

Gemini Surfactants: An Investigation in Drag-Reducing Potential

Undergraduate Thesis

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By

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## Abstract

Drag reduction is an important research area. Due to their unique properties and structure, gemini surfactants are good candidates for drag-reducing additives. This project explored the properties of two different types of gemini surfactants, 12-2-12 and 18-2-18. Various concentrations of surfactants between 0.5-2.5mM with NaSal ratios of 1/10, 1/5, and 1/2 were tested on a cone and plate rheometer to test for viscoelastic properties that may correlate to drag-reducing properties. The 18-2-18 solutions did not exhibit any significant viscoelasticity, and the stability of the solutions is a concern when exploring higher concentrations and counterion ratios. The 12-2-12 solutions exhibited significant viscoelasticity at concentrations of 2.0mM and 2.5mM with NaSal ratio of 1/2. Further studies of this surfactant with higher counterion concentrations are recommended.

## Dedication

Dedicated to my loving parents

## Acknowledgments

I wish to express my sincere thanks to Dr. Zakin, my advisor, for the encouragement and technical help in researching, writing, and finally finishing this project. I would like to thank Andy Maxson for the experiment help, advice, and willingness to answer all my questions. I would like to express my sincere gratitude to my parents, family, and Danny for their constant support and love. I am grateful to my friend, Lisa Steffan, for her kind words when I needed them most.

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## **I. Introduction**

District heating systems have been implemented in buildings throughout the United States, Europe, and Japan. Hot water or cooling water is provided by centralized units, which increases efficiency. The heating and cooling fluids are then pumped to the buildings on the grid, eliminating the need for individual heating and cooling units. The centralized system permits users to control the conditions in each building. A major incentive for district heating and cooling systems is the efficiency and cost effectiveness. Because waste steam to heat the water is used in many cases, much of the operation costs are involved in pumping the fluid (What is district energy 2009). These expenses can be reduced by utilizing drag-reducing additives.

Drag reduction is a turbulent flow phenomenon in which a small concentration of an additive, such as high molecular weight polymers or certain surfactants, causes a reduction of the pressure drop in turbulent flow when compared with that of the pure fluid (Zakin *et al.* 1998). The reduction of the turbulent friction forces can be as great as 80-90% for the many effective drag-reducing systems.

The year 1931 marked the first documented observation of reductions in pressure loss by Forrest and Grierson with wood pulp fibers, but the discovery was relatively unnoticed (Radin 1974, Nadolink and Haigh 1995). Mysels and associates (1949, 1971) discovered that gasoline with aluminum disoaps exhibited drag-reducing behavior, but they were not able to publish the results until after the Second World War in 1949. Toms

(1949, 1977), at the first Rheological Congress in 1948, reported drag reduction of high molecular weight polymers. Research in drag reduction increased in subsequent years (Zakin *et al.* 1998).

The first application for drag reduction was the use in oil pipelines in 1979. Hydrocarbon pipelines had considerable commercial success with concentrations as low as 5 to 25 ppm. In the Alyeska pipeline, the flow was increased by 25% with the addition of high polymer additives, which translates to 500,000 more barrels per day (Burger *et al.* 1982). Since 1979, the effectiveness of the polymers has increased, leading to a reduction of the concentrations by a factor of 12 (Motier and Carrier 1989). As effective as high polymer additives are, high mechanical shear and shear degradation cause the molecules to degrade. The polymer is broken up into smaller segments that no longer exhibit drag-reducing capabilities. Unfortunately, the degradation is irreversible, and therefore high polymer additives are not suitable for recirculating pumping systems, such as district heating systems (Lee 1968, Lee and Zakin 1972).

For recirculating systems, the use of surfactants as a drag-reducing additive is promising. Surfactant systems exhibit self-repairability. Long surfactant micelle nanostructures that are integral to drag reduction are repaired within seconds after exposure to high shear or high extensional stresses. This property makes the surfactant additives well-suited for applications with recirculating pressure driven flows (Zakin *et al.* 1998).

The use of surfactants as an additive in district heating systems can result in lower energy costs. Kroppe and Lipus (2010) found that adding surfactants in a certain district heating system reduced the total cost up to 4%. Ionic, cationic, zwitterionic, and nonionic surfactants have been studied in recirculating systems. Cationic solutions are the most effective for district heating systems, due to their large effective temperature range and insensitivity to mineral deposits in piping (Zakin *et al.* 1998). Unfortunately, the additives also cause a loss in heat transfer, which decreases their utility in district heating systems. However, the micelles are constantly degrading and reforming, so if the micelles were agitated and broken up, they would temporarily be unable to form the effective micelle structure, and the heat transfer ability of the solution would increase. Research is being conducted to find the best method for increased heat transfer (Qi and Zakin 2002).

A unique type of surfactant called gemini surfactants might be very useful in drag reduction because of its special properties. The concentrations for micelle formation are lower for gemini surfactants than regular surfactants, so they may be good candidates for drag reduction (Hait and Moulik 2002). Use of gemini surfactants over conventional surfactants could lead to a large reduction in the concentrations necessary for drag reduction and increased flow. The properties of gemini surfactants' properties suggest they may be good candidates for use as drag reducing agents (Qi 2002).

The purpose of this research project is to perform an exploratory investigation into the drag reduction potential of different gemini surfactants through rheological

testing. With two different gemini surfactants, the main thrust of the project was to determine how various surfactant concentrations and counterion ratios would affect the viscoelasticity of the solution, a property that often accompanies strong drag-reducing behavior (Zakin *et al.* 1998).

## **II. Literature Review**

### **A. Surfactants**

Surfactants received their name from their unusual surface active properties. Surfactants, which have a hydrophilic group and a hydrophobic tail, self-aggregate due to their unique amphiphilic property. The hydrophobic tail is generally an alkyl chain, and the hydrophilic end is polarizable and able to form hydrogen bonds. In aqueous systems, the hydrophilic group prefers to be in the water phase while the hydrophobic parts avoid the water phase. The hydrophobic group either finds a nonpolar phase in the system, or the surfactants self-associate, forming micelles with the hydrophobic groups in the center and the hydrophilic ends in the water phase (Zakin *et al.* 1998).

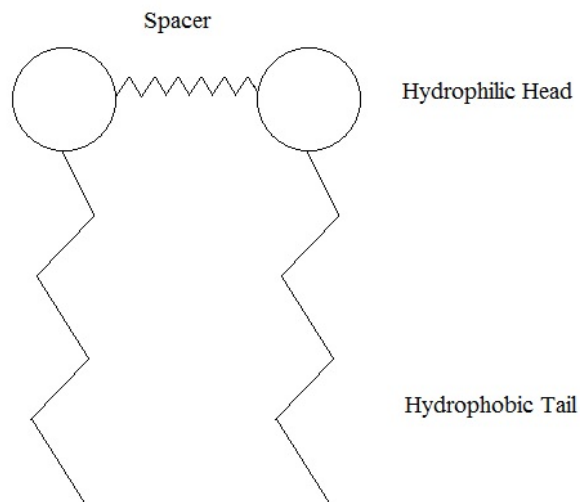
The micellization of the surfactants occurs after a threshold concentration, called the critical micelle concentration (CMC), has been reached. The micelles can form different micelle structures, depending on the concentration. At concentrations above the CMC, micelles generally form spherical micelles and, with increased concentration, the nanostructures form rod-like or worm-like micelles. Drag-reducing cationic surfactant systems have been identified as having long worm-like and entangled micelle structures through the use of cryo-Transmission Electron Microscopy (cryo-TEM) while non-drag reducing systems generally contain only spherical micelles or vesicles. The rod-like micelles are believed to account for drag reduction in surfactant solutions as they impart



viscoelastic behavior to the solutions leading to alteration of the turbulent structure of the flow. The addition of a counterion or salt with the surfactant can prompt rod-like micelles, due to the stabilization from the dispersion of electrostatic charge from polar head groups (Zakin *et al.* 1998).

## B. Gemini Surfactants

Gemini surfactants are made up of two ions with hydrophobic tails that are connected by a spacer group as seen in Figure 1.



**Figure 1: Gemini Surfactant Structure**

These unique surfactants are also frequently referred to as dimeric surfactants (Zana and Xia 2004). This name results from acknowledgement that gemini surfactants are dimers of the quarternary ammonium surfactants:  $C_mH_{2m+1}-(C_{s/2}H_{s+1})N^+(CH_3)_2$  with

Cl- or Br-. Spacer groups are hydrocarbons that can be rigid or flexible with  $s$  number of carbons (Danino *et al.* 1995). The particular ions of the gemini surfactant can vary. The length of the hydrocarbon tails ( $m$  number of carbon atoms) also affects the properties of the solution. Gemini surfactants were found to have much lower CMC values than ordinary surfactants. An increase in the hydrocarbon tail length decreased the CMC two orders of magnitude; a larger spacer group also reduced the CMC (Hait and Moulik 2002). Gemini surfactants appeared in the patent literature as early as 1935 (Zana and Xia 2004).

### **C. Fluid Flow**

Newtonian fluids exhibit a linear relationship of stress and shear rate; Newton's Law of Viscosity applies as shown in Equation 1, where  $\tau$  is shear stress,  $\dot{\gamma}$  is shear rate, and  $\eta$  is viscosity. For many fluids, such as water, Newton's Law of Viscosity describes the behavior adequately. The viscosity is independent of the shear rate (Macosko 1994).

$$\tau = \eta\dot{\gamma} \quad (1)$$

For non-Newtonian systems, the shear viscosity may vary with shear rate. The apparent viscosity is then used to describe these systems, described in Equation 2 below, where  $\eta_{app}$  is the apparent viscosity (Macosko 1994).

$$\tau = \eta_{app}\dot{\gamma} \quad (2)$$

Polymer and surfactant systems exhibit strong non-Newtonian behavior. Shear thinning is defined as a decrease in viscosity with an increase in shear rate; shear thickening is the increase of viscosity with shear rate. Empirical models can be fit to the system experimentally and can range from simple power law models to much more complicated equations with many parameters (Macosko 1994).

#### **D. Viscoelasticity and Rheological Properties**

Most drag-reducing surfactant solutions exhibit viscoelastic properties (Zakin *et al.* 1998). Viscoelasticity is defined as having time-dependent properties of both viscous fluids and elastic solids. For example, if a step strain at time zero is applied, each material will behave very differently. The stress of an elastic solid will be a constant over time. The Newtonian response to a step strain is one spike in the stress at time zero and then zero at time greater than zero. In response to a step strain, the stress over time of a viscoelastic fluid will be a maximum at zero and exponentially decay to zero (Macosko 1994).

For drag-reducing solutions, the first normal stress is generally a good indicator of its drag-reducing potential. Normal stresses are only seen in viscoelastic systems and are defined by Equation 3, where  $N_1$  is the first normal stress,  $\tau_{11}$  is the stress tensor component in the 1 direction acting on the 1 surface, and  $\tau_{22}$  is the stress tensor component in the 2 direction acting on the 2 surface (Macosko 1994).

$$N_1 = \tau_{11} - \tau_{22} \quad (3)$$

Rheometers are used to test the rheological properties of materials, and many different tests can be performed depending on the geometry used. The cone and plate geometry is a good choice to measure the first normal stresses. The first normal stress can be calculated just by the force in the z direction,  $F_z$ , and the radius, R, of the plate as shown in Equation 4 (Macosko 1994).

$$N_{1measured} = \frac{2F_z}{\pi R^2} \quad (4)$$

At high shear rates, inertial forces skew the measurements somewhat. A correction for the normal stresses is given below in Equation 5 where  $\rho_{solvent}$  is the density of the solvent and  $\beta$  is the cone angle (Macosko 1994).

$$N_1 = N_{1measured} + 0.15 * \rho_{solvent} * (\dot{\gamma} * \beta)^2 * R^2 \quad (5)$$

Some dilute surfactant systems have exhibited changes in micelle structure through simple shear. Vesicles that are bilayers or multilayers of surfactants have been shown to transform into giant wormlike micelles that are necessary for drag reduction (Zheng *et al* 2000). This transformation can take place due to the self-assembling property of the surfactant systems under shear. Formation of threadlike micelles under shear is referred to as shear-induced structure (SIS), which generally coincides with increases in shear viscosity and  $N_1$  (Qi 2002).

At low shear rates, dilute surfactant systems have Newtonian-like behavior because the micelles are able to freely move in solution. Increases in shear rate cause the

micelles to begin to orient in the direction of shear which often results in shear thinning. Other solutions may exhibit SIS after shear thinning, which is marked by a steep increase in shear viscosity. This correlates to elastic properties, most notably a large first normal stress difference. The shear-induced structure contains micelles orders of magnitude larger than the previous rod-like micelles. This transformation to SIS is reversible. It is believed that SIS micelle nanostructures may be the source of the drag reduction in surfactant systems (Qi 2002).

### III. Experimental Procedures

#### A. Preparation of Surfactant Solutions

Two different gemini surfactants with dimers of the form  $C_mH_{2m+1}-(C_{s/2}H_{s+1})N^+(CH_3)_2$  with either 2Br<sup>-</sup> or 2Cl<sup>-</sup> were studied. The notation is m-s-m to identify the tail and spacer groups. The two surfactants were 12-2-12 and 18-2-18, described in Table 1.

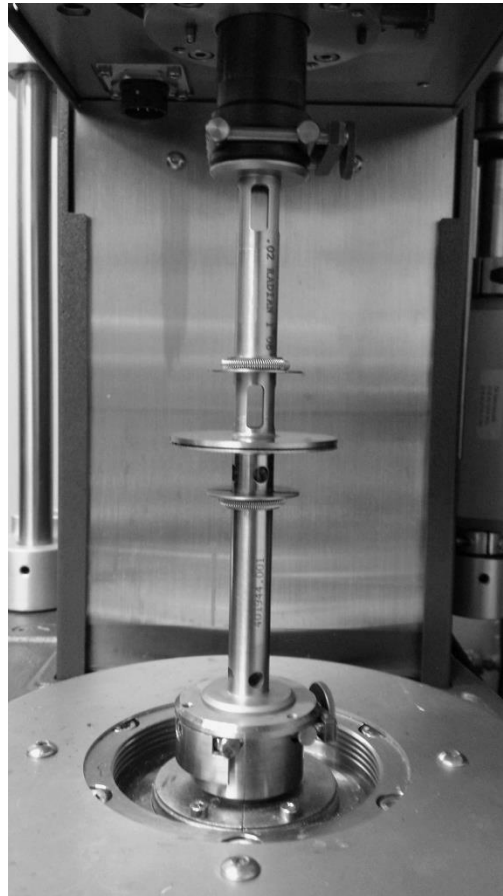
Table 1: Surfactants Tested.

Surfactant	Structure
12-2-12 Gemini Surfactant	$C_{30}H_{68}N_2Br_2$
18-2-18 Gemini Surfactant	$C_{42}H_{92}N_2Cl_2$

Stock solutions of 4mM with solvent of water were made of the 12-2-12, the 18-2-18, and of the sodium salicylate counterion. The surfactants were also tested with no counterion. The gemini surfactant solutions were placed on a stir plate and heated if necessary until the surfactant completely dissolved. The solutions were then measured to make 10mL vials of differing concentrations of the surfactant from 0.5mM to 2.5mM with varied counterion molar ratios of 1/10, 1/5, and 1/2. The solutions were allowed to stand for at least one day before testing to ensure uniform concentration.

## B. Rheological Testing

To test the rheological properties and understand the drag-reducing capability of the gemini surfactant, each solution was tested on the TA Ares G2 instrument.



**Figure 2: The Cone and Plate Setup on the TA Ares Rheometer**

The cone and plate geometry, pictured in Figure 2, was used to obtain accurate measurements of the first normal stress,  $N_1$ , and viscosity. Parameters of the test can be

found in Table 2 below. The solutions were tested at room temperature, approximately 25°C.

**Table 2: Parameters for the Cone and Plate Shear Testing of the Solutions**

Shear rate	10-1000s <sup>-1</sup>
Diameter	50mm
Cone angle	0.02 radians
Loading gap	20mm
Truncation gap	0.0559mm

The samples that were tested are listed in Table 3 below.

**Table 3: The Surfactant Solutions that were tested on the Cone and Plate Rheometer**

Gemini Surfactant	Gemini Concentration (mM)	NaSal Concentration (mM)
12-2-12	2.5	0.0
12-2-12	2.0	0.0
12-2-12	1.5	0.0
12-2-12	1.0	0.0
12-2-12	0.5	0.0
12-2-12	2.5	0.25
12-2-12	2.5	0.5
12-2-12	2.5	1.25
12-2-12	2.0	0.2
12-2-12	2.0	0.4
12-2-12	2.0	1.0
12-2-12	1.5	0.3
12-2-12	1.5	0.75
12-2-12	1.0	0.2
12-2-12	1.0	0.5
12-2-12	0.5	0.25
18-2-18	2.5	0.25
18-2-18	2.5	0.5



18-2-18	2.5	1.25
18-2-18	2.0	0.2
18-2-18	2.0	1.0

0.65mL of each sample was measured with a syringe and discharged on the plate while the gap was at 20mm. Any bubbles on the surface were broken before lowering the stage. The stage was lowered in increments to allow the fluid to evenly coat the geometry. If any liquid was displaced out of the geometry, the fluid was cleaned off before the test began. When the gap was 0.0559mm, the setup was allowed to equilibrate while the normal force readings dropped to 0 or until the normal force readings stopped dropping. This usually took about five minutes. The force transducer was then zeroed, and the start test icon was clicked on the computer. The normal force and viscosity measurements from each run were recorded and are included in the Results and Discussion.

## IV. Results and Discussion

### A. 18-2-18 Solution Results

The 18-2-18 solutions were tested on the cone and plate rheometer, and the data for both viscosity and  $N_1$  were measured and are shown in Figure 3 and Figure 4 for the 2.0mM 18-2-18 and various counterion ratios.

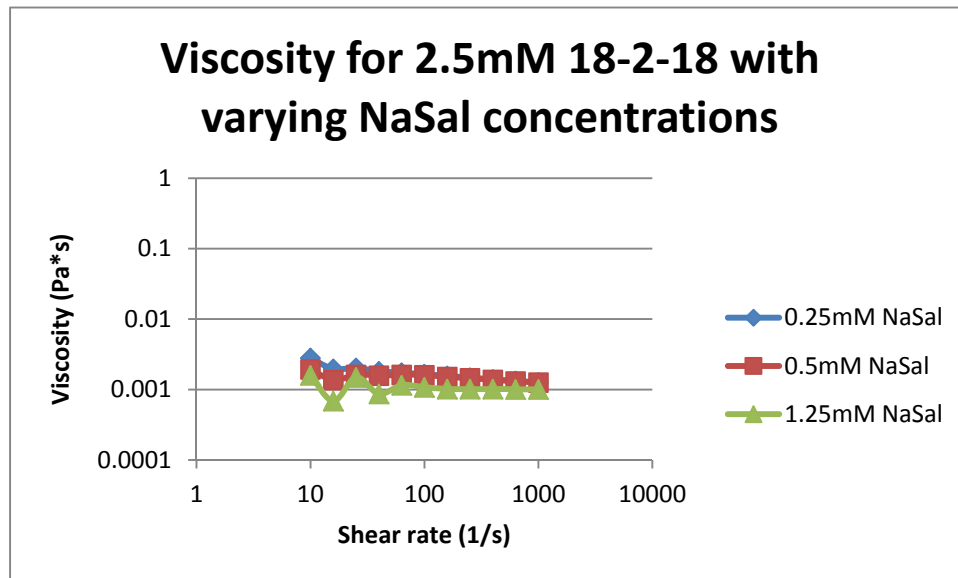
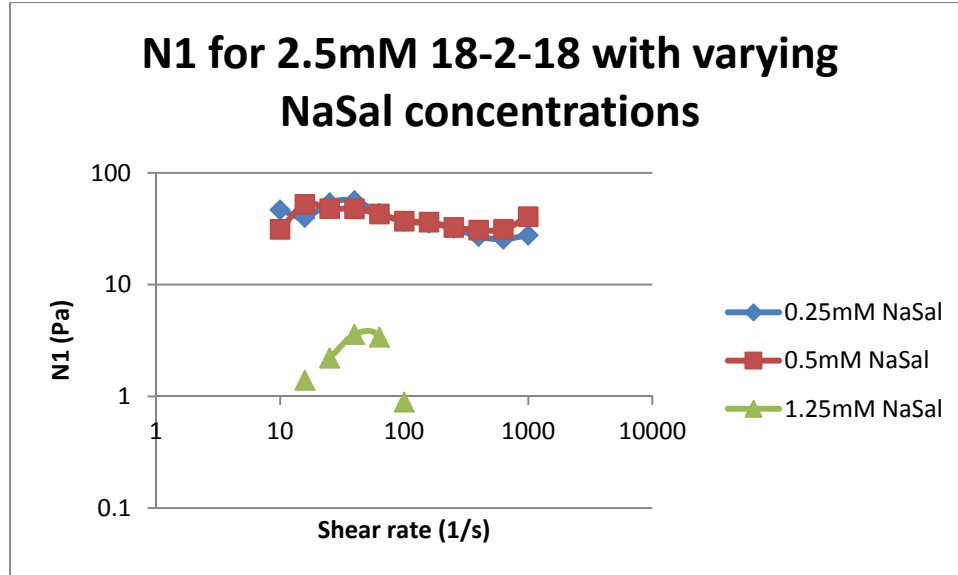


Figure 3: The Viscosity Data for the 2.5mM 18-2-18 with different NaSal Concentrations



**Figure 4: The  $N_1$  Measurements from the 2.5mM 18-2-18 with different NaSal Concentrations**  
 The viscosity data of the 2.5mM 18-2-18 with different NaSal ratios do not

exhibit any SIS behavior. The viscosity is relatively constant with changing shear rate.

The  $N_1$  data does show higher values with the 0.25mM NaSal and 0.5mM NaSal than the 1.25mM NaSal which may be due to separation of the surfactant from the solution which was not detected. The 0.25mM NaSal and 0.5mM NaSal show unusual  $N_1$  behavior because their normal stresses are relatively constant with shear rate while  $N_1$  values of viscoelastic solutions usually are highly dependent on shear rate.

The 2.0mM 18-2-18 solutions were run on the cone and plate rheometer as well, and the data for the viscosity and  $N_1$  measurements are shown below in Figure 5 and Figure 6.

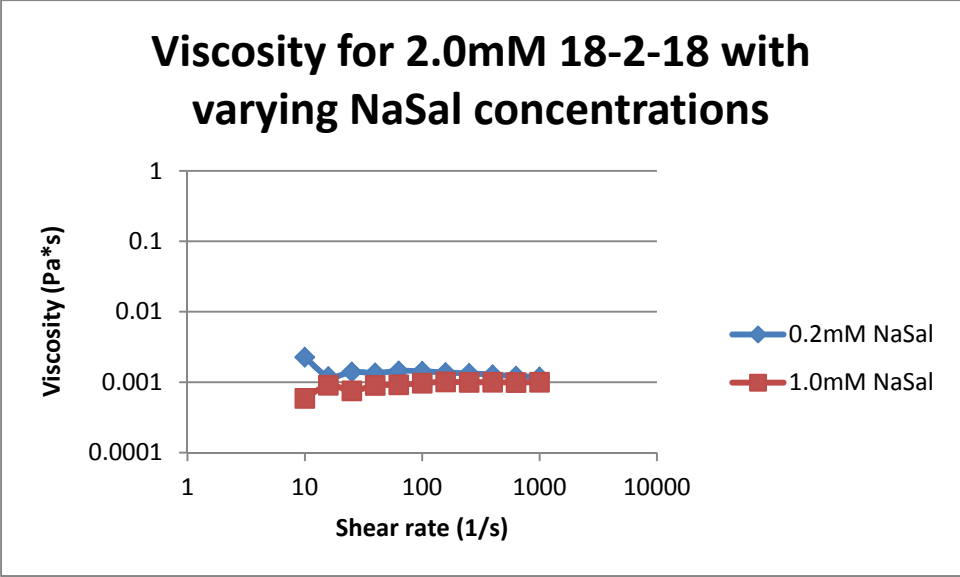


Figure 5: The Viscosity Data for the 2.0mM 18-2-18 with different NaSal Concentrations

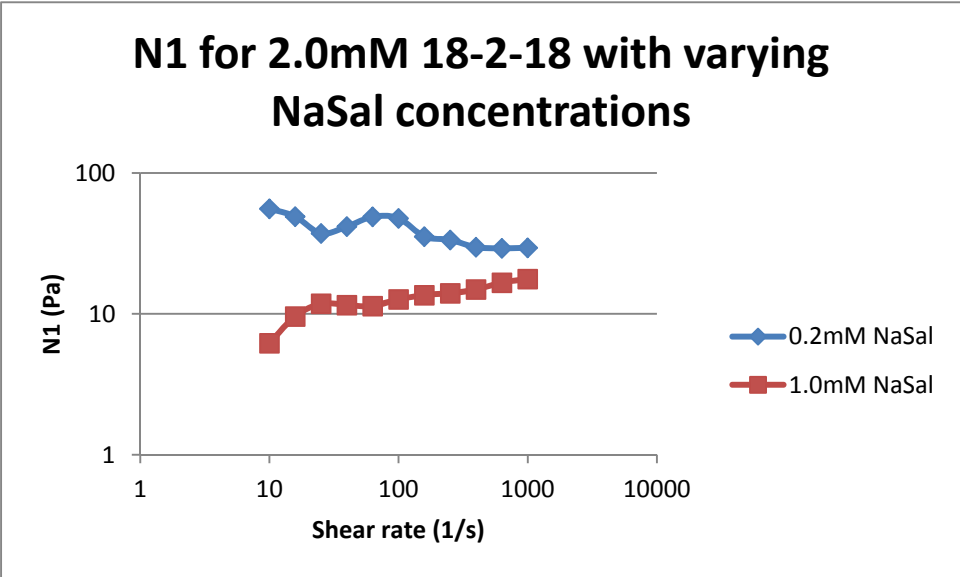


Figure 6: The  $N_1$  Measurements from the 2.0mM 18-2-18 with different NaSal Concentrations

The viscosity data for the 2.0mM 18-2-18 show a constant viscosity with shear rate, showing no SIS behavior. Surprisingly, the  $N_1$  data reveal higher values for the

0.2mM NaSal than for the 1.0mM NaSal. However, the 1.0mM NaSal values of the normal stress increase steadily with increasing shear rate, behavior observed with most viscoelastic solutions.

### B. 12-2-12 Solution Results

The shear viscosity and  $N_1$  data were obtained from the cone and plate rheometer. The 12-2-12 samples were tested without counterion. The graphs of the shear viscosity and  $N_1$  versus shear rate have been included below in Figure 7 and Figure 8.

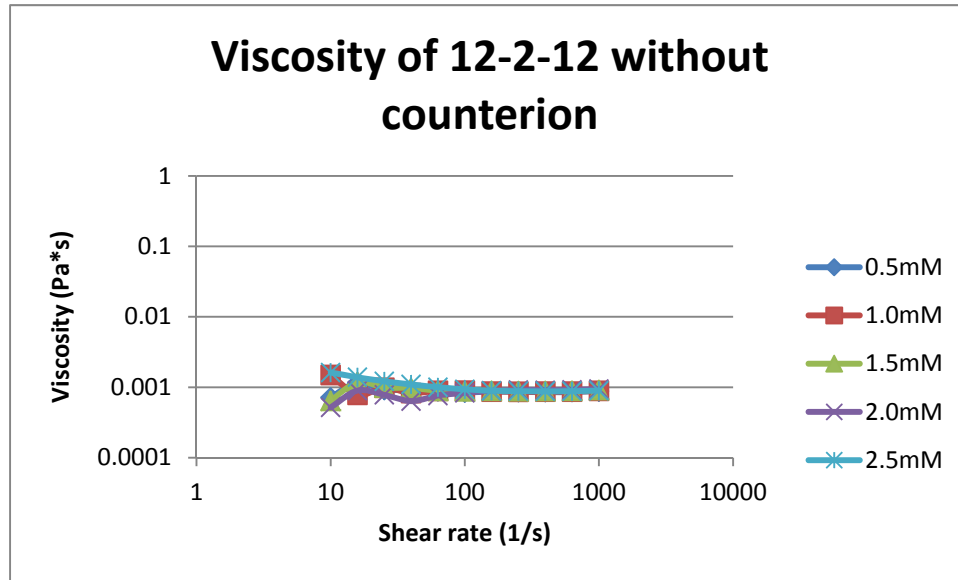


Figure 7: The Shear Viscosity of Different Concentrations of 12-2-12

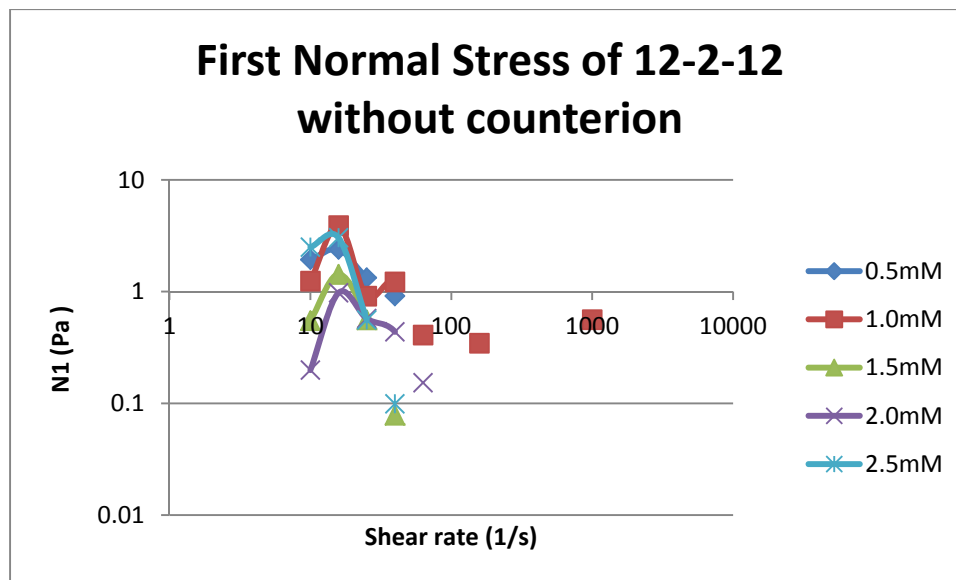


Figure 8:  $N_1$  of Different Concentrations of 12-2-12

The viscosities of all of the samples are around 0.001 Pa\*s, similar to that of the water solvent, and the viscosity is not a function of shear rate. There is no evidence of SIS in the viscosity data. The  $N_1$  graph shows that the highest value is around 8 Pa, which does not indicate any significant viscoelastic behavior of the 12-2-12 solutions without counterion. The 0.5mM 12-2-12 solutions with varying counterion ratios were tested as well and showed similar behavior to the solutions without counterion. Those viscosity and  $N_1$  data are attached in the Appendix.

The 1.0mM 12-2-12 solutions with 1/5 and 1/2 counterion ratios were tested, and the viscosity and  $N_1$  data are shown in Figure 9 and Figure 10.

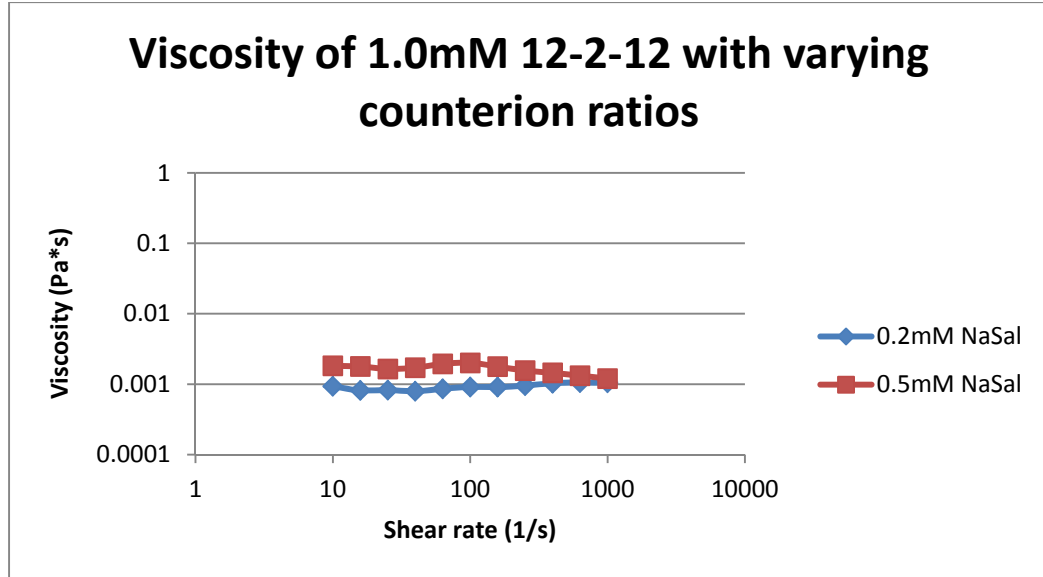


Figure 9: The Viscosity of the 1.0mM 12-2-12 Solutions with different NaSal ratios

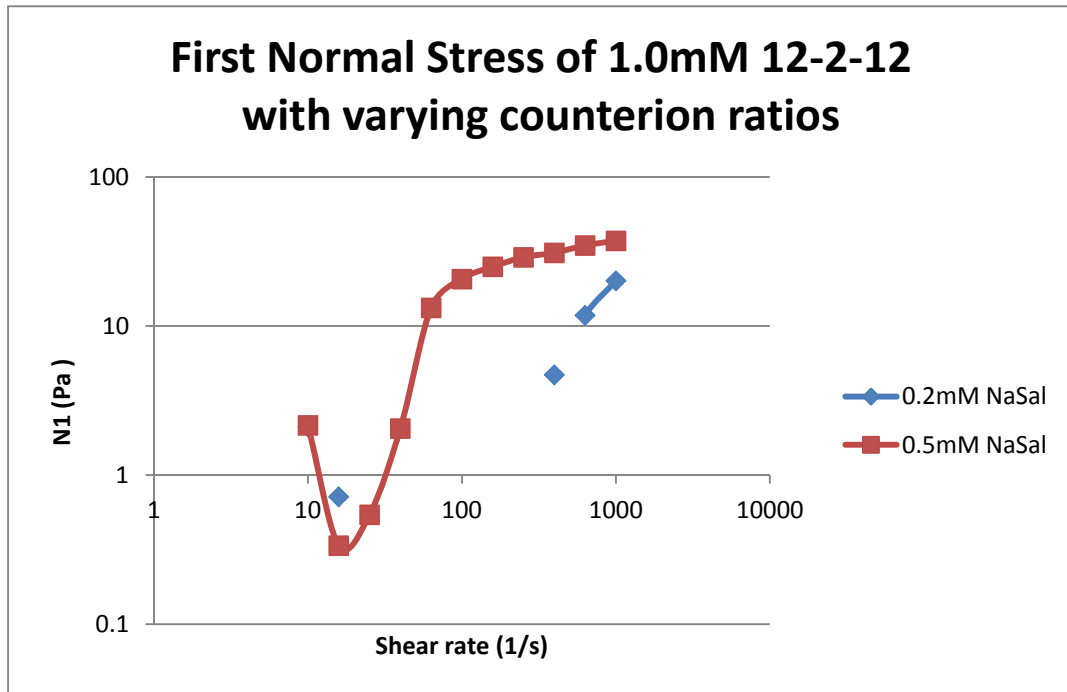


Figure 10:  $N_1$  of the 1.0mM 12-2-12 with different NaSal ratios

The viscosity data of the 1.0mM 12-2-12 are fairly consistent with the 0.5mM NaSal data at shear rate below about  $100\text{s}^{-1}$  showing viscosity of about  $0.002\text{ Pa}\cdot\text{s}$ . At shear rate above  $100\text{s}^{-1}$ , the 0.5mM NaSal solution exhibits shear thinning behavior. The  $N_1$  data for the 0.5mM NaSal concentration suggests that there may be weak viscoelastic forces as the normal force increases to the highest value of 37 Pa. The increase in the  $N_1$  suggests that the micelles may have been beginning to grow and to orient in the direction of the shear flow.

The 1.5mM 12-2-12 data for the viscosity and  $N_1$  are given below in Figure 11 and Figure 12.

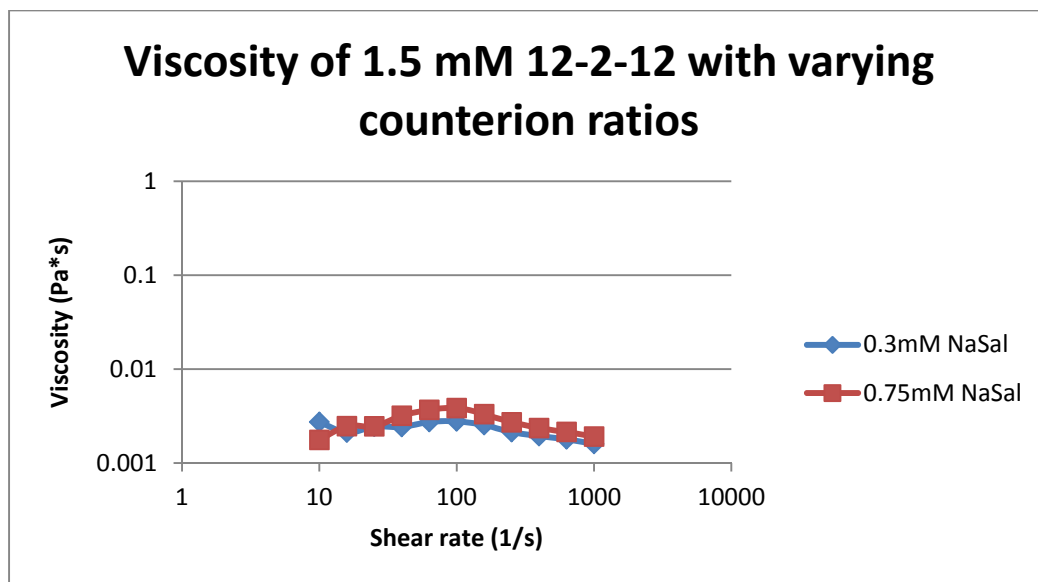
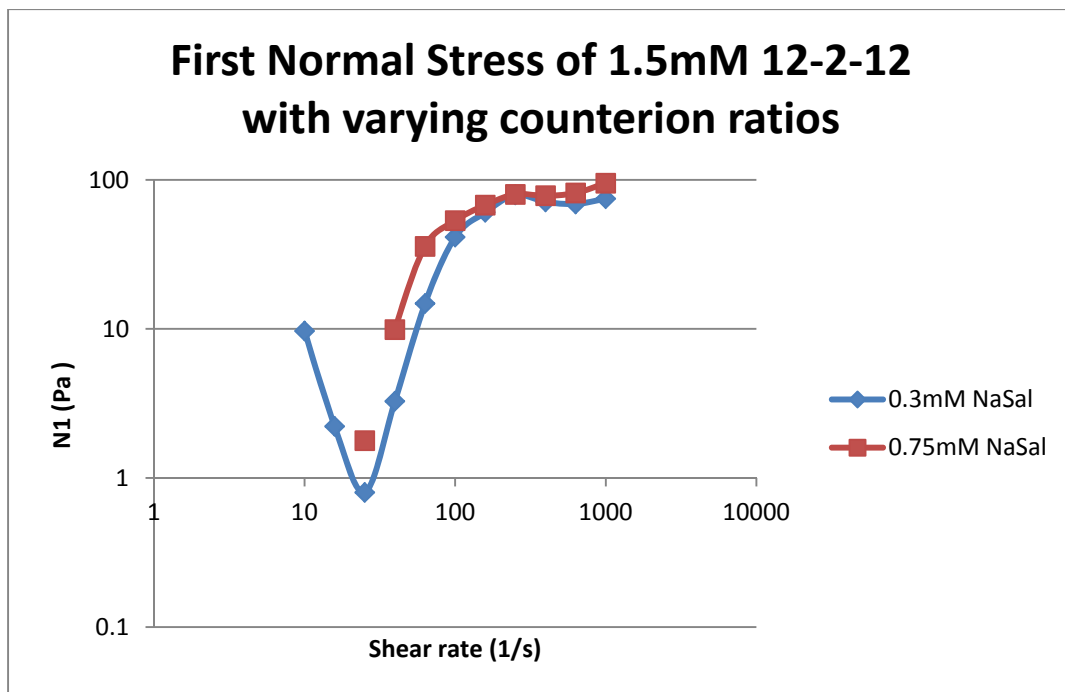


Figure 11: The Viscosity of 1.5mM 12-2-12 with different NaSal ratios





**Figure 12:  $N_1$  for the 1.5mM 12-2-12 with different NaSal ratios**

The viscosities of the 0.3mM and the 0.75mM NaSal solutions are not constant with varying the shear rate. For both the 0.3mM and 0.75mM NaSal concentrations, there is a slight increase to a maximum viscosity, which suggests that SIS may have formed; at higher shear rates, the solutions exhibit shear thinning behavior. The  $N_1$  values exhibit viscoelastic characteristics as the  $N_1$  increases and levels off with increasing shear rate.

The 2.0mM 12-2-12 was tested with different counterion ratios, and the viscosity and  $N_1$  data are shown in Figure 13 and Figure 14.

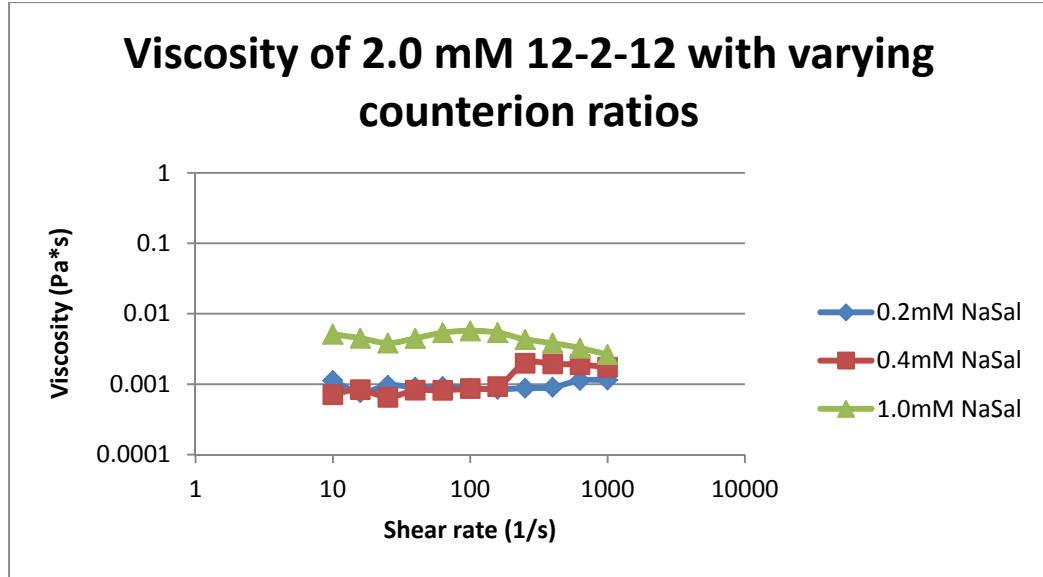


Figure 13: Viscosity of 2.0mM with different NaSal ratios

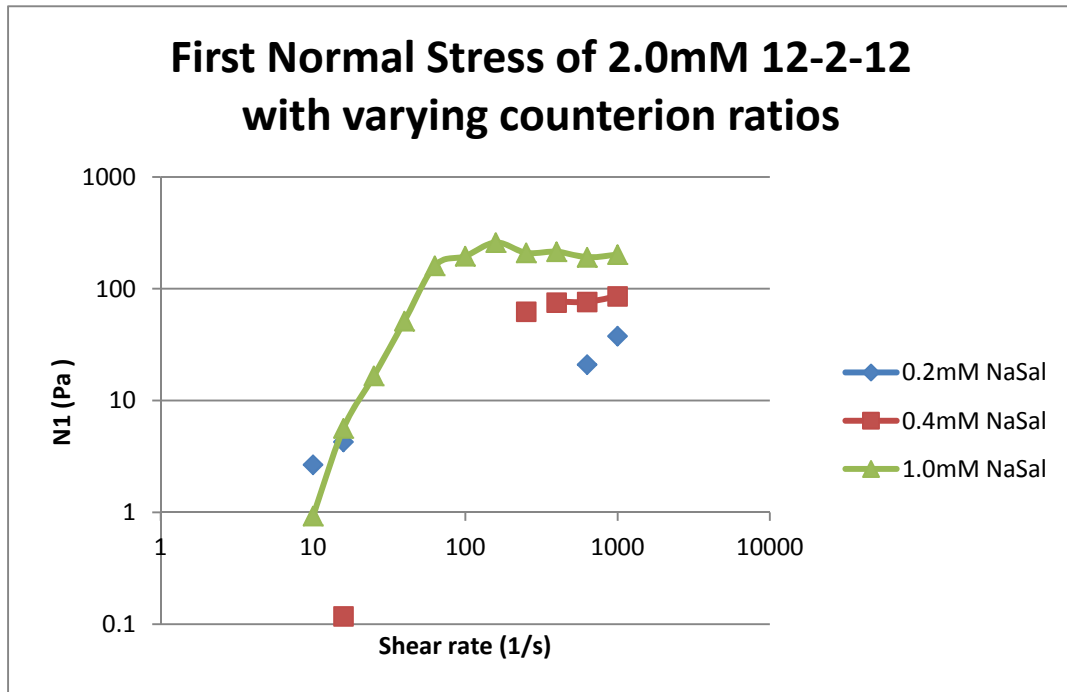


Figure 14: N<sub>1</sub> Data for the 2.0mM 12-2-12 with different NaSal ratios

The viscosity for the 0.2mM NaSal solution appears to not be a function of shear rate. However, the other two samples with 0.4mM and 1.0mM NaSal concentrations are functions of shear rate. The  $N_1$  data indicate that the 0.4mM and 1.0mM NaSal solutions both show viscoelastic behavior. The 1.0mM NaSal values for the  $N_1$  data level off at just over 200 Pa. At a shear rate of  $250\text{s}^{-1}$ , the  $N_1$  for the 0.4mM NaSal solution greatly increases to 62 Pa, accompanied by an increase in the viscosity. The  $N_1$  reaches a maximum of 86 Pa at  $1000\text{s}^{-1}$ . For the 1.0mM NaSal solution, the viscosity reaches a maximum at  $100\text{s}^{-1}$ , which may correspond to formation of SIS. After the maximum, the solution exhibits shear thinning behavior as the viscosity decreases with increasing shear rate.

The highest concentration of 12-2-12 was 2.5mM, and the data from the cone and plate rheometer testing are shown in Figure 15 and Figure 16.

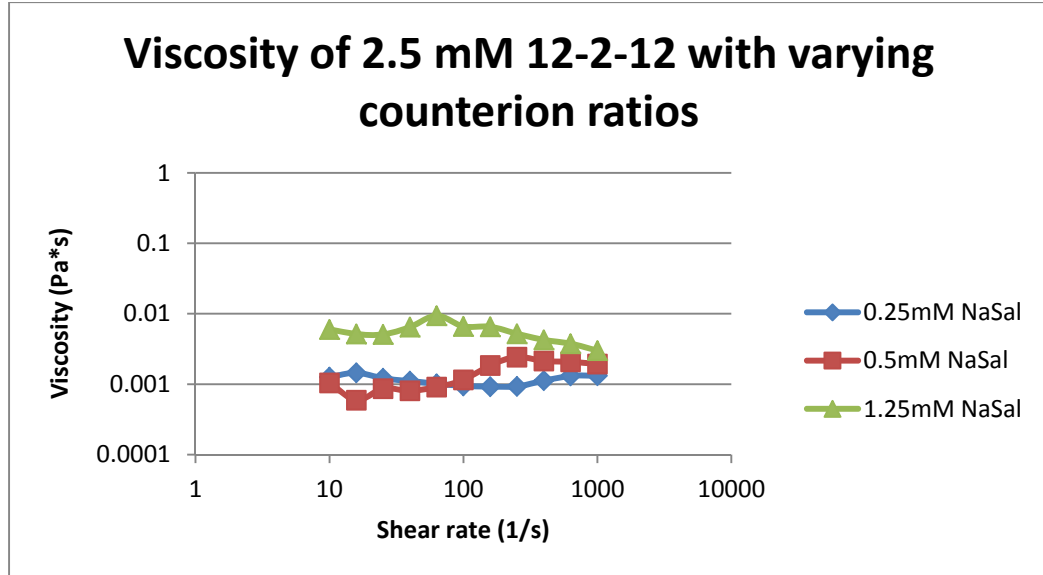


Figure 15: 2.5mM 12-2-12 Viscosity data with different NaSal ratios

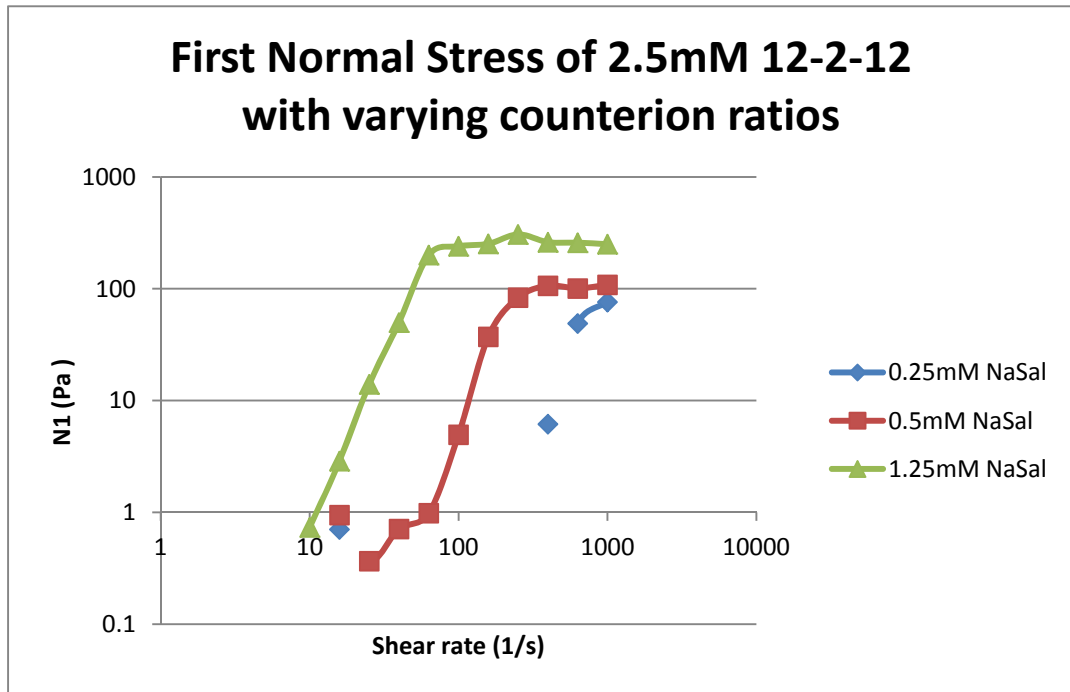


Figure 16: N<sub>1</sub> Data for the 2.5mM 12-2-12 with different NaSal ratios

The 2.5mM data exhibit viscoelastic behavior. The sharp increase in both the  $N_1$  values for the 1.25mM and 0.5mM NaSal solutions correspond to a maximum in the viscosity. The solutions also show shear thinning at high shear rates. The 1.25mM NaSal solution reaches a maximum  $N_1$  value of 306 Pa at  $250\text{s}^{-1}$ ; the 0.5mM NaSal has a maximum  $N_1$  value of 108 Pa at  $1000\text{s}^{-1}$ . At high shear rates, the  $N_1$  of the 0.25mM NaSal solution increased to a maximum of 76 Pa.

The  $N_1$  data reveal trends that increasing concentration and molar NaSal ratio increase the viscoelastic behavior. The maximum  $N_1$  value increased with higher concentrations of both the gemini surfactants and the counterion. The higher the  $N_1$  values, the more viscoelastic the solution is, which increases the likelihood of their having drag-reducing capabilities. The most viscoelastic solutions were the 2.5mM 12-2-12 with 1.25mM NaSal and 0.5mM NaSal and the 2.0mM 12-2-12 with 1.0mM NaSal and 0.4mM NaSal.

## **V. Conclusions and Recommendations**

The 18-2-18 solutions were inconclusive with respect to  $N_1$  data; there were normal stresses that were measured by the rheometer, but they may have been due to errors in the readings for the normal stresses. Alas, the viscosity was not seen to be a function of shear rate, a characteristic of many viscoelastic solutions. If solutions with higher concentrations of surfactant and counterion ratios are stable, large micelles may form, and these solutions might have drag-reducing potential.

The 2.5mM and 2.0mM 12-2-12 solutions with the highest ratio of NaSal have significant  $N_1$  values. The viscosity data also showed SIS behavior, which suggests that entangled, worm-like micelles formed. These micelle structures, as mentioned previously, are believed to be necessary for drag reduction.

For both the 18-2-18 and 12-2-12 gemini surfactants, a higher range of concentrations and counterion ratios should be explored. With increased concentrations and higher NaSal ratios, it is expected that the viscoelasticity of the solutions should increase, and therefore the likelihood of drag-reducing capabilities increased.

From the literature, m-s-m gemini surfactants have been shown to have synergistic properties when mixed with alkyl glucosides and maltosides (Zana and Xia 2004). The synergism that has been investigated may be beneficial in lowering concentrations that are needed for viscoelastic properties. It is recommended that these synergistic interactions be explored as potential drag reduction additives.

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## Appendix

The data for the trial of the 0.5mM 12-2-12 with 0.25mM NaSal can be seen below in Figure 17 and Figure 18.

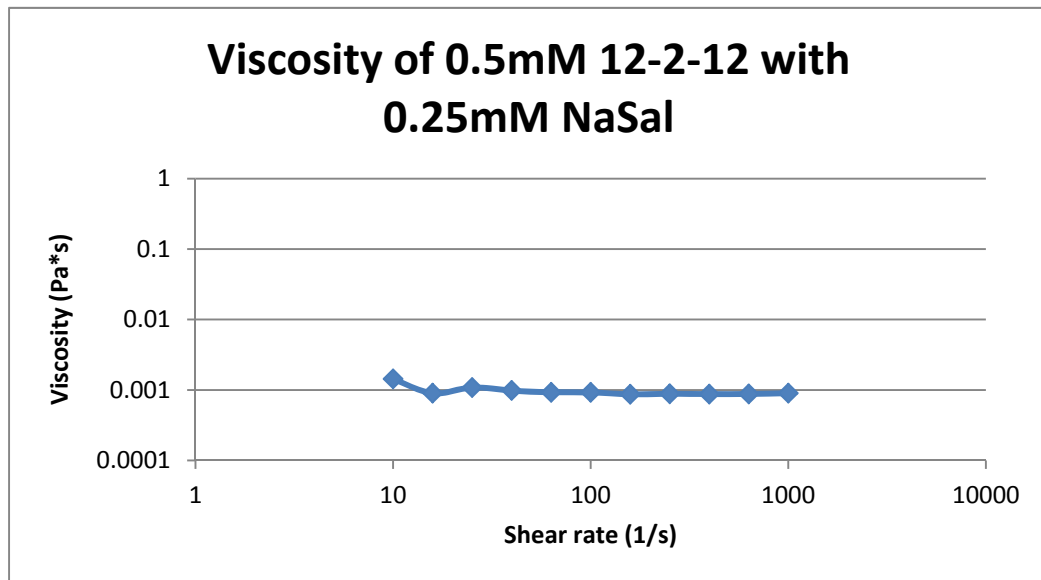


Figure 17: The Viscosity Data of the 0.5mM 12-2-12 with 0.25mM NaSal

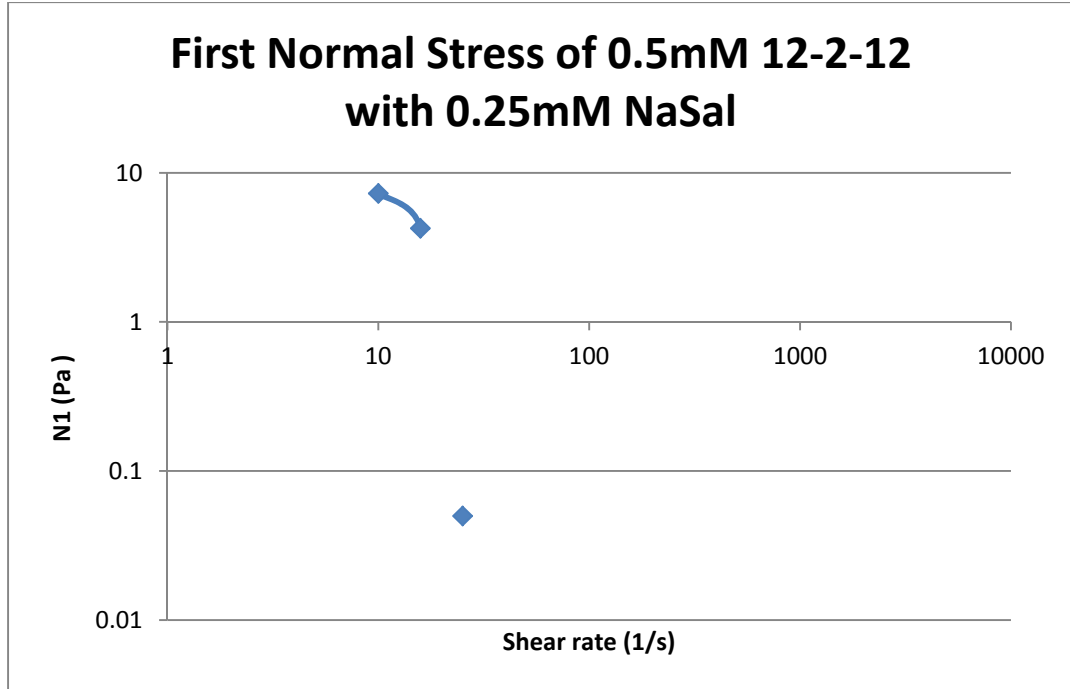


Figure 18: The  $N_1$  Data for the 0.5mM 12-2-12 with 0.25mM NaSal