Transient non-monotonic flow of surfactant solutions in strain- and stress driven flow

Vishweshwara Herle, Peter Fischer, and Erich J. Windhab

ETH Zurich, Laboratory of Food Process Engineering, Institute of Food Science and Nutrition, 8092, Zurich, Switzerland

ABSTRACT

The non-linear rheology of semi-dilute surfactant solution in shear flow is presented. The studied solution shows a pronounced shear-thickening behaviour that is coupled with oscillations of the free rheological parameter and the presence of shear-bands. With the help of rheo-small angle light scattering and optical imaging techniques an attempt is made to correlate the developed flow-induced structures to the flow curve.

INTRODUCTION

It is well known that under certain conditions surfactant molecules in aqueous media can form long rod-shaped aggregates or wormlike micelles. In the linear flow regime the solution can be explained as a simple Maxwell fluid, however, the rheological response is of a complex manner in the non-linear regime. For the latter case, a huge body of very different flow response is observed and discussed in literature over the last few years[1-5]. In general, it is observed that high shear rates disturb the equilibrium structure and kinetics of the surfactant aggregates and, as a consequence, new shear-induced phases and structures are developed during shearing. Depending on the concentration regime of the surfactant solved in aqueous solution (dilute or semi-dilute), the systems may exhibit a shear-thinning or shear-thickening behaviour[6-8,3]. A prominent example is cetylpyridinium chloride and sodium salicylate (CPyCl/NaSal) that normally exhibit shear-thinning behaviour coupled with spurt. But an equimolar mixture of this surfactant and counterion in the concentration regime from 30 to 80 mM/L shows, first shear-thinning and then a pronounced shear-thickening properties with the formation of shear bands[5,9-10].

In the present study, the equimolar surfactant-counterion solution of cetylpyridinium chloride and sodium salicylate was investigated in a transparent parallel-plate geometry using strain- and stress-controlled rheometers. The influence of the gap size on the rheological response function and on the formation of shear bands was discussed with the help of optical imaging and small angle light scattering (SALS) measurements.

EXPERIMENTAL

Solutions of 40mM/l Cetylpyridiunum chloride (CpyCl) and 40mM/l sodium salicylate (NaSal) were prepared in double distilled water with the ratio of salt to surfactant as one. The experiments reported in this contribution were performed using the Rheometric Scientific DSR and ARES rheometers equipped with parallel-plate geometry of 40 mm diameter. A fluid bath was used to maintain the temperature at 20±0.5°C. While DSR was used for stress controlled measurements, ARES was used for strain controlled measurements. SALS images were taken in DSR with the transparent parallel-plate geometry. A 5mW He-Ne laser provided a monochromatic light of wavelength 632.8nm. The scattering images formed on the screen below the sample were captured using a Sony CCD camera (DFW-V 500, Japan). The maximum angle of the scattered light was about 10°. Optical images of the sheared solution were also recorded using a CCD camera fixed below the bottom plate.

RESULTS

Non-Linear Rheology

The flow curves of the investigated fluid in both strain- and stress-controlled experiments are shown in Fig. 1.

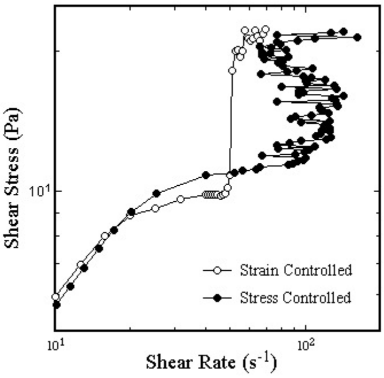

Figure 1. Flow curves for an equimolar (40mMol/l) CpyCl-NaSal solution in stress- and strain- controlled experiments at 20°C

These data were accomplished using parallel-plate geometry of gap 1mm at 20°C. At low shear rates the material shows Newtonian and then shear-thinning behaviour but as soon as the shear rate reaches a critical value, the solution enters in to a shear-thickening regime with the formation of clear and turbid ring like patterns or shear bands. The solution also displays different kind of macroscopic flow behaviour when investigated in strain- or stress-driven experiments. In the non-linear flow regime, above the critical shear rate, where the shear bands are formed, the measured free variable such as shear and normal stress (strain-controlled experiment) or shear rate (stress-controlled experiment) oscillates drastically.

A transient signal of the shear rate in case of stress-controlled experiments is shown in Fig. 2 for a shear stress of 18Pa. This kind of unsteady signal is observed from a shear stress of 12Pa onwards and is because of the shear-induced structures built up in the sample, which changes the shear viscosity in a periodic manner. In all cases (parallel-plate, 1mm gap), the shear rate oscillates with a frequency of 1s. In the shear-thinning regime however, the signal is constant as a function of time. Similar transient behaviour was also observed in strain-controlled experiments by one of us[9].

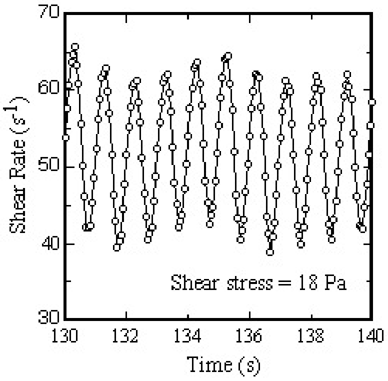

Figure 2. Transient behaviour of the shear rate in stress-controlled rheometer (DSR) at a shear stress of 18Pa

Optical images and SALS patterns

To further investigate the shear banding flow, optical and SALS images of the solution in question were taken in stress-controlled (DSR) rheometer at different stress levels as shown in Fig. 3. Left side of each optical image corresponds to the outer edge of the parallel-plate geometry (1mm gap); black areas correspond to clear sample and the bright areas to the turbid bands.

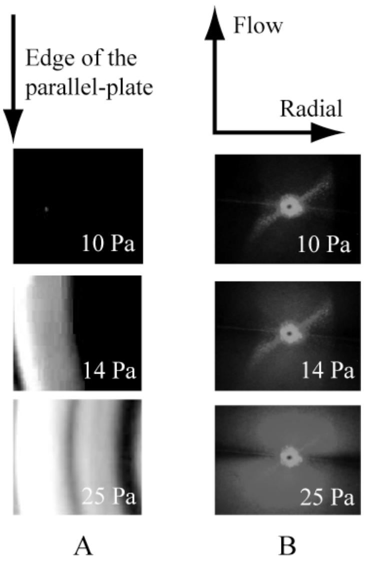

Figure 3. Optical images (A) and SALS patterns (B) of the surfactant solution

The sample is clear in the linear flow regime (10Pa). As the flow enters the non-linear regime, first the solution becomes homogeneously turbid while in the following shear-thickening regime shear-bands are developed with alternating turbid and clear ring-like patterns (14Pa & 25Pa). We also observed that each ring fluctuated between turbid and clear state. The corresponding SALS patterns show butterfly like scattering patterns in the shear-thickening regime and no significant scattering in the shear-thinning regime. This butterfly like scattering pattern is similar to the scattering pattern found in entangled polymer solutions or in viscoelastic surfactant solutions[11].

Further, we investigated the gap dependency of these shear bands in the parallel plate geometry. Experiments were performed with four different gap sizes, 1.0mm, 0.5mm, 0.25mm and 0.1mm. We observed that for all the gap distances studied here, once the critical shear rate is reached, turbid bands start to develop at the outer edge of the parallel-plate and then spread inward. In the non-linear regime, at a shear stress of 25Pa, with decrease in the gap distance the number of turbid bands increase and the intensity of these turbid bands decrease as shown in Fig. 4. For very small gaps like that of 0.1mm, the solution shows multiple bands of very weak intensity only at the outer edges of the parallel-plate geometry. We also observed that decreasing the gap size decreased the higher angle scattering in the SALS patterns (not shown here).

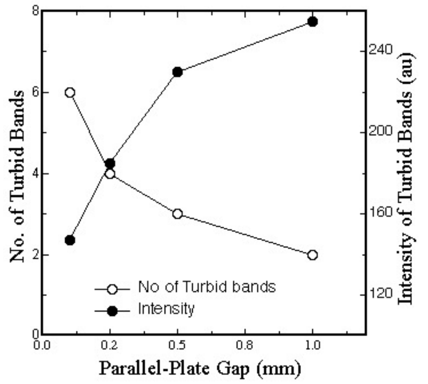

Figure 4. Effect of gap size on the formation of shear bands and their intensity at a shear stress of 25Pa. (The intensity is the average intensity of the outer most turbid band)

DISCUSSION

From the optical and SALS images (Fig. 3) it is clear that the worm-like micelles build up large ring like aggregates. The aggregation of the worm-like micelles and the oscillation of the free parameter can be explained assuming that one of the bands, *e.g.* the turbid one, has a significant higher viscosity than the clear solution. Under constant stress or strain conditions, the two-fold value of the free parameter is now determined by the width, number and the intensity of the generated turbid or clear bands. We observed that, for a gap size of 1mm, at a constant stress in shear banding regime, the shear bands fluctuate from clear to turbid ring like patterns with a frequency of 1s. This causes the shear rate to oscillate (Fig. 2) as the viscosity of the sample is being periodically altered. Lowering the gap size from 1mm to 0.1mm leads to the formation of more number of less intense turbid bands. This means that sample confined in the small gaps will generate low stresses resulting in a shift of the flow curve towards higher shear rates and a later onset of shear-thickening (not shown here). Comparison of the SALS and optical images of the sample at different gap distances suggest that the intense dark bands are due to concentration-fluctuations and as the gap decreases these fluctuations are suppressed due to geometrical restrictions.

CONCLUSIONS

In summary, we reported on the observation that viscoelastic surfactant solutions exhibit a transient band formation in simple shear flow which significantly influences the rheological response function depending on the length scale of the geometry. Due to the geometrical restriction of the flow field, different aggregation forms evolve and the noteworthy point in our experiments is that not only the shear stress (or shear rate) but also the gap distance triggers the formation of shear-induced structures.

ACKNOWLEDGMENT

Financial support for one of us (VH) by ETH Zurich is acknowledged.

REFERENCES

1. Spenley, N. A., M. E. Cates, et al. (1993). "Nonlinear Rheology of Wormlike Micelles." *Phys. Rev. Lett.* **71** (6): 939-942.

2. Schmitt, V., C. M. Marques, et al. (1995). "Shear-Induced Phase-Separation of Complex Fluids - the Role of Flow-Concentration Coupling." *Phys. Rev. E* **52** (4): 4009-4015.

3. Grand, C., J. Arrault, et al. (1997). "Slow transients and metastability in wormlike micelle rheology." *J. Phys. II France* **7** (8): 1071-1086.

4. Berret, J. F. (1997). "Transient rheology of wormlike micelles." *Langmuir* **13** (8): 2227-2234.

5. Fischer P., Wheeler E.K., Fuller, G.G. (2002). "Shear-banding structure oriented in the vorticity direction observed for equimolar micellar solution." *Rheologica Acta* **41**: 35-44.

6. Hu, Y. T., Boltenhagen, P. et al. (1998). "Shear thickening in low-concentration solutions of wormlike micelles. I. Direct visualization of transient behavior and phase transitions." *J. Rheol.* **42**(5): 1185-1208.

7. Hu, Y. T., Boltenhagen, P. et al. (1998). "Shear thickening in low-concentration solutions of wormlike micelles. II. Slip, fracture, and stability of the shear- induced phase." *J. Rheol.* **42**(5): 1209-1226.

8. Rehage, H. and H. Hoffmann (1991). "Viscoelastic Surfactant Solutions - Model Systems for Rheological Research." Mol. Phys. 74(5): 933-973.

9. Fischer, P. (2000). "Time dependent flow in equimolar micellar solutions: transient behaviour of the shear stress and first normal stress difference in shear induced structures coupled with flow instablities." *Rheologica Acta* **39**: 234-240.

10. Wheeler, E. K., P. Fischer, et al. (1998). "Time-periodic flow induced structures and instabilities in a viscoelastic surfactant solution." *J. Non-Newton. Fluid Mech.* **75**(2-3): 193-208.

11. Kadoma, I. A. and J. W. van Egmond (1996). ""Tuliplike" scattering patterns in wormlike micelles under shear flow." *Phys. Rev. Lett.* **76**(23): 4432-4435.