Shear Banding in a Micellar Solution under Transient Flow

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We report on the results of rheological, optical, and small-angle light-scattering experiments performed on a solution of cetyltrimethylammonium bromide and sodium salicylate in water. The solution is subjected to a steplike shear rate and the response of the liquid is studied by recording the transient shear stress, the flow birefringence, and the scattered light intensity. This micellar system shows an enormous "overshoot" of the shear stress at the inception of the flow. A phase transition occurs during this process and the light is strongly scattered by the liquid. When the stationary state is reached, the flow shows the typical two-bands structure already observed in similar systems. [S0031-9007(98)07920-4]

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Molecules of various surfactants are known to aggregate in long reversible micelles in quite a wide range of concentrations of the surfactant or of the salt which is eventually added to the solution. They can form entangled or multiconnected networks which give highly viscoelastic properties to these solutions. Thus we can expect them to reveal nonlinear effects when subjected to the action of shear stresses. In a previous paper [1], one of us has shown by using flow birefringence (FB) that phase transitions could be triggered in a Couette cell when the shear rate $\dot{\gamma}$ reaches a first critical value $\dot{\gamma}_{1c}$: The liquid in the annular gap separates into two bands; the shear stress is the same everywhere in the gap, but the shear rate is different in each band and its value is such that $\dot{\gamma} = \phi_l \dot{\gamma}_l + \phi_h \dot{\gamma}_h$. The subscripts l and h refer, respectively, to the low and high shear rates. When this phase transition happens, the curve $\sigma(\dot{\gamma})$ drawn with the results of a shear controlled rheological experiment shows a characteristic plateau which is the locus of the points representing the stationary states of the two phases. Several indirect methods [small-angle light scattering (SALS) [2], small-angle neutron scattering [3–5], and NMR [6]] lead to the same results: the emergence and the growth with $\dot{\gamma}$ of a highly orientated liquid phase near the moving wall of the device in which the flow takes place.

In the previous flow birefringence experiments, the shear rate was gradually and slowly increased up to and beyond the first critical value $\dot{\gamma}_{1c}$ of the shear rate, and the measurements were all made in a stationary state. In this work we report on the first results of transient flow birefringence, transient shear stress, and SALS experiments performed on a single solution of cetyltrimethylammonium bromide and sodium salicylate in H_2O at the concentration of 0.1 and 0.08 M. This system has been chosen for its highly viscoelastic behavior, and we can expect strong nonlinear effects to take place when such a solution is subjected to shear stresses.

The rheo-optical properties of this solution are studied at a single shear rate of $\dot{\gamma} = 1\ \mathrm{s}^{-1}$; this value corresponds to a point which is already situated in the plateau of the curve $\sigma(\dot{\gamma})$. The FB and SALS experiments are performed in a Couette device and the shear stress measurements with a shear rate controlled rheometer in a cone-plane geometry. Parallel to these quantitative measurements, we are able to observe the flow in the Couette cell directly with a microscope. For the FB measurements, the light (a laser beam at 6328 Å) is propagated along the z axis (vorticity axis) while, in the SALS experiments, the diffusion is observed around a direction belonging to the $(\vec{V}, \vec{\nabla} V)$ plane. Figures 1(a) and 1(b) represent the evolution of three different quantities; the only difference between 1(a) and 1(b) is the time scale. The black squares correspond to the evolution of a quantity called s and proportional to $\sin^2 \delta/2$, where δ is the retardation induced by the flow. Circularly polarized light is used for this recording, so that the average orientation quantified by the extinction angle χ does not take place in the signal. The second curve (open circle) is simply the intensity of the light transmitted by the solution under shear; for this experiment the circular analyzer is removed from the optical bench. Finally, the third curve (full line) represents the behavior of the shear stress σ with the time t. A steplike velocity profile similar to the one used in the optical device is applied to the sample placed in a cone-plane rheometer. The growth and the relaxation of the shear stress is recorded as a function of time. The duration of the optical recordings is approximatively 80 s, and the evolution of σ is studied over the same time interval.

The behavior of s is quite a complicated function of t but well reproducible from one experiment to another, and four different zones can be qualitatively distinguished on the graph: They shall be referred to as zone 1, 2, 3, and 4 in the following.

At the inception of the flow and for a few seconds, the function oscillates very rapidly: The peaks of the function show that $\delta = (2k + 1)\pi$. The retardation reaches 5 or probably even 7π values which is very high for a liquid under shear flow. This large increase of the flow birefringence during the start-up of the flow can easily be followed

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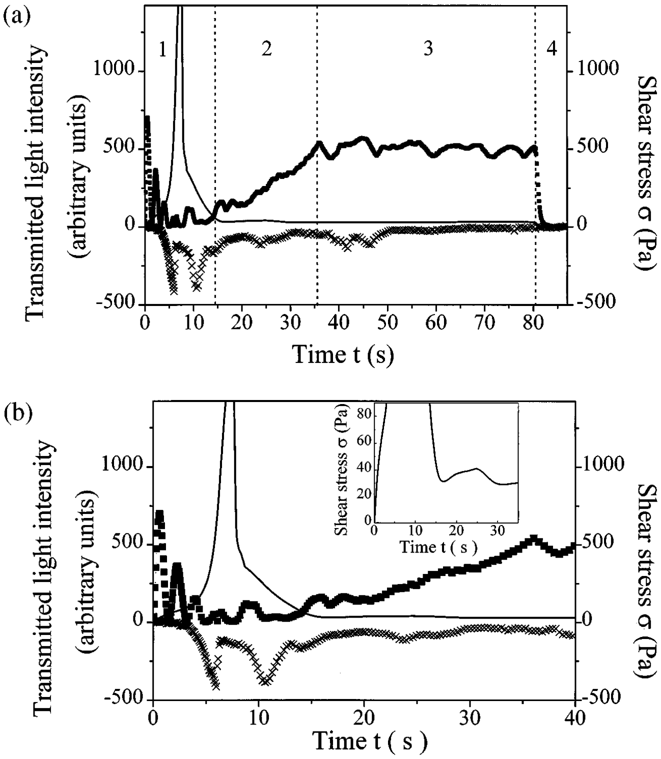

FIG. 1. (a) Variation of the transmitted light intensity (×), of $s = A\sin^2(\delta/2)$ (■), and of the shear stress σ (—) as a function of time t. (b) Variation of the previous three quantities on a shorter time scale. The inset corresponds to an enlargement of the shear stress curve.

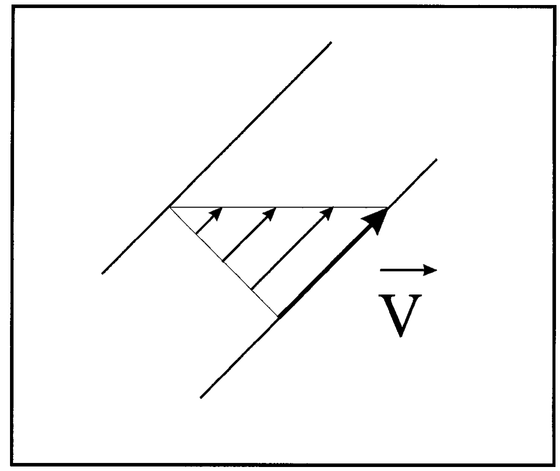

FIG. 2. Schematic description of the gap.

by direct observation of the flow with a magnifying lens or a microscope. A source of white light is now used to illuminate the gap, and we observe the solution between a crossed polarizer and analyzer. During the start-up process of the flow, the solution appears as made up of various colored bands which are propagated very quickly through the gap, indicating that the retardation δ is very important and depends both on time and space; this can easily be seen in the first few photos of Fig. 3 (see, for example, the photos corresponding to $t = 0$ to 5 s). A schematic description of the photos which represents the gap of the cell is given in Fig. 2.

A second striking feature that can be noticed is that the amplitude of the peaks diminishes with time. This behavior can be understood by looking at the intensity curve: As t increases, the transmitted intensity starts to decrease at about 1 or 2 s and goes through two minima before increasing again to the plateau value which is finally reached after nearly 30 s. As for the shear stress, $\sigma(t)$, after a very short period during which it increases smoothly, it shows an inflexion point [7] followed by a huge "overshoot" several tens of times the value corresponding to the plateau. The maximum value is found at stresses larger than 1700 Pa and does not appear on the figure. The liquid cannot bear such a high stress, in a way it "breaks" via a phase transition which could be a liquid crystal one. Then σ drops very quickly and shows a second maximum, the amplitude of which has no comparison with the first one, before reaching the plateau value which starts at the beginning of the third part of the curve $s(t)$. The angular point in the intensity curve which happens around 6 s may be related to the high value of σ.

In Fig. 3 we can see that a drastic change in the flow happens at that particular time (6 s): Patches of different colors appear in the gap; this indicates that the birefringence distribution is nonhomogeneous in the gap. This chaotic variation of Δn may result from rapid variations of the local stresses. The intensity gradually decreases again with t (see the birefringence photos corresponding to $t = 10$ to 15 s). The colors, due to a high retardation, fade slowly; the liquid which initially is translucid starts to look opaque and white like a milky solution over the entire gap, and the turbidity increases sharply as the liquid goes through a phase transition. We notice that during the same time interval, the first overshoot happens in $\sigma(t)$.

The emergence of a bright band, where the particles are strongly oriented, can already be detected near the moving wall at time $t = 14$ s. Maybe the first zone should be split into two subzones, but further experiments appear to be necessary in order to fully understand why the absorption curve presents two minima; we consider that the first zone ends approximatively at 15 s.

Small-angle light-scattering experiments allow the illustration of this shear-induced phase separation. At present these results are only qualitative and appear in Fig. 4, where the flow direction is indicated by the arrow. The first one is taken at $t = 0$ s and, thus, serves as a reference. The only signal which appears on the screen is due to the direct beam: there is no scattering. The second one at 14 s after the inception of the shear flow shows a butterfly-shaped pattern, in which the two peaks are approximatively oriented at 45° from the streamline. These butterfly shapes have been previously observed in polymer solutions [8,9] and more recently in semidilute micellar systems [10–12].

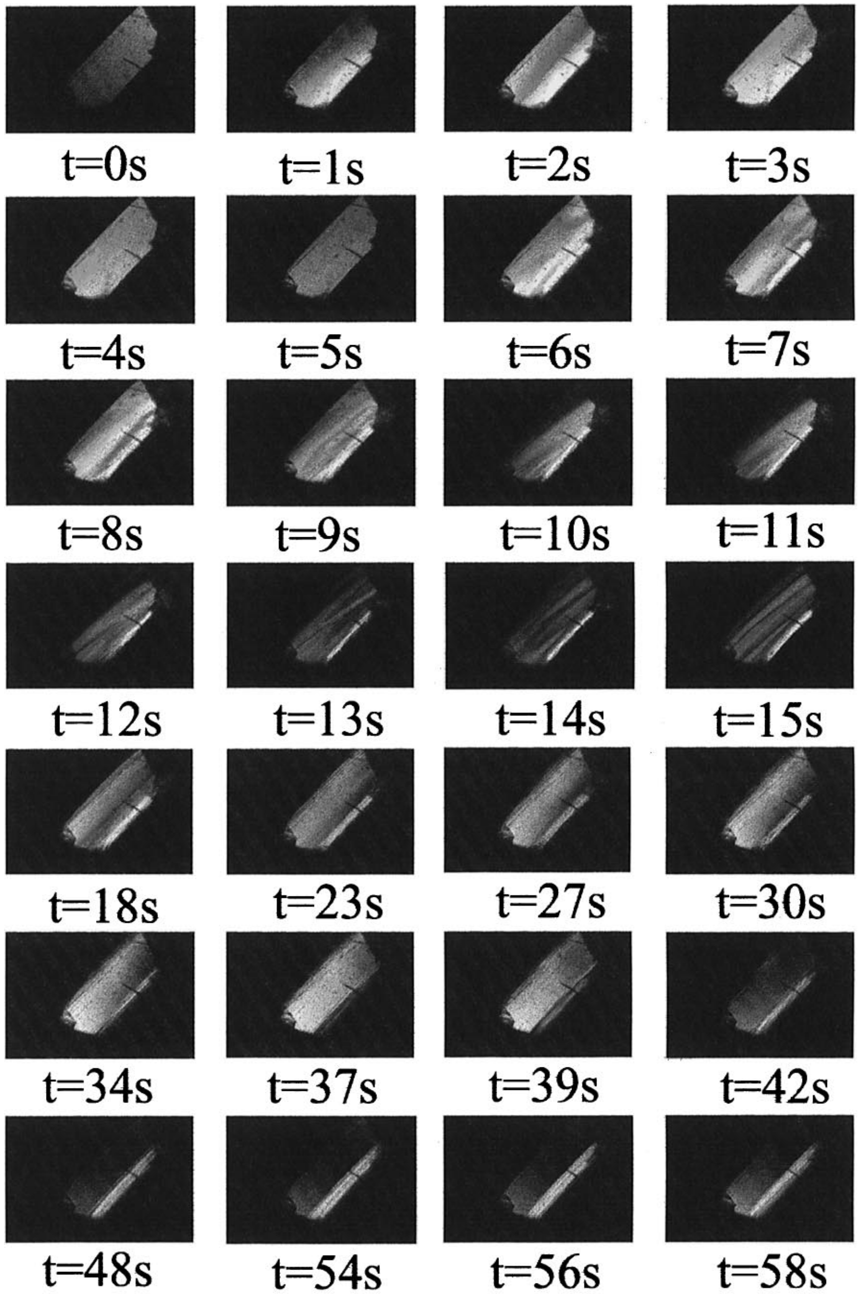

FIG. 3. Visualization of the flow in the gap of the Couette cell placed between crossed polarizers at different moments during the process of inception of the flow.

They could result from the coupling between stresses and concentration fluctuations.

The second zone (2) corresponds to the co-existence of two phases which separate gradually, the liquid becoming translucid again near the fixed wall of the cell first, then nearly over the entire gap. During this time interval (15 to 36 s), the birefringence photos let us see a thin bright band near the moving wall of the cell, whereas the second overshoot happens in the shear stress.

Also in this second zone, we have observed the emergence of a distinct diffraction pattern (not presented here) formed by a principal peak and several secondary peaks when the laser beam propagates through the bright band. This pattern has been observed in the Couette cell when the light is propagated in the z direction. In that case, it lies in the plane $(\vec{V}, \vec{\nabla} V)$ and is perpendicular to the direction of the flow. We do not yet know which "object" could be the cause of this diffraction pattern. However, this observation could lead us to the assumption that it exists as elongated structures in the bright band, strongly aligned parallel to the flow direction.

At the same time, the wings of the butterfly pattern are well separated and orientated parallel to the flow direction, as can be seen in the photos 4(c) and 4(d), taken,

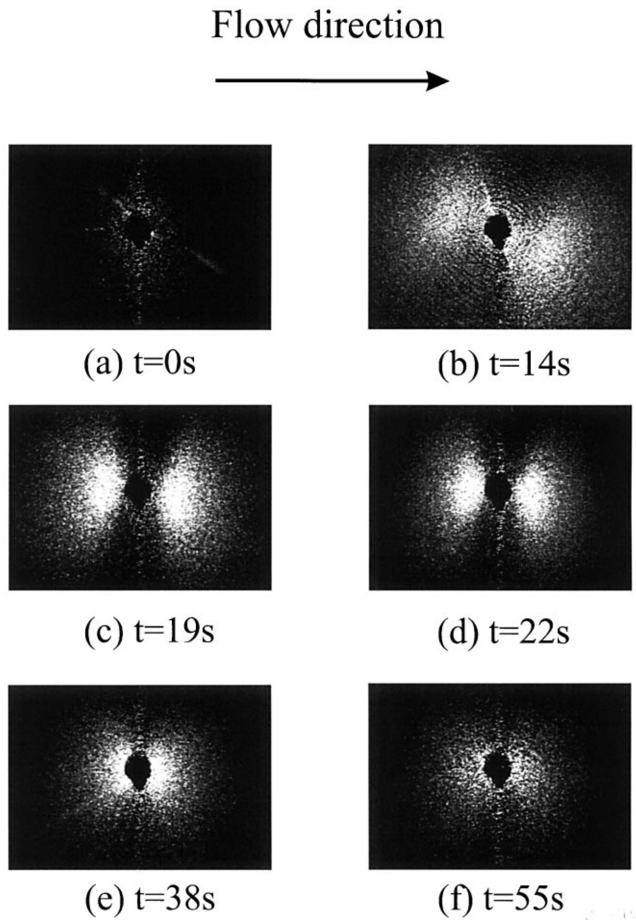

FIG. 4. SALS patterns during the transient experiment of shear flow.

respectively, at 19 and 22 s. This can be interpreted as an enhancement of the concentration fluctuations along the streamline.

But it lasts only until the end of zone 2, where the flow has almost reached a stationary state: In fact, Figs. 4(e) and 4(f) show a strong decrease of the intensity of the peaks. The "separation" between the two lobes, the extension of which is considerably reduced, is less marked. The two phases are completely separated.

In the corresponding part of the curve $s(t)$ in zone 3, δ is nearly time independent; this behavior is similar to the one observed in permanent flows. As for the birefringence pictures ($t = 37$ to 58 s), they show the shear banding flow with the highly orientated phase located near the rotating cylinder and the isotropic band extending in the other part of the gap. A better contrast between the shear-induced structure and the isotropic band is more clearly visible here because of the presence of one branch of the cross of isocline.

At the end of the third part the moving wall is suddenly stopped: The average orientation of the particles is destroyed, the birefringence intensity relaxes and finally disappears.

In order to bring this short article to a conclusion, we can say that the sudden inception of the flow leads to a phase transition which takes place in the entire gap of the Couette cell. After a short period of time, the phases separate, and the flow shows the classical two-bands structure already observed when the shear rate is gradually and slowly increased to a value belonging to the plateau of the curve $\sigma(\dot{\gamma})$. The birefringence and the shear stress reach very high values in the first zone. Transient SALS experiments show that a pattern in the shape of a butterfly appears especially in the second zone where the phases separate; this phenomenon is associated with concentration fluctuations during this phase of the flow. In the third zone, the direct observation of the highly orientated band near the moving wall with a microscope shows long black strings roughly parallel to the direction of the flow; these strings separate small patches of different colors. This indicates that the birefringence is not the same at every point of the band; this might be due to concentration fluctuations which lead to variations of the index of refraction. Further experiments shall soon be performed particularly in birefringence and shear stress measurements in order to fully understand the mechanism underlying this phase transition.

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