Structure and rheology of a shear-thickening wormlike micellar system

Simultaneous formation of vorticity and velocity bands studied by birefringence measurements

1 Vishweshwara Herle, Peter Fischer
2 Joachim Kohlbrecher
3 Cesare Olivero
4 Sebastien Manneville
5 Christophe Baravian
6 Francois Caton

1 Institute of Food Science, ETH Zurich, 8092 Zurich, Switzerland
2 Paul Scherrer Institute, 5232 Villigen, Switzerland
3 Department of Chemistry, University of Calabria, 87036 Consenza, Italy
4 Laboratoire de Physique, ENS Lyon, 69364 Lyon, France
5 LEMTA, CNRS - UMR, Nancy, France
6 Laboratoire de Rheologie, Universite Grenoble, 38041 Grenoble, France
A boring afternoon in the lab
Micellar system under study

System: 40 mMol/L Cetylpyridinium chloride - Sodium salicylate

- Newtonian
- Shear thinning
- Shear thickening
- Formation of alternating vorticity bands

Newtonian and shear thinning regime

- **Newtonian Regime**
  - Transparent

- **Shear thinning regime**
  - Slightly turbid

- **Optical appearance**

- **Graph**
  - Shear Stress (Pa) vs. Shear Rate (s⁻¹)
  - Newtonian Regime: Transparent
  - Shear thinning regime: Slightly turbid

- **Diagram**
  - Stationary Cup
  - Rotating cylinder
  - Sample

London, 4.9.007
Shear thickening regime ($\tau > \tau_c$)

- Formation vorticity bands
- Bands alternate in position
- Shear rate and $\eta$ oscillates

Rheology, flow visualization and SALS -> Stress induced bands
Rheology - transient shear flow

\[ \tau < \tau_c \]

No shear rate oscillations

\[ \tau > \tau_c \]

Shear rate oscillates
Sample never equilibrates!
Methods used & questions asked

Rheology & Flow visualization

Optical appearance (flip-flop) of bands correlated to rheological oscillations?

Influence of geometry?

Triggerd Rheo-Small Angle Neutron Scattering (Rheo-SANS)

Newtonian \textit{clear} = shear thickening \textit{clear}?

Shear thinning \textit{turbid} = shear thickening \textit{turbid}?
Methods used & questions asked

Fast camera, ultrasound Velocity Profiling (UVP), and Rheo-NMR

Wahst is the individual rheology of the clear and turbid bands?

Direct birefringence measurements

Is there really a radial band within the vorticity band (sub-banding)?
Are the oscillations in viscosity and shear rate the same as in the optical appearance of the bands?

Establish via **optical rheometry and SALS** the (obvious) link between ring formation and oscillation of the free parameter.
Instrumentation (optical rheology)

Rheo-Small Angle Light Scattering

Optical Imaging set up

Both set-ups are designed for the Stress controlled rheometer (DSR)

\[ |q| = 0.25 - 10 \mu m^{-1} \]
Analysis of the oscillating signal - FFT

Oscillating shear rate signal from flow curves and oscillating intensity signals from the shear bands

Fast Fourier Transform

Power Spectrum

Shear Stress = 17 Pa
Frequency at \( P_{\text{max}} \) = 0.91 Hz

Shear Stress = 18 Pa

Position I  Position II
Oscillating shear bands in parallel plate device

Rheological signal

Optical and mechanical signals superimpose!

Oscillations are indeed due to the flip-flop of the bands

Amplitude of rate oscillation increases with stress @ constant gap (except for 0.10 mm)

Decrease in gap suppresses the rate oscillations
For a gap of 0.10 mm->NO

0.10 mm is an exception!

Certain length scale is required for band formation
Flow visualization & Rheology

Structural buildup is determined by the rheometer gap

Flow visualization & Rheology

Shear induced structures $\leftrightarrow$ Length scales

Lowering the gap
- Shear thinning instead of thickening
- Intensity of turbid bands decreases
- More number of less intense bands
- Oscillations of the $\dot{\gamma}$ are dampened

Vorticity bands & SANS

What are the structures in these bands?
How to access the structural information in each band?

By triggering the SANS detector and selectively collecting the scattering for each band
**SANS - Set up**

Neutron source: PSI SANS-I

\[ \lambda = 8 \, \text{Å} \]

Detector dist. = 2, 6, and 18 m

\[ q \text{ range} = 0.003 - 0.15 \, \text{Å}^{-1} \]

Suprasil Glass

Outer cylinder dia = 32 mm

Inner cylinder dia = 30 mm

Gap = 1 mm
Newtonian and Shear thinning regime

1. No significant anisotropy is observed
2. Partial alignment of micelles

$x =$ Flow direction  
$y =$ Vel. gradient direction  
$z =$ Vorticity direction

SANS-Trigger Set-up

- Set a threshold value
- Trigger the SANS detector
- Collect the data
1. Triggering the detector helps to separate the scattering information.

2. Transparent state in this regime is structurally different from the one in the Newtonian or shear thinning regime.

3. Both transparent and turbid bands are highly anisotropic.

4. Turbid state is more anisotropic than transparent one.

SANS Analysis for flip-flop bands

$I$ vs $q$ plot

Hayter model for sheared (solid) cylinders
Dia of micelles ~ 40 angstrom
Approx. length of micelles ~ 1200 angstrom

SANS Analysis for flip-flop bands

Anisotropy

\[ A_f = \frac{I(Q)_{\perp} - I(Q)_{\parallel}}{I(Q)_{\perp}} \]

Turbid band correspond to a more anisotrope state

* Croce et. al. 2005, Langmuir
Schubert et. al. 2004, Langmuir
What are the viscosity in the individual bands (Part I)?

How to access the rheology of each band?

Motion of rotation tool captured by high speed camera images
Alternating Vorticity bands

Problems and Questions

• It is difficult to capture the dynamics of the process

• Does the oscillation in the tool really corresponds to the bands?

• If yes, then, when the tool slows down and when it accelerates?

• Finally, what are the structures in these bands?
Vorticity bands - Analysis

Analysis of the bands and the position of the tool using LabView program
Vorticity bands - Analysis

- As the turbid band appears velocity approaches zero
- Implying turbid bands may be of higher viscosity!

What are the **viscosity** in the individual bands (Part II)?

How to access the rheology of each band?

Is the turbid band more viscous than the clear one?

By time-resolved Ultrasound Doppler Velocimetry collecting the shear rate for each band
UVP-Experimental Set-up

UVP @ Newtonian and Shear thinning regime

- No radial banding in stress plateau regime as in conventional systems
- Flow is homogeneous
UVP @ Shear thickening regime ($\tau > \tau_c$)

- **Radial Banding is present**
- **Flow is inhomogeneous**
- **At higher stresses flow becomes chaotic!**
- **Local velocity fluctuates as a function of time**
Local shear rates and time evolution \( (\tau > \tau_c) \)

Local shear rates in each band can be calculated.

This will give an idea about local shear rates.

Position of the interface \( (\delta) \) was monitored.
Local shear rates as a function of time ($\tau > \tau_c$)

In the Stress-plateau regime

$\gamma_1$ and $\gamma_2$ are anticorrelated

$\gamma_2$ and $\delta$ are correlated
We do not see the vorticity bands (all turbid due to seeding):

- The behavior of local shear rates seems chaotic!
- Is the flip-flop of the macroscopic motion hidden?
Possible coexistence of radial and vorticity bands?

Newtonian flow
Shear-thinning flow

Radial shear banding

Vorticity banding

Coupled radial and vorticity banding plus pretty much noise of rheochaos
Vorticity bands & Direct birefringence

Do the sub-bands flip-flop?
How to access the structural information in each band?

By direct birefringence measurement of each band in the “chaotic regime”
Direct birefringence - Set-up

Laser close to inner rotating cylinder

Laser close to outer cylinder

Radial sub-band found in vorticity bands

Inner cylinder (rotating):

- Turbid band
- Clear band

Outer cylinder:

- Turbid band
- Clear band
Radial sub-band found in vorticity bands

Inner cylinder (rotating):
Vorticity bands correlate with the oscillation of the free rheological parameter. Gap effect suggests different lengthscale are relevant for rheological response.

Optical and mechanical signals superimpose!
Summary (2)

Rheo-SANS suggest the highest aligned band to be high viscous

Shear Thinning

\[ \tau < \tau_c \]

Isotropic at rest \rightarrow Partial Alignment

Shear Thickening and vorticity bands

\[ \tau > \tau_c \]

Isotropic at rest \rightarrow Transparent (A) \rightarrow Turbid (B) \rightarrow Strong alignment (anisotropic)
Fast camera experiments show that the creating of turbid band leads to oscillation in viscosity. Due to a phase difference of $\pi/2$ the system never reaches a steady state.

As the turbid band appears, velocity approaches to Zero

Turbid state is more anisotropic than transparent one
Local velocity measurements (Rheo-UVP) and Direct Birefringence measurements show the existence of coupled radial and vorticity banding.
Summary (5)

Is it a Russian Doll ...
...or scrap metal to be sold to China?
Richard Nixon
(quoted by Thomas Pynchon in "Gravities Rainbow",
performed by Ernest in Sherman’s Lagoon)