Shampoo and surfactant solutions—Shear and extensional viscosity

Key Words: shampoo, surfactant, polymer, sodium chloride, shear viscosity, extensional viscosity, shear thinning

Goal: Shampoo is a cosmetic product containing surfactants as the cleansing agents, as well as polymers and NaCl as rheological modifiers. We perform shear rate sweeps with the **VROC® initium one plus** and extensional rate sweeps with the **e-VROC®** on surfactant and shampoo solutions prepared in-house. The goal is to use viscosity measurements to inform on how to improve shampoo formulations for household and industrial container-filling applications.

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Introduction

Shampoos, cosmetic products used to wash the scalp and hair, contain anionic surfactants (up to 40 wt.%) as the primary cleansing agents, as well as polymers (up to 2 wt.%) and NaCl (up to 2.5 wt.%) as rheological modifiers. The shear and extensional viscosity of shampoo products predicts their flow behavior, perceived "thickness", foamability, and storage stability. Although desired shampoo viscosity varies between consumers (male vs. female, adult vs. child), typically non-Newtonian behavior is preferred. Higher viscosities are preferred for low- or no-shear rate situations, like long-term storage stability and holding shampoo in palm of hand before applying it to scalp and hair. Lower viscosities are beneficial for higher shear rate applications, including lathering, squeezing onto palm of hand, and flow in a nozzle in the industrial container filling process. In addition, lower extensional viscosities are desired under extensional deformation, which occurs in flow through a tapered section of a nozzle as well as in strings of shampoo that form upon cessation of flow onto your palm or onto a container in the filling process. In the container filling process, high extensional viscosities can cause strings of shampoo to spill over the bottle cap, leading to improper sealing. Although slowing down the container filling speed can address this problem, this will decrease throughput, which calls for more optimal design of shampoo formulations. Performing shear and extensional rate sweeps with our **VROC®** technology facilitates the development of more desirable shampoo formulations for household and industrial container-filling applications.

Here, we use the **VROC® initium one plus** to measure steady shear viscosity and the **e-VROC®** to measure extensional viscosity as a function of deformation rate for multiple surfactant solutions and shampoo formulations. Our formulations consist of multiple concentrations of the popular and cost-effective anionic surfactant sodium dodecyl sulfate (SDS), the biodegradable nonionic polymer hydroxypropyl methylcellulose (HPMC), and sodium chloride (NaCl). HPMC is used in shampoo products as a thickener, to impart non-Newtonian behavior, and to enhance and stabilize foam for improved lather. Likewise, NaCl is used as a thickener and to magnify rate-thinning behavior. In combination, HPMC and NaCl are added to surfactant formulations to achieve customer preferences without using costly surfactants at high concentrations that could irritate and dry the skin. We study formulations with multiple concentrations of SDS to account for the undiluted and diluted shampoo product during the washing process. Moreover, we use the viscosity measurements to explain the SDS micelle and HPMC polymer structural characteristics present in these formulations.

Experimental

Solutions with varying concentrations of SDS, NaCl, and HPMC in deionized water were prepared at room temperature. Samples containing HPMC were mixed for at least 24 hours to allow the polymer to dissolve fully. The concentrations of SDS and HPMC prepared in this study are well above their critical micelle concentration (CMC) and critical overlap concentration (c^*), respectively. Shear rate sweeps were performed with the **VROC® initium one plus** at 25°C and a combination of the B05 chip (depth = 50 μm & P_{max} = 42 kPa), C05 chip (depth = 50 μm & P_{max} = 200 kPa), and E02 chip (depth = 20 μm & P_{max} = 1800 kPa). The viscosity measured for each shear rate is the average from five segments. Approximately 70 μL of each sample was loaded with the retrieval feature activated such that all segments were performed with only one loaded volume. The flow path was cleaned with the combination of phosphate-buffered saline (PBS), 1% aquet, and acetone solvents. Extensional rate sweeps were performed with the **e-VROC®** at 25°C and a combination of the EA20 chip (depth = 200 μm & P_{max} = 12 kPa) and EC20 chip (depth = 200 μm & P_{max} = 200 kPa). The microfluidic extensional flow channels were cleaned and soaked with 1% aquet solution after testing each sample.

Results & Discussion

The steady-state shear viscosity of solutions with SDS concentrations c_{SDS} = 100 – 1100 mM (~ 3 – 32 wt.%) is plotted as a function of shear rate at 25°C in **Figure 1a**. The error bars, corresponding in length to three times the standard deviation, are smaller than the size of the symbols. Addition of SDS to an aqueous solution leads to an increase in viscosity. All solutions with c_{SDS} = 100 – 1000 mM exhibit Newtonian behavior for the shear rate range probed. The results for c_{SDS} = 1100 mM demonstrate a Newtonian plateau for shear rates 10 – 10,000 s^{-1}, followed by a shear thinning region. The drop in viscosity for shear rates above 10,000 s^{-1} may be due to the alignment of wormlike micelles that move next to each other more easily at higher shear rates.

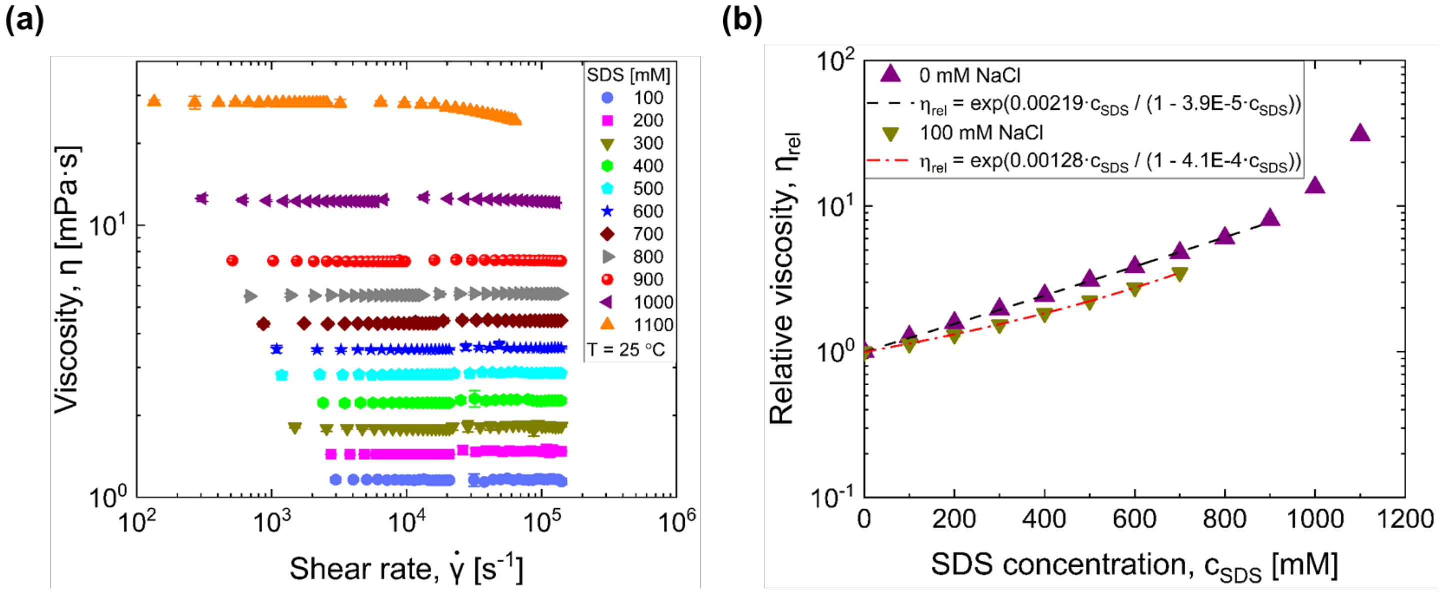

Figure 1: Viscosity of solutions at 25 °C formulated with SDS and NaCl. **(a)** Viscosity versus shear rate for SDS solutions with concentrations c_{SDS} = 100 – 1100 mM. **(b)** Relative viscosity versus concentration of SDS in aqueous solution with or without 100 mM NaCl. Dashed lines are fits to the data based on the Generalized Mooney equation. All error bars correspond to three times the standard deviation.

The relative viscosity $\eta_{rel} = \eta/\eta_s$ as a function of SDS concentration in a solution with or without 100 mM NaCl (~ 0.6 wt.%) is shown in **Figure 1b**. All error bars correspond in length to three times the standard deviation and are smaller than the size of the symbols. Solutions up to c_{SDS} = 700 mM and with added 100 mM NaCl exhibited Newtonian behavior for shear rates up to 140,000 s^{-1} and are not shown here. The viscosity of the sample with concentration c_{SDS} = 1100 mM is calculated from the low-shear rate viscosity plateau prior to the onset of shear thinning. The solvent viscosity η_s = 0.91 is virtually identical for both DI water and the mixture of DI water & 100 mM NaCl. A rise in concentration from c_{SDS} = 0 mM to 700 mM leads to an increase in the relative viscosity from η_{rel} = 1 to η_{rel} = 3.5 and η_{rel} = 4.75 for the solution with and without added NaCl, respectively. The relative viscosity increases due to the tighter packing of micelles, and it exhibits a lower rise for the samples with added NaCl due to the weaker electrostatic repulsion between micelles caused by screening of charges by NaCl ions.

The relative viscosity versus SDS concentration (up to c_{SDS} = 900 mM for 0 mM NaCl and up to c_{SDS} = 700 mM for 100 mM NaCl) is fit using the generalized Mooney equation (Ross & Minton, 1977):

$$\eta_{rel} = \exp\left(\frac{[\eta]\cdot c_{SDS}}{1-\frac{k}{v}\cdot[\eta]\cdot c_{SDS}}\right) \qquad (1)$$

Here, $[\eta]$ is the intrinsic viscosity, k is a “crowding factor”, and v is a parameter whose value is greater than 2.5 for non-spherical particles. The values extracted from the fits are $[\eta]$ = 0.076 and 0.044 dL/g as well as (k/v) = 0.018 and 0.32 for 0 mM and 100 mM NaCl, respectively. The intrinsic viscosities agree with values reported in the literature (Kushner, *et al.*, 1952). For the NaCl-free solutions, the generalized Mooney equation does not adequately fit beyond c_{SDS} = 900 mM, which exhibits a magnified increase in relative viscosity with concentration. The change in behavior for c_{SDS} > 900 mM may be due to a phase transition.

Figure 2a shows the viscosity as a function of shear rate at 25°C for shampoo formulations containing 2 wt.% HPMC and multiple concentrations of SDS and NaCl. The shear rate range covered with the three flow channels is 50 – 100,000 s^{-1}, which spans more than three orders of magnitude. The error bars' lengths correspond to three times the standard deviation and show the high reproducibility of our results. The plots show that addition of 2 wt.% HPMC increases the low-shear rate viscosity by one to two orders of magnitude and leads to shear thinning. For example, while the viscosity of the sample of c_{SDS} = 600 mM (see Figure 1a) remains constant between 1000 and 50,000 s^{-1}, that of the sample of c_{SDS} = 600 mM & c_{HPMC} = 2 wt.% shear thins by 76%. This system contains HPMC polymer chains saturated and physically associated with SDS monomers and micelles, as well as free SDS monomers and micelles. Increasing the concentration from c_{SDS} = 300 to 600 mM increases the viscosity for all shear rates probed, though the increase in viscosity becomes smaller as the shear rate increases. Addition of 100 mM NaCl doubles the low-shear rate viscosity and decreases the higher shear-rate viscosity, hence, it enhances shear thinning. This higher low-shear viscosity increases shelf-stability and helps prevent the formulation from flowing off the palm before application, while the enhanced shear thinning makes it easier to apply over the entire scalp. The rise in viscosity for lower shear rates upon addition of NaCl is due to the screening of electrostatic interactions that lead to decreased repulsion between free SDS micelles and unfolding of the polymer-surfactant complexes. The decrease in viscosity for higher shear rates upon addition of NaCl may be explained by the alignment of wormlike micelles that slide past each other more easily under higher shear rates (Donaldson & Messenger, 1979).

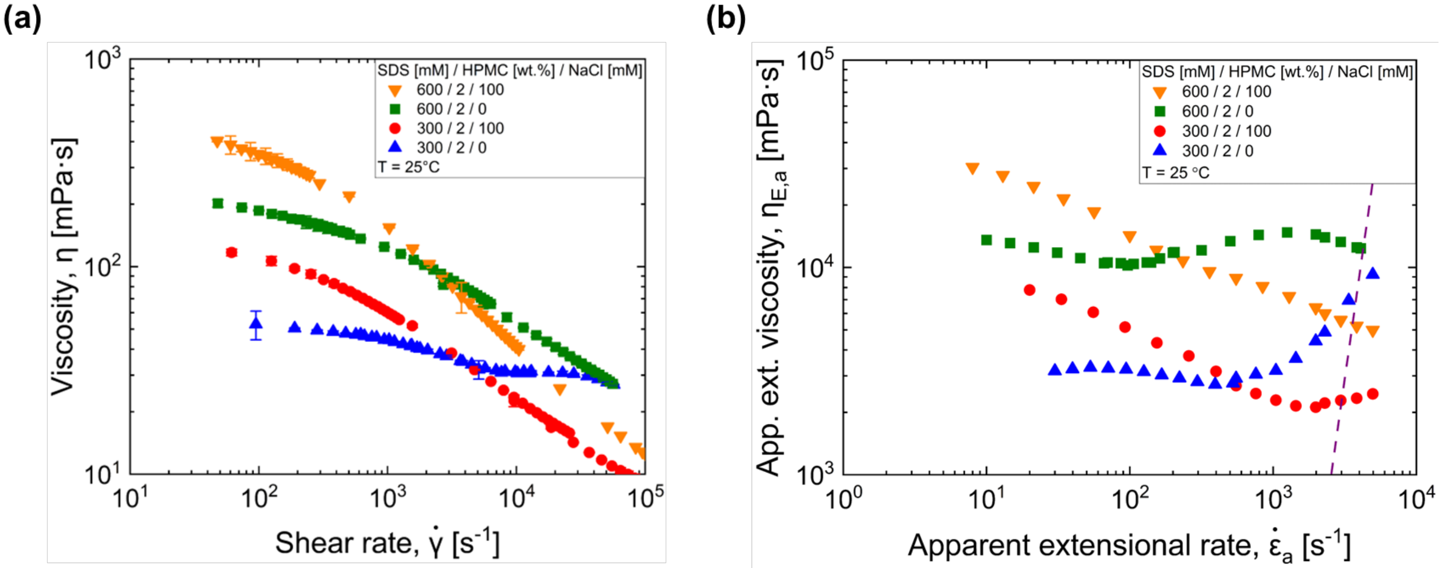

Figure 2: Viscosity of shampoo formulations containing SDS, HPMC, and NaCl at 25 °C. **(a)** Steady shear viscosity versus shear rate. Error bar length corresponds to three times the standard deviation. **(b)** Apparent extensional viscosity versus apparent extensional rate. Dashed line corresponds to Reynolds number Re = 10.

Figure 2b shows apparent extensional viscosity as a function of apparent extensional rate of the four shampoo formulations at 25 °C. Extensional rates span nearly three orders of magnitude. The apparent extensional viscosities are about two orders of magnitude higher than the steady shear viscosities of the same formulations (see Figure 2a), indicating that the stress response is larger under extension than under shear at the same rate. An increase in SDS concentration increases the viscosity for all rates. Analogous to the shear viscosity, the viscosity decreases with increasing deformation rate for the samples with added NaCl. However, the sample with c_{SDS} = 300 mM exhibits an apparent extensional thickening with increasing rate above 2,000 s^{-1}, which is likely caused by turbulent flows in the channel. The dashed line denotes the rates and viscosities resulting in a

Reynolds number of Re = 10, which predicts to the transition from laminar to turbulent flows in the extensional flow channel (Ober, *et al.*, 2013). In comparison to the NaCl-added formulations, the NaCl-free ones show lower viscosities and a more gradual decrease in viscosity for the lower rates. Beyond a critical rate, the NaCl-free formulations show extensional thickening that may be influenced by polymer chain extension and/or secondary flows. Elastic and/or turbulent instabilities can lead to secondary flows in the flow channel. Just like for the shear viscosity results, there is a crossover between the NaCl-free and NaCl-added data such that the NaCl-added formulations exhibit comparatively higher viscosity for lower rates and lower viscosity for higher rates.

Concluding Remarks

Experimental results of shear rate sweeps with the **VROC® initium one plus** and extensional rate sweeps with the **e-VROC®** on solutions containing varying amounts of SDS, HPMC, and NaCl inform on how to formulate shampoo products more aligned to customer preferences and optimal industrial filling processes. The results show that polymer-free solutions with $c_{\mathrm{SDS}} \leq 1000$ mM fail to exhibit shear thinning, while the solution with $c_{\mathrm{SDS}} = 1100$ mM shear thins by only 14%. In addition, the viscosity decreases upon addition of NaCl. Adding HPMC to SDS solutions increases their low-shear viscosity by one to two orders of magnitude and promotes shear thinning. For samples with polymer and SDS, adding NaCl raises the low-deformation rate viscosity but drops the high-rate viscosity. Beyond critical extensional rates, SDS and HPMC formulations without NaCl show extensional thickening that may be influenced by polymer chain extension and/or secondary flows.

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