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LYOTROPIC LIQUID CRYSTALS UNDER SIMPLE COUETTE AND OSCILLATORY SHEAR

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Abstract Small angle neutron scattering (SANS) has been utilized to investigate the flow properties of the discotic micellar isotropic (I), nematic (N) and lamellar (L_α) phases in aqueous solutions of cesium perfluoro-octanate. Under simple shear, no preferred orientation was observed in the I phase. The N phase aligned with the nematic director along the shear gradient velocity, providing the first evidence for a positive value of the viscosity parameter, α_2. The L_α phase oriented with lamellae parallel to the shear plane. A reorientation of the director near the N-L_α transition was witnessed upon cooling from the N phase at a constant shear rate and is attributed, primarily to a change in the value of α_2 as a result of increasing lamellar correlations in the nematic phase. The application of oscillatory shear induced significant shifts in the phase boundaries, including nematic-like order some 7 K into the quiescent I phase.

INTRODUCTION

In recent years, the small angle neutron scattering (SANS) and x-ray diffraction techniques have been employed to probe the dynamical properties of phase transitions in condensed matter systems under shear flow. Significant flow deformation has been realized in colloidal suspensions[1], di-block copolymers[2,3], surfactant solutions[4] and monomer[5-8] and polymer[9] liquid crystals. Shear flow couples to fluctuations within a system and is expected to significantly alter the character of a phase transition and in some cases, transition temperatures are predicted to approach their mean-field values[10]. Interesting results such as shifting of phase boundaries[2,3,8], new critical points[6] and reentrant behavior[5] have been seen in polymer and liquid crystal systems. These effects have been attributed to a reduction of fluctuations as a result of shear flow and may provide insight into the influence of fluctuations on continuous phase transitions.

While some studies of the flow properties of rod-like, thermotropic liquid crystals have been performed, little experimental work has been done[11] on liquid crystals with disk shaped molecules. The flow properties of discotic molecules have been the subject of several theoretical investigations[12], the predictions of which have yet to be tested. We report the results of an experimental investigation into the effects of a couette shear field on the *I*, *N* and L_α phases, of a lyotropic liquid crystal, composed of discotic micelles.

FLOW PROPERTIES OF LIQUID CRYSTALS

In the presence of a shear field, there are three possible configurations for the nematic director, as defined in figure 1 for discotic molecules, along with the characteristic x-ray or neutron scattering patterns in the L_α phase. With the shear velocity, $\mathbf{v} = v\mathbf{x}$, and the gradient velocity ∇v in the **y** direction, the 'a' configuration has $\mathbf{n} \perp (\mathbf{v}, \nabla v)$ plane, which will be referred to as the shear plane. The 'b' configuration has $\mathbf{n} \parallel \mathbf{v}$ while in the 'c' configuration, $\mathbf{n} \parallel \nabla v$. The configuration obtained in a shear experiment depends upon the net balance of torques acting on **n**.

There are several theoretical approaches[8,13,14] for the description of the flow properties of rod-like, thermotropic nematic liquid crystals. The most commonly employed approach is that of Ericksen, Leslie and Parodi[13] (ELP). The predictions of ELP theory agree well with experiment in the *N* phase. However, in systems with a smectic-A (*sm-A*) phase, the growth of pretransitional smectic fluctuations in the *N* phase (near the transition) give rise to new forces which alter the behavior of the nematic director under flow. Bruinsma and Safinya[10], expanding upon a model proposed by McMillan[14], have found that a fluctuation correction must be added to the ELP theory in order to account for this new behavior.

In the limit of high shear, the equation of motion in the *N* phase involves only the viscous torque on **n** :

$$\Gamma_v = -\boldsymbol{n} \times [\gamma_1 \delta \boldsymbol{n} / \delta t + \gamma(\alpha_2 n_y, \alpha_3 n_x, 0)], \tag{1}$$

where α_2 and α_3 are the Leslie viscosity parameters, defined in terms of the rotational and shear viscosities, γ_1 and γ_2 as, $\alpha_2 = (\gamma_2 - \gamma_1)/2$ and $\alpha_3 = (\gamma_2 + \gamma_1)/2$ such that $\alpha_3 > \alpha_2$. In a conventional nematic, consisting of rod-like particles, α_2 is negative and the orientation of **n** depends upon the temperature dependent sign of α_3. In the *N* phase, far from any

underlying *sm-A* phase, α_3 is also negative and the condition of flow alignment requires that **n** lie in the (**v**, ∇**v**) plane at a small angle, θ, with respect to **v**, such that[10] :

$$\tan\theta = \pm\sqrt{\frac{\alpha_3}{\alpha_2}}. \qquad (2)$$

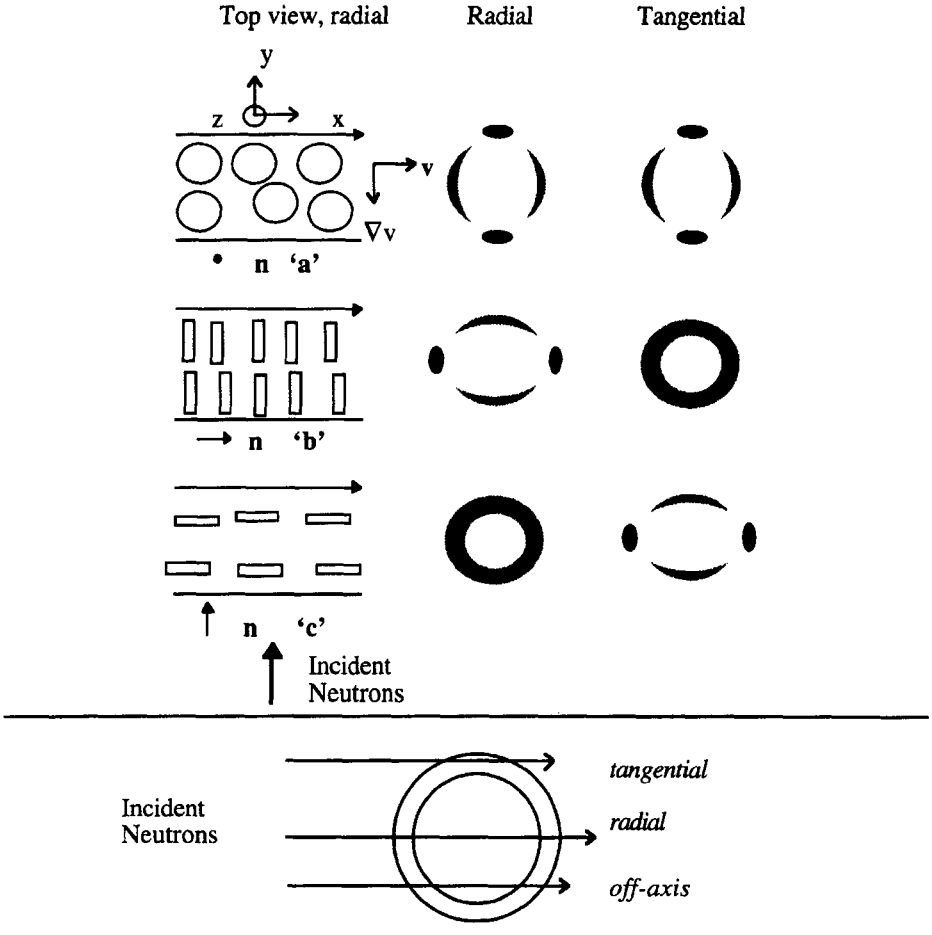

FIGURE 1 The three possible director configurations (a, b, c) for discotic micelles under shear flow along with their characteristic scattering pattern in the radial and tangential geometries. Bottom : Top view of shear cell depicting the *tangential*, *radial* and *off-axis* geometries.

Steady-state solutions require the positive sign and θ is found to be small (typically ~5°, see Fig. 2), which is the 'b' orientation. As the *sm-A* phase is approached, an additional torque due to a flow-induced-fluctuation force renormalizes α_3 to give $\alpha_3^R = \alpha_3 + [\frac{\pi k_B T}{2d^2}]\frac{\tau}{\xi_{\|}}$ [10], where d is the smectic periodicity and $\xi_{\|}$ is the smectic correlation length in the direction of **n**. Consequently, α_3^R increases and becomes positive and the director reorients perpendicular to the shear plane, thus adopting the 'a' orientation.

The theory proposed by Carlsson[12], describing the flow properties of discotics, is an extension of the ELP theory. Based upon molecular symmetry and calculations, by Volovik[12], of the reactive parameter ($\lambda = [\alpha_2+\alpha_3]/[\alpha_2-\alpha_3]$), a reversal of the roles of α_2 and α_3 as compared to rod-like systems is anticipated for disk-like objects. This reversal of roles for discotics leads to **n** being aligned along the flow gradient in the *N* phase. The key to Carlsson's results is the possibility of a positive value of α_2 (and also α_3) for nematics consisting of discotic molecules. While this does not present an unphysical situation, it goes against the common assumption that α_2 must always be negative in the *N* phase. A change in the sign of α_2 near the *N-A* transition is expected and an analogous flow behavior for rods and disks is predicted.

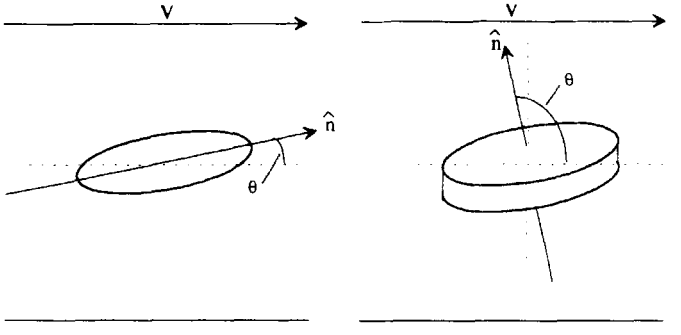

FIGURE 2 Rod-like and discotic molecules under shear flow (from reference 12).

With both α_3 and α_2 positive, the negative sign in Eq. [2] is needed to ensure stability against fluctuations in the orientation of n[12]. Flow alignment then requires **n** to lie at a large angle ~ 90° with the shear velocity. This is the 'c' configuration as described previously. Figure 2 depicts flow alignment for both rod-like and disk-like molecules. Though the angle of alignment is quite different in the two cases, it can be seen from the

figure that the physical situation is very similar. In both cases, it is the longer dimension of the molecule which aligns along the shear flow, suggesting that steric forces play an important role in determining the resulting flow properties of a molecule[12,15].

Currently, no theoretical attempt to consider the effects of smectic fluctuations in the nematic phase of a discotic system has been made. If the analogy between rod-like and discotic systems is further extended, one might expect fluctuations to renormalize the α_2 viscosity parameter ($\alpha_2 \rightarrow \alpha_2^R$).

EXPERIMENTAL

SANS measurements were performed on the NG3 beam line equipped with a 30 meter SANS spectrometer at the National Institute of Standards and Technology's Cold Neutron Research Facility (NIST-CNRF) in Gaithersburg, Maryland. Data were collected, with a two-dimensional-area detector, during three different experimental runs using neutrons of 5.0 and 5.5 Å wavelengths with $\Delta\lambda$ of 15%. For the radial and off-axis configurations, pinhole collimation was used with a sample aperture of 1.2 cm diameter while a vertical rectangular aperture (1.27 cm x 0.1 cm) was used in the tangential configuration. Simple and oscillatory shear flow were obtained by use of the couette shear cell available at NIST. The couette shear cell consisted of two concentric quartz cylinders with a 0.5 mm gap between them. Sample temperature was controlled by a circulating water bath. Temperature stability for earlier runs was ±0.5 K, while for later runs the stability was ±0.3 K. The cell's center could be translated perpendicular to the neutron beam, enabling us to conduct scattering experiments in the radial (neutrons incident along ∇v), the off-axis (neutrons incident oblique to both $\mathbf{v}$ and ∇v) and the tangential (neutrons incident along $\mathbf{v}$) configurations (Fig. 1), thus permitting a three-dimensional determination of the director orientation. Shear rates ranged from 0 to 5835 s^{-1}. Solvent evaporation was minimized with the use of a lid on the shear cell, sealed with an O-ring. Also, counting times were kept short, usually between 5 and 10 minutes to reduce the effects of any concentration drift. Transition temperatures were monitored during the experiment and the sample was replaced with a fresh one if transition temperatures changed significantly.

The mixture of CsPFO and H_2O provided sufficient natural contrast ($\Delta\rho = 4.8 \times 10^{10}$ cm^{-2}), so that no deuteration was required. Data were reduced, using conventional methods and put in *I vs. q* format by taking 20° sector averages in the horizontal and vertical directions of the detector (see Fig. 6). Anisotropy in the resulting data indicated a

preferred orientation of **n**. Experiments were performed at constant temperature while varying γ and as a function of temperature at constant γ in order to examine the behavior of discotic micelles under flow. For ease of interpretation, all temperatures will be expressed as ΔT (= T - $T_{NL\alpha}$), the distance from the N-L_α transition.

RESULTS AND DISCUSSION

Simple Shear

In the isotropic phase of the CsPFO and water system, no preferred orientation, under flow, was observed. This is in contrast to other system[2-6,9] which have shown a shift in phase boundaries under flow.

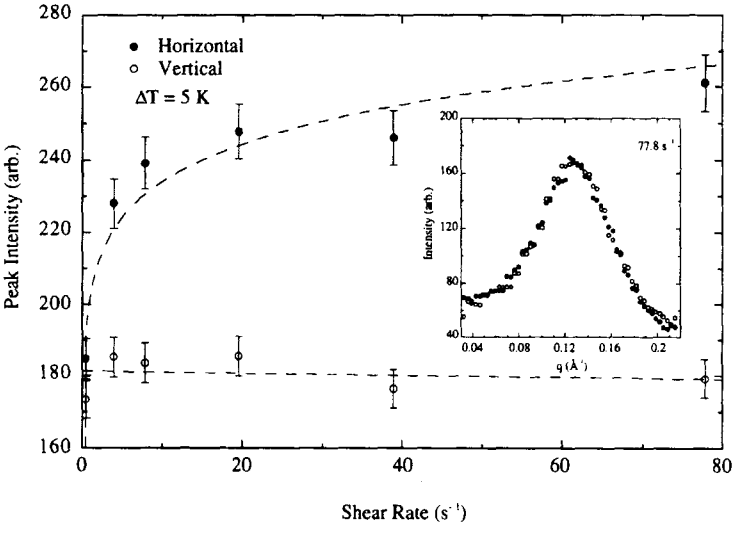

FIGURE 3 Peak intensity vs. shear rate (γ), obtained from analysis of the sector averages in the off-axis position. Inset : Radially obtained sector averages showing two equal intensity peaks and confirming the 'c' orientation.

Measurements performed in the off-axis geometry in the N phase revealed a scattering ring which became increasingly anisotropic with increasing γ and developed into two diffuse peaks in the horizontal direction. This is indicative of **n** being parallel to the shear gradient which is the 'c' configuration. Figure 3 depicts the peak intensity as a function of shear rate for this data and demonstrates the anisotropic growth. The inset to figure 3 shows data obtained in the radial geometry at γ = 77.8 s^{-1}. The appearance of

two equal intensity peaks supports the conclusion of **n** lying along ∇v, as, in the 'c' configuration, with the shear cell in the radial position, neutrons are incident along the axis of a disk (Fig. 1). The scattering peak then corresponds to the diameter of the micelles and gives rise to an equal intensity ring. These results are in contrast to those of rod-like TLC in which **n** aligns along v ('b' configuration) in the *N* phase, but consistent with the predictions of Carlsson for discotics and then represent the first experimental evidence for positive values of the α_2 and α_3 viscosity parameters in the *N* phase.

Orientational behavior of the discotic micelles as a function of temperature at a constant shear rate was also investigated. Three dimensional plots are shown (Fig. 4) for data taken in the off axis geometry with $\gamma = 97.3\ s^{-1}$. At $\Delta T = 5$ K (Fig. 4a), just inside the *N* phase, an anisotropic scattering pattern, appearing as two well defined crescents in the horizontal direction, can be seen. This is indicative of the 'c' orientation, as anticipated

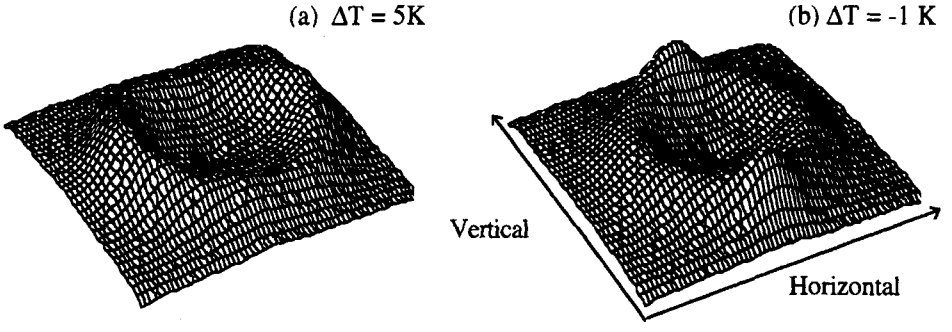

FIGURE 4 Three dimensional plots with the shear cell in the off-axis position at a constant shear rate of 97.3 s^{-1} as the L_α phase is approached from above.

from the previous results. As temperature was reduced toward $T_{NL\alpha}$, this pattern began to appear more uniform, indicating a mixture of the 'a' and 'c' orientations. As the system was cooled below the *N*- L_α transition (Fig. 4b), the scattering pattern again appeared highly anisotropic, but now with peaks in the vertical direction. This behavior is indicative of a 'flip' transition from the 'c' to the 'a' configuration. The peak intensity, determined by sector averaging, is plotted (Fig. 5) as a function of temperature for the off-axis geometry. As seen in the figure, the horizontal intensity is greater than the vertical intensity initially, as expected for the 'c' configuration. This intensity decreases as the temperature was decreased and the vertical sector intensity increases, indicating the reorientation. This is corroborated by the radial data (inset of Fig. 5) which shows equal

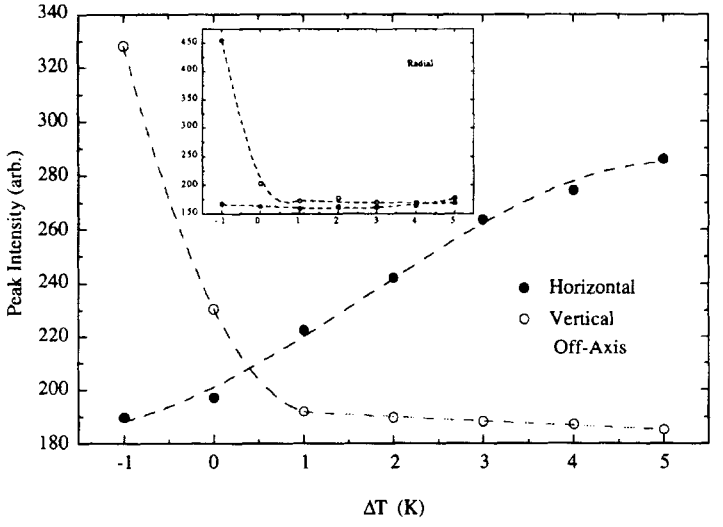

FIGURE 5 Peak intensity vs. temperature for off-axis data ($\gamma = 97.3\ s^{-1}$). Here, the "flip" transition is easily seen in the decrease of the horizontal intensity, as the L_α phase is neared, while the vertical peak intensity increases. Inset : Radially obtained peak intensity as a function of temperature.

intensity at high temperatures and then an increase of the vertical intensity at the transition as would be the case for the 'a' orientation.

The flip transition found here is analogous to the behavior seen for 8CB[5] and suggests a change of sign and renormalization of the α_2 viscosity parameter, due to divergent lamellar fluctuations. This behavior has not been theoretically explored for discotics and is somewhat surprising. In rod-like systems, layers which form with **n** along ∇v or **z** will not be tilted by flow[5,10] and thus give rise to no restoring force and subsequent viscosity renormalization. For disk-like systems aligned as such, shear may move one edge of a disk relative to the other, causing tilt and the resulting restoring force or the individual micelles may begin to distort. Both of these situations could be relieved by the observed reorientation. Additional theoretical and experimental work is needed to answer these questions.

The effect of increasing shear rate at a constant temperature within the lamellar phase was also studied. Figure 6 shows three dimensional plots at different shear rates along with the results of sector averaging, two degrees below the *N*- L_α transition. As shear was increased, two partial rings, corresponding to the diameter and thickness of a micelle emerged (Fig. 6a). The two rings have an anisotropic distribution of intensity, indicating a preferred alignment of the lamellae defined by the discotic micelles. The outer most ring

developed in to two sharp peaks in the vertical direction with increasing γ, while the inner ring took the form of two well defined crescents in the horizontal direction (Fig. 6b). This picture is consistent with **n** being aligned out of the shear plane, along the

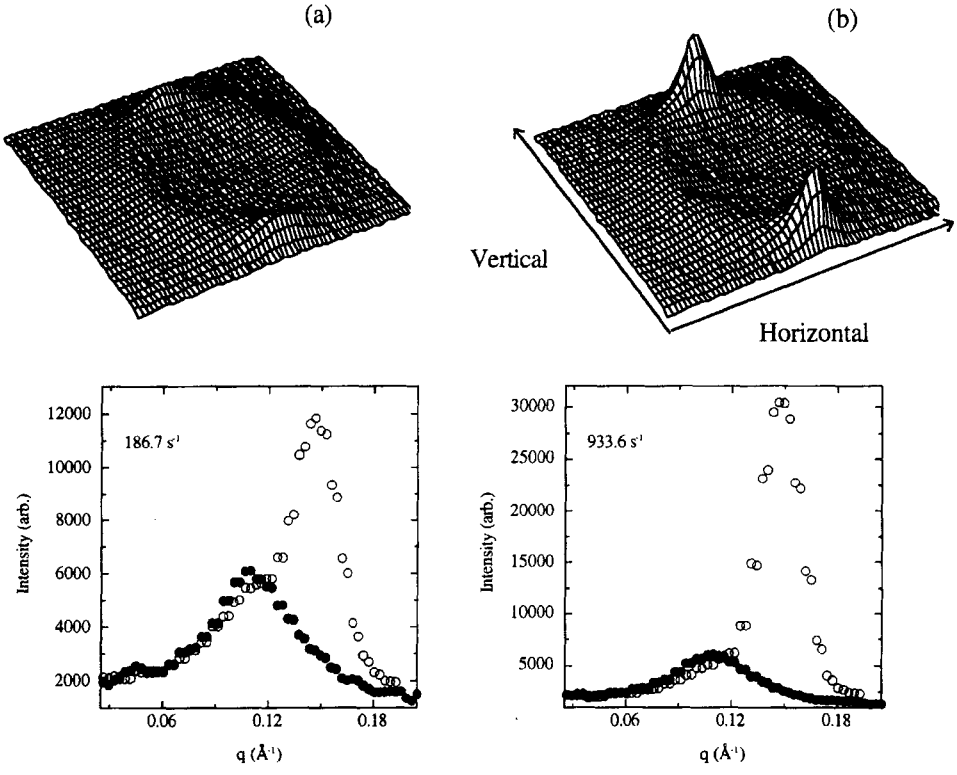

FIGURE 6 Three dimensional plots of radial data in the L_α phase (ΔT = -2 K) along with their sector average. With increasing γ, improved alignment is seen.

z direction, the 'a' configuration. The peaks centered at q = ± 0.146 Å^{-1} became sharper and more intense with increasing γ, indicating that the system became better aligned along this direction, up to 1000 s^{-1}, where the intensity began to saturate. The position of the peaks indicates a layer spacing of 43 Å and the crescents centered at ± 0.113 Å^{-1} indicates an intermicellar spacing within a lamella of 56 Å. Both are in good agreement with independent x-ray measurements[16]. The shear induced alignment was found to be reversible, as a reduction in γ was accompanied by a corresponding reduction in the intensity of the two peaks, with little hysteresis (Fig. 7a). Noticeable in the vertical sector averages (Fig. 6) is a shoulder to the main peak, centered at the same position as the crescents in the horizontal direction. The appearance of this shoulder suggests that some

of the micelles may still remain in the 'c' orientation, forming a boundary layer, and making the flip transition incomplete. Measurements made in the tangential configuration confirmed this notion. Sector averages revealed (inset of Fig. 7b) a sharp peak in the horizontal direction, indicating the presence of lamallae perpendicular to the shear plane. The intensity of this peak (Fig. 7b) was seen to decrease with increasing γ, while the

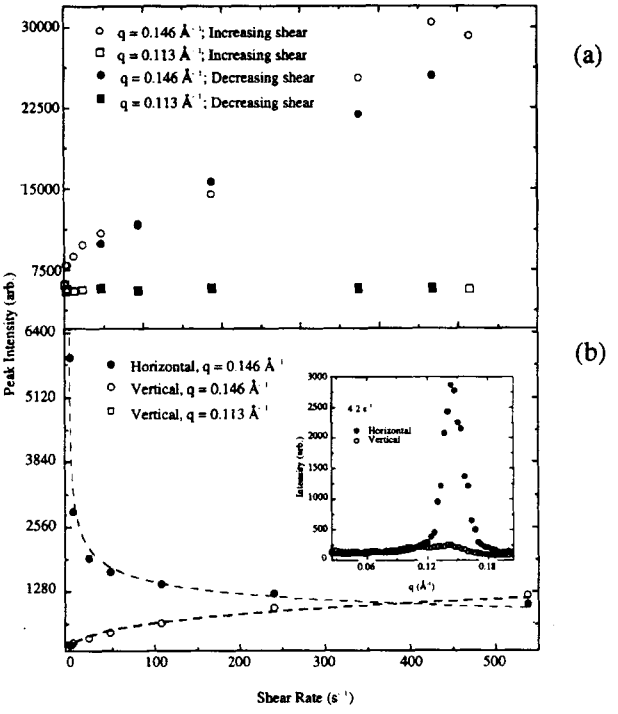

FIGURE 7 Peak intensity as a function of shear rate for the radial and tangential data in the L_α phase. Inset : Radial average of tangential data.

vertical peak increased, indicating a shear-dependent reorientation of the lamallae forming the boundary layer. The presence of a significant number of lamallae oriented perpendicular to the shear plane suggests the cell wall is influencing the orientation and suppressing the flip transition within the boundary layer.

Oscillatory Shear

The temperature dependence of the peak intensity, under oscillatory shear at 5835 s^{-1} and 200% strain is displayed in figure 8. In comparison to the simple shear results, the qualitative features observed under oscillatory shear are the same, just shifted upward in temperature. As seen from the tangential results (Fig. 8a), preferred, nematic-like order

was observed some 7 K into the quiescent isotropic phase, indicating a shift in the *I-N* phase boundary which was not seen under simple shear. Such enhancements of effects[3]

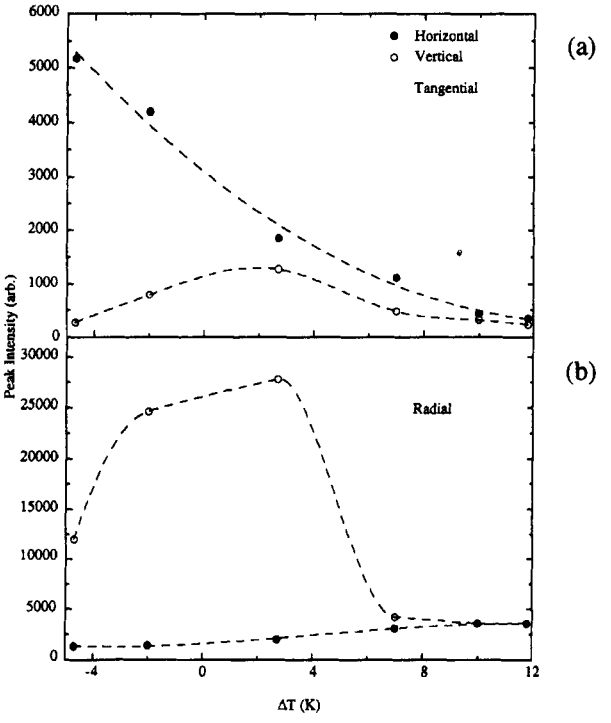

FIGURE 8 Peak intensity as a function of temperature under oscillatory shear. Nematic order is seen some 7K into the quiescent isotropic phase.

under oscillatory shear have also been seen in block copolymer systems where the order-disorder transition was seen to approach its mean-field value. The shear-induced shifts of phase boundaries can be attributed to the damping of critical fluctuations which become stronger as the transition is approached. A similar shift was seen in the N-L_α phase boundary as can easily be seen in comparing the radial data measured as a function of temperature for both the oscillatory and simple shear cases (Figs. 8b and 5, respectively). The peak intensity vs. temperature plots for the two cases show the same shape, only shifted in temperature. In comparing the two plots, the points at which the vertical intensity shows dramatic increase (indicating the onset of flipping) are separated by ~ 7 K. The decrease of intensity observed upon further decrease of temperature suggests that after flipping from the 'c' to the 'a' orientation, the disks begin to flip back. This behavior was not seen under simple shear, but given the large shift in the phase boundary found under oscillatory shear, it may lie outside of the range of temperature explored. Data taken

in the tangential configuration confirms this behavior as the horizontal intensity is seen to increase throughout the temperature range.

SUMMARY

The influence of a shear field on the orientation of the discotic micelles formed by a lyotropic liquid crystal system in its N and L_α phases has been studied. Under simple shear, the N phase was found to adopt the 'c' configuration in accordance with theoretical expectations, providing the first direct evidence of a positive value for α_2. The L_α phase aligned very well with increasing shear in the 'a' configuration. Evidence of a flip transition of the nematic director suggests a renormalization of α_2 and a change in its sign as a consequence of divergent L_α (smectic) correlations. This behavior has not been theoretically explored for discotic molecules, but is analogous to that of rod-like TLC. Significant shifts in the I-N and N-L_α phase boundaries were observed under oscillatory shear, but the qualitative flow behavior remained the same.

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