Behavior of the director reorientation time in glass surfaces of lyotropic liquid crystals in the nematic to biaxial transition

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(Received 21 December 1994; revised manuscript received 23 May 1995)

The surface reorientation process of a lyotropic liquid crystal is investigated in the calamitic (N_c) and biaxial (N_{bx}) nematic phases. It is observed that the surface reorientation process is faster in the biaxial phase and the characteristic time of this process τ_s increases linearly with increasing temperatures, in both nematic phases. The results obtained are discussed and compared to the predictions of a model assuming the gliding of the director at the boundary surfaces. [S1063-651X(96)11905-X]

PACS number(s): 61.30.Gd

I. INTRODUCTION

Nematic liquid crystals can be oriented by external fields (electrical or magnetic) and the equilibrium configuration of the director is strongly related to the boundary conditions. The boundary surfaces play an important role in the liquid-crystal orientation, but the microscopical interactions, even in the most simplest case, are not completly understood [1]. Many theories have been developed to explain surface effects but there are discrepancies between the predictions of different models and different interpretations of experimental results [1]. Despite these difficulties, a phenomenological approach, based on the macroscopic behavior, has obtained some success in the interpretations of experimental results [1–4].

In a lyotropic liquid crystal, a slow reorientation process induced by a magnetic field has been observed. It has been proposed that this process is related to the reorientation of the boundary layers with a gliding of the director at the boundary surfaces [5,6]. If the surface reorientation process is complete, there is no relaxation when the magnetic field is turned off, because the reorientation of the sample is homogeneous. In this paper we investigate the reorientation process of a lyotropic liquid crystal due to a magnetic field in the nematic calamitic (N_c) and biaxial (N_{bx}) phases.

II. EXPERIMENT

The lyotropic sample consists of potassium laurate (28.1 wt %), decanol (7.1 wt %), and water (64.8 wt %) that presents the three nematic phases; $N_d - N_{bx}(15\,^\circ\mathrm{C})$, $N_{bx} - N_c(23\,^\circ\mathrm{C})$, where N_d is the nematic discotic phase. The transition temperatures are determined by measuring the birefringence, as is shown in Fig. 1. The sample is encapsulated in microslides (Vitro Dynamics) 200 μm and 4 mm wide. The inner surface of these microslides was examined in a interferential microscope. The surfaces are plane and no irregularities greater than 0.2 μm were detected and no surface treatment was applied.

The laboratory frame axes are defined with the boundary surfaces at $z=0$ and $z=d$. The director $\vec{n}$ is, initially, in the xy plane everywhere and parallel to the length of the microslide. A magnetic field $\vec{H}$ is applied parallel to the x direction, at 45 ° from $\vec{n}$ (Fig. 2). The choice of an angle of 45 ° eliminates the degeneracy present in a Fréedericksz geometry, when $\vec{H}$ is applied perpendicular to $\vec{n}$.

The orientation process is observed by measuring the transmittance of the sample between crossed polarizers, as a function of the time, when $\vec{H}$ is applied. The polarizers are parallel to x and y axis, respectively, and the light beam is parallel to z. The sample is placed in a thermostat, whose accurancy is about 0.05 °C. Further details about the experimental setup are given in Ref. [6].

III. THEORY

A. Gliding process

When the magnetic field is applied to the uniform oriented sample, the director orients parallel to the magnetic field in the bulk. The reorientation of the sample is uniform except in the thin boundary layers of thickness ξ, where ξ is the magnetic coherence length. The characteristic time of this process is expected to be $\tau_v = \gamma/(\chi_a H^2)$, [7] where γ is the rotational viscosity and χ_a is the anisotropy of the magnetic susceptibility. The rotational viscosity of lyotropic liquid crystals in the nematic phases varies from 1 to 10 P and χ_a is about 10^{-8} (cgs) [8–11]. The bulk reorientation time has been measured for different lyotropic mixtures [8,9], and

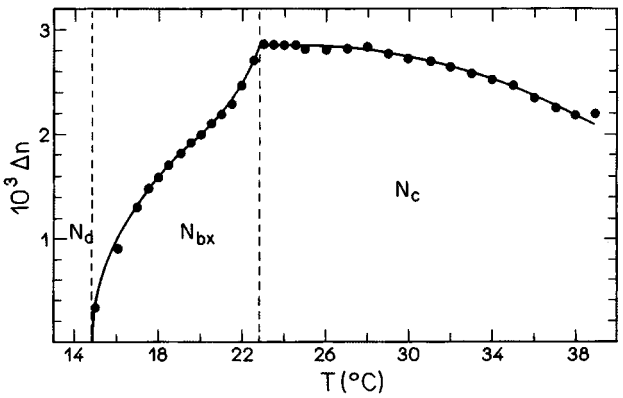

FIG. 1. Birefringence of the lyotropic sample exhibiting the temperature range of the discotic (N_d), biaxial (N_{bx}), and calamitic (N_c) nematic phases. The transition $N_{bx}-N_c$ occurs at $T=23\,^\circ$C.

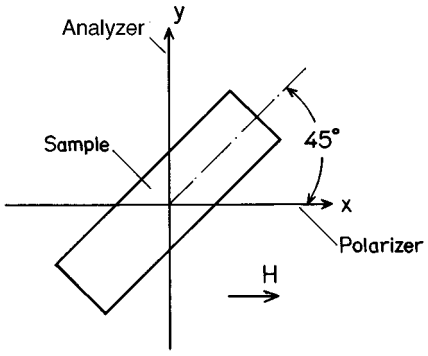

FIG. 2. Definition of the laboratory frame axes. At $t=0$ the director is at 45 ° from the x axis and the magnetic field is turned on.

a value of $\tau_v=36$ s is reported for a nematic calamitic phase of potassium laurate, decanol, and water (KL-DeOH-H_2O) with a magnetic field H of 10 kG [8].

In termotropic liquid crystals the existence of a smectic layer at the boundaries has been proposed [11,13] and there is some experimental evidence to sustain this hypothesis from measurements of the surface order parameter [14] and x-ray scattering [15]. To explain the surface reorientation process observed in lyotropic liquid crystals, in a previous paper we proposed that at the boundary surfaces, there is an amphiphilic bilayer, similar to a lamellar structure. The microscopical structure of the lamelar phase in lyotropic liquid crystal was investigated by Holmes and Charvolin [16] using x-ray and nuclear magnetic resonance. They propose that the bilayer is not a continuous amphiphilic medium, but consists rather of amphiphilic islands surrounded by water.

The bulk applies an elastic torque to the boundary surface layer of thickness ξ, due to their different orientations. In the bilayer, the amphiphilic islands can be considered as anisotropic objects that can also be reoriented by a magnetic field if their surface dimensions are comparable to the magnetic coherence length ξ. Let us call θ_s the angle between the director in the bulk and the mean orientation of the amphiphilic islands at the interface, and a and b are their surface dimensions. The viscous torque per object is $\Gamma_0=ab\xi\gamma\dot{\theta}_s$. If there are N objects at the surface and A is the boundary surface area, then the torque per unit area at the boundary surface layer may be expressed as

$$\Gamma_v=(Nab/A)\xi\gamma\dot{\theta}_s=\alpha\xi\gamma\dot{\theta}_s. \tag{1}$$

This torque is equilibrated by the elastic torque coming from the bulk, which is (per unit area)

$$\Gamma_e=K\frac{\partial\theta}{\partial z}=-K\frac{\theta_s}{\xi}. \tag{2}$$

The equilibrium condition is given by

$$\gamma\alpha\dot{\theta}_s=-K\frac{\theta_s}{\xi^2}. \tag{3}$$

From the solution of the balance of the torque equation one obtains the characteristic time of surface reorientation process, τ_s,

$$\tau_s=\frac{\gamma\alpha}{\chi_a H^2}. \tag{4}$$

The values of γ and χ_a are dependent on the temperature. The parameter α represents the number of objects in a unit area of the boundary surface and may depend on the temperature and also on the magnetic field.

B. Transmittance of the sample

The transmittance of the nonuniform anisotropic sample can be calculated by dividing the sample into many thin layers and considering each layer as an anisotropic homogeneous medium. Let us suppose that there are m layers of thickness ζ_j and θ_j is the angle between the director and the x axis. The incident electric field **E** divides into two components, one parallel to the director (E'_p) and the second perpendicular to the director (E'_t). In a matrix notation, the components of **E** are

$$\begin{pmatrix} E'_p \\ E'_t \end{pmatrix}=\begin{pmatrix} \cos\beta_j & \sin\beta_j \\ -\sin\beta_j & \cos\beta_j \end{pmatrix}\begin{pmatrix} E_p \\ E_t \end{pmatrix}, \tag{5}$$

where E_p and E_t are the components of **E** in the previous layer and $\beta_j=\theta_j-\theta_{j-1}$. The propagation through the layer introduces a phase shift between the two orthogonal polarizations, which will be transformed into E''_p and E''_t

$$\begin{pmatrix} E''_p \\ E''_t \end{pmatrix}=\begin{pmatrix} 1 & 0 \\ 0 & e^{i\delta} \end{pmatrix}\begin{pmatrix} E'_p \\ E'_t \end{pmatrix}, \tag{6}$$

where $\delta_j=2\pi\zeta_j(n_o-n_e)/\lambda$, and λ is the light wavelength and n_o and n_e are the ordinary and extraordinary refraction indices, respectively.

If E_{tm} and E_{pm} are the components of **E** after m layers, the amplitude of the electric field transmitted through the analyzer is

$$E_{pm}=E_{tm}\cos\beta_{m+1}-E_{pm}\sin\beta_{m+1}, \tag{7}$$

where $\beta_{m+1}=\varphi-\theta_m$, and φ is the angle between the analyzer and the x direction and θ_m the maximum distortion angle. The intensity of the transmitted light will be

$$\tilde{I}=E^*_{pa}E_{pa}. \tag{8}$$

Normalizing $\tilde{I}$ to obtain $I_{max}=1$ and $I_{min}=0$, we get

$$I=\frac{\tilde{I}-\tilde{I}_{min}}{\tilde{I}_{max}-\tilde{I}_{min}}. \tag{9}$$

The transmitted light depends on the orientation of the director through the sample, $\theta(z)$. In this analysis we assume that the sample is uniformly oriented parallel to the magnetic field, except in the boundary layers of thickness ξ. Allowing the gliding of the director in the boundary layers, the transmittance of the sample will depend on θ_s:

$$I[\theta_s(t)]=I(t), \tag{10}$$

where $\theta_s(t)$ is obtained from the solution of Eq. (3):

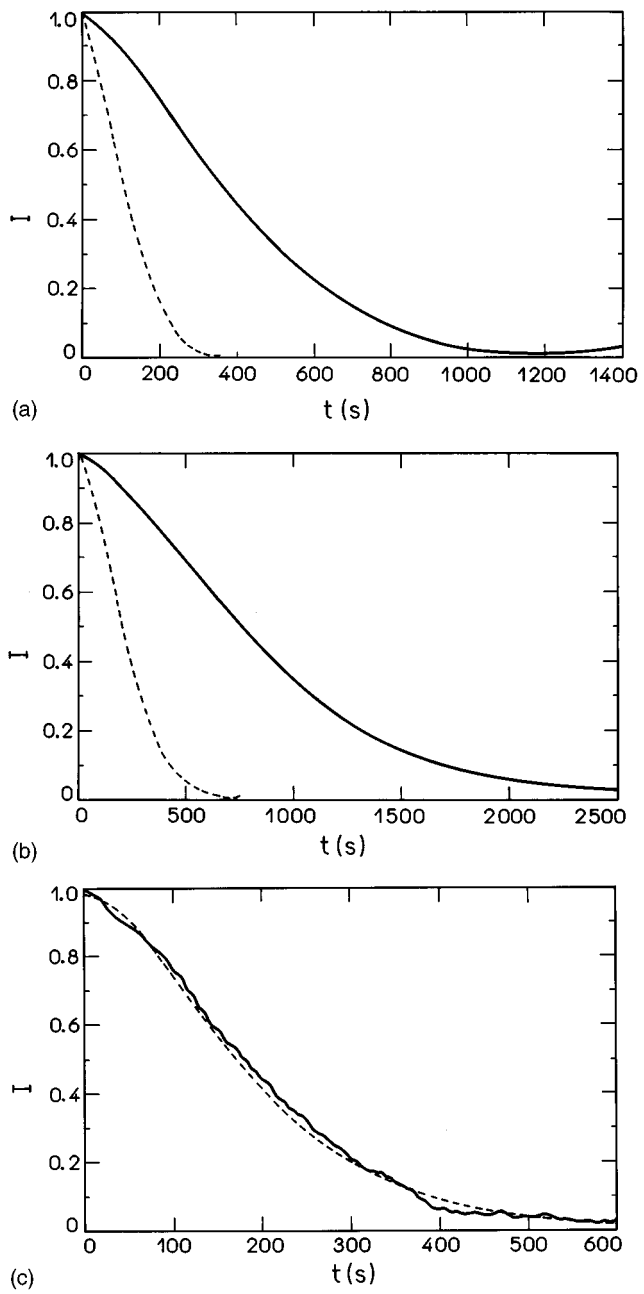

FIG. 3. Experimental curves of transmittance for $H=10$ kG (broken line) and $H=5$ kG (solid line), in the N_{bx} (a) and N_c (b) phase. The temperatures are 21.5 °C and 33 °C, respectively. (c) The broken line represents the transmittance calculated for $\tau_s=280$ s. The experimental curve (solid line) is obtained with $T=25$ °C and $H=10$ kG.

$$\theta_s(t)=\theta_m\exp(-t/\tau_s). \tag{11}$$

According to the geometry of the experiment (Fig. 2) the transmittance is maximum for $t=0$, when H is turned on and decreases with time. The birefringence of the sample is measured by an independent experiment and τ_s is the fitting parameter to the experimental curves.

IV. RESULTS AND DISCUSSION

According to the model presented here, in lyotropic liquid crystals there are two reorienation processes: one with a characteristic time τ_v, related to the reorientation of the director in the bulk, and the second related to the reorientation of the boundary surface layer, with a characteristic time τ_s larger than τ_v.

In this experiment we cannot detect the bulk reorientation process because τ_v is of the same order of magnitude of the time necessary to turn on the magnetic field; that is, about 15 s. However, in a previous experiment, using the same technique of measuring the transmittance and a magnet that could be turned on faster, we estimated $\tau_v\sim$ 20 s for $H=2$ kG and $\tau_v\sim$ 5 s for $H=4.5$ kG [17]. This is in good accordance with the values reported in the literature for this process [8,9].

We measured the transmittance of the samples for different values of H and different temperatures. Typical experimental curves are shown in Fig. 3. The magnetic field is turned on at $t=0$ and the transmittance starts to decrease, reaching a minimum. The final equilibrium configuration corresponds to a uniform oriented sample, with the director parallel to the x axis. The uniformity of the orientation is comparable to what is observed for $t<0$. This orientation remains and there is no relaxation process.

If the magnetic field is turned off before the transmitted intensity reaches a minimum, we observe that the mean orientation of the sample is not yet parallel to the x axis. There is a twist due to the different orientations of the bulk and boundary layers. Therefore, if $H=0$, there will be a relaxation process of the twist distortion [6]. The final orientation of the sample depends on the time with the magnetic field turned on [5].

The orientation process is faster for higher vales of H, as is seen in Fig. 3(a). Comparing the curves obtained, with the same values of H, but in the different nematic phases, we observe that in the biaxial phase, the reorientation process is faster than in the uniaxial phase. The fitting to an experimental curve is illustrated in Fig. 3. The transmittance is calculated using the model of a three-layered sample, discussed in the preceding section. Despite the simplifications of the model, the fitting to the experimental curve is quite good and the uncertainty in the values of τ_s is about 10%.

A. Effects of the temperature

The values of τ_s obtained for different temperatures are plotted in Fig. 4, with $H=5$, 8, 10, and 11 kG. It is noticed that τ_s increases with increasing temperatures in both biaxial and uniaxial phases. Within the accuracy of our measurements, we observe that the increase of τ_s is linear with the temperature and faster in the biaxial range. The measurements of τ_s in the biaxial phase close to the transition to the discotic phase are particulary difficult because small fluctuations of temperature disturb the orientation of the sample. For $T-T_c>-4$ °C the uncertainty of τ_s become greater than 10%. However we can observe the qualitative behavior of τ_s in the calamitic and biaxial nematic phases.

In the uniaxial phase, the surface reorientation time increases slowly compared to the increasing in the biaxial phase. This behavior is observed for low and high magnetic fields; however, the effects of the temperature are more pronounced with a low magnetic field ($H=5$ kG). The ratios $\Delta\tau_s/\Delta T$ are shown in Table I, for different values of H, in

TABLE I. Dependence of the ratio $\Delta\tau_s/\Delta T$ (s/°C) with the magnetic field in the N_{bx} and N_c phases.

H (kG)	N_{bx}	N_c
5	97	18
8	20	5
10	29	3
11	33	7

the uniaxial and biaxial domains. In the biaxial phase, $\Delta\tau_s/\Delta T$ is about five to six times larger than in the uniaxial phase. With increasing values of H, the ratio $\Delta\tau_s/\Delta T$ becomes smaller and seems to reach a constant value; about 30 s/°C in the biaxial phase and $\sim$ 5 s/°C in the uniaxial phase.

The effects of the temperature on the surface reorientation process can be qualitatively analyzed by considering the microscopical structure of the uniaxial and biaxial nematic phases. X-ray diffraction experiments in lyotropic liquid crystal [18,19] have shown that the amphiphilic aggregates preserve the same shape and are locally organized in a lamellar structure in the three nematic phases. The micelles are biaxial, with dimensions of about 85×50×26 Å, where the smaller dimension corresponds to the bilayer thickness. The correlation length perpendicular to the bilayer is about six to eight times the micellar dimension, without any significant change at the biaxial to uniaxial nematic transition [20]. This point is consistent with the requirement that the local structure remains the same in the three nematic phases.

In this view, the different nematic phases are just a macroscopical consequence of different orientational fluctuations. In the biaxial nematic phase the fluctuations are restricted to small oscillations around the principal axes of symmetry, fixed in the micelle (Fig. 5). There is a correlation between the orientation of the micelles in three directions of the space. The uniaxial nematic phases are generated when the orientational fluctuations are full rotations around the director. Naturally, the micellar dimensions vary with concentration and temperature; however, these variations are negligible at the second order $N_{bx}-N_c$ transition.

When the magnetic field is applied to the lyotropic liquid crystal in the N_{bx} and N_c phases, the micelles in the bulk orient with their longest dimension parallel to $\vec{\mathbf{H}}$. If the interactions in the bulk are comparable to the nematic-surface interactions the orientation of the bulk can be transmitted to the adjacent micelles in the boundary surface layers. Our experiment shows that this surface reorientation process is faster in the N_{bx}. Small variations of the temperature produce a more significant variation of τ_s in the N_{bx} phase than in the N_c phase. We associate this behavior with the different orientational fluctuations in the biaxial and uniaxial nematic phases.

In the biaxial phase, there is a long-range orientational order along the three directions of space. The distortions imposed onto a small domain propagate to the neighbor domains in the three directions of the space. When the temperature is increased towards the transition to the N_c phase, the amplitude of the orientational fluctuations around the m axes becomes larger, up to $T>T_c$, when there is no orientational order along the ℓ and n axes. The increasing amplitude of the orientational fluctuations can be seen as a thermal noise,

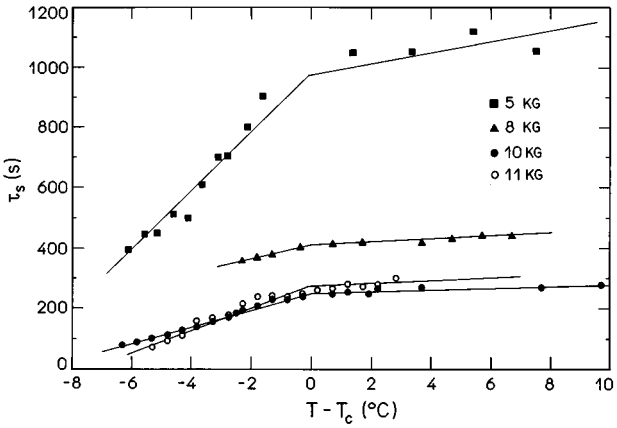

FIG. 4. Dependence of τ_s on the temperature in the biaxial and uniaxial domains with different values of magnetic field.

which hinders the propagation of the elastic torque through the boundary layers.

Another factor that affects the propagation of the elastic torque is the average volume of a micelle; that is, $V_{bx}=ABC$, in the biaxial phase. In the calamitic phase, due to orientational fluctuation around the m axis, the average volume of a micelle is $V_c=AB^2$. Therefore, the orientation of a micelle in the calamitic phase involves a greater volume than in the biaxial phase.

In the biaxial phase, close to the transition to the discotic phase, the orientational fluctuations around the l axis become larger. If the sample is cooled down small homeotropic domains appear that propagate through the sample after some time. More experimental work is being done in order to determine τ_s in this range of temperature, where the orientational fluctuations play an important role.

In the domain of the calamitic phase, the increasing of the temperature does not induce a significant effect on the orientational fluctuations, except close to the transition to the isotropic phase, when the orientational order along the director is lost.

B. Effects of the magnetic field

In Fig. 6, τ_s is plotted as a function of H, for different values of $T-T_c$, in the uniaxial [Fig. 6(a)] and biaxial [Fig. 6(b)] domains. We observe that it is possible to fit a straight line to the experimental points, in the uniaxial and biaxial domains, except for $T-T_c=-6$ °C, where the fitting is very poor. The exponents of H, $\tau_s\sim H^{-\omega}$, for different values of

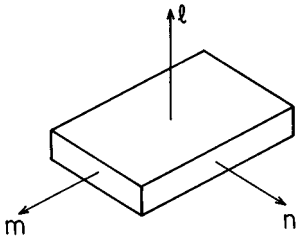

FIG. 5. Schematic representation of the amphiphilic aggregates. A, B, and C are the dimensions of the micelle along the l, m, and n axes, respectively.

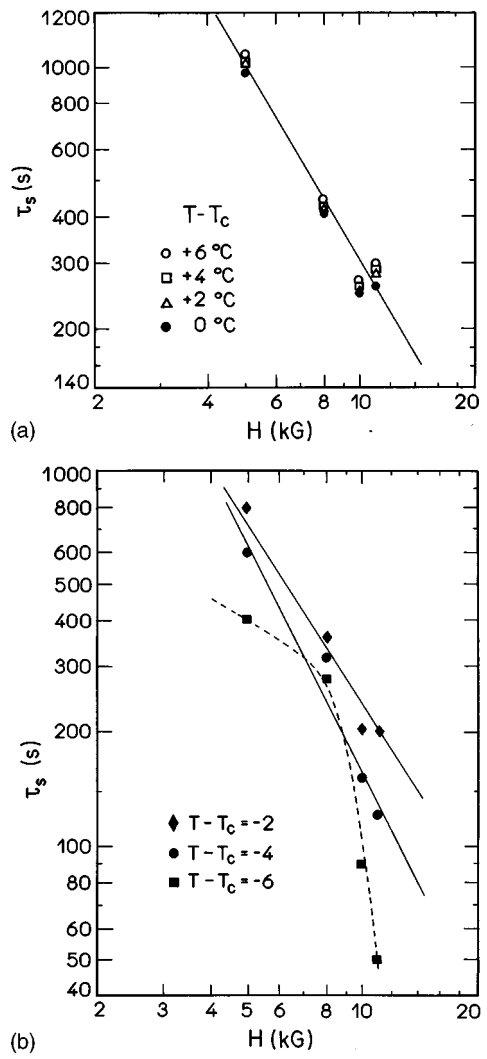

FIG. 6. Dependence of τ_s on H, in the uniaxial (a) and biaxial (b) phases.

$T-T_c$ are presented in Table II with the respective values of τ_s. We observe that τ_s is proportional to $H^{-1.8}$ in the uniaxial phase. Within the experimental error in the determination of the exponent, which is about ± 0.3, this result is in good accordance with what is expected from Eq. (4) ($\tau_s \sim H^{-2}$). In the biaxial phase, Eq. (4) still holds, within the temperature range of 4 °C below T_c, as is clear from Fig. 5(b).

For a given temperature, the values of γ and χ_a are constant in Eq. (4). Assuming $\gamma = 1$ P and $\chi_a = 10^{-8}$ (cgs units) and with the experimental values of τ_s, we investigate the behavior of the parameter α with the magnetic field. We assume that γ and χ_a are constant in the temperature range considered and we calculate $\alpha(H)$ for different values of $T-T_c$. The results are illustrated in Fig. 7 and we notice that, in the uniaxial phase, α is almost constant for $H \leqslant 10$ kG, with a mean value $\bar{\alpha} \cong 260$. With magnetic fields higher than 10 kG, the value of α increases very fast and jumps to $\alpha \sim 350$ for $H = 11$ kG. This behavior is observed for different temperatures in the uniaxial domain and also at the transition temperature, $T-T_c = 0$ °C [Fig. 6(b)].

TABLE II. Dependence of τ_s (s) on H for different values of $T-T_c$. The sample is the biaxial phase for $T-T_c < 0$. The last column represents the exponent of H, with $\tau_s \sim H^{-\omega}$.

$T-T_c$ (°C)	5 kG	8 kG	10 kG	11 kG	ω
−6	400	280	90	50	
−4	600	320	150	120	2.0
−2	790	360	200	200	1.8
0	970	410	250	270	1.7
2	1010	420	255	280	1.8
4	1050	430	260	290	1.8
6	1080	440	270	300	1.8

The values of α in the uniaxial phase, shown in Table III, are about three times smaller than what was found in a previous work, with the same lyotropic mixture, but with different composition [6]. In that case, the phase sequence was different (isotropic-calamitic nematic-isotropic) and α was approximately constant for H between 3 and 14 kG.

In the biaxial domain, for $T-T_c = -2$ °C, α is almost constant, although there is a tendency for α to be slightly larger for $H = 8$ kG. This behavior is present in the two curves with constant temperatures, $T-T_c = -2$ °C and $T-T_c = -4$ °C. The curves $\alpha(H)$ must be examined with some care, because we assumed the same values of γ and χ_a for all the temperatures. This does not change the shape of the curve $\alpha(H)$, but may cause only a shift of the curves.

The rotational viscosity of a lyotropic liquid crystal has been measured as a function of the temperature, in the uniaxial nematic phases [10]. The results obtained showed that in the N_c phase, there is a rapid decrease of γ when the temperature is lowered approaching the transition to the biaxial phase and that the decreasing of γ is faster than the order parameter. However, there are no measurements in the biaxial phase and it was not possible to obtain an expression $\gamma(T)$. If we take into account the dependence of γ with the temperature and assume that χ_a is proportional to the birefringence, in the uniaxial phase, the curves $\alpha(H)$ would be shifted to higher values of α for values of $T-T_c$ close to the transition to the biaxial phase. We still expect α to be smaller for lower temperatures, since the decrease of γ is faster than the order parameter, and χ_a is often assumed to be proportional to the birefringence (which in lyotropics is proportional to the order parameter).

TABLE III. Dependence of α on H for different values of $T-T_c$. The values listed were calculated assuming that τ_s is proportional to H^{-2}, $\gamma = 1$, P, and $\chi_a = 10^{-8}$ (cgs units).

$T-T_c$ (°C)	5 kG	8 kG	10 kG	11 kG
−4	150	205	150	145
−2	198	230	200	242
0	243	262	250	327
2	253	269	255	339
4	263	275	260	351
6	270	280	270	363

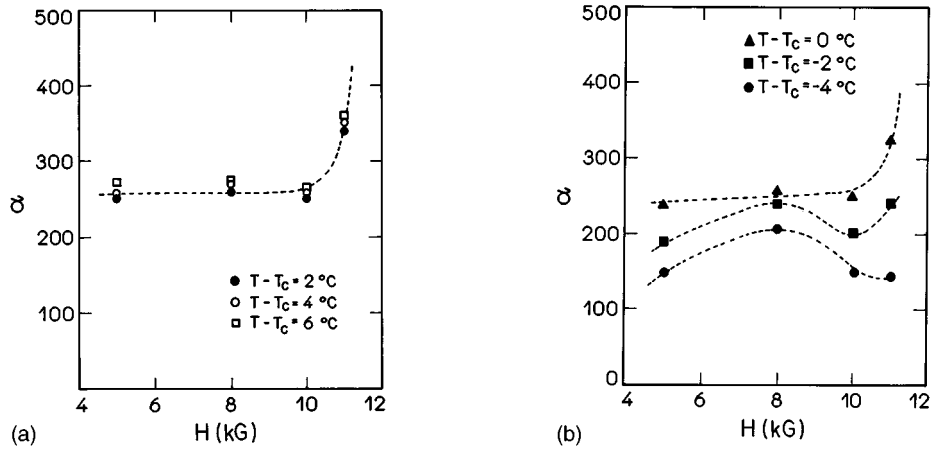

FIG. 7. Dependence of the parameter α on the magnetic field in the calamitic (a) and biaxial (b) nematic phases. The broken lines are only a guide to the eyes.

In the biaxial phase, for $T-T_c=-6\,^{\circ}\mathrm{C}$, the sample is in a temperature range closer to the transition to the discotic nematic phase (N_d). In the N_d phase the anisotropy of the magnetic susceptibility is negative and the director orients parallel to H. Therefore, we expect χ_a to become very small when the temperature is lowered approaching the transition to the N_d phase. The decreasing of γ and χ_a close to the transition would not allow a discontinuous increasing of α close to the N_d transition. However, the explicit dependence of γ and χ_a with the temperature is required to obtain more precise values of α and its dependence on the temperature.

V. CONCLUSIONS

In this work we investigate the behavior of τ_s in the calamitic uniaxial and biaxial nematic phases, for different intensities of applied magnetic field. Within the temperature ranges considered, we observed a linear dependence of τ_s on the temperature, which is more pronounced in the biaxial phase and for low intensities of the magnetic field.

The experimental results show that the model proposed, allowing the gliding of the director at the boundary surfaces, can be extended to the biaxial phase, within a range of 4 °C below the transition temperature. Close to the N_d phase ($T-T_c=-6\,^{\circ}\mathrm{C}$) the predictions of the model [Eq. (4)] are not valid, probabily due to the orientational fluctuations around the director, that become larger in the N_d phase and degenerate one of the three axes of symmetry present in the N_{bx} phase [17].

The parameter α is related to the microscopical structure of the boundary surface layer and it is known that the dimensions of the micellar aggregates are very influenced by the composition of the sample [18]. Thus, the differences observed in the values of α and its behavior may be related to the different composition of the samples.

The fluid dynamics of biaxial nematics have been examined in detail by many authors [21–25]. The analysis leads to 12 viscosities and 12 independent elastic constants for a incompressible biaxial nematic [20]. If the fluid is considered to be compressible 15 viscosities are required to describe the flow and hydrodynamical properties [22]. Nevertheless, the form of the expression for the elastic energy density with so many elastic constants is too complex for practical use. Even in the case of uniaxial nematics, when only three independent elastic constants are required, the solutions of the equilibrium equations are usually prohibitive and the one constant approximation is often very useful.

Although the analysis presented in this work is qualitative, it is possible to obtain some insight into the surface orientation process and its relation with the microscopical structure of the lyotropic nematic phases. It is important to remark that more experimental work is required to determine how γ and χ_a depend on the temperature in the nematic phases, especially in the biaxial phase. This would allow a more precise determination of the parameter α in the different nematic phases, a better description of the microscopical structure at the boundary surface layers and its interactions with the bulk and the substrate.

The authors are very grateful to Professor A.M. Figueiredo Neto for his critical reading and helpful discussions and to FAPESP and CNPq for the financial support.

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