy (which allows the measurement of Δn and δn simultaneously), and the optical microscope with Berek compensator (light wavelength $\lambda = 546$ nm), which allows the measurement of Δn. In laser conoscopy, the orienting procedure was the same as that previously described. We started the measurements with the sample in the N_D phase and the temperature was decreased until the crossover of $N_B^- - N_B^+$, where the orientation of the sample was lost, and we observed a pattern similar to that shown in Figure 3 d. In the N_B^+ phase, we cannot orient the sample to measure the birefringences. In the N_C phase, the fringes reappear and the birefringences can be measured (see Figure 6 a). In the microscope with the Berek compensator, after about 10 h with the magnetic field applied parallel to the biggest glass surface of the microslide, we succeeded in orienting the N_B^+ phase. Different from the laser conoscopy, in the microscope, we can only measure Δn in the three nematic phases. Figure 6 b shows Δn as a function of the temperature. The experimental errors are bigger than those from the laser conoscopy because only the first-order fringe is present in the pattern. By comparing the birefringence behavior shown in Figure 2 a with that of Figure 6 b, we can identify the region where the anomalous effect occurs for the N_B^+ phase. A final remark can be made about the measurement of birefringences and simple inspection of Figure 3 c and e. Despite the fact that the patterns are similar, calculation of the birefringences takes into account the numerical angular positions of the conoscopic fringes along the two axes (1 and 2). This gives values of birefringences that characterize the phase.

The difficulty in aligning the sample in the N_B^+ phase by means of the orientational procedure usually employed in lyotropics in the presence of the magnetic field, as observed in
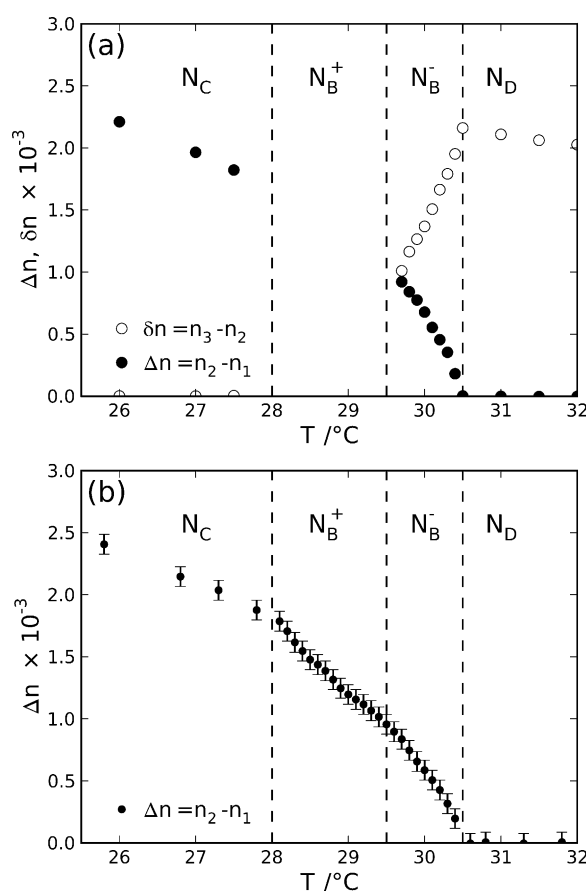

Figure 6. Sample d6 showing the anomalous behavior. a) Laser conoscopy experiment: birefringences [$\Delta n = n_2 - n_1$ (●); $\delta n = n_3 - n_2$ (○)], as a function of temperature. b) Polarized optical microscope with a Berek compensator experiment: birefringence [$\Delta n = n_2 - n_1$ (●)] as a function of temperature.

particular, in the conoscopy measurements, may be due to a decrease in $\Delta\chi$. The hydrocarbon chains are mainly responsible for $\Delta\chi$ in lyotropic nematics with hydrocarbon surfactants, which, in the presence of a magnetic field, orient preferentially perpendicularly to the magnetic field.[15,16] One can imagine two mechanisms that can lead to a decrease in $\Delta\chi$ for the

sample in this phase: 1) a decrease in ordering of the carbon chains in micelles due to the temperature change; and 2) assuming that the chains of the molecules in the bilayer are preferentially oriented perpendicularly to the magnetic field,[17] the number of molecules in the bilayer and in the caps that close the micelle, preventing contact of the inner part of the micelles with the solvent, are almost equivalent. Hypothesis 1 seems to be improbable because the anomalous behavior does not occur in mixtures d1 and d2. Let us discuss hypothesis 2 in more detail in the framework of the IBM model. In this context, the DDeOH molecules are mainly located in the flat part of the micelle and DDTMABr is mainly located in the more curved parts (the caps) of the micelles.[18] Because the number of carbon atoms in both aliphatic chains is the same, the contribution of both types of molecules to $\Delta\chi$ is expected to be equivalent. Considering the sketch of an orthorhombic micelle of Figure 1a, when the magnetic field is applied in the plane (α,β), due to the negative sign of $\Delta\chi$, molecules in the bilayer do not experience any torque due to $\vec{H}$. However, the molecules in the caps are not in an energetically favorable (orientational) configuration. Averaging the contributions from all molecules (flat surface and caps) may lead to a decrease in the mean $\Delta\chi$ of the sample in this phase. As previously discussed,[10] the micellar shape anisotropy changes as a function of the temperature, that is, the dimensions of the micelles change and give rise to particular shapes that trigger the orientational fluctuations which characterize each nematic phase. Our results indicate that, in the particular shape anisotropy that triggers the orientational fluctuations of the N_B^+ phase, the effective value of $\Delta\chi$ leads to the anomalous behavior observed in these particular mixtures. An almost equivalent number of carbon chains from the surfactant and cosurfactant in the flattest part and caps of the micelles seems to be important for this behavior. It is worth stressing that, in the case of the N_B phase, the magnetic field alone may orient just one of the phase axes.

To investigate the dimensions of micelles in the three nematic phases, SAXS experiments were performed with lyotropic samples placed in thin glass capillaries. Samples were oriented according to the procedure described above for laser conoscopy, and different geometries of the director (in the case of the uniaxial phases) or directors (in the case of the biaxial phase), with respect to the X-ray beam direction, were investigated. Figure 7a and b shows the SAXS patterns of the N_D (N_C) phase with the director $\vec{n}$ perpendicular (perpendicular) to the beam and perpendicular (parallel) to $\vec{H}$.
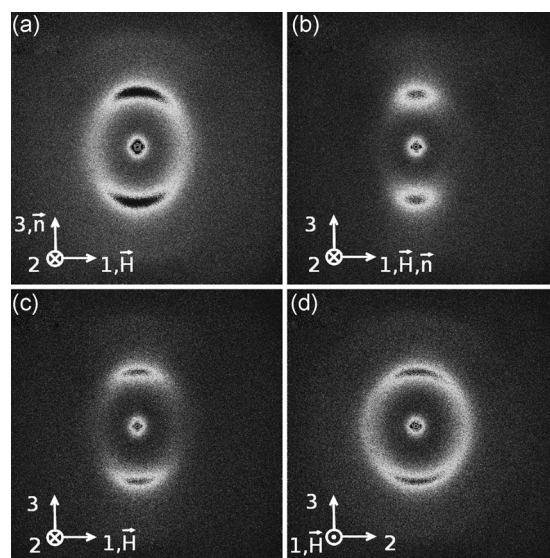

Figure 7. SAXS patterns of sample d3: a) N_D phase with the director $\vec{n}$ perpendicular to the beam and perpendicular to $\vec{H}$; b) N_C phase with the director $\vec{n}$ perpendicular to the beam and parallel to $\vec{H}$; c) N_B phase with $\vec{H}$ perpendicular to the beam; d) N_B phase with $\vec{H}$ parallel to the beam.

Figure 7c and d shows two planes of the biaxial reciprocal space image, with $\vec{H}$ perpendicular and parallel to the beam, respectively. Analysis of these patterns follows the procedure described in refs. [12, 19], and the dimensions of the micelles (A',B',C') in the N_B phase were evaluated (Figure 8). Let us briefly point out the main hypothesis made in this evaluation. The available volume per micelle $(V_a = s_1^{-1}s_2^{-1}s_3^{-1})$ is obtained directly from the band positions in the patterns, in which $s = (2\sin\theta)/\lambda$ is the scattering vector modulus, 2θ is the scattering angle and λ is the X-ray wavelength. In the case of the N_B
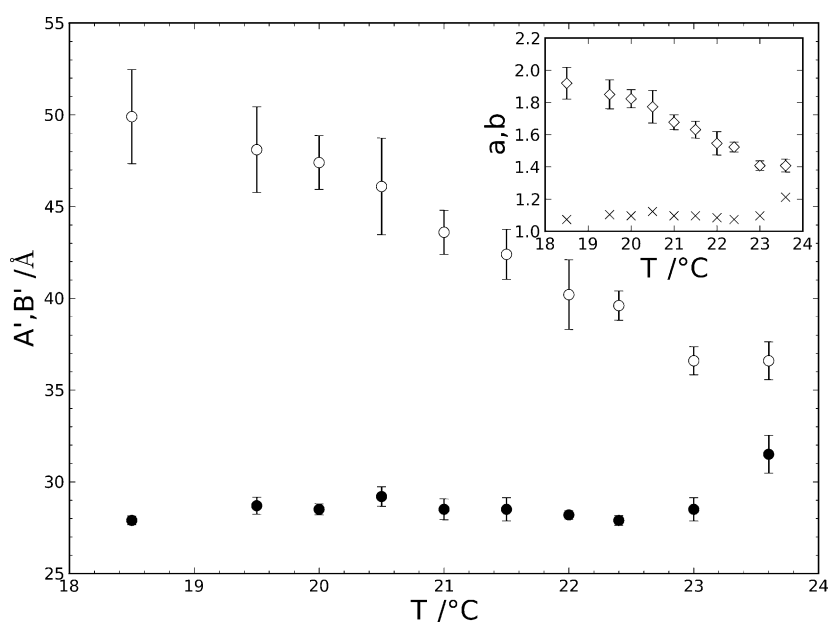

Figure 8. Dimensions of the micelles in the N_B phase domain [A' ($\circ$), B' ($\bullet$), $C' \approx 3$ nm] evaluated from the X-ray scattering vector modulus (s_i^{-1}; $i = 1, 2, 3$) for sample d3. In the inset, micellar shape anisotropies $a = A'/C'$ ($\diamond$) and $b = B'/C'$ ($\times$).

phase, s_i ($i=1,2,3$) values were associated directly with the repeating distance along the three orthogonal directions of the laboratory frame axes. In the case of the N_D phase, oriented with $\vec{n}\|3$, the scattering band in the plane (1, 2) is a result of the convolution of the bands originating from orientational fluctuations of the micelles around axis 3. In the case of the N_C phase, oriented with $\vec{n}\|1$, the scattering band in the plane (2, 3) is a result of the convolution of bands originating from orientational fluctuations of the micelles around axis 1. Because we are only interested in the micelle dimensions in the N_B phase, we did not proceed to the deconvolution procedure to obtain these dimensions in the N_D and N_C phase domains. To evaluate the micellar dimensions, we assume that, as in the case of the potassium laurate/decanol/water mixture, the water layer around the micelles has a thickness of about 1.8 nm, and the main amphiphile bilayer thickness is $C' \approx 3$ nm. The micellar shape anisotropy, defined as ($1{:}b=B'/C'{:}a=A'/C'$), is much smaller (see the inset in Figure 8) than that encountered in the case of the potassium laurate mixture, for which the micellar shape anisotropy was (1:2:3). In our mixture, it varied, approximately, from (1:1.1:1.8) near the N_C phase to (1:1.2:1.4) near the N_D phase. This small phase anisotropy supports the assumption that the number of amphiphilic molecules in the flattest region of the micelles is not so different from that of molecules in the caps. With the micellar dimensions evaluated as described above, we could calculate the percentage difference between the surfaces of the flattest part of the micelle ($A'\times B'$) plus the lateral cap ($A'\times C'$) and the end cap surface ($B'\times C'$) with respect to the total area of the flattest part and the caps. Figure 9 shows these results as a function of the temperature. Our results indicate that, when this number reaches values of the order of 50%, that is, the evaluated surface of the flattest part and the lateral cap of the micelle is about three times the surface of the end cap, the anomalous behavior regarding the loss of sample orientation takes place.
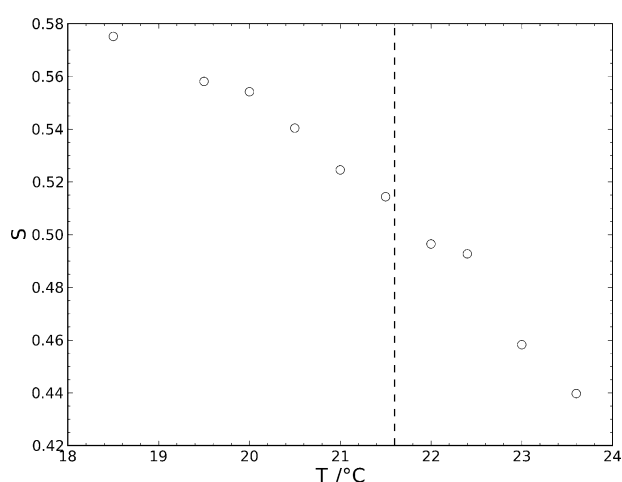
3. Conclusions

A new lyotropic mixture composed of DDTMABr/NaBr/DDeOH/water was investigated by using laser conoscopy, polarized light microscopy, and SAXS. This mixture presented three nematic phases. For a particular range of concentrations of DDTMABr, the sample in the N_B phase presented anomalous behavior in the presence of a magnetic field when compared with that of all other lyotropic mixtures reported in the literature: in the crossover between the N_B^- and N_B^+ phases, the sample orientation was lost, which prevented measurement of the birefringences. SAXS experiments allowed evaluation of the micellar dimensions in the framework of the IBM model, which revealed that the shape anisotropy them of was much smaller than that measured in the potassium laurate/1-decanol/water mixture. This led to a smaller value of the anisotropy of diamagnetic susceptibility, which could explain weakening of the magnetic coupling responsible for sample alignment.

Experimental Section

Samples

DDTMABr, NaBr, and DDeOH were purchased from Sigma, Carlo Erba, and Fluka, respectively. Lyotropic liquid-crystalline samples

Table 1. Compositions of the lyotropic liquid-crystalline mixtures. X is the concentration of the constituent (in percent mole fraction); N_D–N_B and N_B–N_C represent the phase transition temperatures from discotic to biaxial and from biaxial to calamitic nematic phases, respectively.

Sample	$X_{DDTMABr}$	X_{NaBr}	X_{DDeOH}	X_{H_2O}	N_D–N_B [°C]	N_B–N_C [°C]
d1	4.97	0.32	1.85	92.87	19.85	13.45
d2	5.01	0.32	1.85	92.82	22.40	17.45
d3	5.06	0.31	1.85	92.77	23.25	19.00
d4	5.10	0.32	1.85	92.73	26.25	22.40
d5	5.15	0.32	1.85	92.68	28.05	24.80
d6	5.20	0.31	1.85	92.64	30.45	27.90
d7	5.24	0.31	1.85	92.60	32.45	30.30

were made by dissolution of DDTMABr in a mixture of NaBr, DDeOH, and water, with appropriate compositions (Table 1). After weighing all constituents in a test tube, successive mixing by vortex and centrifugation were applied to obtain homogeneous samples. No heat was necessary in the preparation of the samples. To help the alignment process of the samples in the presence of the magnetic field, a small amount of water-based ferrofluid from Ferrotec was added, about 1 μL per 1 mL of the lyotropic mixture. We verified that, at these small concentrations of ferrofluid, the transition temperatures did not change, within our accuracy.

Laser Conoscopy

Laser conoscopy[10] was the technique used to measure the birefringences ($\Delta n, \delta n$) of the different nematic phases as a function of T. It was particularly useful because the birefringences of lyotropics were of the order of 10^{-3}, and samples about 2 mm thick were necessary to obtain accuracy in the order of at least 10^{-4} in these

Figure 9. Evaluation of the percentage difference between the surfaces of the flattest part of the micelle ($A'\times B'$) plus the lateral cap ($A'\times C'$) and the end cap ($B'\times C'$) with respect to the total area of the flattest part and caps: $S=[(A'\times B'+A'\times C')-(B'\times C')]/[(A'\times B')+(B'\times C')+(A'\times C')]$. The vertical dashed line indicates the crossover from N_B^+ to N_B^-.

measurements. Another advantage of this technique comes from the fact that, at a given temperature, both birefringences were simultaneously measured.

The laboratory frame axes were chosen as follows: two orthogonal axes 1 and 2 defined the horizontal plane; axis 3 was perpendicular to this plane and parallel to the laser beam propagation direction. A static magnetic field ($H = 3.05$ kG; Walker Sci. electromagnet), parallel to axis 1, helped in the orientation of the samples. Lyotropic samples were placed in a cell made of two circular optical glasses and a glass O-ring, which left a liquid-crystalline film 2.5 mm thick. The experimental setup had a HeNe laser ($\lambda = 632.8$ nm), a Neocera LTC-21 temperature control with a precision of $0.01\,°C$, and a Julabo refrigerated/heating water-bath circulator with a precision of $0.01\,°C$.

The orientation of the N_D and N_B phases was a crucial aspect of the technique. To obtain high-quality conoscopic patterns, it was essential to have well-oriented samples. To obtain well-oriented N_D and N_B samples, we rotated the sample ($\pm 30°$) several times around axis 3 in the presence of $\vec{H}$. After this procedure, inspecting the symmetry of the conoscopic pattern allowed the quality of the sample orientation to be checked and measurement of the birefringences. This procedure was repeated at each temperature. In the case of the N_C phase, the sample was left at rest in the presence of $\vec{H}$. More details may be found in ref. [1].

Polarized Light Microscopy

A Leitz Orthoplan-Pol microscope was used to observe the liquid-crystalline textures. Samples were encapsulated in rectangular flat glass microslides, 300 μm thick, placed in an INSTEC temperature controller device. A magnetic field of about 300 G was applied to the sample in the plane perpendicular to the light propagation direction.

Small-Angle X-ray Scattering

The SAXS experiments were performed on a Bruker AXS NanoStar system with a VANTEC-2000 detector and a Xenocs X-ray microfocus source and beam delivery system. The sample to detector distance of 66.7 cm was measured with a silver behenate sample.

Lyotropic sample d3 was put in a glass capillary tube of 1.5 mm diameter. The sealed capillary was placed in a temperature-controlled sample holder with a precision of $\pm 0.1\,°C$. Two permanent magnets were attached to the sample holder, which generated a magnetic field of about 800 G in the sample position.

A monodomain of each nematic phase was achieved with an alignment procedure similar to that described in the laser conoscopy experiment. The laboratory reference system was defined with axis 3 along the vertical direction and parallel to the capillary long axis, axis 1 parallel to the magnetic field direction, and axis 2 perpendicular to both axes.

Measurements at different temperatures were performed on the lyotropic sample. At a given temperature, the sample was irradiated in both relative orientations of the magnetic field direction with respect to the X-ray beam direction, that is, parallel and perpendicular. Each diffractogram took 10 min for data acquisition.

Prior to analysis, spatial, nonlinear, and beam center corrections were applied to the data, as far as background (water) and detector noise subtractions. For background subtractions, frames for water at different temperatures were measured.

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