Structure and Rheology of Surfactant Solutions

Weizhong Zou#, Taraknath Mandal #, Mike Weaver+, Peter Koenig‡, Sumanth Jamadagni, Geoffrey Reynolds, and Ronald G. Larson#

# Department of Chemical Engineering, University of Michigan, Ann Arbor, MI 48109
+ Analytic Sciences, The Procter & Gamble Company, Mason, OH 45040
‡ Computational Chemistry, Modeling and Simulation, The Procter & Gamble Company, West Chester, OH 45069

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Weizhong Zou, Taraknath Mandal, Peter Koenig, Mike Weaver
The Challenge of Multiple Length and Time Scales in Surfactant Solutions

Sodium dodecyl sulfate

$10^{23}$ degrees of freedom!

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

Increase surfactant/salt concentration

- Citronellol
- Limonene
- Vanillin

10% SLES

No additives

Linalool

DPG

Cumene

Linalool

Long worms

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

PMF = \Delta \mu_n^0 = \mu_n^0 - (\mu_n^{-1} + \mu_1^0)

\mu_n = \mu_n^0 + k_B T \ell n(X_n)

M_n \leftrightarrow M_{n-1} + M_1

n surfactants

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

n-1 surfactants

\[ X_n = X_{n-1} X_1 \exp\left(-\frac{\Delta \mu_n^0}{k_B T}\right) \]
Simulation of scission energy using weighted histograms

\[ L \propto \exp \left( \frac{\Delta G_{\text{sciss}}}{kT} \right) \quad c(L) \sim \exp(-L/L) \]


Use bead count in region to bias simulation towards scission/fusion.


\[ V_s = \frac{1}{2} k N(\{x_i, y_i, z_i\}, v) - N_0 \]

Peter Koenig, P&G

Taraknath Mandal
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
Pointer algorithm: simulation of ensemble of micelles

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

Fitting Data

Procter and Gamble is using this predictive method in their research into design of shampoos and body washes.

\(<L> = 1.6 \mu m\)

\(l_p = 112 \text{ nm}\)

\(\tau_{br}/\tau_{rep} = 1.8\)
Lamellar Gels for Hair Conditioners

Additives

- Salts (NaCl/EDTA)
- Perfumes
- Preservatives

Forms a lamellar gel network of
1. regularly spaced bilayers with
2. trapped interlamellar water and bulk water

Self-assembly of surfactants in water

• In these cosmetic emulsions, critical packing parameter $\sim 1$
  • Form lamellar bilayers

• Two different phases of lamellar bilayer structures depending on the temperature:
  • Liquid crystalline (L$\alpha$) phase – above gel transition temperature
  • Gel phase (L$\beta$) phase – below gel transition temperature

Hydrocarbon chains in the bilayer can exist in a number of physical states:

- Disordered state
- Ordered state: Hexagonally packed
Solid-like Creep Response and “Apparent Yield-Stress”

- **< 18 Pa**: Solid-like creep response, with $\gamma \propto t^{0.25}$
  - Partial strain recovery

- **> 18 Pa**: Apparent yielding behavior, with $\gamma \propto t^{1.35}$
  - No strain recovery, flows like a fluid
**Materials:**
Ternary system lamellar gel network seeded with fluorescent tracer particles (diameter 1.5 μm, 0.1 vol%).

**Instruments:**
- MCR 702 rheometer
- Cone (2°) and plate geometry
- Fluorescent microscope

Example of velocimetry raw data

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Input: rotation speed → shear rate

Test output: torque → stress

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