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Classification

Physics Abstracts

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Effects of Shear on the Smectic A Phase of Thermotropic Liquid Crystals

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Abstract. — The rheological behaviour of the smectic A phase of the thermotropic liquid crystal 4-cyano-4'-octylbiphenyl (8CB) is examined. X-ray scattering studies under shear flow were performed to probe changes of structures. We found that in a certain range of temperatures two states of orientation of lamellae exist. These two steady states of orientation are separated by a first order dynamic transition that becomes continuous at T_c (a temperature different from that of the smectic/nematic transition). At low shear rates, the smectic A phase is non-Newtonian: its viscosity η varies as $(T_c - T)^{1/2} \cdot \dot{\gamma}^{-1/2}$ (where $\dot{\gamma}$ is the shear rate and T the temperature). In this regime, the structure of the system is compatible with multilamellar cylinders oriented along the flow direction. At high shear rates, the system becomes Newtonian, its layers are then oriented perpendicular to the shearing plates (as already noticed by Safinya *et al.* [1]).

1. Introduction

Dynamics of complex fluids such as polymers, micelles, colloids has drawn much interest in the past few years. While the static properties of those systems are rather well understood, much less is known concerning their dynamic properties [2]. Under shear flow, most of those complex fluids exhibit non-Newtonian behaviour (ie, the viscosity depends on the shear rate [3]). One goal is to understand the rheology and viscoelasticity of complex fluids in terms of their microstructures. Whether a fluid is Newtonian or not depends certainly on how much its microstructures are altered by the flow. Therefore, it turns out that in order to better comprehend flow properties of complex fluids, one has to probe the distortion of their microstructures under shear flow.

Some time ago, in order to address this very general issue, investigations on lyotropic lamellar phases under shear flow have been started [4]. Such lamellar phases are long-range ordered phases that are stabilized either by weakly screened electrostatic repulsion or undulation forces [5]. In some systems, this layered structure may persist over very large ranges of dilution [6]. It then turns out that such systems are unique to study static and dynamic properties of membranes since the intermembrane distance and therefore elastic moduli can be modulated over several orders of magnitude by dilution [7]. Such systems have been extensively studied. Today, most of their equilibrium properties are considered well-understood both from a

microscopic point of view (stack of interacting membranes) and from a macroscopic one (two-component smectic A elasticity) [8, 9]. However, the rheology of those systems has received very little attention over the years despite their importance in food and cosmetics processings, lubrication, and biological systems [10].

Using different techniques such as light scattering, conoscopy, neutron scattering and microscopic observations, it has been shown that lyotropic lamellar phases present under shear flow three steady states of orientation separated by dynamical transitions [11]. At low and high shear rates, the layers orient parallel to the shearing plates. For intermediate shear rates, there exists a state made of monodisperse, closed-packed multilayered vesicles whose size is precisely fixed by the shear rate. A direct and promising application of this phenomenon is to allow the preparation of monodisperse spherulites with a controllable size ranging from a few microns to a tenth of it that can encapsulate specific molecules [12]. The passage from one steady state to another corresponds to out of equilibrium transitions [13]. It is therefore possible to present a so-called orientation diagram which generalizes the concept of phase diagram to systems under shear flow. Such a diagram is of particular interest for rheologists since each steady state corresponds to a particular viscoelastic regime of the system. At high and low shear rates, the system is Newtonian, whereas in the onion state (i.e. in the state made of closed-packed multilayered spherulites), it becomes non-Newtonian.

In this paper, we investigate the rheology of the smectic A phase of a thermotropic liquid crystal (8CB) in a relatively large range of temperatures (from 29 °C to the smectic/nematic temperature of transition $T_{N/A} = 33$ °C). It has been shown that under shear flow thermotropic smectic phases develop rectangular focal domain patterns as a result of an undulation instability [14]. The underlying question of our work is to find out whether or not, under shear flow, lamellar thermotropic phases present similarities with lyotropic phases. In particular, does 8CB under shear flow also present stationary states separated by dynamic transitions? Both phases are lamellar. However, thermotropic smectic A phases are one-component systems and therefore the distance between layers is fixed [15]. In a previous study [1], C. Safinya *et al.* found that indeed under shear flow, the smectic phase of 8CB also exhibits steady states of orientation. At high shear rates, contrary to lyotropic lamellar phases, the layers orient perpendicular to the shearing plates. At lower shear rates, no spherulites are formed: instead domains of layers oriented perpendicular and parallel to the shearing plates coexist.

We focus here on the rheology of the smectic A phase of 8CB. As for lyotropic systems, we show that most rheological properties can be well understood in terms of a so-called orientation diagram.

2. Experimental

8CB was kindly provided by Safinya (Exxon/UCSB). Its transition temperatures were determined by observation between crossed polarizers under a thermostated microscope (Leitz). The temperature was controlled within 0.1 K. The smectic A/nematic and nematic/isotropic temperatures of transition were found to be 33 °C and 40 °C, respectively. Rheological measurements were made with a thermostated Carrimed rheometer CSL 100 with a plane/cone and a Couette geometry. The stress was imposed, and the shear rate was measured. All measurements were made when the stationary state was reached (ie, the shear rate becomes independent of time). Close to the transition between orientation states, the transient time was particularly long (several hours). In the plane/cone geometry, the cone angle was 2 degrees and its diameter 4 cm. The Couette cell which we used was a Mooney cell: it consists of two concentric cylinders whose radii are 24 and 25 mm with the inner cylinder ending with a cone shape at the bottom. Here again the temperature was controlled within 0.1 K.

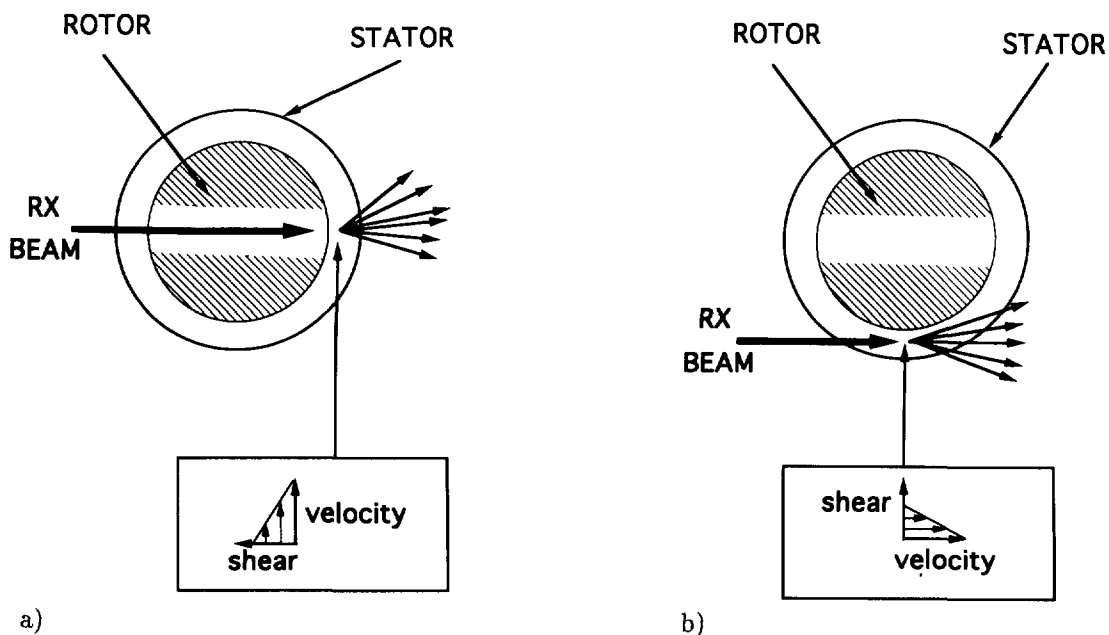


Fig. 1. — a) Geometry of the X-ray experiment in the (V, Z) configuration. b) Geometry of the X-ray experiment in the $(\dot{\gamma}, Z)$ configuration.

X-ray scattering measurements were performed on a home-made line using the $\text{Cu K}\alpha$ radiation of an 18 kW rotating anode X-ray generator. A flat pyrolytic graphite (002) monochromator delivered a $1 \times 1 \text{ mm}^2$ beam onto the sample. The scattered radiation was collected on a two-dimensional detector purchased from Mar Research (Hamburg, Germany). The detector system was an imaging plate (Fuji Photo Film Co. Ltd) read out by scanning with a He-Ne laser. The diameter of the circular plate is 180 mm and the pixel size $150 \mu\text{m} \times 150 \mu\text{m}$. The intensity map was stored as a 1200×1200 pixel numerical image on a VAX station. The sample-to-detector distance was 830 mm through helium in order to lower absorption and diffusion. The instrumental resolution in reciprocal space was about $1.8 \times 10^{-2} \text{ \AA}^{-1}$ in both vertical and horizontal directions. The Couette X-ray shear cell consists of two concentric cylinders whose radii were 19.5 and 20 mm. The outer cylinder rotates, while the inner one is kept fixed. The 8CB was confined between those cylinders. To a good approximation, the velocity profile can be considered to be linear with a constant shear rate $\dot{\gamma} = V/D$ (where V is the velocity of the rotor and D the gap between the two shearing cylinders). The inside temperature is controlled within 0.05 K. By translating the shear cell, one can probe the X-ray scattering occurring in the (V, Z) and $(V, \dot{\gamma})$ planes (Fig. 1).

3. Results

3.1. RHEOLOGY MEASUREMENTS. — Figure 2a shows the stress (σ) versus the shear rate ($\dot{\gamma}$) for the smectic-A phase of 8CB. The temperature is $31 \text{ }^\circ\text{C}$. At low shear rates, up to 700 s^{-1} (region I), the stress varies as $\dot{\gamma}^{1/2}$ (Fig. 2b). Consequently, in this region, the viscosity η varies as $\dot{\gamma}^{-1/2}$. At higher shear rates (region II), the stress is proportional to the shear rate (see Fig. 2a). In this region, the fluid is Newtonian and its viscosity is of order of that of nematic ($\eta = 0.036 \text{ Pa}\cdot\text{s}$). The transition between regions I and II is discontinuous: it occurs

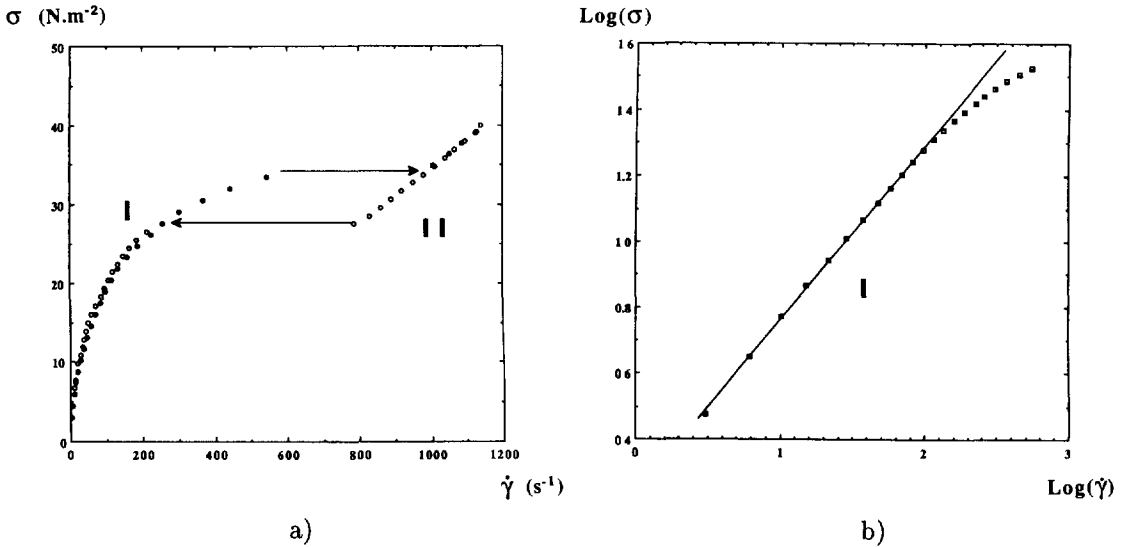


Fig. 2 — a) Rheology measurement: stress versus shear rate for 8 CB at 31 °C in the plane/cone geometry. b) Same data as in Figure 2a in a log-log plot, but limited to region I. The best fit gives: $\log(\sigma) = 0.193 + 0.497 \cdot \log(\dot{\gamma})$.

through a jump in shear rate (Fig. 2a). This transition is reproducible, however the critical shear rates are somewhat variable. Indeed, since the system presents a hysteresis (Fig. 2a), any mechanical perturbations (such as vibrations, for instance) may induce the transition.

3.2. X-RAY SCATTERING UNDER SHEAR FLOW. — We performed X-ray scattering under shear flow in regions I and II, in order to determine whether this discontinuous transition could be related to changes in the orientation of 8CB.

At low shear rates (region I), X-ray data in the plane containing q_v (parallel to the fluid velocity) and q_z (parallel to z) reveals a Bragg peak for $q_z = 0.19 \text{ \AA}^{-1}$ and $q_v = 0$ (Fig. 3a). In the plane q_z and q_γ (parallel to the shear), the scattering peak is isotropic (Fig. 3b). In real space, the structure of smectic phase in region I is therefore compatible with multilamellar cylinders oriented along the flow direction (Fig. 4).

At very high shear rates, (region II), X-ray data in the planes (q_z, q_v) and (q_z, q_γ) show a maximum of intensity occurring for $(q_z = 0.19 \text{ \AA}^{-1}, q_v = 0)$ and $(q_z = 0.19 \text{ \AA}^{-1}, q_\gamma = 0)$, respectively (Figs. 5a and 5b). This demonstrates that the director n of molecules is along the z direction. In this region, the layers are oriented perpendicular to the shearing cylinders (Fig. 6). Note that this orientation of layers has already been observed [1]. Note also that there exists a splitting of the peaks into two peaks very close in Figure 5b. We do not know the origin of this effect but it is systematic.

For intermediate shear rates, both shear structures coexist. There, the X-ray spectra are a superposition of high and low shear patterns. Note that this occurs because the shear rate is fixed. If the stress were fixed, such an intermediate region would not exist (Fig. 2a).

3.3. TEMPERATURE STUDIES: ORIENTATION DIAGRAM. — We systematically studied the rheology of the smectic A phase of 8CB for temperatures ranging from 29 °C to the smec-

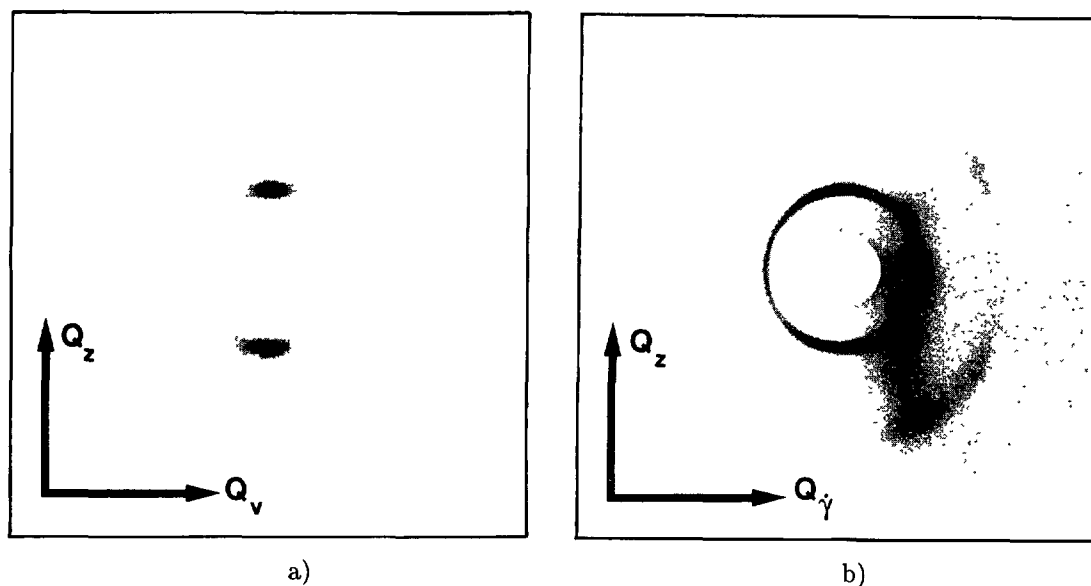


Fig. 3. — a) X-ray scattering data in the (q_v, q_z) plane. The temperature is 31.2°C and the shear rate is 200 s^{-1} . b) X-ray scattering data in the (q_γ, q_z) plane. The temperature is 31.2°C and the shear rate is 200 s^{-1} .

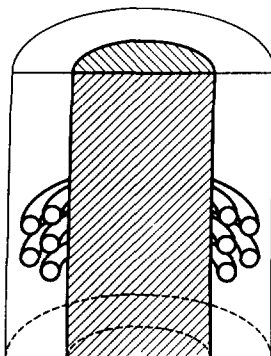


Fig. 4. — A structure of the material in real space compatible with results from Figures 3a and 3b.

tic/nematic temperature of transition: $T_{A/N} = 33^\circ\text{C}$.

When the temperature is increased, the transition between region I and II occurs at lower shear rates (Fig. 7). For temperatures higher than 31.9°C , the smectic A phase is Newtonian for all shear rates experimentally accessible, with a viscosity η of order of that of a nematic, while the nematic state occurs only at 33°C . For such temperatures, the structure adopted by the system is similar to that of region II. It was not possible to observe experimentally the transition for temperatures lower than 30.6°C because of stress limitations due to the cell geometries used. In region I we always have $\sigma = C(T) \cdot \dot{\gamma}^{1/2}$. The slope $C(T)$ is strongly temperature dependent (Figs. 8 and 9). Indeed, $C(T)$ is found to vary as $(T_c - T)^{1/2}$ with $T_c = 31.83^\circ\text{C}$ (Fig. 10). Note that this temperature is more than 1°C below $T_{A/N}$, and that

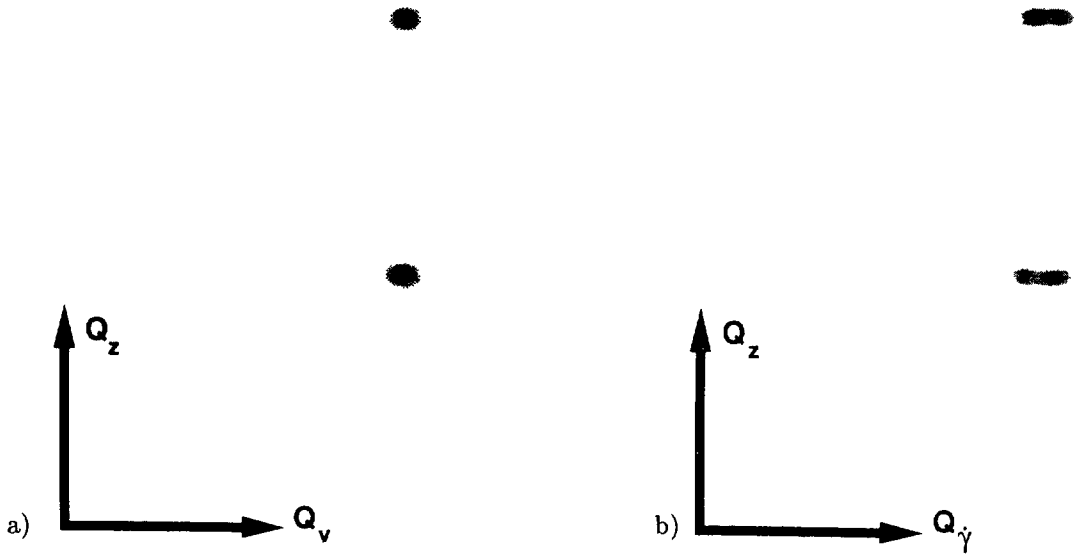


Fig. 5. — a) X-ray scattering data in the (q_v, q_z) plane. The temperature is 31.2°C and the shear rate is 800 s^{-1} . b) X-ray scattering data in the $(q_{\dot{\gamma}}, q_z)$ plane. The temperature is 31.2°C and the shear rate is 800 s^{-1} .

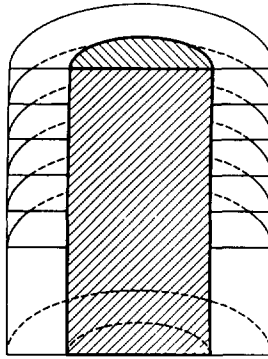


Fig. 6. — Structure adopted in real space by 8CB under shear flow. The experimental conditions are those of Figures 5a and 5b.

the critical point therefore does not correspond to the smectic/nematic transition. Besides, this temperature T_c seems to correspond to the temperature above which only state II is found as a function of shear.

From the previous results, it is possible to present an orientation diagram of the system under shear. Such a diagram represents for different temperatures the steady states adopted by the system under shear flow. It can be either represented in a $(\dot{\gamma}, T)$ plane or a (σ, T) plane (Figs. 11 and 12). Note that in the (σ, T) representation, no coexistence domains between cylinders and oriented lamellae exist. In terms of equilibrium phase transition vocabulary, this means that σ plays the role of a field variable and $\dot{\gamma}$ that of a density one. It is also interesting to note that the amplitude of the jump in shear rate between regions I and II varies linearly with temperature (Fig. 13).

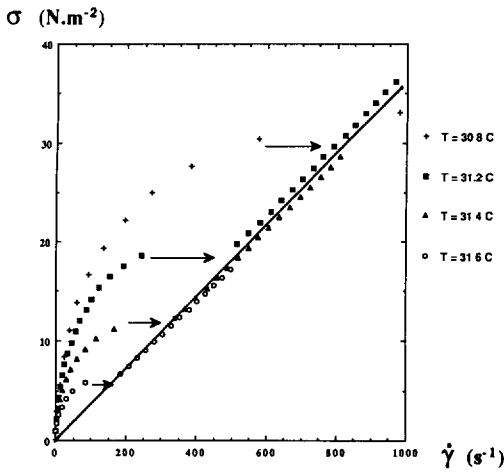


Fig. 7

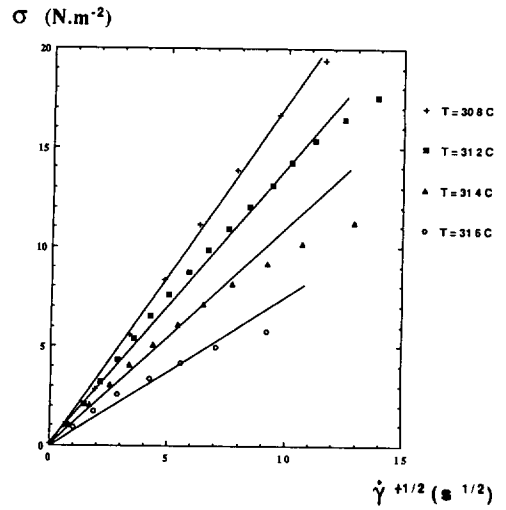


Fig. 8

Fig. 7. — Rheology measurement: stress *versus* shear rate for 8CB at different temperatures, in the plane/cone geometry.

Fig. 8. — Plot of stress *versus* square root of shear rate for the same data as in Figure 7. The representation is limited to region I.

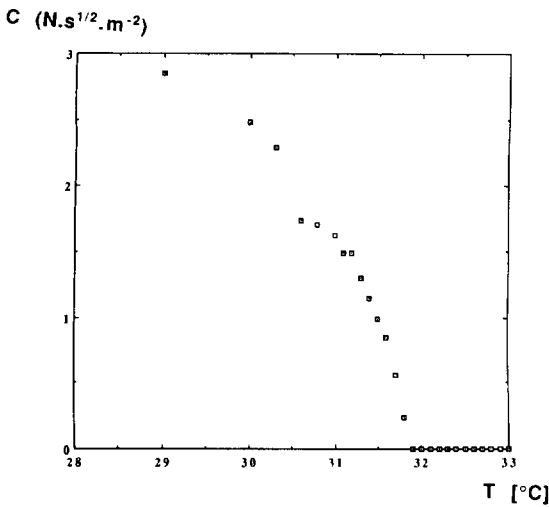


Fig. 9

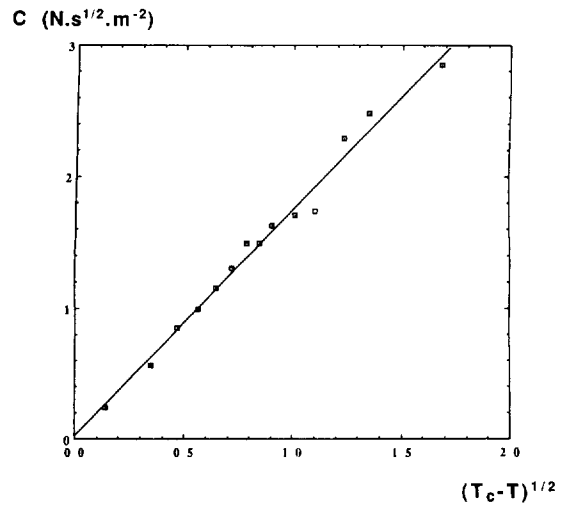


Fig. 10

Fig. 9. — Slope of the stress *versus* the square root of shear rate C , in region I for different temperatures.

Fig. 10. — C *versus* $(T_c - T)^{1/2}$ where $T_c = 31.83$ °C is the critical temperature and T the temperature. $C = 1.7397 \times (T_c - T)^{1/2}$.

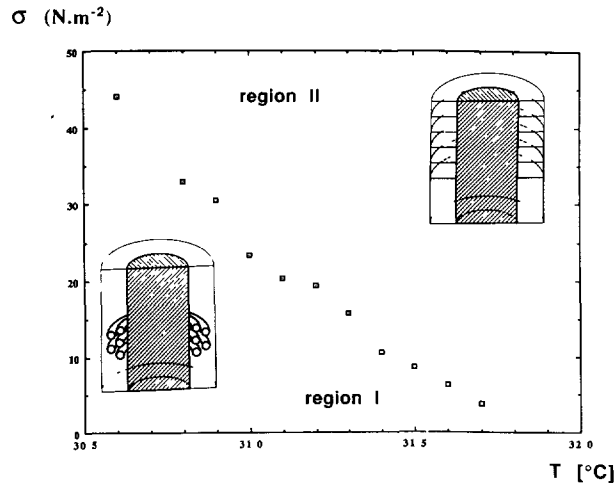


Fig. 11. — Orientation diagram in the (σ, T) representation.

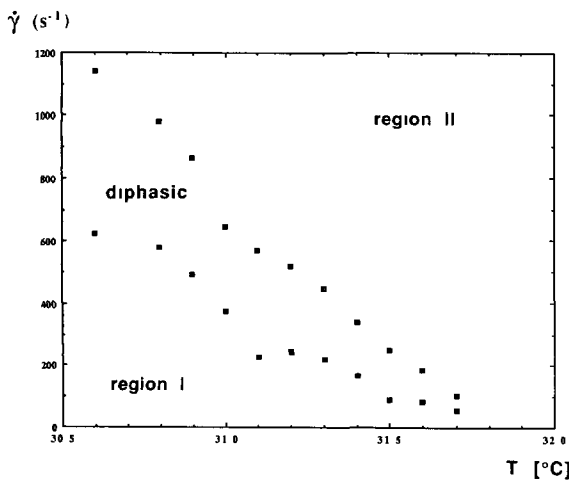


Fig. 12

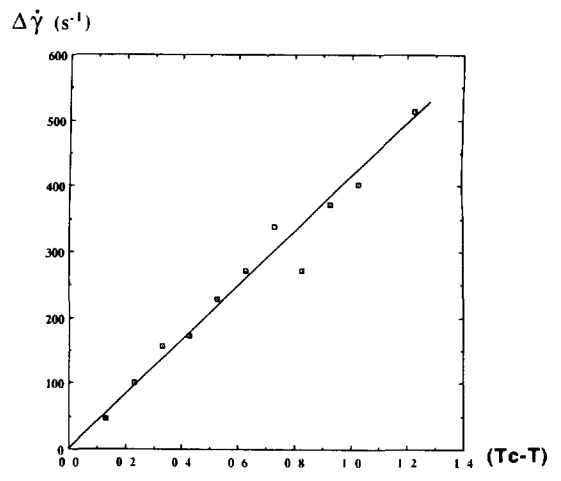


Fig. 13

Fig. 12. — Orientation diagram in the $(\dot{\gamma}, T)$ representation

Fig. 13. — Amplitude of the jump shear rate between regions I and II versus $(T_c - T)$.

4. Conclusion

In summary, the smectic A phase of 8CB presents under shear flow two states of orientations separated by a first-order dynamic (subcritical) transition. This transition becomes continuous (critical) at $T = T_c$, a temperature different from that of the smectic/nematic transition. At low shear rates, the structure of the system is compatible with the presence of multilamellar cylinders oriented along the flow. In this region the fluid is non-Newtonian. its viscosity varies

as $\dot{\gamma}^{-1/2}$. At higher shear rates, the system becomes Newtonian. This corresponds to an orientation of layers perpendicular to the shearing plates. As for lyotropic lamellar phases, all information can be summarized in an orientation diagram.

Acknowledgments

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References

- [1] Safinya C. *et al.*, *Phys. Rev. Lett* **66** (1991) 1986-1989.
- [2] Gelbart W.M., Ben Shaul A , Roux D , Solutions of surfactants (Eds UCLA University Press) (to be published).
- [3] Evans D.J., Hanley H.J.M. and Hess S., *Phys. Today* (jan 1984),
Doi M., Edwards S.F., The theory of polymer dynamics (Science Publication Oxford, 1986).
- [4] Diat O., PhD thesis, Effets du cisaillement sur les phases lyotropes: phase lamellaire et phase éponge, Université de Bordeaux I France (1992).
- [5] Nallet F., Roux D., Prost P.J., *J. Phys. France* **50** (1989) 3147;
Roux D., Safinya C., *J. Phys. France* **49** (1988)307
- [6] Roux D., Bellocq A.M., Physics of amphiphiles, V. Degiorgio, M. Corti Eds. (North Holland, Amsterdam, 1985).
- [7] Nallet F., Roux D., Milner S.T., *J. Phys. France* **51** (1990) 2333.
- [8] Roux D., *Mat. Res. Soc. Symp. Proc.* **177** p. 91
- [9] Brochard F., de Gennes P.G., *Pranama Suppl* **I** (1975) 1.
- [10] See for instance Reed R.L., Healy R.N., Improved oil recovery by surfactant and polymer flooding (Academic Press, New-York, 1977).
- [11] Diat O., Roux D., Nallet F., *J. Phys. II France* **3** (1993) 1427.
- [12] Diat O., Roux D., *J. Phys. II France* **3** (1993) 9,
Roux D., Diat O., French Patent n° 9204108.
- [13] Roux D., Nallet F., Diat O., *Europhys Lett.* **24** (1993) 53-58.
- [14] Ostwald P , Kleman M., *J. Phys. Lett. France* **43** (1982) L411-L415.
- [15] See for instance de Gennes P.G., Liquid crystals (Oxford University Press, London, 1974).