

Bistability in non-Newtonian flow: Rheology of lyotropic liquid crystals

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We study the rheological properties of self-assembled surfactant structures: lyotropic liquid crystals exhibiting plane lamellar and “onion” (concentric bilayer) textures. Both systems behave similarly: they are gel-like and exhibit extreme shear-thinning behavior. We demonstrate that this results in a hysteresis in the stress-strain curve when the stress is imposed. Controlled shear-rate experiments reveal the origin of the hysteresis by demonstrating the existence of two extrema in the stress-strain curve. The bistability leads to the formation of shear bands in the system and is illustrated by demonstrating the existence of sudden jumps in the viscosity of the fluid, following the viscosity of the fluid in time. [S1063-651X(98)01208-2]

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The flow behavior of “complex fluids” such as polymer or surfactant solutions is of both practical and fundamental interest [1,2]. The large length scales present in these systems, when compared to molecular dimensions, can lead to interactions between the flow field and the structure of the complex fluids. A structural change can affect the viscosity of the fluid and thus, in turn, modify the flow field. It is the purpose of this paper to show that such a cascadelike event can lead to bistable systems that exhibit a hysteretic flow behavior.

The effect of shear on the structure of surfactant solutions has attracted much attention lately [2–9]. The experimental situation is reviewed in a recent paper by Porte *et al.* [2]. One of the key questions is the physical origin of the stress plateau observed in stress-strain curves. Such plateaus have been observed for a variety of systems; for surfactant systems principally in lamellar phases [3,4] and systems forming giant micelles [5–9]. However, very similar observations have also been made for thermotropic liquid crystals [10] and polymer solutions and melts [11]. For the latter, the resulting spurt (or velocity oscillations) are believed to be responsible for the phenomenon of melt fracture, which is an important limitation of the speed with which polymeric fibers can be spun from a melt [11].

For all these “complex fluids,” it is not clear whether the observed stress plateau is due to a mechanical instability, or whether the shear induces a nonequilibrium phase transition [2]. Several authors argue in favor of a mechanical instability [5,7,8,11], whereas other groups interpret their data as a shear-induced phase transition [3,4,6,9,10]. As is evident from some very recent work, the situation is still very much unclear [12].

In order to investigate this question, we study the rheology of lyotropic liquid crystalline phases. We study aqueous solutions containing 7% by weight of AOT [sodium bis (2-ethylhexyl) sulfosuccinate, obtained from Sigma] as an anionic surfactant, and vary the amount of sodium chloride added to the solution. The equilibrium phase behavior of this system has been studied in detail by Gosh and Miller [13]. At high salt ($0.9 < c < 1.35$ wt %) a flat lamellar phase is

found, the lamellae consisting of bilayers of surfactant molecules; water separates the different bilayers. At low salt concentrations ($0 < c < 0.9$ wt %), the bilayers roll up around each other to form spheres, called “onions.” Upon a first inspection of the samples, a large difference between the two regions of the phase diagram is immediately evident. The plane lamellae, at higher salt, are fluid with a viscosity roughly that of water. The onions, on the other hand, form a turbid gel with a much higher viscosity. Even more surprising is the observation that if one shakes the bottle containing the flat lamellar phase, one obtains a similar high-viscosity gel.

The rheological characterization of these phases was performed on a Rheologica Stress-Tech rheometer, which imposes either the shear stress or the shear rate. The measurements were performed in a Couette cell with a diameter of the inner cylinder of 25 mm and a gap of 1 mm and, for the higher shear rates, a cone and plate geometry (cone diameter 55 mm, cone angle 0.5°). First, consider the gel phase found for the onion spheres. We present only the data for the 0.5 wt % NaCl sample, which are representative for the rest of the samples in this region of the phase diagram. Imposing, in the first experiment, the shear stress and measuring the non-Newtonian viscosity of this sample, we found it to be strongly shear thinning. In a narrow region of shear rates, the viscosity was found to decrease roughly as the inverse first power of the shear rate. Plotting the imposed shear stress as a function of the shear rate, an almost horizontal plateau can be observed [Fig. 1(a)]. The surprise now comes when we perform the exact same measurement, but instead of increasing the stress, we start from a high value and decrease the stress. The two curves superimpose at low and high stress, but in the region of the stress plateau, they are distinctly different. It appears that we observe a hysteresis loop: the measurements performed while increasing the stress tend to remain at a high viscosity in the region of the plateau, whereas by decreasing the stress, low viscosities are found. A second surprise comes when, instead of imposing the stress, we impose the shear rate and measure the resulting stress. It can be observed that in the plateau region, the mea-

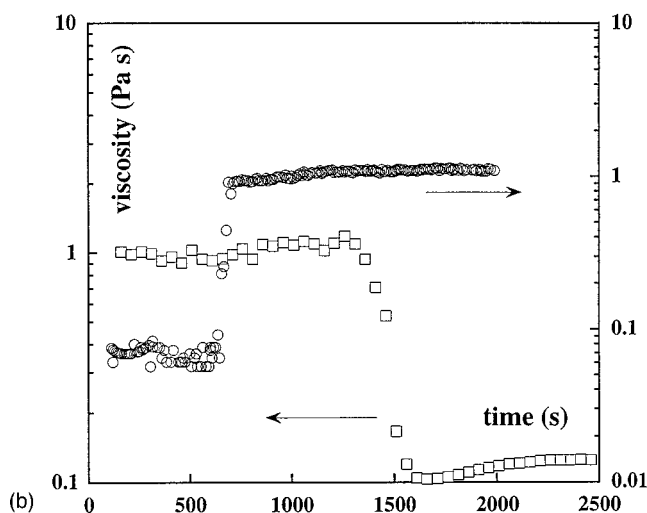
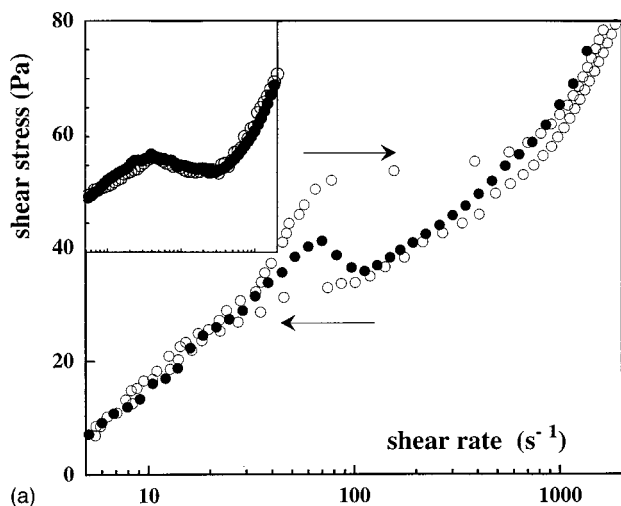


FIG. 1. (a) Shear stress as a function of the shear rate for the 0.5 wt % salt sample in the onion region of the phase diagram. The measurement represented by the filled circles is obtained by fixing the shear rate, and shows two extrema. This leads to the observation of a hysteresis when the shear stress is fixed (open circles, the arrows give the sense of the measurement). Inset: measurements with imposed shear rate obtained on two different samples prepared independently for a 0.7 wt % salt sample on the same scale. (b) Viscosity as a function of time for the 0.5 wt % salt sample (squares) at an imposed stress of 35 Pa. Circles are for a sample within the lamellar phase (1 wt % NaCl, presheared before the measurement) at an imposed stress of 20 Pa. For both cases, a large and almost discontinuous jump in the viscosity is observed after very long times, demonstrating the bistability of the system.

sured curve is different from the other two. For imposed shear rate, the stress exhibits a maximum and bends down before increasing again. The observation that we succeed in measuring the part of the curve with a negative slope implies that these states are at least dynamically stable on the time scale of our measurement. To demonstrate the reproducibility of the measurements, in the inset we show two stress-strain curves for two different samples. These measurements then reveal the reason for the observed hysteresis: for a given stress, the system is bistable, with an energy barrier between the two states.

These findings would imply that the shear rate is a multi-

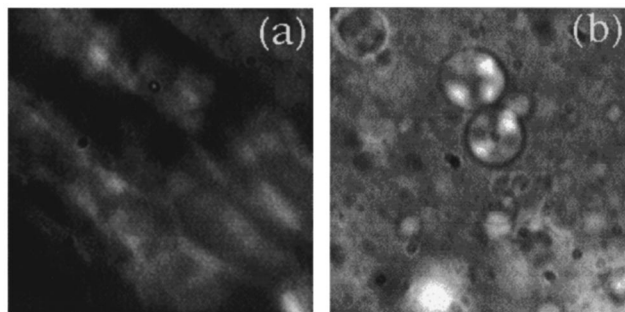


FIG. 2. Polarization microscopy images of (a) the presheared lamellar phase at 1 wt % salt; one observes the presence of large Burgers-vector defects in the sample. (b) The onion phase at 0.5 wt % salt; crosses, characteristic of birefringent droplets can be clearly observed. Picture sizes are $100 \times 100 \mu\text{m}$.

valued function of the shear stress: by imposing a certain stress, more than one value for the shear rate, and consequently for the viscosity should be found. In order to validate this hypothesis, in Fig. 1(b) we depict the results of two of such measurements. Imposing the stress, we observe the viscosity to reach a steady value, which, after quite a while, transits abruptly to a second and different value. The transition times are not completely reproducible. This is completely consistent with the observed bistability; the distribution of transition times should probably be a rather broad Poisson distribution, as the transition is likely to be due to a random process. The conclusion is that, indeed, the system is bistable, and that, consequently, the viscosity is not a single-valued function of the stress. The results reported in Fig. 1(b) also account for the large hysteresis observed for the case of imposed shear stress. As can be observed in the figure, the lifetime of the initial state is very large; typically about 1000 s. The viscometry measurements, on the other hand, are performed by taking a point typically every 30 s, after which the stress is changed. As this time interval between the data points is much smaller than the typical transit time, this accounts for the observed large hysteresis.

A behavior very similar to that of the onion spheres can be observed for the flat lamellar phases found at somewhat higher salt concentrations. However, for this case, the observations do depend on the shear history of the sample. Rested samples have viscosities that are very low, a few mPas (milli-Pascal seconds). However, if these samples are sheared (typically 200 s at 100 s^{-1}), a dramatic increase in the viscosity of the sample is the result: we observe a shear-induced gelation. The gel phase is stable for periods of several tens of minutes to even several weeks, depending on the salinity of the sample. Observing the fluid and gel-like samples using polarization microscopy, the difference between the two appears to be that there are a large number of defects present in the gel phase. An image of the pre-sheared gel phase, which reveals the presence of a large number of defects, is shown in Fig. 2. Similar observations on an equilibrium lamellar biogel were made recently by Warriner *et al.* [14], who conclude, in agreement with our observations, that the defects stabilize the gel phase. A typical example (1 wt % salt) of the rheological properties of the lamellar gel is depicted in Fig. 3. Imposing the shear rate, a similar behavior as was reported for the onions spheres is

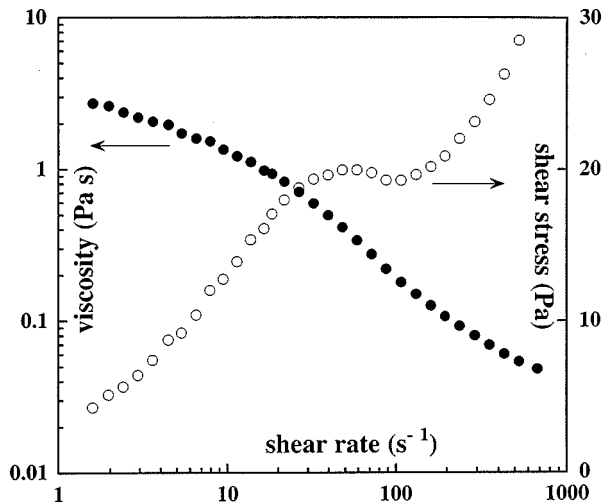


FIG. 3. Shear stress and viscosity as a function of shear rate for the 1 wt % salt sample in the lamellar region of the phase diagram. The sample was presheared for 200 s at a shear rate of 100 s^{-1} . The measurements were performed by imposing the shear rate, and display a behavior very similar to that observed in Fig. 1 for the onion phase.

found: the shear stress exhibits a maximum, and, at somewhat higher shear rates, a minimum.

The question now rises how this compares to previous measurements on similar systems. The usual way to measure non-Newtonian viscosities is by imposing the stress rather than the shear rate. A plateau for the stress, similar to the one we report here, has been observed, as explained above, on a number of systems [2–12]. The existence of such a plateau implies a nearly discontinuous jump from one value to another and thus could imply that the system is bistable. Transitions between two distinctly different values of the viscosity have also been observed in surfactant [7] and polymer [11] solutions. However, to the best of our knowledge (and that of Porte *et al.* [2]), clear evidence for a true bistability has not been obtained before [15]. We report here two extremal points and a negative slope in the stress-strain curves for an imposed shear rate, which leads to hysteresis when the stress is imposed. The combination of imposed stress and shear rate measurements, together with the observed viscosity jumps in time, allow us to demonstrate unambiguously a bistable flow behavior in non-Newtonian fluid flow.

What happens in the flow is immediately evident if we compare the results to those obtained for so-called “power-law fluids” for which the non-Newtonian behavior is modeled by a power-law dependence of the viscosity on the shear rate: $\eta = m \gamma^{n-1}$, with γ the shear rate; m and n are constants characterizing a given fluid over a certain range of shear rates [1]. Within this model, Newtonian behavior is retrieved for $n = 1$; shear-thinning fluids have $n < 1$. If one calculates the velocity profile of such a power-law fluid in the Couette geometry used for our experiments, one finds for the tangential velocity [1] $v_\theta = \Omega r [(R/r)^{2/n} - 1] / [(1/\kappa)^{2/n} - 1]$, with Ω the angular velocity, r the radial coordinate, and κ the ratio of the diameters of the inner and outer cylinder. It is immediately evident from this equation that a singularity appears in the flow problem for $n \rightarrow 0$. Mathematically, the singular point $n = 0$ could be associated with a change of the type of

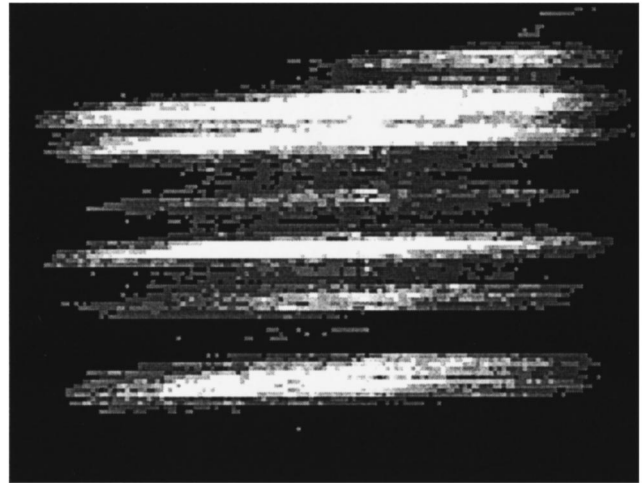


FIG. 4. Flow visualization experiment in a transparent Couette cell for the 1.2 wt % salt sample at a shear rate of 200 s^{-1} , demonstrating the formation of shear bands in the system. Picture size is $2 \text{ cm} \times 2 \text{ cm}$. The horizontal direction is the velocity, the vertical one the vorticity direction.

the hydrodynamic equations (a Hadamard instability [16]), although no constitutive equation for this surfactant system is known from which such a rigorous conclusion may be drawn.

What happens in our system is exactly what is described above. The first extremum of the (shear-rate imposed) stress-strain curve in Fig. 1(a) is in fact the point where $n = 0$, i.e., the viscosity decreases as the inverse first power of the shear rate. From the equation it follows that when $n \downarrow 0$ the tangential velocity is no longer a simple linear function of r (neglecting small logarithmic correction), but has a large spatial variation. This implies that the shear rate $\partial v_\theta / \partial r$ is no longer constant over the cell gap. As the viscosity, in turn, depends on the shear rate, also the viscosity will vary spatially. The consequence is that very large shear gradients will develop, which may destabilize the system. For a power-law fluid with a vanishingly small n , practically all of the shear will be concentrated in a region close to the rotating inner cylinder of the Couette cell [1]; the shear gradient diverges for $n \rightarrow 0$.

The physical manifestation of the development of such large shear gradients is the appearance of so-called “shear bands,” separation of the flow in regions of high and low shear, in the solution [5–8]. A simple flow visualization experiment indeed shows the appearance of shear-banding instabilities. The experiment is performed in a transparent glass Couette cell with the outer cylinder of radius 50 mm turning at variable speeds; the gap is 1 mm. In order to visualize the flow field, “Kalliroscope” particles (Kalliroscope corporation) are added to the surfactant solution. These particles are widely used for flow visualization; they are flakes that move in the flow, and reflect light when viewed under the right angle. Thus, without flow, the solution is dark, whereas with flow the regions of stronger flow will appear more luminous. A small density of particles added (approximately 0.5 g/liter) does not significantly alter the structure of the surfactant solution even after two days, as observed by phase contrast microscopy. We observe that at

low rotation speeds, the solution appears homogeneous. For rotation speeds corresponding to shear rates for which a stress plateau was observed, the aspect becomes inhomogeneous. We discuss here the typical results obtained for a presheared lamellar phase at 1.2% salt, having a viscosity very similar to that shown in Fig. 3. For rotation speeds corresponding to $0 < \dot{\gamma} < 100 \text{ s}^{-1}$, the flow is homogeneous; the picture is not worth showing. However, for higher speeds, $100 < \dot{\gamma} < 350 \text{ s}^{-1}$ the flow is clearly disordered, with the sudden appearance of dark and light regions (Fig. 4), corresponding to the appearance of shear bands in the flow in the vicinity of the instability point. Within this velocity interval, the number of bands increases with increasing speed. At even higher speeds the inhomogeneity disappears again, either because the shear bands disappear altogether, or because they become too small to be observed. It should be noted here that, although the observed pattern is reminiscent of the usual Taylor vortices, the critical Taylor number for the onset of instability is much larger than the one realized in the experiment [17]. Also, the pattern is not likely to be due to elastic instabilities [17], as the normal stress effects in these solutions are small.

Returning, now, to the original question whether the stress plateau corresponds to a mechanical instability or a nonequilibrium phase transition [2], it appears that, in fact, the problem is ill posed. If a nonequilibrium phase transition would occur in the system, with the strain rate as “effective order parameter” [2], one would expect the transition to occur at a well-defined shear rate. Instead, what happens is that, near the inflection point of the stress-strain rate curve, very large shear gradients will develop, i.e., the shear rate is no longer

uniform, which implies that the surfactant concentration varies spatially. Different regions in the flow having different surfactant concentrations can lead to the formation of surfactant aggregates that are different from those found in equilibrium, which, in turn, may affect the local viscosity. Thus, the observed mechanical instability is likely to both result from and entail a redistribution and restructuring of the surfactant structures. Similar observations have been made for plug flow of suspensions of solid particles: very large velocity gradients develop in the vicinity of the wall, with almost all the solid particles depleted from this region. Also for this case, the nonuniform spatial distribution of both the particles and the shear rate results from a dynamic coupling between the flow field and the distribution of particles.

In conclusion, we have demonstrated a bistability in the non-Newtonian flow behavior of lyotropic liquid crystalline phases. This can be concluded from a hysteresis observed in controlled stress experiments, together with a “metastability loop” observed in controlled shear rate experiments. The bistability of the system entails rather abrupt changes in the viscosity of the system, which accounts, for instance, for instability of the velocity in controlled stress experiments. The coupling between the hydrodynamics and the structure of the surfactant aggregates is at the origin of the observed bistability.

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