The Dynamics and Stability of Viscoelastic Wormlike Micelle Solutions in Strong Extensional Flows

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Surfactant Solutions

- Surfactants used as rheological modifiers and detergents in a host of industrial applications and consumer products
  - Applications include ink jet printing, agrochemical spraying, enhanced oil recovery, ground water remediation …
  - Consumer products include soaps, shampoos, cosmetics, inks and paints
- Surfactants are composed of a hydrophilic head and a long hydrophobic tail
- When dissolved in water can self-assemble into large aggregate
Why Wormlike Micelles and not Spheres or Bilayers?

- Isrealachvili (1992) demonstrated that the morphology of the micelle depends primarily on the character of the surfactant and the quantity of salt.

  - Surfactants with large head groups tend to form spherical micelles.

  - Surfactants with small head groups tend to form wormlike micelles.

  - Surfactants with bulky tails (double chained) tend to form bilayers.
Dynamics of Wormlike Micelle Solutions

- To relieve stress, entangled micelles can *reptate* past each other

![Diagram showing reptation](image)

- Or wormlike micelles can *break* and *reform*

![Diagram showing breaking and reforming](image)
Steady Shear Rheology

- Rheology is a very sensitive bulk measure of molecular and supramolecular structure of a material.
- CPyCl and NaSal mixed in 100mM NaCl solution with a 2:1 molar ratio.
- Concentration of CPyCl was varied between $50 \leq \text{mM} \leq 200$.
- High shear rate behavior indicative of shear banding.
Shear Rheology – Linear Viscoelasticity

- Small Amplitude Oscillatory Shear probes linear response of viscoelastic fluids

\[ \gamma = \gamma_0 \sin \omega t \]

\[ \tau = G' \sin \omega t + G'' \cos \omega t \]

\[ G' \rightarrow \text{Storage Modulus} \ldots \text{elasticity of fluid} \]

\[ G'' \rightarrow \text{Loss Modulus} \ldots \text{viscosity of fluid} \]

[Graph showing Storage and Loss Modulus, \( G' \) & \( G'' \) vs. Angular Frequency, \( \omega \) [rad/s]]

Maxwell Model

\[ \eta \]

\[ G \]

Characteristic Relaxation Time

\[ \lambda = \eta / G \]
Shear Rheology – Linear Viscoelasticity

- Small Amplitude Oscillatory Shear probes linear response of viscoelastic fluids
  - $G'$ → Storage Modulus … elasticity of fluid
  - $G''$ → Loss Modulus … viscosity of fluid

- Cates showed that when $\lambda_{\text{break}} \ll \lambda_{\text{rept}}$

$$\lambda = \left( \frac{\lambda_{\text{rept}} \lambda_{\text{break}}}{m} \right)^{1/2}$$

- Deviations at high frequencies due to Rouse-like modes can be used to determine $\lambda_{\text{break}} \approx 200\text{ms}$

- Plateau modulus can determine mesh size of entangled micelle network

$$\zeta_m = \left( \frac{kT}{G_0} \right)^{1/3}$$
Shear Rheology – Summary Equimolar Solutions

- Viscosity, relaxation time and elastic modulus of CPyCl/NaSal solutions increase monotonically with surfactant concentration.

<table>
<thead>
<tr>
<th>CPyCl/NaSal [mM]</th>
<th>50/25</th>
<th>100/50</th>
<th>150/75</th>
<th>200/100</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zero-shear viscosity</td>
<td>$\eta_0$ [Pa-s]</td>
<td>2.84</td>
<td>31.5</td>
<td>86</td>
</tr>
<tr>
<td>Plateau modulus</td>
<td>$G_0$ [Pa]</td>
<td>4.2</td>
<td>27</td>
<td>60</td>
</tr>
<tr>
<td>Maxwell relaxation time</td>
<td>$\lambda$ [s]</td>
<td>0.772</td>
<td>1.44</td>
<td>1.592</td>
</tr>
</tbody>
</table>

- This is not true for all surfactant solutions
  - CTAB/NaSal solutions for example do not exhibit nice monotonic growth

<table>
<thead>
<tr>
<th>CTAB/NaSal [mM]</th>
<th>10/10</th>
<th>17.5/17.5</th>
<th>25/25</th>
<th>50/50</th>
<th>75/75</th>
<th>100/100</th>
<th>150/150</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zero-shear viscosity</td>
<td>$\eta_0$ [Pa-s]</td>
<td>5.0</td>
<td>41</td>
<td>68</td>
<td>62</td>
<td>55</td>
<td>39</td>
</tr>
<tr>
<td>Plateau modulus</td>
<td>$G_0$ [Pa]</td>
<td>0.28</td>
<td>1.2</td>
<td>2.5</td>
<td>10.9</td>
<td>26.2</td>
<td>48.8</td>
</tr>
<tr>
<td>Maxwell relaxation time</td>
<td>$\lambda$ [s]</td>
<td>18</td>
<td>35</td>
<td>27</td>
<td>5.7</td>
<td>2.1</td>
<td>0.8</td>
</tr>
</tbody>
</table>
Filament Stretching Rheometry

The fluid filament experiences a transient uniaxial extensional flow field as it is stretched.

We can simultaneously measure stress and flow induced birefringence of the fluid filament during stretch and relaxation.

\[ \varepsilon = -2 \ln \left( \frac{R_{\text{mid}}}{R_0} \right) \]

\[ \langle \tau_{zz} - \tau_{rr} \rangle = \frac{F_z}{\pi R_{\text{mid}}^2} + \frac{1}{2} \rho g \left[ \frac{L_0 R_0^2}{\pi R_{\text{mid}}^2} \right] - \frac{\sigma}{R_{\text{mid}}} \]
• All wormlike micelle solutions show significant strain hardening.

• At large extension rates, all solutions fail with rupture near axial midplane at a constant value of extensional stress independent of extension rate.

• At lower extension rates, filaments fail through elasto-capillary thinning.

→ Interestingly, failure occurs at tensile stresses larger than that at rupture.
Filament Failure Mechanism

- At large extension rates, filaments do not fail due to elasto-capillary thinning, but through rupture near the axial midplane.

- Failure at constant stress likely stems from breakdown of entangled micelle structure

- Expect this to be the maximum tensile stress that could be supported by micelle network

- Increase in maximum tensile stress under elasto-capillary thinning suggest changes to the micelles or the micelle network at low extension rates.

150/75mM CPyCl/NaSal

\[ De = \lambda \Delta \varepsilon = 2.6 \]
\[ \Delta t_{\text{rupture}} = 11\text{ms} \]
• Sharp increase in the maximum extensional viscosity at low extension rates.

• At large extension rates, stress at rupture is independent of extension rate so the final Trouton ratio at failure decreases with increasing extension rate.

• In no experiments is a steady state extensional viscosity reached before filament fails.
- Sharp increase in the maximum extensional viscosity at low extension rates.

- At large extension rates, stress at rupture is independent of extension rate so the final Trouton ratio at failure decreases with increasing extension rate.

- In no experiments is a steady state extensional viscosity reached before filament fails.
• We have seen the complex behavior of wormlike micelles in shear and extensional flows, what about flows with mixed kinematics?

• To test, we performed a detailed experimental study of flow of a wormlike micelle solution past a series of falling spheres.

• Applicable to flows of consumer products like paints and shampoo, to enhanced oil recovery, micron and nano-particle suspensions, microrheology....

• Complex extensional rheology behavior results in a new class of flow instabilities unique to wormlike micelle solutions.
Drag correction factor $K(a/R, Re, De)$

- Shear thinning causes drag reduction on sphere
- Development of extensional stress in wake, $De > 2$, slow sphere considerably
- At larger Deborah numbers, $De > 4$, the flow becomes unstable.

\[ U_{stokes} = \frac{2a^2(\rho_s - \rho)g}{9\eta_0} \]

$U = \text{measured terminal velocity}$
New Flow Instability

• Above a critical Deborah number, $De > 4$, the motion of the sphere becomes unstable
• Instability not observed for spheres falling through polymer solutions.

\[ De = 6.6 \quad Re = 1.7 \times 10^{-3} \]
Motion of sphere is initially stable (a-c)

At a random location and time, the sphere abruptly accelerates (d)

Sphere decelerates and elasticity causes the velocity of the sphere to oscillate (e-i)

Amplitude of the oscillations decay and the motion of the sphere is again stable (j-l)
Would like to determine the extent of micelle deformation in the wake.

Sedimenting sphere imaged through crossed linear polarizers.

Pockets of highly deformed fluid appear to pinch off in the wake of the sphere.

After being pinched off the deformation in these regions decays with time.
Flow Instability Mechanism

• We believe flow instability is related to filament rupture in extensional rheology.

• From birefringence data we can approximate maximum deformation of wormlike micelle in wake.

• Maximum deformation of micelle corresponds to almost 90% of the finite extensibility.

• Good agreement with deformation just prior to filament rupture in extensional flow.
Flow of Wormlike Micelle Solutions Past a Confined Cylinder

- Flow past a single cylinder is qualitatively similar to flow past a sphere
  - Difference is that extensional flow in wake is biaxial rather than uniaxial.
- Is a benchmark problem for both computational and experimental studies
Pressure Drop Measurements – Steady State


Newtonian Response

Extensional Thickening Response

Shear Thinning Response

- Newtonian response for
  \[ De \frac{\lambda \bar{U}}{R} < 1 \]

- Normalized pressure drop decays quickly with increasing flow rate for
  \[ 1 < De < 5 \]

- Normalized pressure drop begins to plateau for \( De > 5 \).

- No shear banding is observed.

- Instability is only observed for the 50mM/50mM CTAB/NaSal at both 5:1 (●) and 10:1 (□) aspect ratios and not the 100mM/50mM CPyCl/NaSal (▲) at 5:1.
Flow Induced Birefringence Measurements

- Polarizers crossed at $0^\circ$ and $90^\circ$ to highlighting shear flow.
- CTAB/NaSal at $De = 3$

- Contours of shear stress $\tau_{xy}$ at a $De = 3$
- Comparison shows excellent qualitative agreement

More FIB results

- Polarizers crossed at 45° and 135° to highlighting extensional deformation.
- CTAB/NaSal at $De = 3$

- Contours of tensile stress $\tau_{xx}$ at a $De = 3$
- Comparison shows excellent qualitative agreement

FIB Variation with Deborah Number

- Polarizers crossed at 45° and 135° to highlighting extensional deformation.
- Strong extensional tail observed in wake of cylinder.
- Tail grows with increasing Deborah number.
- Stark differences observed between FIB of the two fluids.
- CTAB/NaSal unstable above $De > 4.5$
FIB Variation with Aspect Ratio

- Polarizers crossed at 45° and 135° to highlighting extensional deformation.

- Increasing aspect ratio shifts everything to higher Deborah number.

- Critical Deborah number for onset of instability shifts from $De = 4.5$ to $De = 6.0$ as aspect ratio increases from 5:1 to 10:1.

- Interaction between shear flow from confining walls and extensional flow not needed for instability.
Movies of CTAB/NaSal Instability – Side View

$De = 10$
Movies of CTAB/NaSal Instability - Top View

De = 8
pre-instability

De = 8
post-instability

De = 16

De = 8
• Velocity profiles at low Deborah number agree well with previous measurements of flow of polymer solutions past confined circular cylinder.
Why is CTAB unstable and CPyCl is not?

- Can differentiate velocity profile in wake of cylinder to calculate the extension rate.
- Can integrate extension rate forward with time to calculate accumulated strain.
- Now have quantified strength of extensional flow in wake of cylinder.
Why is CTAB Unstable and CPyCl is Not?


- Extensional rheology could explain the difference
- CPyCl/NaSal solutions capable of supporting larger stress before rupture.  
  \( \tau_{\text{rupt}} = 2.7 \text{kPa for CTAB/NaSal vs. } \tau_{\text{rupt}} = 8.5 \text{kPa for CPyCl/NaSal} \)
- CTAB/NaSal strain hardens and ruptures more quickly making rupture likely in flow past single cylinder where strains of \( \varepsilon \sim 2.5 \) and Deborah numbers of order \( De = 1 \) were found.
Flow Through a Periodic Array of Cylinders (PAC)

- Periodic array of cylinders a natural extension to flow around a single cylinder
- Additionally, this geometry is a good approximation of flow through porous media
- Can investigate the effect of size and spacing of cylinders to determine effect of forcing micelles through a number of strong shear and extensional regions
Pressure Drop Measurements – Steady State


- Newtonian response for $De \cdot \frac{\bar{U}}{R} < 1$
- Normalized pressure drop decays quickly with increasing flow rate for $1 < De < 5$
- Normalized pressure drop begins to increase again for $De > 5$.

- No shear banding is observed.
- Instability is only observed for the 50mM/50mM CTAB/NaSal (●) and not the 100mM/50mM CPyCl/NaSal (▲) solution.
Elastic Flow Instability ($De = 10$)

- At high Deborah numbers, elastic instability in CTAB solution presents itself, resulting in large asymmetrical deformation around the PAC.
- This can be observed in streakline images, PIV or FIB measurements.
Semi-Dilute Regime – Branched vs. Linear Micelles

- The kinematics and details of micelle break-up and reformation depends on surfactant type and salt concentration.

- Micelles want to minimize number of endcaps.

- In the limit of low salinity, electrostatic repulsions keep the micelles from interacting leading to linear micelles (a).

- For high salinity, electrostatic screening makes higher curvature and interaction possible leading to interconnected networks (c) or branched micelles (b).

- Transition from (a) to (b) occurs when three-point junctions become more energetically favorable than endcaps.
Stress Relaxation – Additional Mechanisms for Branched Micelles

• To relieve stress, entangled micelles can pass right through each other forming temporary branch points along the way.

  ![Temporary Branch](image)

• Once a branch point is formed, it can move along the micelle with no energy penalty.
  
  - This is very different from branched points in polymers which are fixed and often make it difficult to move entangled polymer through reptation.

• In polymer melts and solutions, branches hinder mobility resulting in increased elasticity, viscosity and relaxation times.

• How does branching affect the rheology of wormlike micelles?
Branched Wormlike Micelles - Composition

- Typically form wormlike micelles by combine charged surfactants with salts.
- We will focus on the systems developed by Raghavan and Kaler (2000, 2002) who mixed cationic and anionic surfactants to form linear and branched wormlike micelles.

Octyl Trimethyl Ammonium Bromide (C₈TAB)

\[
\begin{align*}
\text{CH}_3 & \quad \text{Br}^- \\
\left[ C_n\text{H}_{n+1}-\text{N-CH}_3 \right] & \\
\text{CH}_3 & 
\end{align*}
\]

Sodium Oleate (NaOA)

\[
\begin{align*}
\text{O} & \\
\left[ C_7\text{H}_{15}-\text{CH}=\text{CH} -C_8\text{H}_{16} -\text{C-O}^- \right] & \\
\text{Na}^+ & 
\end{align*}
\]
Shear Rheology – Effect of Changing Concentration

Chellamuthu and Rothstein, J. Rheology, 52 (2008) 865-884.

- Holding the ratio of the two surfactants fixed (70/30 C₈TAB/NaOA) and increasing concentration, the viscosity increase before going through a plateau.

- Two solutions with very different composition can have the same viscosity. Why?
  → The maximum represents a transition from linear to branched micelles.

- The transition from an entangled network of linear micelles to an increasingly branched system can be seen in the Cryo-TEM images of Danino et al. (2001)
The extensional viscosity appears to mirror the non-monotonic behavior of shear viscosity.

However, if one plots Trouton ratio \( Tr = \frac{\eta_E}{\eta_0} \), then at the onset of branching the strain hardening is eliminated and the response becomes Newtonian \( Tr_{Newt} = 3 \).

The additional stress relief mechanisms available to branched systems are appear to be extremely effective at reducing stress, especially in extensional flows.
Conclusion

- The break-up and reformation of wormlike micelle solutions in strong shear and extensional flows can lead to a host of new and interesting phenomena and flow instabilities.

Acknowledgements

Support

- NSF
- 3M Non-Tenured Faculty Award
- John Healy Foundation
- UMass MRSEC

Students

- Sheng Chen
- Erik Miller
- Avinash Bhardwaj
- Manoj Chellamuthu
- Geoff Moss