"Tuliplike" Scattering Patterns in Wormlike Micelles under Shear Flow

Ignatius A. Kadoma and Jan W. van Egmond
Department of Chemical Engineering, University of Massachusetts at Amherst, Amherst, Massachusetts 01003
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Using small angle light scattering we report on the formation of a string phase in a semidilute solution of wormlike micelles (0.03*M* CTAB/0.24*M* NaSal) under simple shear flow. The string phase appears as a bright narrow streak in the scattering pattern normal to the flow direction. We also study the relaxation behavior after cessation of flow, and using the Brochard–de Gennes model we are able to estimate the stress relaxation time τ_s and diffusion coefficient D_c of the dominant relaxation mode. [S0031-9007(96)00227-X]

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"Wormlike" micelles are highly flexible locally cylindrical aggregates of amphiphilic molecules. Typical radii are ~20–25 Å, with persistence lengths ~150 Å and average lengths of the micelles approaching several microns [1,2]. Accordingly, the static and quasistatic properties of these solutions are very similar to those of conventional polymer molecules [3]. However, unlike ordinary polymers, the micellar chains can reversibly break and recombine on a time scale dependent on the system and on the physicochemical conditions. This property has crucial consequences on their flow behavior and has been the object of both theoretical [3–6] and experimental [7–12] research.

In the rheology community, a considerable amount of attention is presently being focused on shear-induced transitions in complex fluids. Recent studies conducted by Kume and Hashimoto [7] and van Egmond, Werner, and Fuller [8] have reported shear-induced phase transitions in semidilute solutions of polystyrene. Also, using small angle neutron scattering (SANS) to probe individual micelles, shear-induced phase transitions of various *concentrated* wormlike micelle systems [10,11] have been reported. In this Letter, however, we use small angle light scattering (SALS) to probe clusters of micelles, and report on a shear-induced phase transition in a *semidilute* solution of *wormlike micelles*. We also investigate the relaxation behavior of the new phase following cessation of shear flow.

The system under investigation was a semidilute solution consisting of 0.03*M* cetyltrimethylammonium bromide (CTAB) and 0.24*M* sodium salicylate (NaSal) in distilled water, prepared with a salt to micelle ratio of 8:1. The solution was allowed to equilibrate for 2 days prior to any experiments. All experiments were performed at room temperature. A linear parallel plate flow cell, consisting of two glass windows separated by a gap width of 1 mm, was utilized as a shearing device. The lower plate of the parallel plate cell was driven by a linear stepping Compumotor while the upper plate was held stationary, thus providing true simple shear flow between the plates with a maximum available strain of 70 units. An 8 mW Uniphase He-Ne laser provided a source of monochromatic light of wavelength 632.8 nm. The light propagates along the velocity gradient axis thus allowing for light scattering in the plane of flow. Light scattered by the sample is projected onto a flat nonreflecting screen, whose plane is placed perpendicular to the direction of incident light. A small aperture in the screen allows transmitted light to pass. Time-resolved scattering patterns were then digitized and stored, using a two-dimensional charge coupled device array detector connected to a computer, at a typical rate of 12–15 images/s.

The scattered intensity I_S can be written as the following Fourier transformation of the equal time spatial correlation function of concentrations:

$$I_S(\theta) = A \int d\mathbf{x} \langle \delta c(\mathbf{x}) \delta c(0) \rangle e^{i\mathbf{q}\cdot\mathbf{x}} = \frac{A}{c} S(\mathbf{q}), \quad (1)$$

where $S(\mathbf{q})$ is the structure factor, $\delta c(\mathbf{x})$ is the fluctuation in concentration at the position $\mathbf{x}$, and $\mathbf{q}$ is the scattering vector.

Time-dependent evolution of the structure factor $S(\mathbf{q}, t)$, including relaxation on cessation of flow, was measured using our SALS apparatus. Experiments were run at shear rates ranging from 1 to 25 s^{-1}. Above a critical shear rate, $\dot{\gamma}_c \approx 2\ s^{-1}$, a bright streak normal to the flow was noticed, its intensity growing with increasing shear rate. At very high shear rates ($\dot{\gamma} > 100\ s^{-1}$), however, the system became unstable and no measurements could be performed. In this paper we report on the experiments conducted at a shear rate of 15 s^{-1} and a temperature of 23 °C. Figure 1 shows the time-dependent growth and orientation of the anisotropic structure factor $S(\mathbf{q}, t)$ in the flow field. The direction of flow is as indicated, with the flow starting at $t = 0$ and stopping at $t = 5.0$ s. A distinct "tuliplike" pattern—consisting of a narrow bright streak with 4 "leaves"—evolves along the vorticity axis; see Fig. 1(b). Its intensity and anisotropy grow with time, and the orientation remains along the vorticity axis. The model here is one of highly elongated one-dimensional strings, oriented in the flow direction; see Fig. 2. The strings *A* have a micelle concentration higher than that of the matrix *B*. These concentration

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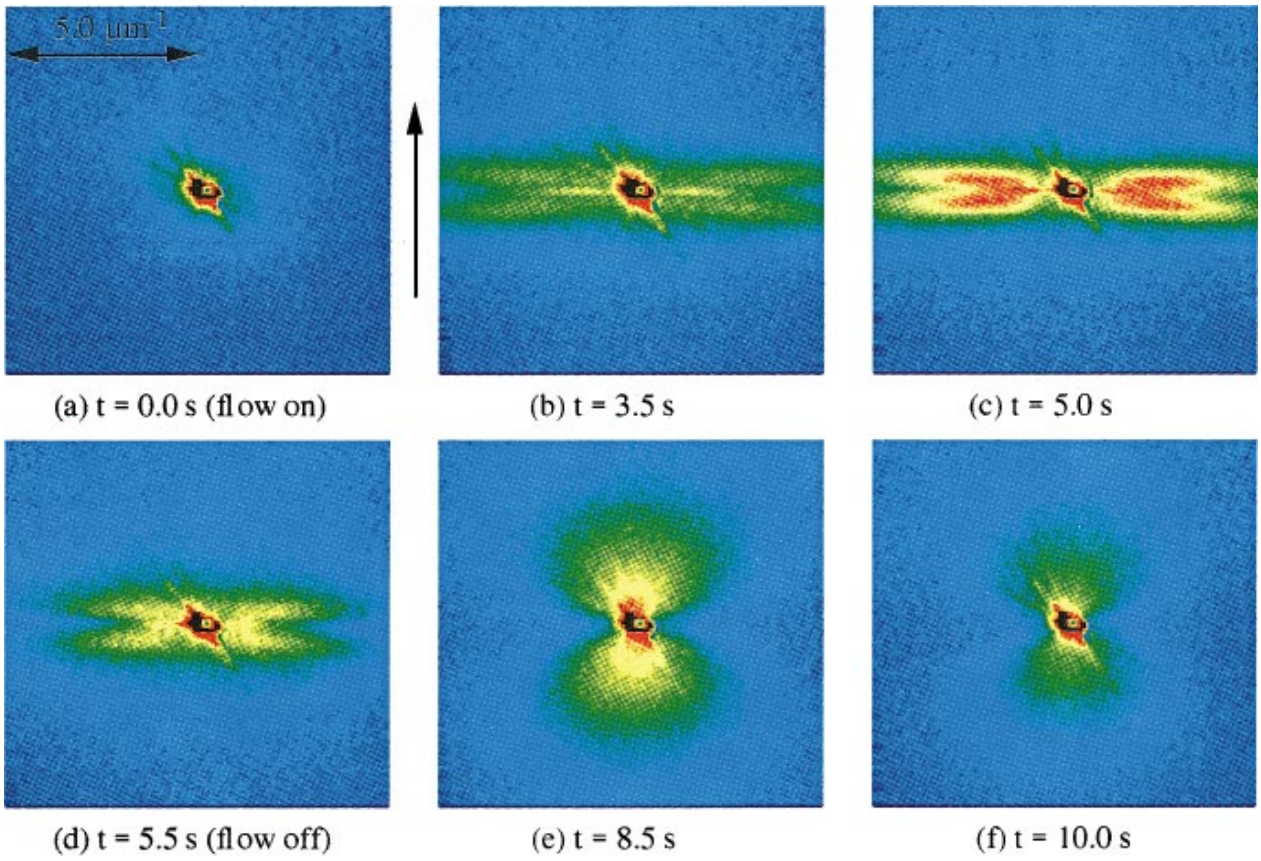

FIG. 1(color). Time-dependent response to shear flow of structure factor for $0.03M$ CTAB/$0.24M$ NaSal. $T = 23\,^{\circ}\mathrm{C}$, $\dot{\gamma} = 15\ \mathrm{s}^{-1}$.

fluctuations normal to the flow give rise to the narrow bright streak along the vorticity axis. The strings may also have internal fluctuations due to concentration and/or orientation as illustrated by regions "*a*" and "*b*." These internal fluctuations are thought to be responsible for the leaves. Moreover, since the length scale of the internal fluctuations λ is shorter than Λ, the average length scale of the fluctuations due to the strings, we would expect the leaf pattern to occur at larger scattering angles than the narrow bright streak. This string phase is thought to be a result of flow alignments and suppression of scission mechanisms, as suggested by Cates and Turner [13].

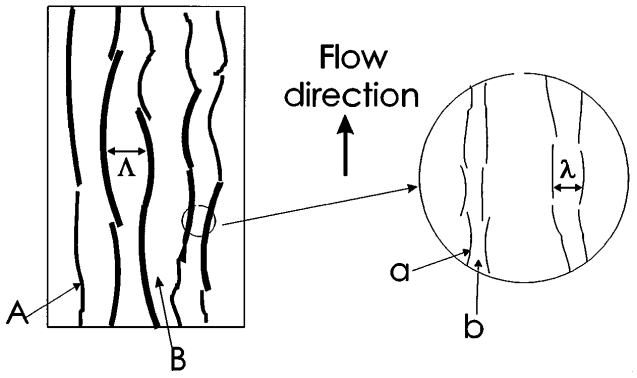

FIG. 2. Schematic of concentration fluctuations in micelle solutions at $\dot{\gamma} = 15\ \mathrm{s}^{-1}$.

On flow cessation the narrow bright streak collapses rapidly, Fig. 1(d), and is surprisingly followed by a sudden increase in $S(\mathbf{q}, t)$ along the flow axis, Fig. 1(e). The increase in $S(\mathbf{q}, t)$ forms a "butterflylike" pattern along the flow axis, which initially grows in intensity and then gradually disappears. The butterflylike pattern is thought to be a consequence of the breaking up of the elongated strings creating concentration fluctuations along the axes of the strings in the direction of flow. At the same time, the alignment of the strings is destroyed. This latter effect suppresses the intensity of the butterfly pattern and also reduces the lateral spread of the bright streak until the scattering pattern finally disappears.

Quantitative analyses were performed on each time-resolved scattering pattern after cessation of flow. Figure 3 shows the relaxation of $\Delta S(\mathbf{q}, t)$ along the flow axis. The initial increase of $\Delta S(\mathbf{q}, t)$, as mentioned earlier, is thought to be a consequence of the breaking up of the elongated strings along their axes during relaxation; however, as the alignment of the strings is destroyed, $\Delta S(\mathbf{q}, t)$ decreases with time. Owing to the similarity of worm-like micelles to polymers, the Brochard–de Gennes model [14], originally developed for polymer systems, was used to fit the data. According to this model the relaxation of $\mathbf{q}$

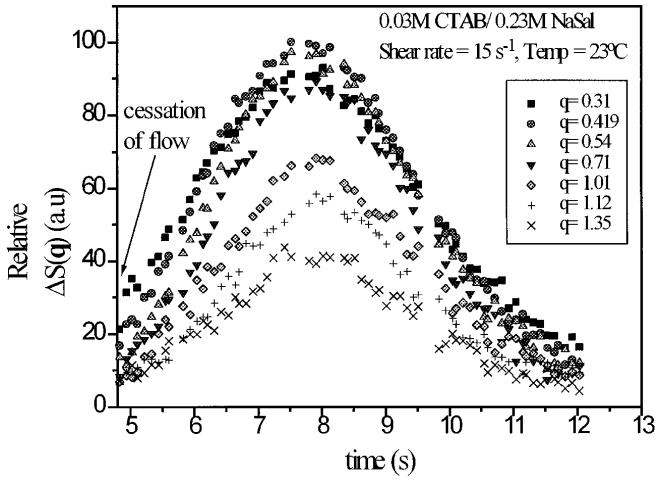

FIG. 3. Plot of relative $\Delta S(\mathbf{q}, t)$ along the flow axis vs time at various q values following the cessation of flow.

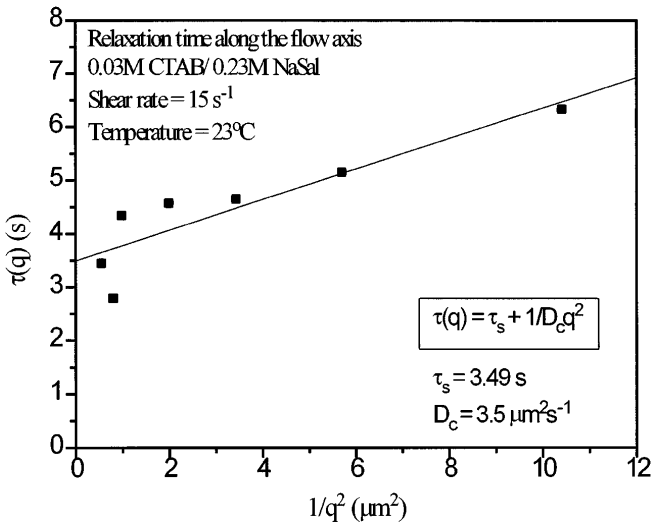

FIG. 4. Relations time $\tau_1(\mathbf{q})$ vs $1/q^2$ along the flow axis; $T = 23\,^{\circ}\mathrm{C}$, $\dot{\gamma} = 15\ \mathrm{s}^{-1}$.

modes is due to a coupling of diffusion and the relaxation of elastic stresses. This is represented as

$$S(\mathbf{q}, t) = A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2}, \tag{2}$$

where the characteristic time of the slow mode is

$$\tau_1(q) = 1/D_c q^2 + \tau_s \tag{3}$$

and that of the fast mode is

$$\tau_2(q) = (D_g q^2 + 1/\tau_s)^{-1}. \tag{4}$$

Here D_c is a cooperative diffusion coefficient, D_g is the fast diffusion coefficient, and τ_s is a stress relaxation time. The decrease of $\Delta S(\mathbf{q}, t)$ with time for each q mode was normalized and fitted by Eq. (2). Since the ratio of the preexponentials, $A_1/A_2 \sim 15$, which is much greater than 1, the slow mode dominates the fast mode. A line of best fit through a plot of $\tau_1(q)$ vs $1/q^2$ (Fig. 4) shows that Eq. (3) is a fairly good assumption. From this line of best fit, the stress relaxation time τ_s, determined from the y intercept, was found to be 3.49 s. Also, from the slope, the cooperative diffusion coefficient D_c was found to be 3.5 $\mu\mathrm{m}^2\,\mathrm{s}^{-1}$. A comparison between these quantitative results and birefringence and mechanical rheology measurements are underway.

In summary, we have shown the existence of a shear-induced phase transition in a semidilute micellar solution of CTAB/NaSal with surfactant to salt ratio of 1:8, at a shear rate of 15 s^{-1}. The induced phase is thought to consist of highly elongated strings oriented in the flow direction as evidenced by a tuliplike SALS pattern. The bright streak, at small q values, is attributed to large length scale concentration fluctuations between the oriented strings and the surrounding matrix, while the leaves are due to smaller length scale orientation and/or concentration fluctuations within the highly oriented string phase. At cessation of flow, the butterflylike pattern along the flow axis is thought to be a consequence of the breaking up of the strings creating fluctuations along their axes in the direction of flow. This behavior is similar to that observed in semidilute solutions of polystyrene [7,8]. By following the relaxation behavior of the structure factor $\Delta S(\mathbf{q}, t)$ after the cessation of flow, we were able to quantitatively estimate a stress relaxation time τ_s and a cooperative diffusion coefficient D_c. This was done by fitting plots of $\Delta S(\mathbf{q}, t)$ vs time with the Brochard–de Gennes model for semidilute solutions of polymer solutions. The observed scattering pattern is certainly not unique to the proposed flow-induced structure. Other mechanisms could account for the observed structure factor; e.g., these patterns are characteristic of phase transitions in block copolymers, blends and binary polymeric solutions [15], and also shear-induced defects of nematic liquid crystalline polymers [16]. A direct visualization of the structure by means of shear microscopy will provide a deeper understanding of the physics underlying these patterns. This investigation together with birefringence and mechanical rheology measurements are in progress. In addition, the effect of the concentration of NaSal on this phase transition is being investigated and will appear in future publications.

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