

Rheological Characterization of a Novel Viscoelastic Surfactant for Subsurface Applications

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ABSTRACT

The use of viscoelastic solutions are applied in a variety of products including fluids for subsurface applications. These solutions are considered self-assembled micellar structures that lengthen into flexible, wormlike structures and entangle to reminisce viscous polymer solutions. Factors such as surfactant concentration, salinity, temperature, pH, electrostatic interaction, chemical structure and shear rate are critical to the self-assembly and growth of the micellar structure, thus decoupling the effects can provide insight on the level of dependency each parameter partakes among altering micellar structures. This study reflects the work completed to develop and control viscoelastic properties for Duomeen TTM (DTTM) with NaCl. The results suggest that salinity has the highest impact in altering viscosity, while an increase in surfactant concentration magnifies this viscoelastic behavior. Additional degrees of freedom for DTTM/NaCl include the pH effect from amine protonation and atypical viscoelastic response with changes in temperature.

Keywords: viscoelasticity, surfactant, rheology, molecular self-assembly, shear thinning

1 INTRODUCTION

The use of viscoelastic surfactant solutions are applied in a variety of products ranging from fluids in oil and gas industries to drug delivery and everywhere in between. Also known as “living polymers” due to its breaking and reforming mechanisms, these solutions are considered self-assembled micellar structures that lengthen into flexible, wormlike structures and entangle to resemble viscous polymer solutions [1]. Factors such as surfactant concentration, salinity concentration, salt type, temperature, pH, electrostatic interaction, tail length, head group composition and shear rate are critical to the self-assembly and growth of the micellar structure, therefore decoupling the effects can provide insight on the level of dependency each parameter contributes among altering micellar structures [2]. It is well known that the type and amount of salt in the solution triggers viscoelastic behavior, however some cationic surfactant solutions can furthermore be tuned or induced by changes in pH and temperature.

To conceptualizes the geometrical relation on how surfactant molecules will structuralize and aggregate, a

qualitative model called the packing parameter is based on the influence of the volume (v) and maximum length (l) of the tail, as well as the effective head group area (a) of the surfactant molecules [3]. Different micellar structures are associated with a packing parameter range, these include; spherical ($P < 0.33$), wormlike ($0.33 < P < 0.5$), vesicles ($0.5 < P < 1$) and lamellar ($P=1$).

$$P = \frac{v}{al} \quad (1)$$

External factors such as salt, pH and temperature can reduce or enlarge the effective head group area, which ultimately changes the packing parameter ratio if the tail length and volume is assumed fixed. For instance, upon the addition of salt, the effective head group size shrinks from reduction of electrostatic repulsion and stern layer from salt interaction, decreasing “ a ” thus increasing the packing parameter. Therefore, salt addition results in structural transformation of self-assembled micelles in solution [3].

Viscoelastic surfactants with multi-component amine headgroups, such as N,N,N' trimethyl-N'-tallow-1,3-diaminopropane (DTTM) shown in Figure 1, are tremendously water soluble due to its large-hydrophilic, polar head when protonated under acidic conditions. The larger polar heads, based on packing parameter, change the micellar aggregation state to a smaller, less entangled structure due to molecular repulsion. As pH increases, the effective head size shrinks and viscosity rises due to deprotonation of the molecules. This characteristic of pH-controlling micellar structure in amine surfactants is useful in biological, drug delivery and industrial applications.

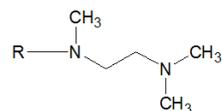


Figure 1: Chemical Structure of Duomeen TTM

Using a rheometer, shear rate analysis was conducted to describe the viscoelastic properties of Duomeen TTM for solutions ranging from 0.2 to 2 wt% DTTM and 5 to 25 wt% NaCl. The ability to fine tune viscoelasticity and rheological behavior based upon altering the solution’s properties is an engineering novelty to optimize performance and efficiency for subsurface applications.

2 RESULTS AND DISCUSSION

This section decouples the degree of freedoms that impact the viscoelasticity of the solution. First, the effects of salinity and surfactant concentration will be analyzed followed by the influence of changes in pH and temperature.

2.1 Effects of Salinity

The type and amount of salt plays a significant role in developing viscoelastic solutions. Using a weakly, non-binding salt, such as NaCl, requires a high concentration to screen electrostatic repulsion amongst molecules and alter micellar structures [4]. The Cl⁻ ions shrink the double layer around each surfactant's head group allowing the surfactant molecules to compact into micelles and grow into micellar chains. Based on the packing parameter, as salt concentration increases, the effective head group decreases leading to a rise in packing parameter and transformation in micellar structure.

From Figure 2, the addition of NaCl can change the viscosity by three orders of magnitude at 1 wt% DTTM. At a fixed shear rate of 1 and 10 s⁻¹, the transition slope displays the fluid shifting from Newtonian to a pseudoplasticity state. It can be seen at low salinities around 5 to 10 wt% NaCl, the fluid acts Newtonian where viscosity is independent of shear rate. It is important to note that at high salinities the viscosity appears to approach a plateau, most likely resulting in maximum entanglement due to thermodynamic and hydrodynamic limitations or micellar branching [5].

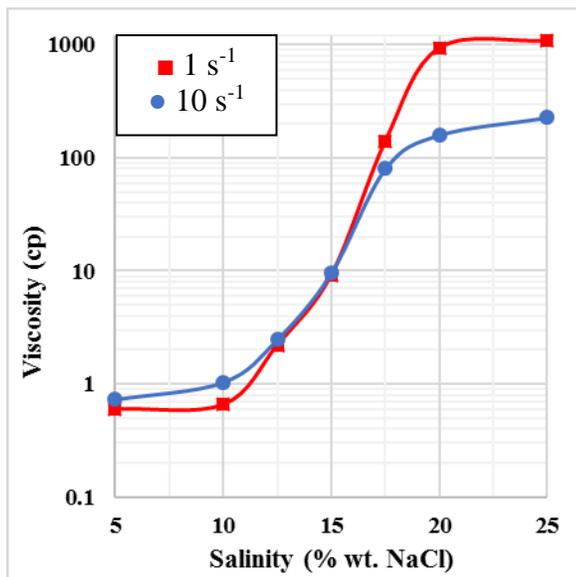


Figure 2: Viscosity profile at constant shear rate with changes in salinity (NaCl). Fixed parameters: 1% wt. DTTM solution and pH=6 conducted at 40°C.

In another perspective, Figure 3 visualizes the transition zones from Newtonian to viscoelastic behavior. Viscosity profiles of four surfactant concentrations were used against steady-state shear rate at three different salinities: 20 wt%, 15 wt%, and 10 wt% NaCl. At a shear rate of 1 s⁻¹, the viscosity at 20 wt% NaCl drops nearly a magnitude every time the surfactant concentrations are halved. As surfactant concentration increases, the micelles overlap and entangle into a transient network due to a larger presence of surfactant molecules in the solution [2].

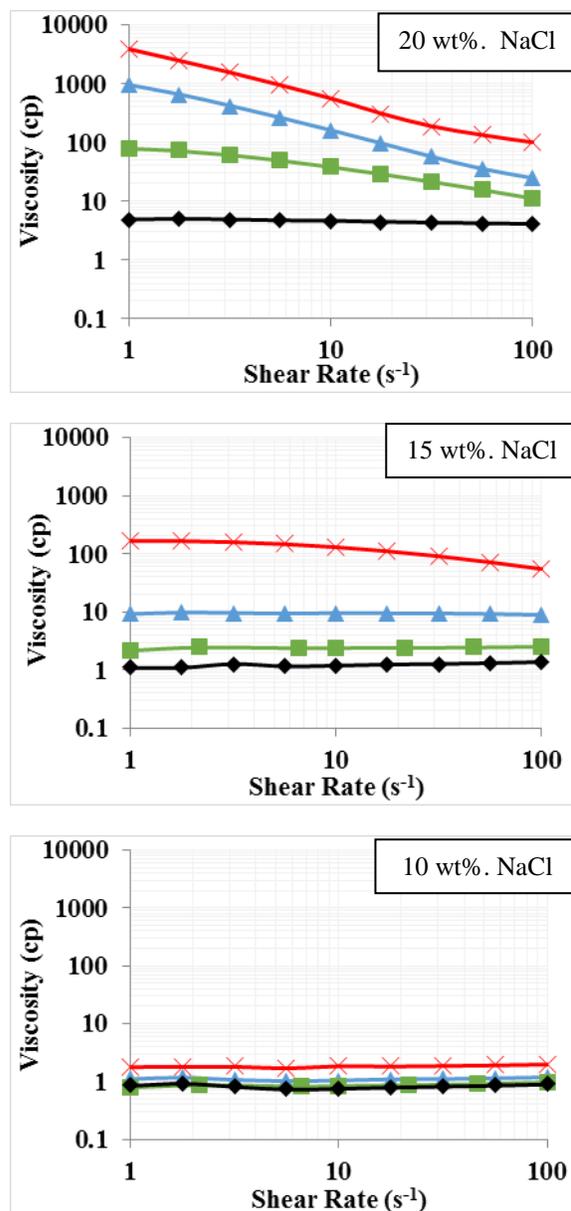


Figure 3: Steady-state shear rate at 40°C with 20 (A), 15 (B) or 10 (C) wt% NaCl. Surfactant concentrations legend: (X) = 2, (▲) = 1, (■) = 0.5, and (◆) = 0.2 wt% DTTM.

Shear thinning (pseudoplasticity) shown at high salt concentrations can be attributed to the disentanglement of the system and alignment of the wormlike micelles under shear flow [6-9]. This alignment causes degradation of viscosity since the micellar structure orients to minimize friction causing the solution to move as a single object [10]. Furthermore, shear thickening occurs at low salt concentrations causing a viscosity increase of 0.2 mPa·s. This instability is most likely attributed to the formation of micellar connections under shear [11].

2.2 Effects of pH

Duomeen TTM is characterized as a nonionic compound at high pH, but protonates into a cationic surfactant under acidic conditions. For diamine surfactants, the protonation process ionizes each nitrogen ion in the head group, where each surfactant molecule initially obtains an H^+ ion for a single nitrogen ion then another round for the second nitrogen ion. Effects of protonation on viscosity have been well established for amine cationic surfactants [12-13]. Based upon the packing parameter, as the head group increases from protonation (adding 2 H^+ ions), the “a” parameter from Eq. 1 increases leading to smaller aggregate structures due to all molecules having the same ionic charge. However when pH increases, the effective head group becomes smaller due to the reduction of ionic repulsion causing micelles to transform into cylindrical, vesicles, or lamellar structures. To support this relationship, Maeda stated for tetradecyldimethylamine oxides, the viscosity can be greater at the half-ionized state (half cationic/half nonionic) since the micelle size exhibits a maximum and the CMC of the solution is at a minimum. Wang contributed more about the effects of protonation on pH with a surfactant containing a multi-amine headgroups called, bis(amidoethyl-carbamoylethyl) octadecylamine where he concluded that at a low pH, the surfactants are fully protonated forming small micelles due to repulsion of similar-charged head groups and become globule vesicles at higher pH since deprotonation decreases repulsion leading to large micellar aggregates.

Figure 4 displays how viscosity changes with steady-state shear rate (1 and 10 s^{-1}) based on the addition of HCl from 3 wt% to 30 wt% Both shear rates overlap and converge at higher HCl concentrations. In terms of viscoelasticity, all solutions observed to be polymer-like at some degree before conducting the experiment, even at a pH considerably lower than the full protonation pH of the chemical. This can be due to the amount of Cl^- ions from the 20 wt% NaCl salt solution and added HCl providing enough electrostatic screening to reduce repulsion among surfactant molecules. This effect is counteracted by the amount of H^+ ions present in the solution that push to form smaller micelles.

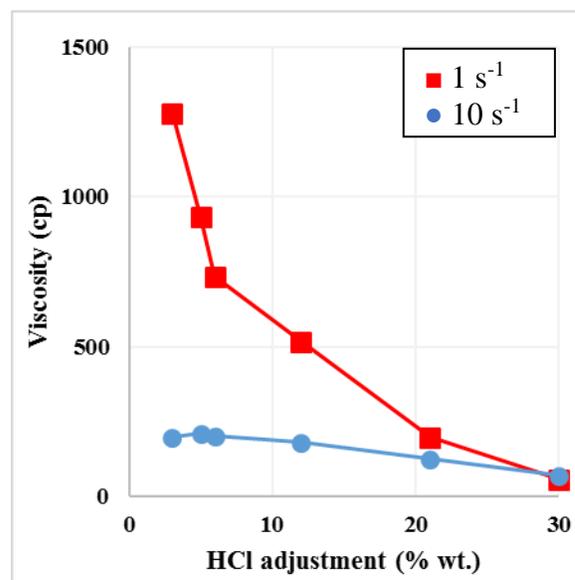


Figure 4: Viscosity profile at constant shear rates with changes in the amount of HCl added to the surfactant solution. The effect of pH on viscosity decreases as shear rate increases. Fixed parameters: 1% wt. DTTM solution and 20% wt. NaCl conducted at 40°C.

2.3 Effects of Temperature

Uncommon viscosity behavior is exhibited for this surfactant. In particular, viscosity increases with temperature until it reaches an inflection point where the viscosity begins to deteriorate afterwards. This trend can possibly be attributed to the micelles continuing to entangle as temperature increases until the inflection point where the onset of micellar branching occurs leading to a decrease in viscosity due to minimization of free energy.

Figure 5 characterizes how temperature changes with steady-state shear rate (1 and 10 s^{-1}) of 1 wt% DTTM solution at 20 wt% NaCl. It can be seen that at low shear rates, the viscosity is more dispersed with respect to temperature ranging from 1076 mPa·s at 50°C to 109.4 mPa·s at 80°C, then as shear rate increases, the viscosity profiles become concentrated at all temperatures. This suggests that temperature plays an important role in altering apparent viscosity in low shear environments, which displays representative behavior of wormlike micelles [14]. When focused on a fixed shear rate at 1 s^{-1} , the viscosity increase at low temperatures can be visually seen as well as the inflection point around 50 °C and the viscosity drop-off afterwards. This “enhancement” in viscosity suggests that not all of the micelles entangled to form wormlike micelles at low temperatures [15]. As the temperature increases, micelles elongate and entangle into chains until the competing effect of temperature surpasses the growing process. When this happens the inflection point occurs and viscosity begins to decline. It seems at higher shear rates, the inflection point shifts to a higher temperature and the peak magnitude is compressed.

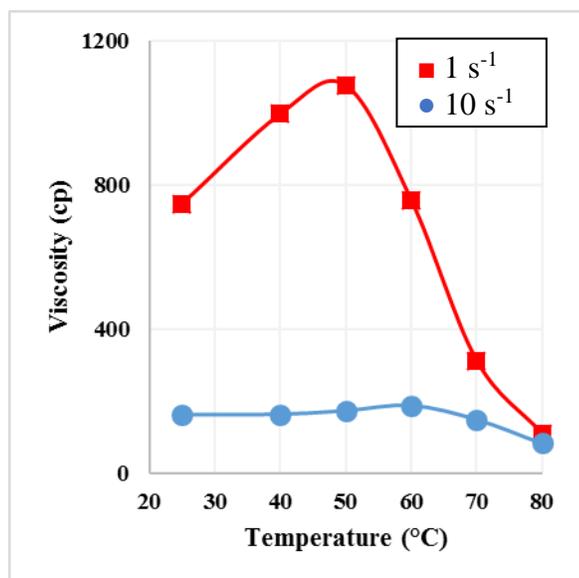


Figure 5: Viscosity profile at constant shear rates with changes in temperature. Critical temperature “inflection point” occurs around 50°C at 1 s⁻¹ and 60°C at 10 s⁻¹. The increase in viscosity can be attributed to the entanglement of the system having a higher effect on viscosity than thermal degradation. Fixed parameters: 1% wt. DTTM solution and 20% wt. NaCl at a pH=6.

3 CONCLUSION

Duomeen TTM endures trigger-induced viscoelasticity with changes in salinity, surfactant concentration, pH, temperature under steady state shear. The addition of salt is the most important factor for enhancing the viscosity for this chemical, while increasing surfactant concentration amplifies this effect on viscosity at moderate to high salt concentrations. The pH effect resembles the behavior of amine surfactants due to the protonation and deprotonation of the surfactant molecules. Additionally, compelling results were found for temperature where viscosity initially increases then decreases as temperature ramps up. In all, this information provides insight in ways to optimize the rheological response of DTTM when exposed to variations of temperatures and other environmental factors in subsurface applications.

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