Shear-induced orientational effects in discotic-liquid-crystal micelles

Boualem Hammouda
Room E151, Building 235, National Institute of Standards and Technology, Gaithersburg, Maryland 20899

Joseph Mang and Satyendra Kumar
Department of Physics, Liquid Crystal Institute, Kent State University, Kent, Ohio 44242
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Small angle neutron scattering was used to investigate the orientational ordering of a lyotropic mixture of cesium-perfluoro-octanoate (CsPFO) in water under simple Couette and oscillatory shear. The discotic-liquid-crytstal micelles were found to orient mostly parallel to the moving shear cell walls (i.e., vertically). A partial "flipping" of the orientation was observed in the smectic phase, whereby lamellae were seen to orient horizontally. Oscillatory shear produced orientational effects as well as shear-induced shifts of the phase transition boundaries. Interesting competing "bulk" and "wall" effects were also observed.

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INTRODUCTION

Present thermotropic liquid-crystal display devices are based on the alignment of the nematic phase. Much effort is being made to develop devices that use the smectic-*C* phase. Lyotropic liquid crystals readily form the smectic-*C* phase and are much simpler model systems to investigate. The cesium-perfluoro-octanoate (CsPFO) system, for example, is of particular interest because it exhibits micellar nematic and smectic (neat soap) phases over an unprecedented range of concentration and temperature [1–3]. Aqueous solutions of CsPFO are characterized by isotropic, nematic, and smectic phases of discotic micelles with well defined sizes (diameter and thickness). The small angle neutron scattering (SANS) technique was used to investigate the orientational ordering of a lyotropic mixture of CsPFO in water (55% concentration) under shear. These micelles become orientationally and positionally ordered without any appreciable change in their shape and size. Previous investigations have shown that when an externally applied magnetic field [3] or shear field [4] is used to orient the sample, the scattering patterns are highly asymmetric and allow the monitoring of the nematic director orientation in the various phases.

A number of investigations used *in situ* shear along with scattering techniques to monitor the rheology of various "soft" materials. These have included shear-induced crystal-like ordering of colloidal suspensions [5], alignment of thermotropic liquid crystals [6], of liquid crystal polymers [7], and of wormlike micelles [8] as well as morphological changes in various copolymer systems [9,10]. To our knowledge, this is the first time that oscillatory shear has been applied to lyotropic liquid crystals in conjunction with a scattering technique.

EXPERIMENTS

The SANS measurements were performed on the NG3 instrument at the National Institute of Standards and Technology Cold Neutron Research Facility (NIST-CNRF) in the following configuration: wavelength of 5 Å, wavelength spread of 15%, sample-to-detector distance of 1.85 m, and tight presample collimation in order to avoid resolution effects. Measurement times ranged from 5 to 20 minutes. The Couette flow shear cell used in these experiments [11] has two concentric vertical cylindrical parts (the stator and the rotor) made out of quartz (6-cm diameter and 2-mm thickness) with a 0.5-mm gap for the sample. The stator comprises a hollow aluminum block (inside the quartz cylinder) for temperature control (using a circulating bath) and allows for a horizontal neutron beam to be used either radially or tangentially to the shear cell (see Fig. 1). Whereas the "radial" geometry measures scattering wave vectors (**Q**) in the vertical plane formed by the shear and neutral directions, the "tangential" one yields information in the shear and shear gradient directions. A circular aperture (1.27-cm diameter) was used with the radial geometry while a vertical rectangular aperture (1.27 cm × 1 mm) was used with the tangential geometry. Two modes of shearing (simple Couette and oscillatory shear) have been used for various shear rates (up to 4000 s^{-1} for steady simple shear and at a fixed shear rate of 5835 s^{-1} and a strain of 200% for the oscillatory shear) and a range of temperatures. For the CsPFO-water concentration used (55% CsPFO), the isotropic-to-nematic and nematic-to-smectic phase transition lines are estimated (optically) to be 52 and 47 °C, respectively. Due to the high natural contrast of the liquid-crystal micelles with respect to water, no deuteration was necessary. Measurements were taken at three main sample temperatures corresponding to the isotropic phase (54 °C), the nematic phase (49.7 °C), and the smectic phase (45 °C). A few measurements at other temperatures well into the isotropic phase (58.8 and 57 °C) or deep into the smectic phase (42.3 °C) have also been taken. SANS data were reduced using standard methods (empty cell and blocked beam subtractions, transmission correction, etc.) and 20° sector averages were formed in order to obtain scattered intensities [$I(Q)$ data] in the vertical and horizontal directions for both the radial and tangential geometries.

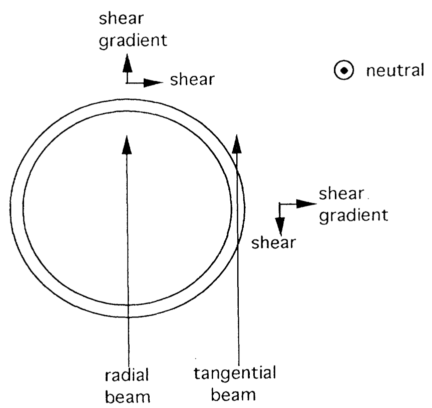

FIG. 1. Top view of the neutron beam geometry with respect to the cylindrical shear cell.

RESULTS

The $I(Q)$ scattering patterns are consistently characterized by peaks located at $Q_1=0.113$ Å^{-1} and $Q_2=0.146$ Å^{-1} (Fig. 2 shows two examples). These peaks are either prominent or suppressed in the horizontal or vertical directions depending on the alignment of the disklike micelles. The low-Q "inner peak" (Q_1) represents the center-to-center interdistance of micelles that lie parallel to each other in an edge-to-edge configuration (see, for example, the A configuration in Fig. 3) while the high-Q "outer peak" (Q_2) represents the interdistance between micelles that are face-to-face (see, for example, the B configuration in Fig. 3 along the velocity direction). The heights of these four peaks (two in the vertical and two in the horizontal directions) are essential clues used to infer discotic alignment, i.e., to make a choice among the three reasonable alignment possibilities shown in Fig. 3. A few observations and results are discussed here.

For simple Couette shear, no shear-induced shifts of the phase transition lines were observed to within our temperature control accuracy (0.3 °C). This means that the outer peak remains a uniform ring for the quiescent isotropic temperature [Fig. 4(a)], but yields distinct spots along with a weaker halo in the nematic and smectic phases. In the following, anisotropy of the outer ring will be monitored through an anisotropy ratio (ratio of the maximum intensity in the horizontal to that in the vertical directions). In the tangential beam geometry, this anisotropy ratio is constant with shear rate $\dot{\gamma}$ in the nematic phase [Fig. 4(b)] and decreases with shear rate in the smectic phase [Fig. 4(c)]. Figure 4(c) shows that the anisotropy ratio R obeys a power law in the smectic phase (at 45 °C) as $R \sim \dot{\gamma}^{-0.59\pm0.03}$ in the tangential geometry. It is interesting to note that the tangential anisotropy ratio in the smectic phase, R_s, is higher than that in the nematic phase, R_n, at low shear rates, but $R_s < R_n$ at high shear rates [compare Figs. 4(b) and 4(c)]. Based on these observations, one can conclude that simple shear can distinguish clearly between the three phases.

Still with simple shear, monitoring the variation of R with temperature instead (at fixed shear rate), one can see that the nematic phase is characterized by discotic micelles aligned parallel to the moving shear cell walls (C configuration in Fig. 3) while, in the smectic phase, a fraction of the micelles have a perpendicular orientation (A configuration in Fig. 3). This is observed as an increase of the value of R at 49.7 °C in the tangential geometry case in Fig. 5(a). This "flipping" of the smectic layers was observed for other systems [4,6,9]. It can be attributed primarily to changes in the values of the Ericksen viscosity parameters α_2 and α_3 [4,6].

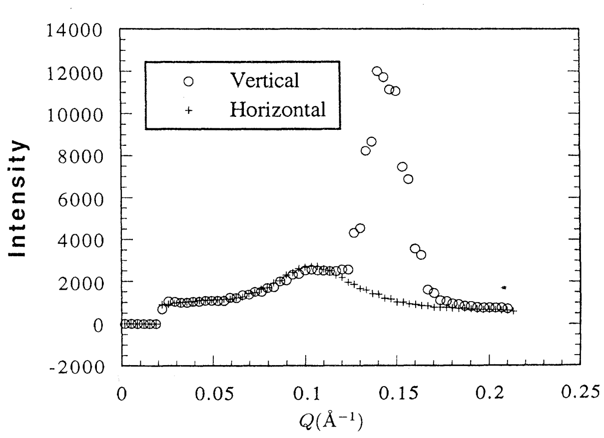

FIG. 2. Typical SANS intensity averaged along vertical and horizontal sector slices for oscillatory shear (5835 s^{-1}) at 42.3 °C, with a radial beam geometry. Both the inner ($Q_1=0.113$ Å^{-1}) and outer ($Q_2=0.146$ Å^{-1}) peaks are visible in the vertical direction.

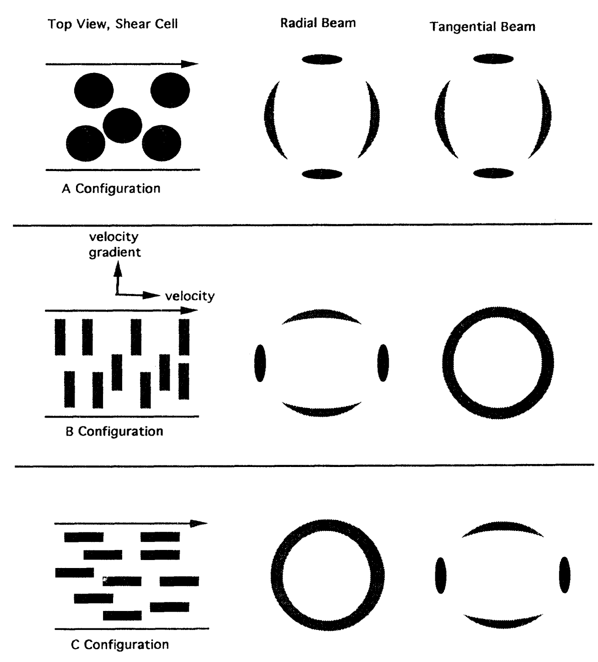

FIG. 3. Schematic view of the three possible (so-called Miesowicz) orientations of the discotic micelles under shear. Only pure C configuration and mixtures of A and C configurations have been observed.

In the case of oscillatory shear with fixed shear rate (5853 s^{-1}), the same trend is pretty much preserved but with a temperature shift upward [see Fig. 5(b)]. Shear-induced shifts of phase transition temperatures can be attributed to the damping of critical fluctuations that become stronger close to transition lines. In block copolymers, for example, the order-disorder transition temperature is also raised and becomes closer to its mean-field prediction when reciprocating shear is applied [9]. The value of R at 54 °C (tangential) corresponds to the maximum discotic alignment parallel to the shear cell walls and is reminiscent of the quiescent nematic phase even though this temperature corresponds to the quiescent isotropic phase. Note that in this case, shear-induced alignment ($R \neq 1$) persists even at 58.8 °C. The flipping pro-

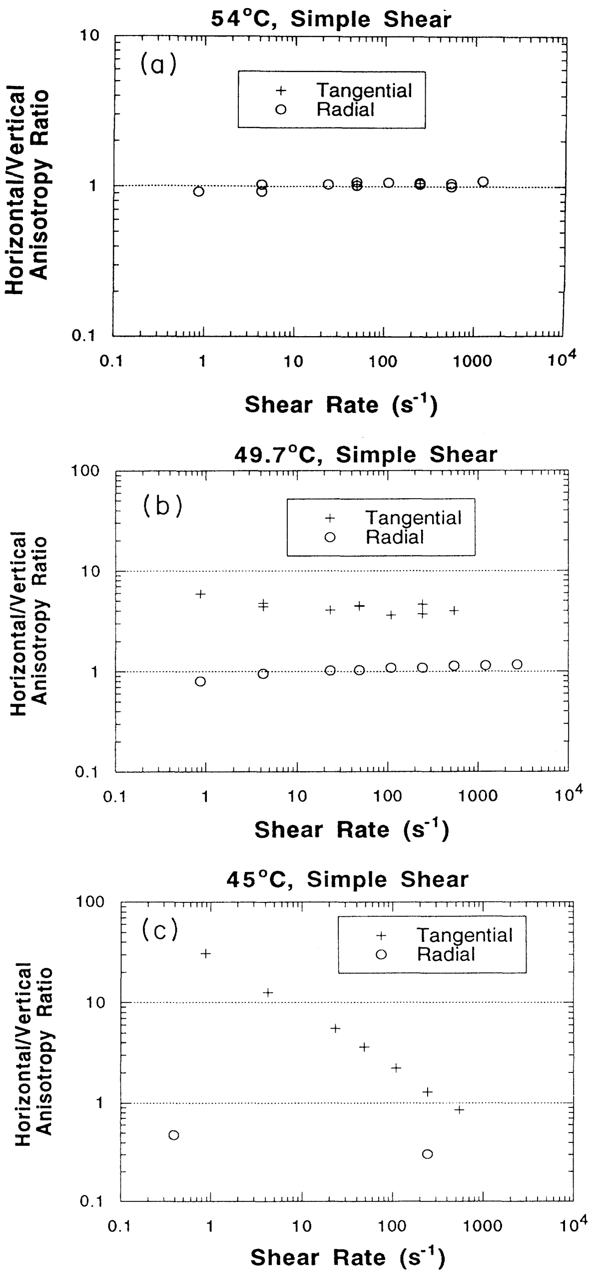

FIG. 4. Variation of the ratio of the outer peak intensities in the horizontal and vertical directions (anisotropy ratio) with shear rate (simple shear) for the tangential and radial beam geometries and the following sample temperatures: (a) 54 °C (isotropic phase), (b) 49.7 °C (nematic phase), and (c) 45 °C (smectic phase).

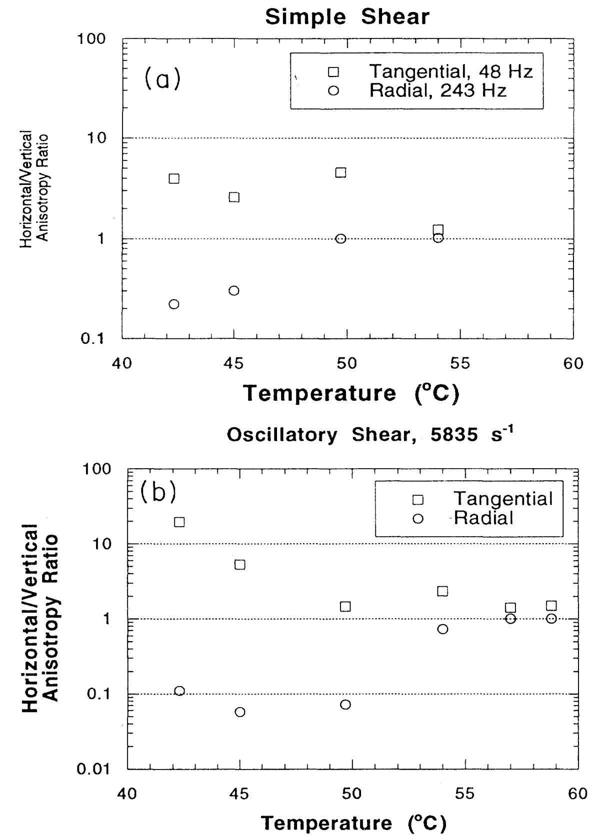

FIG. 5. Variation of the ratio of the outer peak intensities in the horizontal and vertical directions with temperature for the tangential and radial beam geometries in the case of (a) simple shear and (b) oscillatory shear.

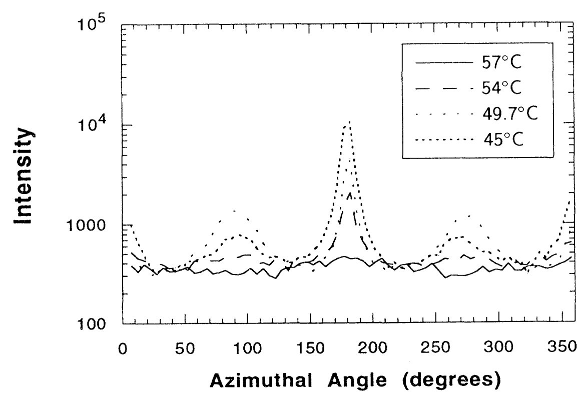

FIG. 6. Variation of the SANS intensity at $Q=0.146$ Å^{-1} (location of the outer peak) with azimuthal angle in the detector plane for a tangential beam geometry and oscillatory shear (5835 s^{-1}). The SANS intensity was averaged over a range $\Delta Q=0.014$ Å^{-1}.

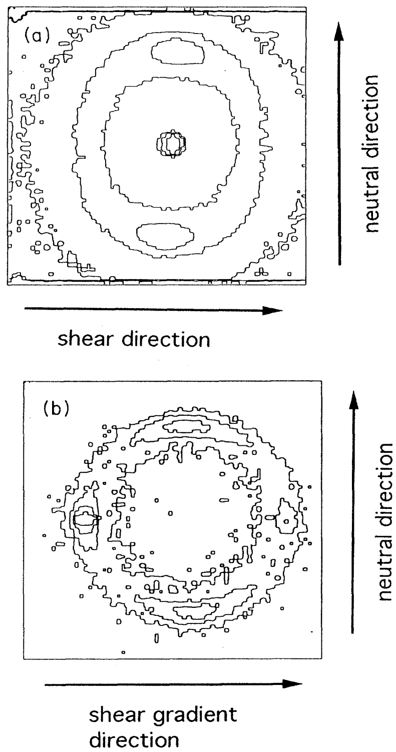

FIG. 7. Contour plots of the SANS data taken at a shear rate of 5835 s^{-1}, at a sample temperature of 49.7 °C, using oscillatory shear (a) with a radial beam geometry (an inner ring and two outer peaks in the vertical direction can be observed), and (b) with a tangential beam geometry (a weak outer ring and four outer peaks in the vertical and horizontal directions can be observed). Because the tangential beam geometry does not sample a uniform scattering volume, the left horizontal peak is higher than the right one.

cess (seen as a contribution from vertical spots in the tangential geometry of Fig. 3) was observed for 45, 49.7, and 54 °C, but not for 42.3, 57, or 58.8 °C. It seems strange that for simple shear, the flipping process was observed in the smectic phase and not in the nematic phase, while for oscillatory shear, this process was observed in what corresponds to the quiescent nematic phase but not in the quiescent smectic phase. These experimental facts have, however, been verified. Another observation consistent with this conclusion is shown in Fig. 6 as a plot of the outer peak intensity with varying azimuthal angle (with respect to the horizontal axis) in the detector plane using oscillatory shear and a tangential beam geometry. For decreasing temperature one sees a gradual buildup of the horizontal peaks (located at 0° and 180°), which is consistent with an increase of the alignment parallel to the shear cell walls. The vertical peaks (located at 90° and 270°), however, first increase then decrease with decreasing temperature which is consistent with an increase then a decrease of the flipping process with decreasing temperature. This is attributable to the competition of two effects: an increase of the fraction of micelles that have "flipped" and lie in the *A* configuration of Fig. 3 (bulk effect) and at the same time an increase of the size of the micellar layer aligned vertically in the *C* configuration of Fig. 3 (wall effect) when the sample temperature is decreased. At first, the bulk effect dominates whereas at low enough temperatures the wall effect takes over the whole sample volume. The anisotropy ratio for the radial beam geometry shown in Fig. 5(b) shows a behavior consistent with this conclusion. To our knowledge, such a behavior has not been predicted or observed before.

Another conclusion is that tangential beam geometry is more useful than the radial one and that results based only on the radial beam geometry could be misleading. Figure 7(b), for instance, shows that only a fraction of the discotic micelles are oriented horizontally (i.e., have "flipped"). This fact could not have been inferred by looking at Fig. 7(a) alone. Actually, in all of the measurements taken in these experiments, there was not a single instance where the flipping was complete (i.e., corresponding to the *A* configuration of Fig. 3).

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