Alternating Vorticity Bands in a Solution of Wormlike Micelles

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We report on structural characterization of vorticity bands formed in a wormlike micellar solution by Rheo–small-angle neutron scattering and video imaging experiments. Below a critical shear stress τ_c in Newtonian and shear-thinning regime, only a minor flow alignment of the micelles is observed. Above τ_c , in the shear-thickening regime, alternating transparent and turbid bands are formed. Triggered small-angle neutron scattering shows different anisotropic patterns in both bands indicating strongly aligned structures. By high-speed video imaging, we show that such an alignment of micelles does not correspond to a phase of lower viscosity.

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Viscoelastic solutions of wormlike micelles (WMs) can be obtained by adding counterions or cosurfactants to certain cationic surfactants [1]. In the nonlinear flow domain, dilute and semidilute solutions of WM may exhibit complex rheological behavior due to the formation of shear-induced structures (SIS) macroscopically leading either to shear-thinning [2,3] or shear-thickening response [4–7]. The formation of SIS in most cases is not observed in the entire sample but is associated with shear bands, i.e., the formation of spatially inhomogeneous regimes. This leads to different stress or strain levels in the sheared solution and is expressed theoretically by multibranched constitutive equation [8–10]. In most cases the shear bands develop in the velocity gradient direction (e.g., radial direction in Couette flow) while vorticity bands have also been observed for semidilute shear-thickening WM solutions [6]. Shear bands, additionally, have a transient character: in velocity gradient bands, the boundary fluctuates radially and for the vorticity bands investigated in this Letter the bands undergo a flip-flop–like change axially (see video in Ref. [11]). This spatiotransient behavior of shear bands with different structure and, consequently, viscosity manifests itself in oscillations of the overall rheological signals or rheochaotic behavior [5,7,12–14]. While much of the theoretical work addresses the radial shear bands [9,13,15], only a few attempts have been made towards explaining the shear-thickening vorticity banding as seen in our system [16].

In this Letter, we report on the structural investigation of an equimolar semidilute solution of cetylpyridinium chloride (CPyCl) and sodium salicylate (NaSal) with triggered Rheo–small-angle neutron scattering (Rheo-SANS) and video imaging experiments to clearly distinguish between the structures in vorticity bands as well as their spatiotemporal appearance. The system exhibits a Maxwell-like flow behavior ($G_0 = 6.3$ Pa and relaxation time $\lambda = 0.02$ s) in the linear regime and a rich nonlinear rheological response associated with distinct optical behavior [6,14,17,18]: (i) at rest and in the Newtonian flow region the sample is opti-

cally transparent; (ii) in the shear-thinning regime the solution turns slightly turbid; and (iii) in the shear-thickening regime transparent and turbid bands appear in the vorticity direction of the flow geometry. These vorticity bands alternate in their position (flip-flop), forcing the free parameter (shear rate $\dot{\gamma}$, apparent viscosity η) to oscillate under controlled shear stress conditions. Once a critical shear stress τ_c is applied to the system, the bands appear without incubation time and oscillate with a frequency and amplitude that depends on the applied shear stress and gap size [18]. Even though this particular WM solution has been studied for over a decade now, several questions still remain unanswered whereof two are discussed in this Letter: (a) whether the transparency and turbidity observed below τ_c are of similar structural or orientational origin as above τ_c and (b) if the difference in the microstructure within the vorticity bands is influencing the local viscosity of each band and the macroscopic flow response.

The cationic surfactant CPyCl, the salt NaSal, and deuterium oxide (D_2O) were obtained from Fluka (Buchs, Switzerland) and used without further purification to prepare equimolar solution of 40 mM CPyCl and NaSal. Rheo-SANS experiments were performed on the SANS-I beam line at PSI, Villigen, Switzerland. A controlled-stress Rheometric Scientific® DSR rheometer equipped with a neutron-transparent concentric cylinder shear cell made of SuprasilTM glass was set up in the neutron beam. The shear cell consists of a stationary outer cylinder of 32 mm and an inner cylinder of 30 mm diameter (1 mm gap and $T = 22$ °C). The shear cell was mounted in radial beam position, with the neutron beam passing through the sample along the velocity gradient (y) direction, probing the structure of the micelles in the flow-vorticity (x - z) plane. The neutron wavelength was fixed at 8 Å. Data were collected on a two-dimensional ^3He detector at distances of 2, 6, and 18 m covering a momentum transfer q of $0.003 \leq q \leq 0.15$ Å⁻¹. After correction for background radiation, empty cell scattering, detector efficiency, and conversion to an absolute scale using direct beam intensity, the 2D

intensity maps were 20° section averaged in flow (x) and vorticity (z) directions for further analysis.

Figure 1 displays the linear and nonlinear flow curve (stress controlled) and corresponding 2D SANS patterns for the quiescent state (0 Pa) and under imposed shear stress for the WM solution [18]. At low shear stresses ($\tau \leq 5$ Pa) the solution exhibits Newtonian behavior, which is associated with an isotropic intensity map. With an increase in shear stress ($6 \leq \tau \leq 13$ Pa) shear-thinning becomes evident and SANS patterns become elongated in the vorticity direction (z) indicating shear-induced alignment of the WMs [19]. Comparing the anisotropic scattering patterns to those of other semidilute and concentrated WM systems [2,20], wherein similar onset of shear-thinning properties were observed, the system at hand shows a weak anisotropy in the shear-thinning regime, with absence of any two-lobed or butterfly-like patterns.

The apparent viscosity of the solution significantly increases above the critical shear stress of $\tau_c \approx 13$ Pa with the appearance of transient oscillations of shear rate and viscosity. Furthermore, in this shear-thickening regime, alternating vorticity bands appear in the form of transpar-

FIG. 1 (color online). Nonlinear and linear (inset) flow curves for a 40 mM CPyCl-NaSal WM solution and the corresponding SANS intensity maps at rest (0 Pa) and at different elevated shear stresses. The dotted ellipse in the flow curve shows the region where the solution exhibits shear-thickening ($13 \leq \tau \leq 23$ Pa) while the bars indicate the minimum and maximum shear rate during flip-flop motion at constant shear stress. The inset shows the linear flow behavior indicating a Maxwell behavior. Displayed scattering patterns were collected at 6 m detector distance, corresponding to a q range of $0.008 - 0.06 \text{ \AA}^{-1}$. Coordinates x , y , and z correspond to the flow, velocity gradient, and vorticity directions, respectively. The neutron beam passes through the sample along the velocity gradient y direction.

ent and turbid concentric rings [Fig. 2(a)]. To elucidate the microstructures in these vorticity bands separately, triggered SANS experiments were designed so that scattering patterns could be obtained exclusively from turbid or transparent bands, despite their spatiotransient appearance. Triggering was achieved by an external trigger signal, a He-Ne laser beam, which was passed orthogonally to the neutron beam to detect the nature of the bands, either turbid or transparent. Measured laser intensity was fed to a Labview-based computer program which allowed us to enable or disable the neutron detection depending on the transmitted laser intensity. Figure 2(b) shows the scattering patterns obtained by triggering the neutron detector for transparent and turbid bands. Two remarkable features emerge from this triggered experiment. First, the intensity maps show two-lobed patterns oriented in the vorticity (z) direction as compared to the spherical and elliptical patterns in Newtonian or shear-thinning flow, respectively, (Fig. 1). Such two-lobed patterns indicate a higher degree of anisotropy, i.e., a stronger alignment of the wormlike chains in the flow (x) direction [2,21,22] compared to the shear-thinning regime below τ_c . Second, there is a considerable difference between the patterns obtained from the transparent and turbid states. For the turbid state, the overall scattering intensity in vorticity (z) direction is enhanced and intensity in the flow (x) direction is diminished as compared to the transparent state indicating that the turbid state is more anisotropic than transparent state.

To quantify these intensity maps, the 20° sector averaged scattering intensity I was calculated in the flow (x) and vorticity (z) directions and plotted against momentum transfer q as shown in Fig. 3 for both transparent and turbid regions. The experimental data were fitted using the

FIG. 2 (color online). (a) Formation of vorticity bands in the shear-thickening regime at 21 Pa, as visualized by a high-speed digital video camera. The small white rectangle shows the approximate position of the neutron beam. (b) 2D SANS patterns obtained by triggering the Neutron detector for transparent (left) and turbid (right) regions at a detector distance of 6 m ($0.008 \leq q \leq 0.06 \text{ \AA}^{-1}$) (see also Fig. 3).

Hayter-Penfold model for sheared solid cylinders [23], shown as solid lines in Fig. 3. The data are in good agreement with the model in the high q region (>0.06) which gives the diameter of the micelles. We obtain an average micellar diameter of 44 Å. The model did not give any large differences in micelle diameter for transparent or turbid bands, meaning the overall cross-sectional area of micelles remains identical in both states. The inset in Fig. 3 shows the scattering anisotropy A_f as a function of τ . The anisotropy factor is defined as $A_f = [i_z - i_x]/i_z$ with $i_{x,z} = \int I_{x,z}(q) dq$ and $I_z(q)$ and $I_x(q)$ as the intensities in the vorticity and flow directions, respectively [22]. We observe that anisotropy index gradually increases with the shear stress until the critical stress of $\tau_c \approx 13$ Pa is reached. Above τ_c , in the shear-thickening flow, A_f is significantly higher (triangular symbols) indicating a high degree of orientation.

In summary, the SANS intensity maps [Fig. 2(b)] and A_f values indicate that both the oscillating transparent and turbid bands consist of highly anisotropic structures as compared to the structures in the shear-thinning regime. This answers the first question raised in the initial part of the Letter: the optical properties are due to the different structural alignment of the micelles under flow and above τ_c generally a higher degree of orientational ordering is observed with the turbid vorticity band having the highest anisotropy.

The second question raised concerns differences in the viscosity within each vorticity band and the overall oscillation of the macroscopically detected viscosity signal. To

FIG. 3. Scattering intensity I as a function of momentum transfer q for transparent (open symbols) and turbid bands (closed symbols) obtained from triggered measurements. Square symbols represent 20° sector average in vorticity direction and circles represent the same in flow direction. The inset shows the anisotropy factor A_f as a function of shear stress τ . The gray circles are calculated A_f for $\tau < \tau_c$ and triangular symbols are for $\tau > \tau_c$, i.e., in the vorticity banding regime. Open triangle corresponds to transparent band and closed triangle to the turbid band.

address this point, we investigated the banding regime by flow-visualization methods with the same Couette shear cell used for Rheo-SANS. With a high-speed digital video camera (NAC MemreCam fx RX6), images of alternating vorticity bands and the position of the inner rotating cylinder were captured simultaneously at a rate of 100 frames per second. The grayscale intensities of the images were analyzed to obtain the average intensity of the bands, I , while the corresponding angular position θ and the angular velocity ω of the rotating inner cylinder were detected using a position marker at the rotating tool.

Figure 4(a) shows a series of video snapshots of the vorticity bands: frames *ii* and *iv* show a complete clear solution appearing between states of turbid bands nucleating either in the upper part (frame *iii*) or lower part (frames *i* and *v*). It should be noted that the clear image is of much shorter duration and until now only a flip-flop like spatial change in axial position has been seen and discussed [6,14,18]. The corresponding intensities of the bands are depicted in Fig. 4(b) along with the angular position θ of the inner rotating cylinder of the Couette geometry. It is clear from the figure that the rotating cylinder displays a pulsating motion ($f \approx 2$ Hz) [6], which is correlated to the appearance and disappearance of the bands (a plot of θ vs time should be linear if the rotation of the cylinder is continuous). From the angular position θ the angular velocity $\omega = d\theta/dt$ is calculated and is shown in Fig. 4(c). The region A marked in Fig. 4(c) shows the region wherein the angular velocity ω of the tool (black symbols) gradually increases, which corresponds to the appearance of a fully transparent region (square symbols). In region B, [Fig. 4(c)] the angular velocity ω of the rotating cylinder decreases to zero and even shows a negative value; i.e., the inner cylinder is forced to rotate backwards. This correlates with the appearance of a turbid band [square symbols in Fig. 4(c)]. As the angular speed ω can be directly related to the macroscopic shear rate $\dot{\gamma}$ these results indicate a higher viscosity for the system in the presence of turbid bands. A striking feature of Fig. 4(c) is a phase shift of $\sim \pi/2$ between the two signals indicating that the structure formation is not in line with the rheological response function. It is because of such a phase difference between the shear rate (imposed by a constant shear stress above τ_c) and the SIS (structural change manifested in anisotropy A_f) that the system never reaches a stationary state and continues to maintain alternating vorticity bands and the oscillation of the free rheological parameter. A similar observation was made by Hu *et al.* [5] for dilute shear-thinning systems showing a phase shift between the structure formation and the development of the shear stress. In their system this phenomena was, however, slower due to the low concentration of both surfactant and counterion.

In conclusion, by triggered Rheo-SANS experiments, we showed that the observed transparent and turbid optical appearance in Newtonian, shear-thinning, and shear-thickening flow regimes is caused by different structural

FIG. 4. Coupling between structure and flow: time evolution of macroscopic band morphology and the rotation of the inner cylinder of the shear cell. (a) Vorticity bands as seen through the transparent concentric cylinders in the flow-vorticity (x - z) plane. Images i to v cover one period which is approximately 1 s. The white dotted rectangle shows the area used to extract the average grayscale intensity of the bands and the dotted line in the middle shows the approximate boundary between the bands. The corresponding intensities of the images i – v are shown in (b). (b) Average intensity I of vorticity bands (open squares) and angular position θ of the inner rotating cylinder of the Couette geometry (closed circles) as a function of time. A higher intensity corresponds to a turbid band and a lower intensity to a transparent one. (c) Average intensity I and angular velocity $\omega = d\theta/dt$ of the rotating tool (closed circles) as a function of time. Regions marked A and B indicate appearance of transparent and turbid bands, where the angular velocity ω of the tool increases and decreases, respectively.

arrangements of the WMs expressed by the anisotropy factor A_f , with the turbid band having the highest anisotropy. The Rheo-SANS experiments further provide the micellar diameter of 44 Å, but it would be too premature to speculate on the mesoscale structure of the vorticity bands. Video imaging experiments indicate that the turbid band exhibits a high viscous flow response and that a phase shift between the structural buildup in the bands and the rheological response function forces the sample to exhibit continuous oscillations in the free rheological parameter. However, this finding leaves us with the somewhat puzzling result that the turbid vorticity band composed of highly aligned structures has a higher viscosity than the less anisotropic transparent vorticity band. In a forthcoming investigation we will address (i) the transient structure formation in an extended q range to elucidate micellar length and the question, and (ii) if a nematic ordering

which would suggest a reduced viscosity of the turbid band [6,24] is indeed applicable for the investigated system.

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