Wormlike Micelle Rheology

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Sponsors: Procter and Gamble, NSF
The Challenge of Multiple Length and Time Scales in Surfactant Solutions

10^23 degrees of freedom!

http://www.ifnh.ethz.ch/vt/research/projects/vivianel
Micellar solutions: the salt curve

Increase surfactant/salt concentration

- Citronellol
- Limonene
- Linalol
- Vanillin

10% SLES

No additives

- Cumene
- Linalool

DPG
Snapshots of micelles with 100 SDS molecules

<table>
<thead>
<tr>
<th></th>
<th>GROMOS45A3</th>
<th>OPLSAA</th>
<th>CHARMM36</th>
<th>OPLSU A</th>
<th>GROMOS53A6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid crystal phase formed in small region, 4 O share 1 Na⁺</td>
<td>Intermediate</td>
<td>Head groups are spread out</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Sodium-oxygen condensed patch

larger aggregates form “bicelles”

larger aggregates form cylinders

: S
: O
: CH₂, CH₃
: Na⁺, Cl⁻
CTAC in NaSal: Stable Threadlike Micelle

Equal molar Sal⁻/CTA⁺

3.28M NaCl

Ordering of Atoms

Packing density: \( n_L \approx 21-27/\text{nm} \)

Experiments: 21-28/\text{nm}

Head group: 2D hexagonal lattice

Hydrophobic tail: radially oriented
Umbrella Sampling

Weighted Histogram Analysis Method (WHAM)

PMF \( w(z) \)

\( z = r \), radial coordinate

molecular dynamics (MD) simulations:

\[ m_i \frac{d^2 v_i}{dt^2} = f_i \]

density \( \rho(z) \)

Video from student Kyle Huston
Potential of Mean Force

n= 60 SDS surfactants

1\textsuperscript{st} window

20\textsuperscript{th} window

<table>
<thead>
<tr>
<th>$\Delta G^0$</th>
<th>SDS</th>
<th>C12E5</th>
</tr>
</thead>
<tbody>
<tr>
<td>-RT ln(CMC) (experiment)</td>
<td>8.8 kT</td>
<td>13.6 kT</td>
</tr>
<tr>
<td>Atomistic Simulation*</td>
<td>9.7 kT</td>
<td>13.1 kT</td>
</tr>
</tbody>
</table>

*SDS Micelle Aggregation Number: n = 60
*C12E5 Micelle Aggregation Number: n = 54

Micelle Size Distribution
(inferred from potentials of mean force)
Yuan and Larson, JPC B (2015)

\[ X_n = X_1^n \exp \left( -\frac{1}{k_B T} \sum_{j=2}^{n} \Delta \mu_j^0 \right) \]

\[ X_n = X_{n-1} X_1 \exp \left( -\frac{\Delta \mu_n^0}{k_B T} \right) \]

\[ \Delta \mu_n^0 = \mu_n^0 - (\mu_{n-1}^0 + \mu_1^0) \]
Micelle Size Distribution

(inferred from potentials of mean force)

Yuan and Larson, JPC B (2015)

\[ \Delta \mu_n^0 = \mu_n^0 - (\mu_{n-1}^0 + \mu_1^0) \]

\[ X_n = X_{n-1}X_1 \exp \left( -\frac{\Delta \mu_n^0}{k_BT} \right) \]
Scission free energy
From coarse-grained Martini MD – WHAM simulations

\[ \Delta G_{\text{sciss}} (R = 0.6) = 27 K_B T \]
\[ \Delta G_{\text{end}} (R = 0.6) = 13.5 K_B T \]
Length scales in threadlike micelles

Persistence Length

Entanglement Length

Mesh Size

Average Micelle Length

d = 2r_{cs}

Time scales: micelle breakage time, reptation time

Micellar relaxation dynamics

Reptation:
Edwards, De Gennes,
\[ \tau_{\text{rep}} \sim L^3 \]

Micelle breakage & Re-joining:
M.E. Cates (1989):
\[ \tau_{\text{break}} \sim 1/L \]

Slide from Peter Koenig, P&G
Breakage

Reptation

Recombination

Contour length fluctuations

Pointer algorithm: simulation of ensemble of micelles

\[ G(t) = G_N \mu^2(t) + \text{Rouse} + \text{bending modes} \]

Including Bending Modes

From Oelschlaeger et al., Langmuir, 2009

diffusing wave spectroscopy

\[ G'(\omega) \mu (i \tau_p)^{3/4} \]

Morse & Macintosh

\[ \frac{\partial \phi}{\partial t} \approx D_\phi \frac{\partial^2 \phi}{\partial s^2} \quad D_\phi \equiv \frac{B}{\zeta} \]

\[ B(\omega) = \frac{2^{3/4} k_B T}{l_p} (i \omega \tau_p)^{3/4}, \tau_p = \frac{\zeta l_p^3}{k_B T} \]

\[ G'(\omega) = \text{RE} \left[ \frac{L B(\omega)}{15} \right], G''(\omega) = \text{IM} \left[ \frac{L B(\omega)}{15} \right] + \omega \eta_s \]

\[ l_p = \frac{b_K}{2} \]

\[ \zeta_\perp = \frac{4 \pi \eta_s}{\ln (0.6 \xi / d)} \]
Micelle Parameters from Rheology

Key parameters from mechanical rheometry:

- \( G_N \)
- \( \tau_{\text{rep}} \)
- \( \zeta \)
- \( \omega_{\text{max}} \)
- \( \omega_{\text{min}} \)
- \( l_p \)

From neutron scattering or molecular simulations:

- \( b_r / b_{\text{rep}} \)

Obtain from Diffusing Wave Spectroscopy:
Result and analysis

- Results

6.67 wt% SLE1S, 3.10 wt% NaCl with solvent viscosity $\eta_s = 0.9$ cP at 25°C

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Mechanical data</th>
<th>DWS data</th>
<th>Combined data</th>
</tr>
</thead>
<tbody>
<tr>
<td>$G_N$ (Pa)</td>
<td>115</td>
<td>105</td>
<td>115</td>
</tr>
<tr>
<td>$\zeta$</td>
<td>2.49</td>
<td>1.16</td>
<td>1.82</td>
</tr>
<tr>
<td>$\langle L \rangle$ (μm)</td>
<td>1.45</td>
<td>1.60</td>
<td>1.59</td>
</tr>
<tr>
<td>$\alpha_e$</td>
<td>1.35</td>
<td>1.41</td>
<td>1.36</td>
</tr>
<tr>
<td>$d$ (nm)</td>
<td>4</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>$l_e$ (nm)</td>
<td>155</td>
<td>161</td>
<td>153</td>
</tr>
<tr>
<td>$l_p$ (nm)</td>
<td>116</td>
<td>114</td>
<td>112</td>
</tr>
</tbody>
</table>

Average fitting deviation < 5%

$\zeta \equiv \frac{\bar{r}_{br}}{\bar{r}_{rep}}$, $\alpha_e \equiv \frac{l_e}{l_p}$
Effect of Persistence Length $l_p$
Effect of Breakage Rate, $\zeta$
Micelle Parameters obtained from Pointer Algorithm

SLE1S

Branching
Scission Free Energy from Rheology

SLE1S/CAPB

\[ \langle L \rangle \propto \exp(\frac{\Delta G^{sciss}}{2k_B T}) \]

\[ \Delta G^{sciss} = 24 - 28 k_B T \]

The average micelle length \( \langle L \rangle \) and the average aggregation number \( \langle n \rangle \) are given by:

\[ \frac{\rho \pi d^2 \langle L \rangle N_A}{4M} = \langle n \rangle \approx 2\chi^{0.5} \exp \left( \frac{\Delta G^{sciss}}{2k_B T} \right) \]

\( \chi \) is the mole fraction of the surfactant, \( \Delta G^{sciss} \) is the free energy of breakage.

\( M \) = mass of surfactant; \( \rho_s \) = density of surfactant; \( d \) = micelle diameter, \( N_A \) = Avogadro’s number.
Current Work:
Adding Branches to Simulation Method

Constrained diffusion model

\[ x_i = \text{displacement} \]

Diffusion
\[
x_1 = \sqrt{\frac{6k_B T \Delta t}{\zeta_{14}} n_{14}}.
\]
Current Work: Adding Branches to Simulation Method

Constrained diffusion model

\[ x_i = \text{displacement} \]

\[ F_2 = 0 \]

\[ x_1 + x_2 + x_3 = 0 \]

Diffusion

\[ x_1 = \sqrt{\frac{6k_BT\Delta t}{\zeta_{14}}} n_{14} + \frac{(F_1 - F_4)\Delta t}{\zeta_{14}} \]
Current Work:
Adding Branches to Simulation Method

Constrained diffusion model

\[
\begin{align*}
F_2 &= 0 \\
x_2 &= \text{displacement} \\
F_3 &= 0 \\
x_1 + x_2 + x_3 &= 0
\end{align*}
\]

Diffusion

\[
x_1 = \sqrt{\frac{6 k_B T \Delta t}{\zeta_{14}} n_{14} + \frac{(F_1 - F_4) \Delta t}{\zeta_{14}}}
\]

Constraint

Kirchhoff Circuit model

\[
\begin{bmatrix}
1 & 0 & 0 & a_{41} & 0 & 0 & -a_{41} \\
0 & 1 & 0 & 0 & a_{42} & 0 & -a_{42} \\
0 & 0 & 1 & 0 & 0 & a_{43} & -a_{43} \\
0 & 0 & 0 & 1 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 1 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 1 & 0 \\
-1 & -1 & -1 & 0 & 0 & 0 & 0
\end{bmatrix}
\begin{bmatrix}
\Delta x_{41} \\
\Delta x_{42} \\
\Delta x_{43} \\
F_1 \\
F_2 \\
F_3 \\
F_4
\end{bmatrix}
= \begin{bmatrix}
b_{41} \\
b_{42} \\
b_{43} \\
0 \\
0 \\
0 \\
0
\end{bmatrix}
\]

\[
a_{ij} = \frac{\Delta t}{\zeta_{ij}}, \quad b_{ij} = \sqrt{\frac{2 k_B T \Delta t}{\zeta_{ij}}} n_{ij}
\]

\[
\begin{align*}
U_2 &= 0 \\
U_3 &= 0 \\
U_4 &= 0 \\
U_1 &= 0 \\
I_1 + I_2 + I_3 &= 0 \\
I_1 &= i_1 + \frac{(U_1 - U_4)}{R_{14}}
\end{align*}
\]
Modelling of branched micelles: micelle architecture
Modeling of Branched Micelles: Budding Process

Budding process

$\varsigma_{bd} = \frac{\tau_{bud}}{\tau_{br}}$

Nucleation process
Buds = nucleation seed

Add buds
Rejoining
Sprouting
Remove un-sprouted buds
Short Sprouts

Additional relaxation
Constrained diffusion

Additional relaxation
Constrained diffusion
reptate
reptate
reptate
Modeling of Branched Micelles: Results

Total number of micelles: 2500;
Average micelle size $\langle M \rangle$: 4 μm;
Dimensionless breakage time $\zeta_{br}$: 0.003;
Dimensionless budding time $\zeta_{bd}$: 0.33;
Micelle entanglement length $l_e$: 100 nm;
Micelle persistence length $l_p$: 50 nm;
Micelle diameter $d$: 4 nm;

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System composition

- Linear micelle (35 wt%)
- Lightly branched micelle (60 wt%)
- Highly branched micelle (5 wt%)

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Strand length distribution

Average strand length $\langle L_{st} \rangle = 2.2$ μm

Number of branch junctions per micelle size $\langle \beta \rangle = 0.09$ per μm

---

Number of branch junctions per micelle size $\langle \beta \rangle = 0.09$ per μm
Modeling of Branched Micelles: Effect of Branching

\[ G^*(\omega) = F\left[G_N \mu^\alpha(t, \langle M \rangle, \alpha_e, \zeta_{br}, \beta)\right] + G^H(\omega) \]

- **Storage and loss modulus**
- **G** indicates the storage modulus.
- **H** indicates the loss modulus.
- **F** is the frequency-dependent function.
- **G_N**: plateau modulus
- **zeta_br**: dimensionless reaction time
- **alpha_e**: semi-flexibility
- **M**: average micelle size
- **beta**: branching level
- **d**: micelle diameter

**Lightly branched micelles**

- \( \langle M \rangle = 4 \mu m \)
- \( \beta = 0.09 \) per \( \mu m \)
- \( G_N = 132.8 \) Pa
- \( \zeta_{br} = 0.003 \)
- \( \alpha_e = 2 \)
- \( l_p = 50 \) nm

**Unbranched micelles**

- \( \langle M \rangle = 4 \mu m \)
- **Linear micelles**

**Decrease of viscosity by 3 fold**

- **Modified genetic algorithm**
- **Contribution from low frequencies**
- **Contribution from high frequencies**
Coarse-Graining Complex Mixtures

Obtained with assistance of COSMOtherm software (Klamt et al.), as described in Liyana-Arachchi, Jamadagni, Eike, Koenig, and Siepmann, J Chem Phys 142 (2015)

<table>
<thead>
<tr>
<th>Common Name</th>
<th>Chemical Structure</th>
<th>Common Name</th>
<th>Chemical Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dodecyl Sulfate (C3T)(C3)(C3)(SO4)</td>
<td><img src="image" alt="Dodecyl Sulfate" /></td>
<td>Heliotropin (CDO)(O2yC)</td>
<td><img src="image" alt="Heliotropin" /></td>
</tr>
<tr>
<td>Lauryl Ether Sulfate (C3T)(C3)(C3)</td>
<td><img src="image" alt="Lauryl Ether Sulfate" /></td>
<td>Linalool (BTN)(CCD)(CDC1)</td>
<td><img src="image" alt="Linalool" /></td>
</tr>
<tr>
<td>-EO)n(SO4)</td>
<td><img src="image" alt="Lauryl Ether Sulfate" /></td>
<td>Allyl Amyl Glycolate (PPT)(COSR)(IPT)</td>
<td><img src="image" alt="Allyl Amyl Glycolate" /></td>
</tr>
<tr>
<td>Cocamidopropyl Betain (C3T)(C3)(C2P)(C3ta)</td>
<td><img src="image" alt="Cocamidopropyl Betain" /></td>
<td>Undecavertol (DCCT)(PL2)(C4T)</td>
<td><img src="image" alt="Undecavertol" /></td>
</tr>
<tr>
<td>-NC2)(ACE)</td>
<td><img src="image" alt="Cocamidopropyl Betain" /></td>
<td>beta-Ionone (CDMC)(CDM)(P3O)</td>
<td><img src="image" alt="beta-Ionone" /></td>
</tr>
<tr>
<td>Cumene (TLB)(TLA)(IPBb)</td>
<td><img src="image" alt="Cumene" /></td>
<td>Synambran (CDMC)(CTMC)(CrDM)(OCR)</td>
<td><img src="image" alt="Synambran" /></td>
</tr>
<tr>
<td>Isopropyl Myristate (C3T)(C4)(C4)(IPBc)(IPBb)</td>
<td><img src="image" alt="Isopropyl Myristate" /></td>
<td>Synambran (CDMC)(CTMC)(CrDM)(OCR)</td>
<td><img src="image" alt="Synambran" /></td>
</tr>
<tr>
<td>Dipropylene Glycol (DPGA)(DPGB)(DPGC)</td>
<td><img src="image" alt="Dipropylene Glycol" /></td>
<td>Synambran (CDMC)(CTMC)(CrDM)(OCR)</td>
<td><img src="image" alt="Synambran" /></td>
</tr>
</tbody>
</table>

Tang, Koenig, McConaughy, Weaver, Eike, Wang, Zou, & Larson, to be submitted (2015)
Impact of perfume raw materials on viscosity

Experimental viscosity and DPD result

\[ \log P_{ow} = \log \left( \frac{[PRM]_{octanol}}{[PRM]_{water}} \right) \]

\[ p = \frac{V}{\alpha l} \]
Summary

- Atomistic molecular simulations, combined with umbrella sampling (weighted histograms), can yield free energies for micellization of spherical micelles, for breakage of thread-like micelles, and potentially for branch formation.
- Coarse-grained, micelle-level models, allow inference of micelle properties, such as length, breakage time, and persistence length, from rheological properties.
- The inclusion of branch formation into micelle models is now feasible.
- Surfactant additives, such as perfumes, influence micelle properties, and thereby the rheology. Molecular simulations are beginning to allow assessment of these relationships, opening the possibility of de novo design of surfactant system.
End