

Investigation of Industrially-relevant Wormlike Micellar Networks

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Background

Cleansers formulated for personal and home care applications often owe their unique rheology to the presence of an entangled network of dynamic, “wormlike” surfactant micelles (WLMs). The physical properties of the wormlike micellar structure are dependent on many things, e.g., surfactant level and type, electrolyte type and concentration, presence and level of co-surfactant, etc. These products are often formulated to have a “desirable” texture and flow behavior based on the product type and target market. While the flow behavior of the product is primarily determined by the physical properties of the micellar network, these products are often formulated in a “trial and error” manner due to a limited understanding of how parameters like surfactant type and electrolyte quantitatively affect the texture and flow behavior of industrially-relevant systems where surfactant / co-surfactant systems are more complex than the model wormlike micellar systems which are often studied.

In the late 1980s, Cates used a combination of polymer “tube model” and reptation theories to develop a model linking the rheological behavior of WLMs to their microstructure in the regime where the breakage time is much longer than the reptation time, and where the micelles are long enough to be appreciably entangled but not branched.¹ This theory was expanded and tested by Cates and others in the early 1990s, and scaling laws for various rheological properties were determined.²⁻⁶ Most notably, select rheological properties were found to scale with surfactant concentration as:

- **Zero shear viscosity:** $\eta_0 \propto c^{3.5}$
- **Plateau modulus:** $G_0 \propto c^{2.25}$
- **Terminal relaxation time:** $\tau \cong (\tau_{br}\tau_{rep})^{1/2} \propto c^{1.5}$
- **Micelle breakage time:** $\tau_{br} \propto c^{-1/2}$
- **Entanglement length:** $l_e/\bar{L} \propto c^{-1.75}$
- **Average micelle length:** $\bar{L} \propto c^{0.6}$

Experimentally, when micelles are possibly branched, scaling exponents were found to decrease for the zero shear viscosity and plateau modulus (2.42 and 1.85, respectively), and increase for the entanglement length (-0.88).⁶

More recently, Larson and coworkers developed a “pointer algorithm” which utilizes a simulation of an ensemble of thousands of micelles to estimate physical parameters such as \bar{L} , G_0 , and τ_{br} . However, this algorithm performs best when high-frequency rheological data,

which is often only accessible by means other than mechanical rheometry, e.g., diffusing wave spectroscopy (DWS), is included.⁷

The above scaling exponents are valid for a small range of the “phase diagram” of surfactant and electrolyte concentration. Applied systems of WLMs are often formulated in regimes outside of the parameter space where the above scaling rules should apply; furthermore, co-surfactants are also added, and the ratio of surfactant to co-surfactant is another variable that is often adjusted to achieve the desired rheological texture while balancing formula cost.

It would be desirable to explore the phase space of surfactant concentration, electrolyte concentration, and surfactant / co-surfactant ratio for an industrially-relevant WLM system to determine the most economical means of achieving desirable rheology and texture.

Objective

The primary objective of this work is to explore and understand the effects of varying surfactant concentration, surfactant / co-surfactant ratio, and salt concentration on the physical properties of the micellar network, and how the changes in these physical properties affect the rheology and flow properties of the formulas in terms of aesthetically-relevant measures. For example, the above scaling relations may not hold for the conditions of many applied WLM systems where micelle branching is likely present as these products are often formulated at or near the peak in the viscosity vs. electrolyte concentration curve. Furthermore, electrolyte has a monotonic effect on the plateau modulus, but a non-monotonic effect on the relaxation time and thus zero shear viscosity, and electrolyte affects the micelles differently for different surfactant / co-surfactant ratios. It would be advantageous to explore the phase space of surfactant concentration, electrolyte concentration, and surfactant / co-surfactant ratio in terms of the micellar properties obtained by the pointer algorithm and develop scaling laws which will help in determining if desirable rheological textures can be obtained by different means, e.g., by using less surfactant but more electrolyte at a different surfactant / co-surfactant ratio, thus reducing formula cost.

A secondary objective is to understand the effect of “aging” and of certain co-ingredients on the physical properties of the micellar network, and in turn on the flow behavior of the final product. For example, are some surfactant / co-surfactant ratios more or less prone to any change in zero shear viscosity upon “aging” at elevated temperature, pH drift, or preservative spike? If so, it would be advantageous to understand what is changing within the micellar network and how negative effects, i.e., decreasing zero shear viscosity, can be mitigated through the addition of ingredients that affect the micellar microstructure in a way that can counteract these negative effects.

Materials and Methods

A two-surfactant system of sodium lauryl ether sulfate (SLES) and cocamidopropyl betaine (CAPB) in water will be used, with sodium chloride as an electrolyte. Stock solutions of specific

surfactant active levels and ratios will be made at J&J Consumer, Inc. with a portion of the water reserved (water hole). These stock solutions will be sent to NIST for addition of appropriate levels of salt and seeding particles (for DWS), and the balance of water will be added.

The linear viscoelastic properties of the solutions will be measured by mechanical rheometry and DWS. This linear viscoelastic data will be used with the pointer algorithm of Larson et al.⁷ to determine physical properties of the micellar network.

This data will give insights into the effect of surfactant level, ratio, salt concentration, etc. of industrially-relevant systems on the microscopic micellar parameters governing the rheology and flow behavior:

- Average micelle length
- Breakage and reputation timescales
- Micelle flexibility and persistence length

Scaling relations can then be developed for variations in surfactant & electrolyte level, and surfactant / co-surfactant ratio, and possibly explained through the results of the pointer algorithm.

Outline of experiments

Formulas will be at a pH of 4.5, 12% by weight total active surfactant concentration, SLES:CAPB ratios of:

- 75:25
 - Dilutions of 0 – 50 %
 - 0.5 – 6 % NaCl added at each dilution
- 50:50
 - Dilutions of 0 – 50 %
 - 0.5 – 6 % NaCl added at each dilution
- 35:65
 - Dilutions of 0 – 50 %
 - 0.5 – 3.5 % NaCl added at each dilution

Select additives for consideration include:

- Sodium benzoate (preservative)
- Citric acid / sodium hydroxide (for pH adjustment)
- Polysorbate 20 (micellar thickener)

References

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