B.S. HONORS THESIS

RHEOLOGY OF DRAG REDUCING SURFACTANT SYSTEMS

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I. Introduction

District energy systems are an environmentally friendly and energy efficient method for heating and cooling buildings in an urban district. District heating and cooling systems consist of a central station, which distributes hot water, chilled water, or steam through a network of pipes for consumer use. These types of systems have become increasingly popular throughout the world and are most commonly used in densely populated areas. District cooling systems, which are the focus of this research project, consist of a system where a liquid is cooled at a central station. This liquid then exchanges heat with a secondary system in a building in order to cool it.

Typically, district cooling systems use pure water as the transporting liquid. Water, however, is less efficient in these systems than some solutions can be. For instance, water can only be cooled to a temperature of about 5 ^oC due to its 0 ^oC freezing point. The temperature of the warmed liquid to be re-circulated in district cooling systems is typically 15 ^oC. This results in a temperature difference of 10 ^oC. This temperature difference can be increased by replacing the water with a solution which allows the initial temperature to be lower. For example, by using a 20% ethylene glycol / water solution the initial temperature can be reduced to about -5 ^oC. This will produce a temperature difference of 20 ^oC doubling the amount of heat transfer that can occur in the system for a given mass of fluid. This in turn will reduce the volume of liquid necessary to produce the same amount of cooling and in turn decrease the required size of the district cooling system.

Drag reduction is another factor that can be used in district cooling systems to help boost the economic benefits of such systems. Drag reduction occurs when a small amount of an additive such as a surfactant or polymer causes a reduction in the turbulent friction[9]. This reduction in friction causes the pressure drop in the pipe flow to be less than that of the pure fluid leading to a decrease in the pumping requirements of such systems. This is beneficial in district cooling systems because the pumping energy amount to about 15% of the total energy load. Several types of additives have been studied which cause this drag reducing phenomenon to occur. These include surfactants, polymers, aluminum disoaps, and fibers. Surfactants are the focus of this research due to their ability to self-repair upon mechanical degradation. Degradation occurs when a molecule undergoes a region of high shear such as a pump. This is common in district cooling systems because these systems are recirculating flow systems with multiple pumps.

Surfactants are molecules which contain a hydrophobic tail and a hydrophilic head group. Surfactants can be further classified by their hydrophilic group. The different types of surfactants are anionic, nonionic, zwitterionic, and cationic. Surfactants behave in a characteristic manner in aqueous solution. In these solutions the hydrophobic groups avoid contact with water by forming micelles. In micelles the hydrophilic parts, which are polar, contact the water allowing the non-polar, hydrophobic, parts to concentrate in the center of the micelle. The micelles form different structures in aqueous solutions including spherical, rod-like, lamellar, and vesicles. The types of surfactant as well as the structure of the micelle both contribute to the drag reducing properties of the molecule.

The main objective of this research project was to determine the rheological properties of surfactant solutions and to compare these with their drag reducing properties. Rheological properties can be better understood by noting that rheology is the study of the deformation and flow of matter in terms of stress, strain, temperature, and time. This research project focused on the rheological properties of shear viscosity, first normal stress difference, shear stress, and shear induced structure. The project was part of a larger research project, which aimed at developing practical drag reduction systems for use in district cooling. Surfactant solutions with promising drag reduction characteristics were the focus of the rheology measurements. The rheology research aimed to determine how these drag reducing solutions behave under stress.

There were several objectives for the research project. The first object was to test anionic, cationic, and zwitterionic surfactant solutions, which were promising drag reducers, to determine their shear viscosity, shear stress, and first normal stress difference at varying shear rates. For each of these rheological properties any consistent trends in the data and behavior were determined and compared to the drag reducing properties. The second objective was to find a correlation between the first normal stress difference and the appearance of shear induced structure (SIS). The apparent SIS occurs when a solution's viscosity, which normally decreases as shear rate increases, undergoes a quick rise with increasing shear rate. A goal of the project was to determine if there was a relationship between SIS behavior and normal stress difference behavior. The final objective of the research project was to study the behavior of shear stress as a result of a constant shear rate. In these experiments, the solutions were stressed at a constant shear rate to determine the shear stress behavior of each solution vs. time.

II. Literature Review

A. Drag Reduction

Drag Reduction is a phenomenon in which the friction of a liquid flowing in a duct in turbulent flow is decreased by using a small amount of an additive. This is beneficial because it can decrease pumping energy requirements. Some current applications where drag reduction has been applied include district heating and cooling systems and oil transmission pipelines[8],. Different types of additives can be used in these systems and include surfactants, fibers, aluminum disoaps, and high polymers. Drag reducing additives are effective because they reduce the turbulent friction of a solution. This results in a decrease in the pressure drop across a length of conduit and likewise reduces the energy required to transport the liquid.

An important aspect of drag reducing additives which impacts their performance is their ability to self repair[9]. This is the ability of a group of molecules to return to its original form after its structure has been altered as a result of high shear. High molecular weight polymers and aluminum disoaps both degrade when subject to high shear and generally cannot reform. Therefore, they cannot be effective in recirculation systems such as district cooling systems because pumps are required to recirculate the fluid and these pumps apply high shear stress to the fluid. This causes polymer chains to break into smaller segments which do not have the ability to revert to their original form. Aluminum disoaps degrade similarly to polymers. These disoaps do, however, have the ability to recombine into their original structure, but this takes several days in which the additive has no drag reducing capability. Surfactants on the other hand are able to repair themselves in a matter of seconds upon degradation from shear. This characteristic makes surfactants a good candidate for recirculation systems.

B. Surfactants

The term surfactant came from the contraction of "surface active agent." This contraction describes surfactants because a predominant characteristic of surfactants is their ability to lower the surface tension of liquids[7]. Surfactants are able to do this because they are amphiphilic compounds. This means that they have a hydrophilic head group and a hydrophobic tail group. The hydrophobic head group is a polar group which is usually (but not always as in nonionics) ionizable and capable of forming hydrogen bonds. In contrast the hydrophobic tail group is a nonpolar group which is typically a long chain alkyl group[9]. Due to this unique structure surfactants show characteristic behaviors when in an aqueous solution. The hydrophobic group repels water in solution while the hydrophilic group is attracted to the polar water molecules. This causes the hydrophobic groups to cluster together in a hydrocarbon phase in order to avoid contact with the water while the hydrophilic polar groups surround them and are in contact with the water. The aggregates formed are called micelles.

There are several types of surfactants which include anionic, cationic, zwitterionic, and nonionic surfactants. Anionic soap surfactants are water soluble and have a negative charge when in aqueous solutions[6]. They give good drag reduction results when the shear stress is not too high i.e. lower flow rates. They are, however, very sensitive to hard water metal ions such as Ca^{2+} and Mg^{2+} which make them insoluble in water. Anionic surfactants also cause some problems when exposed to air because they have the tendency to form foam[9]. This can result in complications is many systems that do not have the ability to handle foam formation. For these reasons they have not been considered good candidates to be drag reducing agents.

Cationic surfactants, as opposed to anionic surfactants, have a positive charge when immersed in aqueous solutions. These surfactants are not affected by the metal ions in tap water as were the anionic surfactants. Cationic surfactants produce good drag reduction results over a wide temperature range. Some other positive characteristic of cationic surfactants are that they are relatively stable and they have good self-reparability[9]. The major disadvantage is that they do not biodegrade readily which could cause problems if leaks or spills occur.

Zwitterionic surfactants have both negative and positives charges on the head group of the molecule. Since these surfactants contain both types of charges, it may cause the surfactant molecule to be sensitive to the ions present in water or solutions which may decrease the stability of these types of surfactants. One beneficial characteristic of zwitterionic surfactants is that they are readily biodegradable and less toxic than some other surfactants. This is very important in district cooling systems because, if leaks or spills occur in the system, the environment will not be polluted by the additive.

Nonionic surfactants, unlike the three surfactants discussed above, have no charge on their head groups. These types of surfactants are stable and are able to self-repair quickly after degradation from high shear. Similar to zwitterionic surfactants, nonionic surfactants are also less toxic than most and are rapidly biodegradable. However, they are generally only effective as drag reducing agents over a relatively narrow temperature range near their upper consolute or cloud point temperature.

C. Micelles

Surfactants have the ability to group themselves in consistent patterns due to the hydrophobic and hydrophilic components of the molecules. The hydrophobic ends of the surfactants group themselves together when in aqueous solutions because these ends are nonpolar and repel the polar water molecules. Conversely, the hydrophilic or polar ends of surfactants are attracted to the water molecules. This causes the surfactants to form clusters called micelles.

Micelles form into several different shapes including spherical, rod-like, lamellar, and vesicles. Typically, at low concentrations micelles are spherical in shape as shown in Figure 1b. When the concentration of the surfactant is increased or the temperature of the solution is decreased the micelles may form into rod-like micelles, which are shown in Figure 1c. Drag reducing systems are generally believed to be composed of long rod-like micelles. Another method that has been used to promote the formation of rod-like micelles is the addition of salts or conterions to the solution. This disperses the positive repulsive charges on the ionic headgroups and stabilizes the micelles allowing them to grow in size[9].

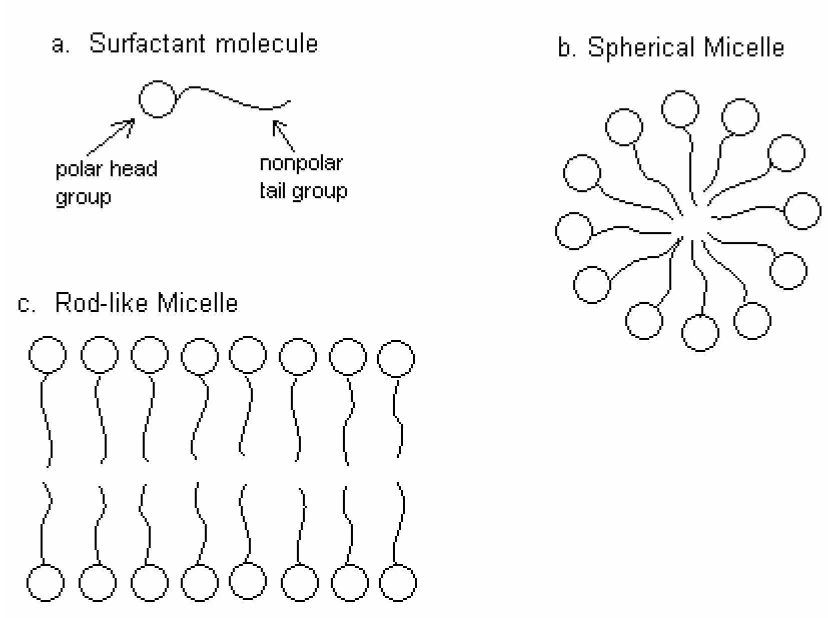

Figure 1: Micelle Structures

D. Rheology

Rheology is the study of the flow and deformation of matter. Rheological properties of many different substances including paint, plastics, rubber, and lubricants are important to their applications. Typically, the rheological properties of non-Newtonian materials are studied to develop models to understand the behavior of such solutions. Most drag reducing surfactant solutions are non-Newtonian even at low concentrations. These types of solutions have unusual rheological behavior because of the presence of the micelles. For example, surfactant solutions undergo structural changes when they self repair themselves upon removal from high shear[5]. Several rheological properties are important to study in order to develop a better understanding of a solution's behavior. These properties include shear viscosity, shear-induced structure, first normal stress difference, and shear stress.

E. Shear Viscosity

Viscosity is a property of a fluid which is a measure of its resistance to flow. Viscosities can be measured using a viscometer, which has the ability to determine changes in viscosity with time or with shear rate or shear stress. Viscometers can also detect if a solution undergoes shear thinning or thickening with time. Shear thinning is when a solution's viscosity decreases with increasing shear while shear thickening is the opposite, where a solution's viscosity increases with increasing shear[1].

A particular solution's composition can have a dramatic effect on its viscosity. For example, at high shear rates dilute surfactant solutions with micelles will exhibit viscosity close to that of water while the viscosity of the pure surfactant is much greater than that of water[5]. Also, the addition of salts to surfactant solutions may increase or decrease the viscosity of the solution depending on the concentrations of both the surfactant and salt[3].

F. Shear Induced Structure (SIS)

Shear induced structure (SIS) is a phenomenon that occurs when a shear thinning solution undergoes a sudden increase in viscosity as the shear rate applied to the solution increases. According to Yunying Qi[5] this coincides with a change in the structure of the micelles at a critical shear rate causing formation of a "shear induced structure". The sizes of these structures may be orders of magnitude larger than the rod-like micelles resulting in a large increase in viscosity. This increase forms a peak in the viscosity because the structures are not stable and as the shear rate increases further, shear thinning will occur again. The critical shear rate at which SIS occurs is a function of the concentrations of all components in a solution as well as the temperature and geometry used in a rheometer. Although this is the typical explanation for SIS behavior, no detailed understanding of this phenomenon has been reached

G. First Normal Stress Difference

The first normal stress difference, N_1, is a characteristic of viscoelasticity. Viscoelasticity is a property of materials which behave as both liquids (viscous behavior) and solids (elastic behavior). It has been suggested that first normal stress difference can be used to correlate a solution's viscoelacticity to its drag reduction characteristics[5]. Furthur, it has been found that for many drag reducing surfactant solutions there is a relationship between the occurrence of increase in shear viscosity (SIS) and normal stress difference[5].

III. Experimental Methods

A. Materials

All of the surfactants and counterions used for this research project are listed below in Table 1.

Table 1: List of Materials

Material	Classification
Beraid DC DR 620	Zwitterionic Surfactant
SPE98300	Zwitterionic Surfactant
DR0206	Zwitterionic and Anionic Surfactant
Oleyl Betaine	Zwitterionic Surfactant
Oleyl Trimethylaminimide	Zwitterionic Surfactant
Ethoquad O12	Cationic Surfactant
Trilon A	Sequestering agent
Formaldehyde	Biocide
Sodium Dodecyl Benzenesulfonate (SDBS)	Anionic Surfactant
Sodium 2-hydroxy benzoate (NaSal)	Salt
Sodium Nitrite	Salt, Corrosion Inhibitor
Ethylene Glycol (EG)	Solvent
Glycerin	Solvent
Propylene Glycol (PG)	Solvent

B. Viscosity Measurements

The viscosities of all of the solutions that were investigated in this project were measured using two different rheometers, the ARES and the MCR 300 Rheometers, both of which are made by TA Instruments. The viscosity tests were run at shear rates ranging from 0.1 to 1000 s^{-1} to determine the viscosity for each shear rate. For each of these tests a plot of the viscosity vs. the shear rate was prepared.

To perform this type of test using the ARES rheometer, a steady rate sweep test was run using an initial rate of 0.1 s^{-1} and a final rate of 1000 s^{-1}. Five points were generated per decade, i.e. 1, 1.58, 2.51, 3.98, and 6.31 s^{-1}. Each point was measured for 30 seconds with a 30 second delay between them in which steady state was reached. Couette geometry was used for these tests. Approximately 8mL of solution was used for each test and was loaded into the couette tool using a syringe. No temperature control was available for the viscosity measurements using the ARES rheometer, therefore, these tests were performed at room temperature and were subject to some fluctuation in temperature.

Using the MCR 300 rheometer, viscosity curve tests were run to determine the viscosity. These tests were also run with an initial shear rate of 0.1 s^{-1} and a final shear rate of 1000 s^{-1}. The measuring time was fixed at 60 seconds and had 5 points per decade. The tests run on this rheometer used the cone and plate geometry with a cone angle of 1 degree. The amount of sample tested was approximately 0.6 mL and was applied to the plate using a syringe. Temperature was controlled in these viscosity tests. All of the solutions were tested using the MCR 300 at a low temperature of either -2, 0, or 2 ^{o}C and a higher temperature of 25 ^{o}C.

The viscosity measurements obtained using the ARES and the MCR 300 show the behavior of solutions under shear. Using the plots of viscosity vs. the shear rate, values of shear rate can be found at which a solution undergoes an apparent shear induced structure (SIS). This SIS phenomenon occurs when the viscosity increases to a peak value as the shear rate increases. This is important because it is believed that the SIS is observed when micelle structure changes because of the shear applied to the solution.

C. First Normal Stress Difference Measurements

The first normal stress difference (N_1) measurements could be obtained only with the MCR 300 rheometer with cone and plate geometry. These measurements were obtained concurrently with the viscosity measurements. Therefore, the procedure for this test is the same as the viscosity measurement tests on the MCR 300 and shear rates varied from 0.1 to 1000 s^{-1}. The tests were performed at temperatures of either -2, 0, or 2 ^oC and 25 ^oC. From these measurements, the first normal stress difference vs. the shear rate could be plotted at the same time as the viscosity vs. the shear rate. This is important because any correspondence between SIS behavior and N_1 behavior could then be easily found.

D. Constant Shear Rate Measurements

The constant shear rate measurements were performed using both the ARES and the MCR 300 rheometers. These tests were carried out by applying a constant shear rate to a solution for a fixed amount of time. When the time period expired the shear was removed and the solution was allowed to relax back to its non-stressed form. These tests were conducted using two variables to determine how they influenced the behavior of the shear stress. These variables are the length of time a constant shear is applied and the magnitude of the shear rate applied to the solution.

To execute these types of tests using the ARES rheometer a step rate test was run. This type of test is a transient, strain-controlled test. The time and magnitude of the shear rate applied to the solution was set as well as the time for observing stress relaxation after removal of the shear. In these tests, which were run at room temperature, the temperature was not controlled. Couette geometry was used with approximately 8 mL of sample. Step rate tests were also run using the MCR 300. Again, the initial time and magnitude of the shear rate were specified as well as the time to measure the relaxation of the solution. The temperature was controlled for these tests at either 0 or 25 ^oC. Cone and plate geometry was used with a cone angle of 1 degree and approximately 0.6 mL of sample.

IV. Results and Discussions

A. Viscosity and First Normal Stress Difference Results

Several different surfactant solutions were tested to determine the viscosity and first normal stress difference behavior of each solution. These surfactant systems included Beraid DC DR 620, SPE98300, DR0206, Oleyl Betaine/SDBS, and Oleyl Trimethylaminimide in several solvents (water, 20% ethylene glycol / water, 30% glycerin / water, and 25% propylene glycol / water). All of the solutions that were tested had been previously tested for drag reduction.

i. Beraid DC DR 620

The surfactant Beraid DC DR 620 was the first surfactant system that was investigated. The structure of this zwitterionic surfactant can be seen in Figure 2.

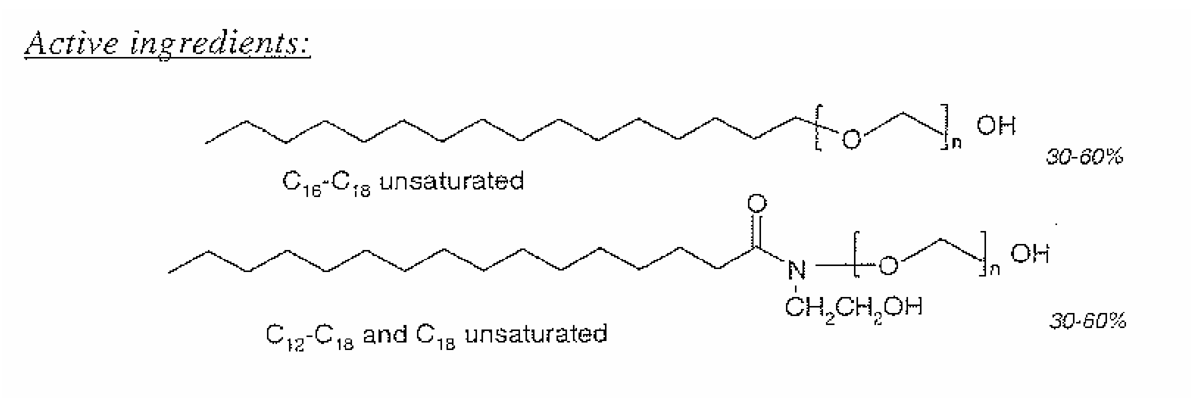

Figure 2: Structure of Beraid DC DR 620[11]

The first solution of Beraid DC DR 620 that was tested for viscosity and first normal stress difference was 1.0 wt% Beraid DC DR 620 in water. The solution was tested using the ARES and the MCR 300 rheometers. For this solution and all others to follow, the plots of the results will indicate which rheometer and temperature was used for a particular test. The plots of the shear viscosity vs. the shear rate and the first normal stress difference (normal force) vs. the shear rate obtained for this solution are shown in Figures 3 thru 5.

This solution demonstrates apparent SIS behavior at all temperatures tested as well as with both rheometers. N_1 values of this solution are quite high and are fairly constant with no rise at any shear rate. Table 2 summarizes the results for SIS behavior, N_1 behavior, and the maximum percent drag reduction (%DR) for this solution and all other Beraid DC DR 620 solutions.

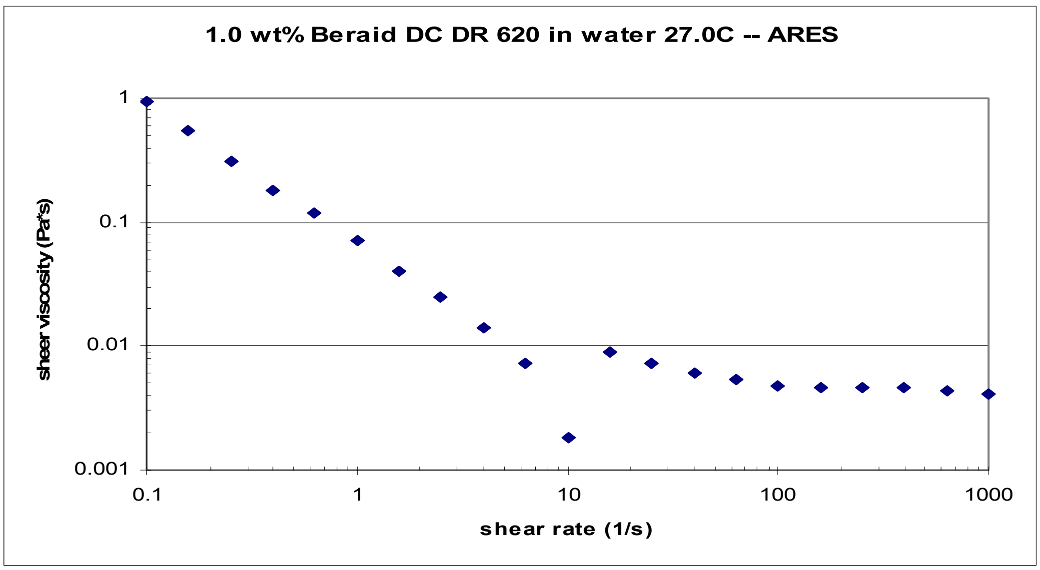

Figure 3: 1.0 wt% Beraid DC DR 620 in water 27.0 °C – ARES

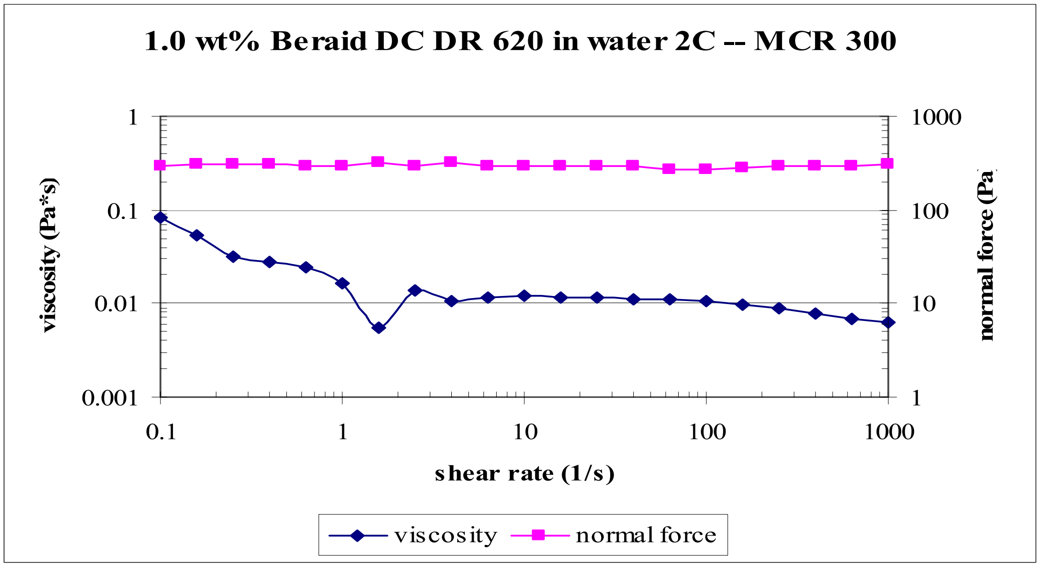

Figure 4: 1.0 wt% Beraid DC DR 620 in water 2 °C -- MCR 300

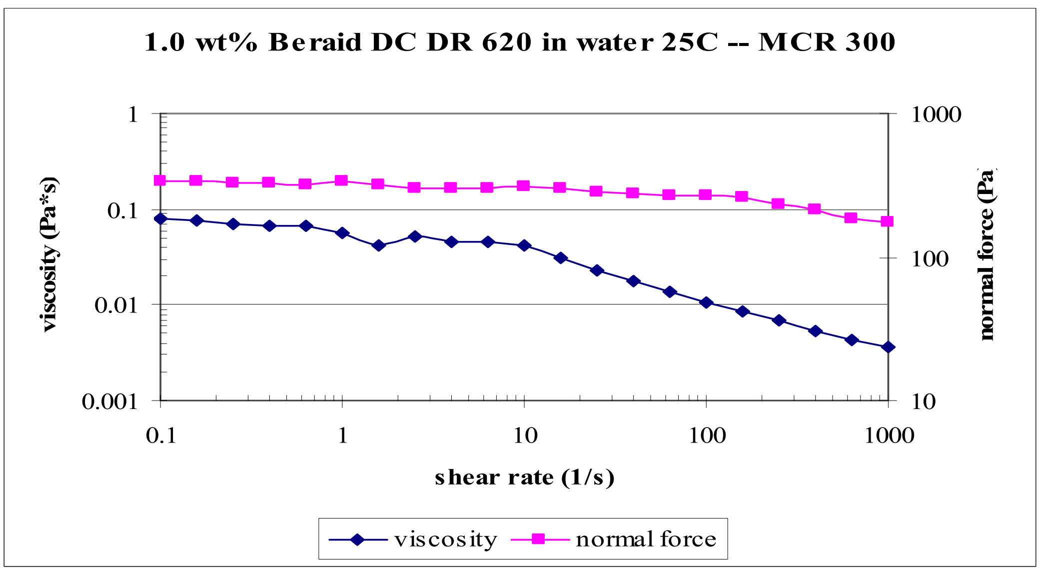

Figure 5: 1.0 wt% Beraid DC DR 620 in water 25 °C -- MCR 300

The next solution tested included the addition of sodium nitrate to the previous solution. The addition of sodium nitrate was chosen for two reasons, first it is a corrosion inhibitor and second it has been suggested by Akzo Nobel to be a drag reducing enhancer. The addition of salt produced the solution 1.0 wt% Beraid DC DR 620 + 30mM $NaNO_2$ in water. The results for this can be found in Figures 6 thru 8. This solution again does not show a rise in N_1 as the shear rate increases. Apparent SIS behavior is observed only at room temperature.

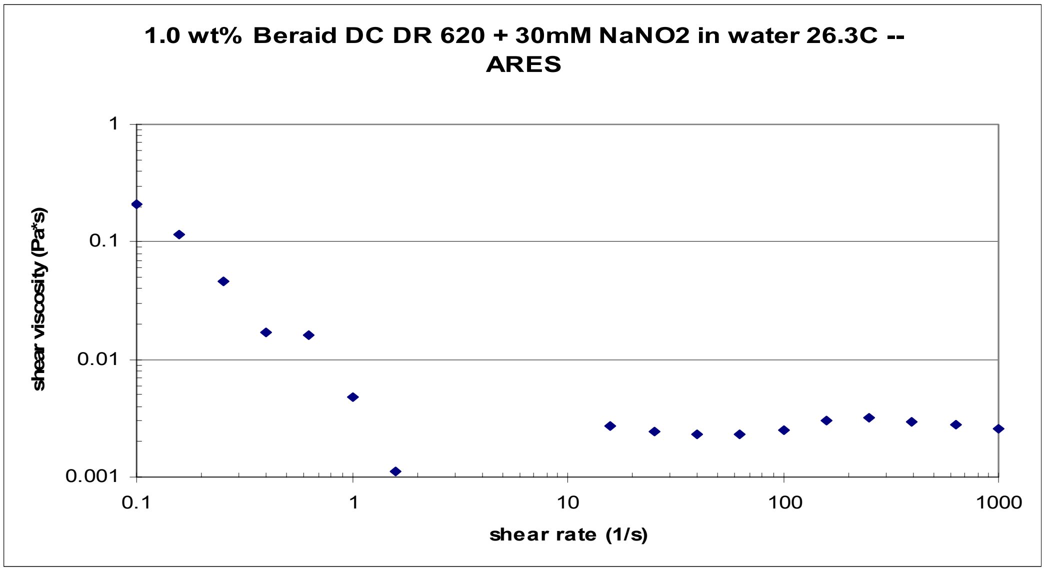

Figure 6: 1.0 wt% Beraid DC DR 620 + 30 mM $NaNO_2$ in water 26.3 °C -- ARES

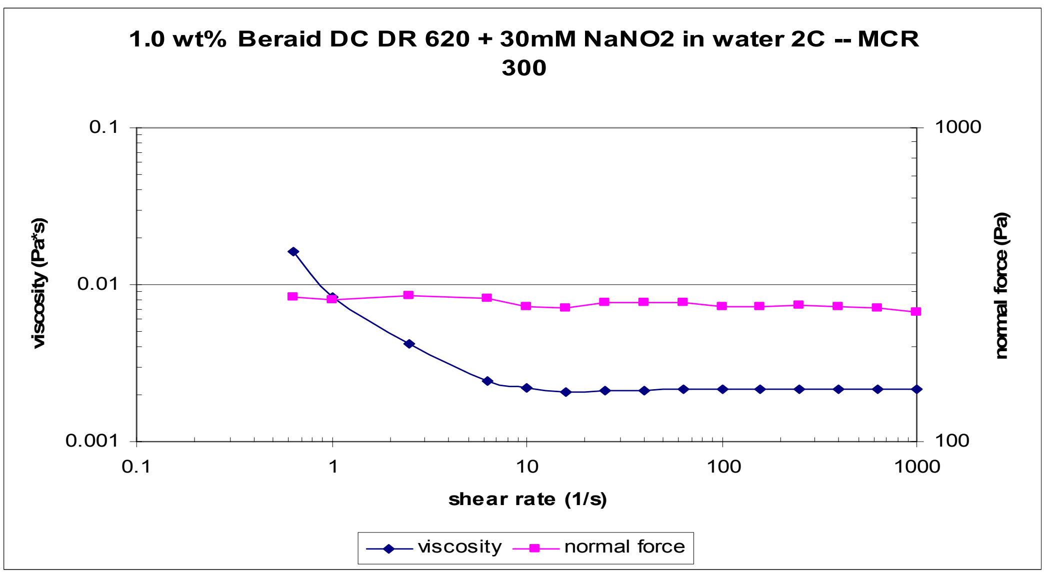

Figure 7: 1.0 wt% Beraid DC DR 620 + 30 mM $NaNO_2$ in water 2 °C – MCR 300

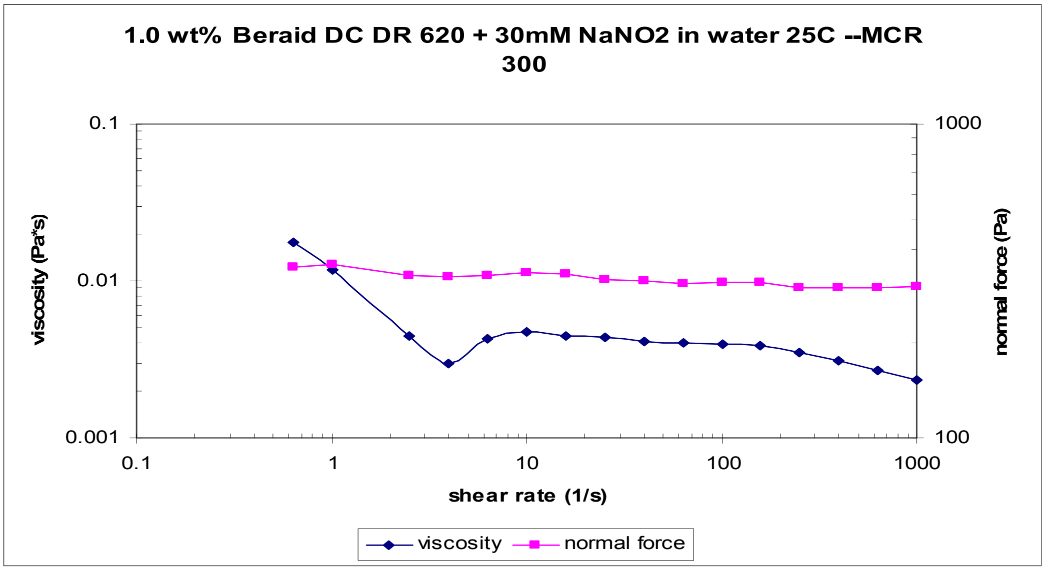

Figure 8: 1.0 wt% Beraid DC DR 620 + 30 mM $NaNO_2$ in water 25 °C – MCR 300

The next Beraid DC DR solution tested was 1.0 wt% Beraid DC DR 620 in 20% ethylene glycol (EG) / water. The results are shown in Figures 9 - 11. This solution has SIS at all tested temperatures. It also displays a slight rise in N_1 at a shear rate near 250 s^{-1} at -2 °C.

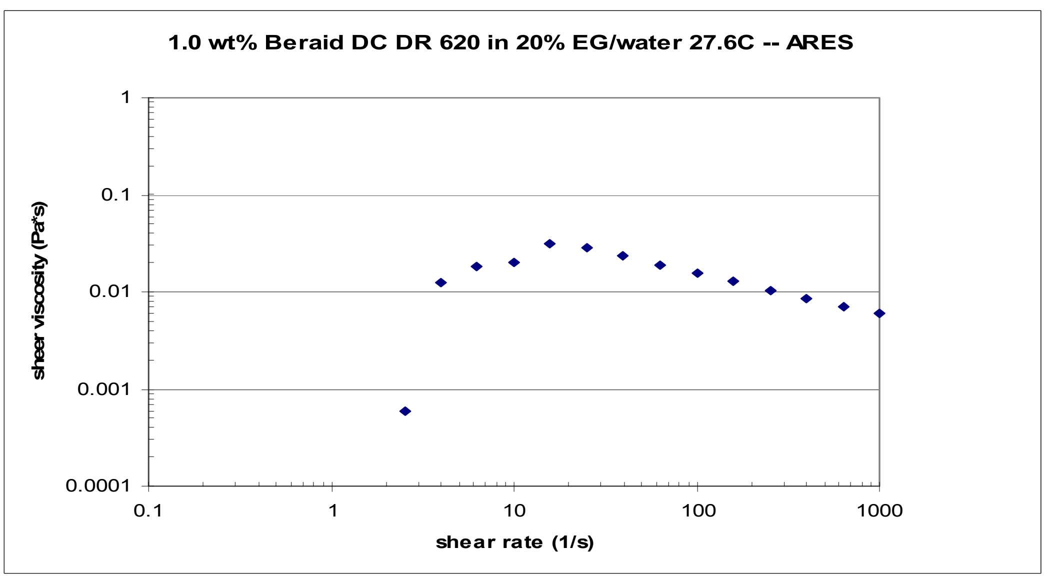

Figure 9: 1.0 wt% Beraid DC DR 620 in 20% EG/water 27.6 °C – ARES

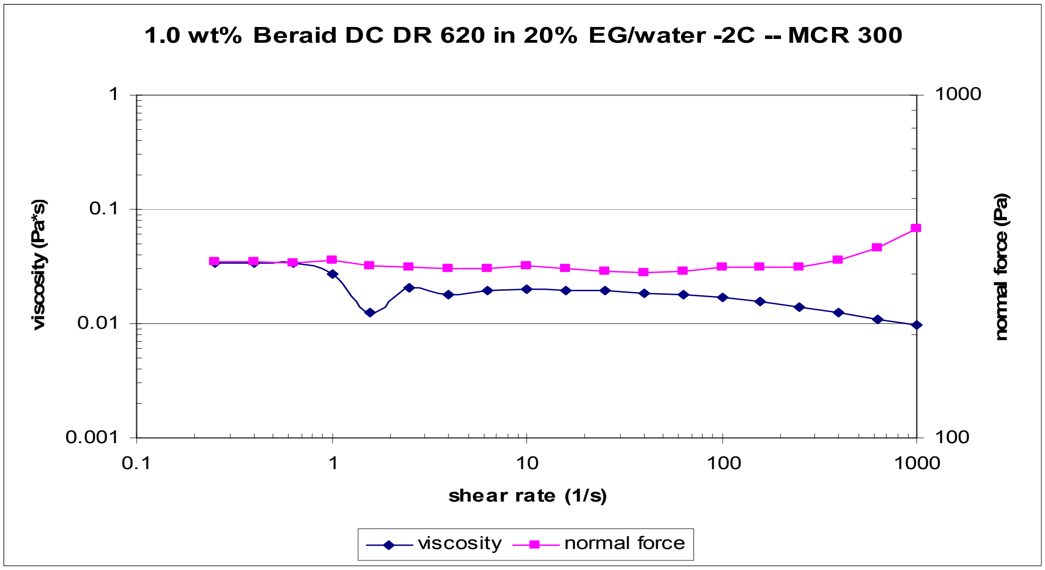

Figure 10: 1.0 wt% Beraid DC DR 620 in 20% EG/water -2 °C – MCR 300

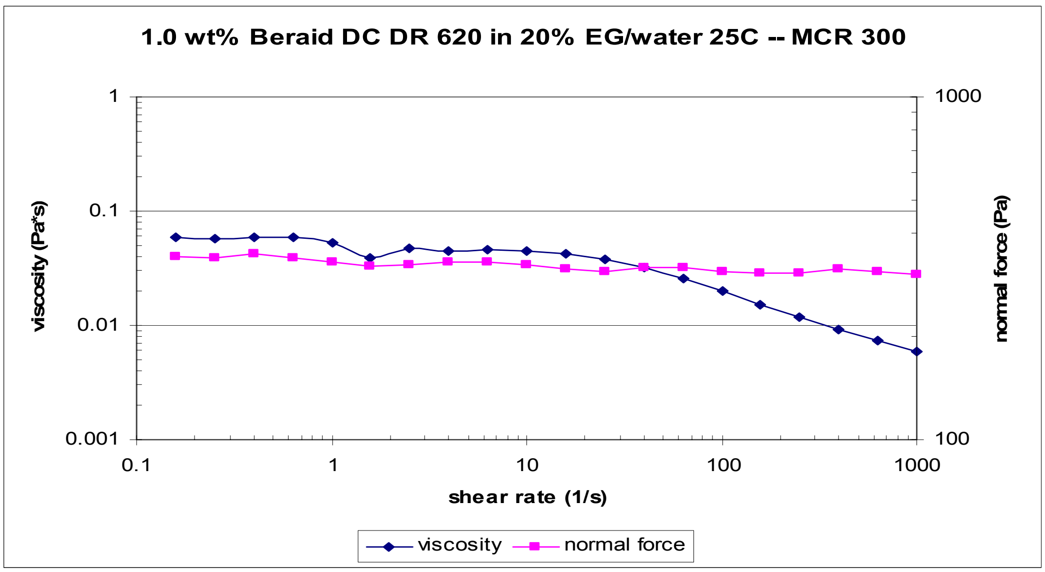

Figure 11: 1.0 wt% Beraid DC DR 620 in 20% EG/water 25°C – MCR 300

The next solution tested was 1.0 wt% Beraid DC DR 620 + 30mM $NaNO_2$ in 20% EG / water. The results are shown in Figures 12 thru 14. This solution has SIS behavior at all tested temperatures. There is no rise in N_1 at any shear rate or temperature tested.

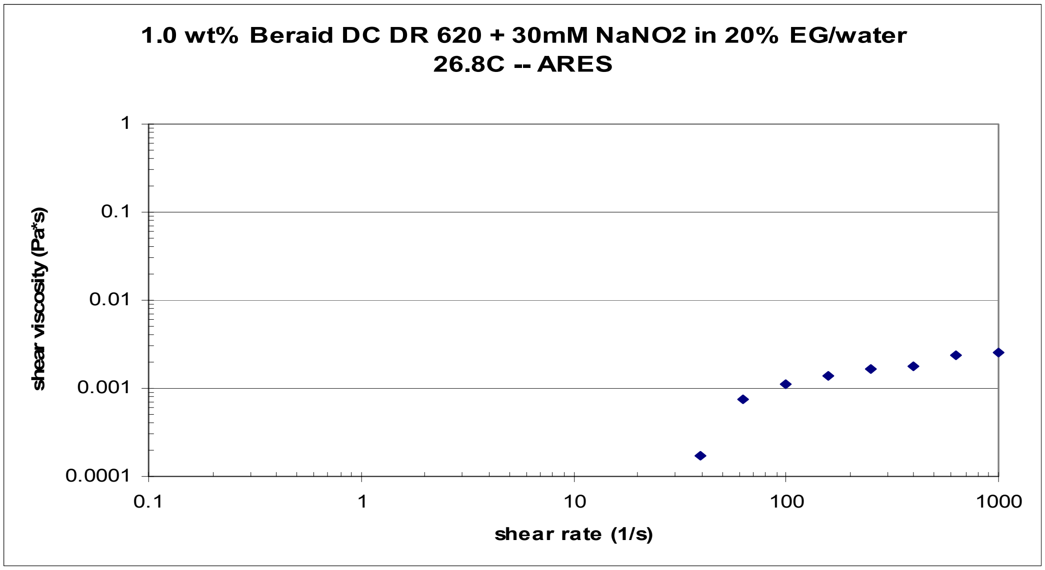

Figure 12: 1.0 wt% Beraid DC DR 620 + 30mM NaNO2 in 20% EG/water 26.8°C – ARES

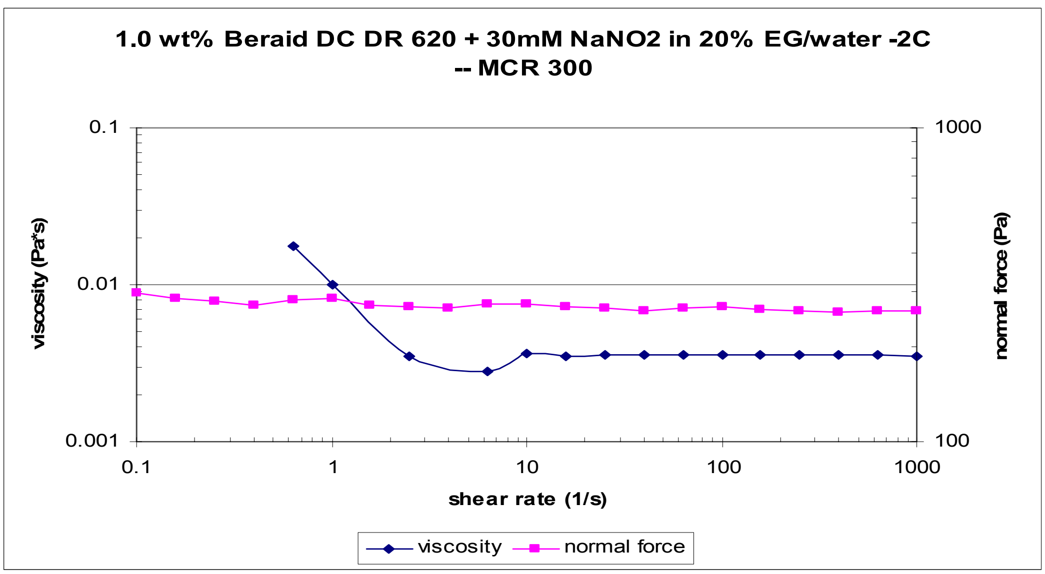

Figure 13: 1.0 wt% Beraid DC DR 620 + 30mM NaNO2 in 20% EG/water -2°C – MCR 300

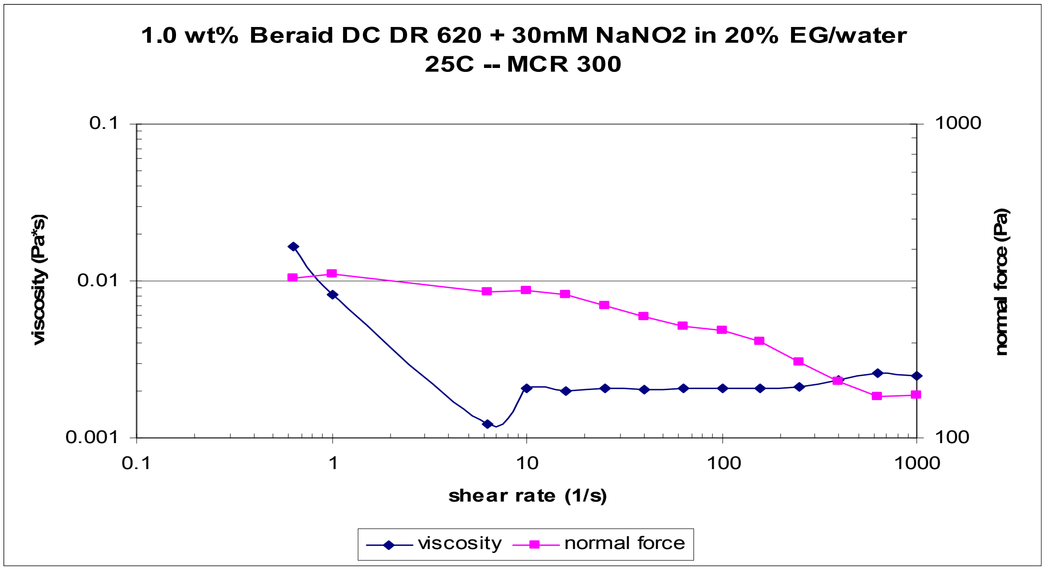

Figure 14: 1.0 wt% Beraid DC DR 620 + 30mM NaNO2 in 20% EG/water 25°C – MCR 300

Next, the solution of 1.0 wt% Beraid DC DR 620 in 30% glycerin / water was tested. The results can be found in Figures 15 thru 17. This solution shows large apparent SIS behavior at room temperature and slight SIS at -2 °C. In the low temperature test, N_1 increases around the shear rate associated with the second apparent SIS.

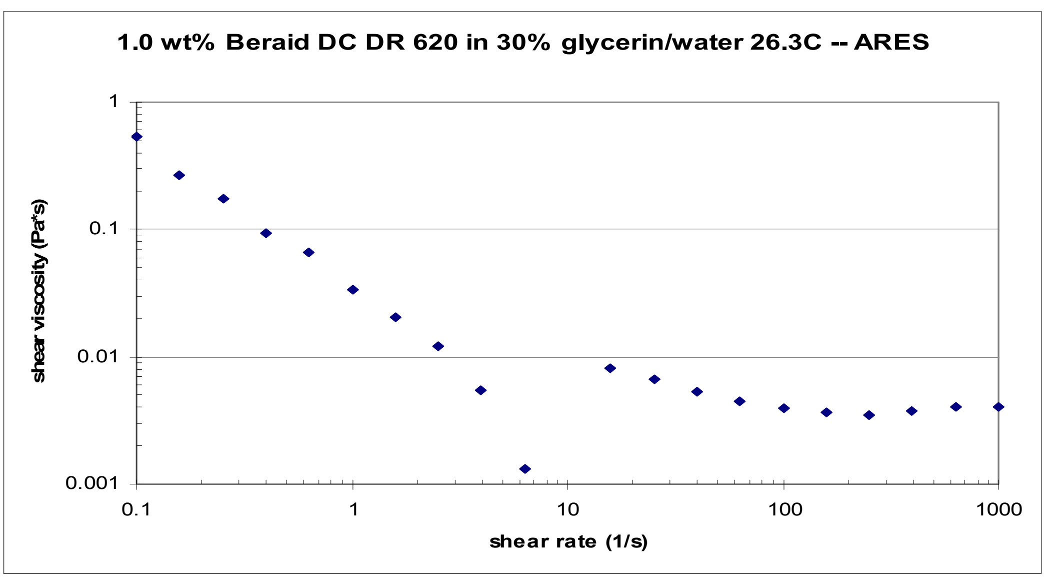

Figure 15: 1.0 wt% Beraid DC DR 620 in 30% glycerin/water 26.3°C – ARES

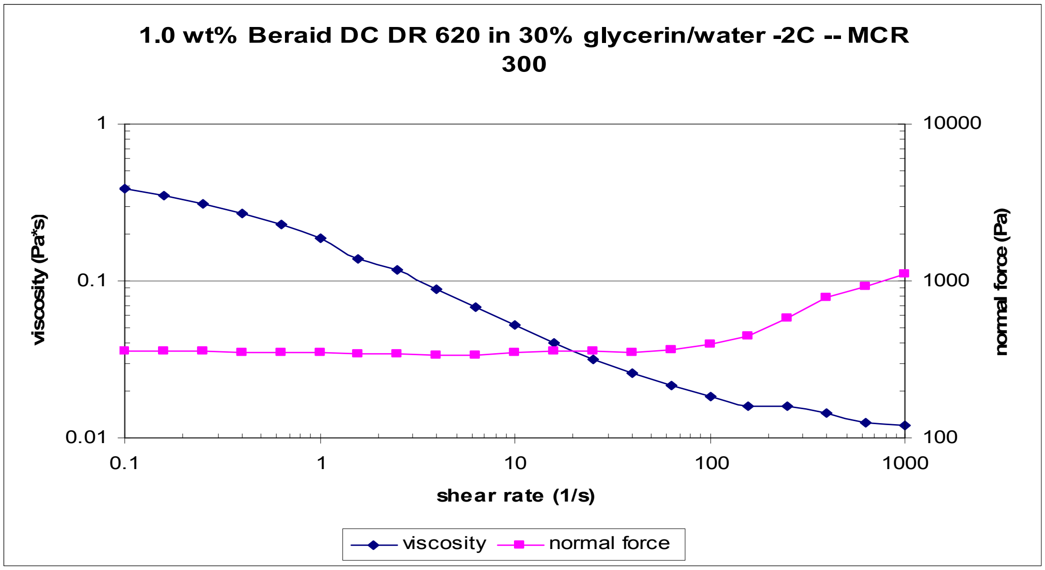

Figure 16: 1.0 wt% Beraid DC DR 620 in 30% glycerin/water -2°C – MCR 300

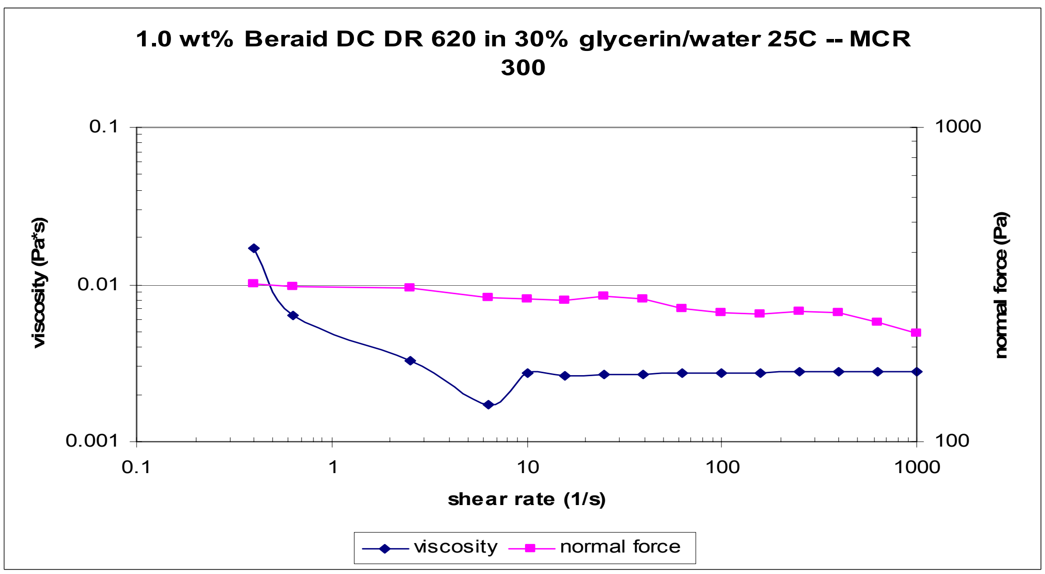

Figure 17: 1.0 wt% Beraid DC DR 620 in 30% glycerin/water 25°C – MCR 300

The solution of 1.0 wt% Beraid DC DR 620 + 30mM $NaNO_2$ in 30% glycerin / water was tested. The results are shown in Figures 18 thru 20. Similar to the solution without salt, the tests show that SIS occurs at all temperatures tested. Also, the N_1 values at low temperature rise near the shear rate for the second apparent SIS.

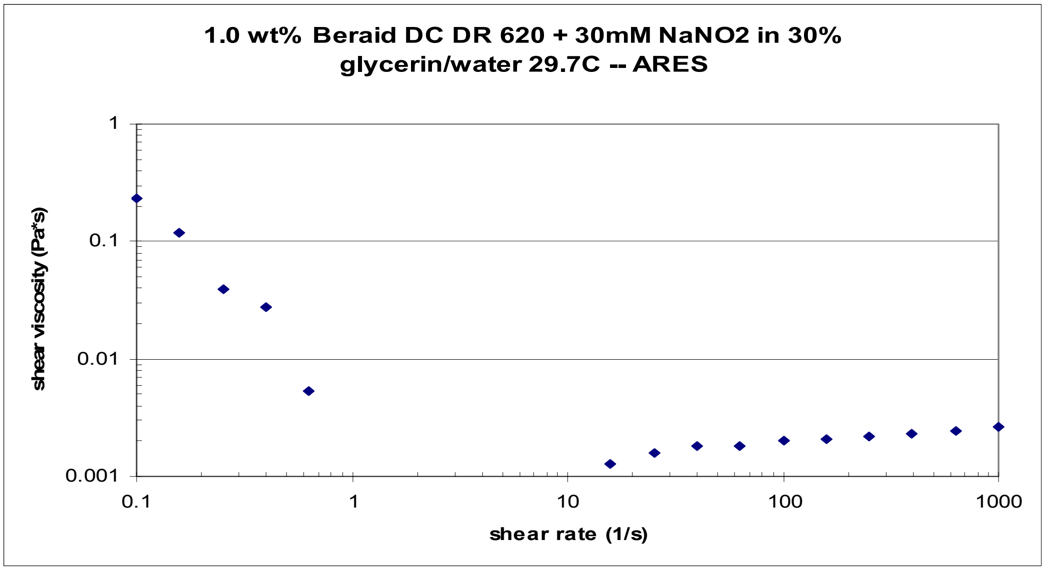

Figure 18: 1.0 wt% Beraid DC DR 620 + 30mM $NaNO_2$ in 30% glycerin/water 29.7°C – ARES

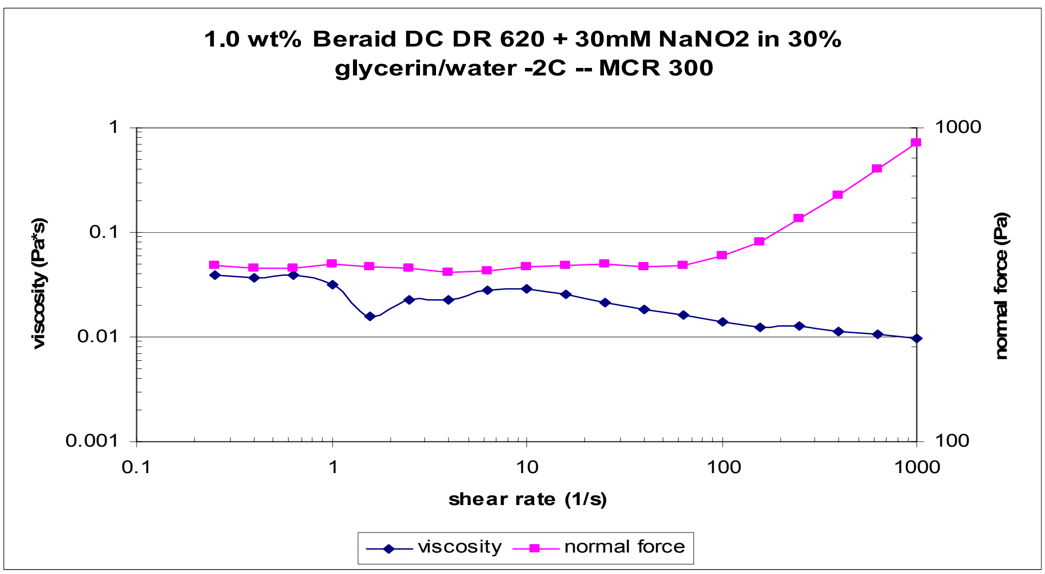

Figure 19: 1.0 wt% Beraid DC DR 620 + 30mM $NaNO_2$ in 30% glycerin/water -2°C – MCR 300

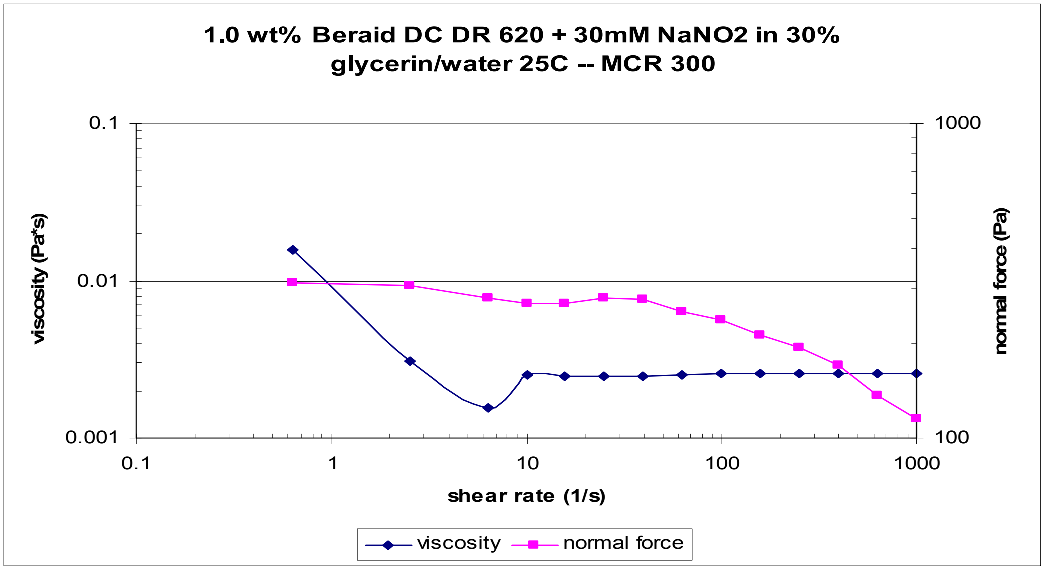

Figure 20: 1.0 wt% Beraid DC DR 620 + 30mM $NaNO_2$ in 30% glycerin/water 25°C – MCR 300

The final solvent in which 1.0 wt% of the Beraid DC DR 620 surfactant was tested was a solution of 25% propylene glycol (PG) / water. The results from the tests for this solution can be found in Figures 21 thru 23. The data obtained from the ARES rheometer do not give conclusive evidence as to the occurrence of SIS. The tests from the MCR 300 do, however, show apparent SIS behavior at both temperatures. The N_1 in both of these tests does not have a rise at any shear rate and it actually decreases above a shear rate of 10 s^{-1} at 25 °C.

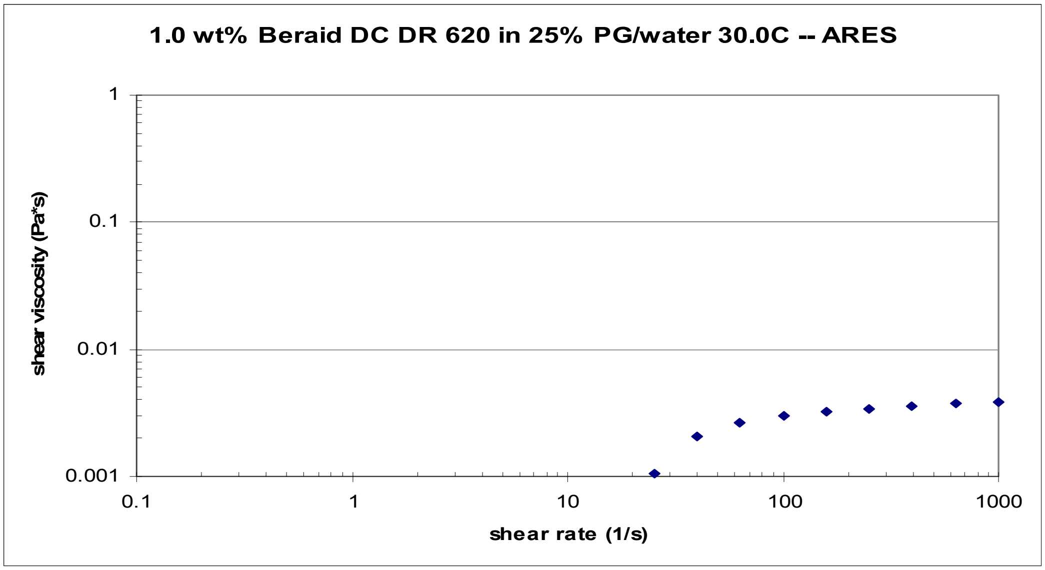

Figure 21: 1.0 wt% Beraid DC DR 620 in 25% PG/water 30.0°C – ARES

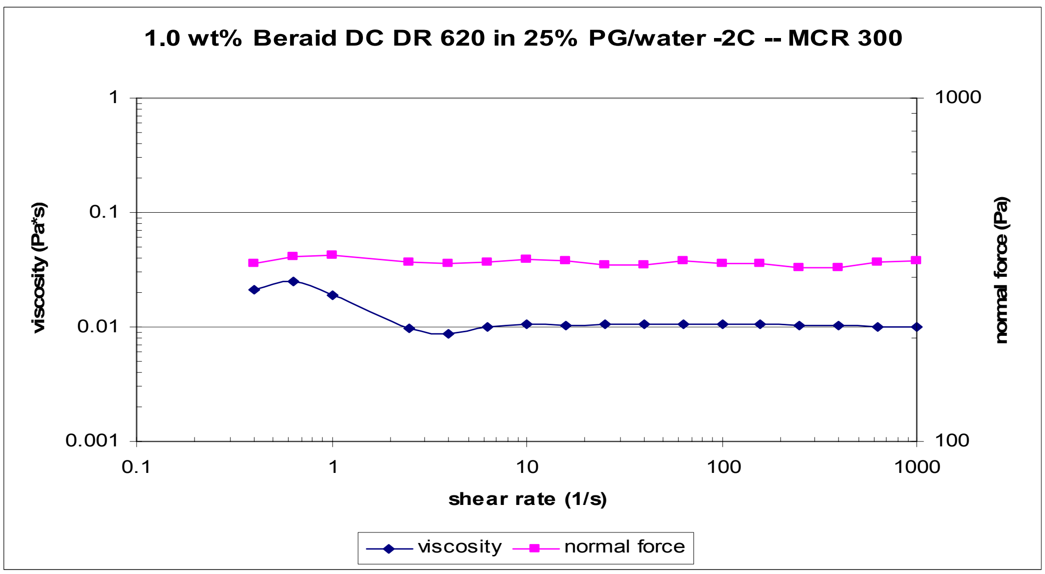

Figure 22: 1.0 wt% Beraid DC DR 620 in 25% PG/water -2°C – MCR 300

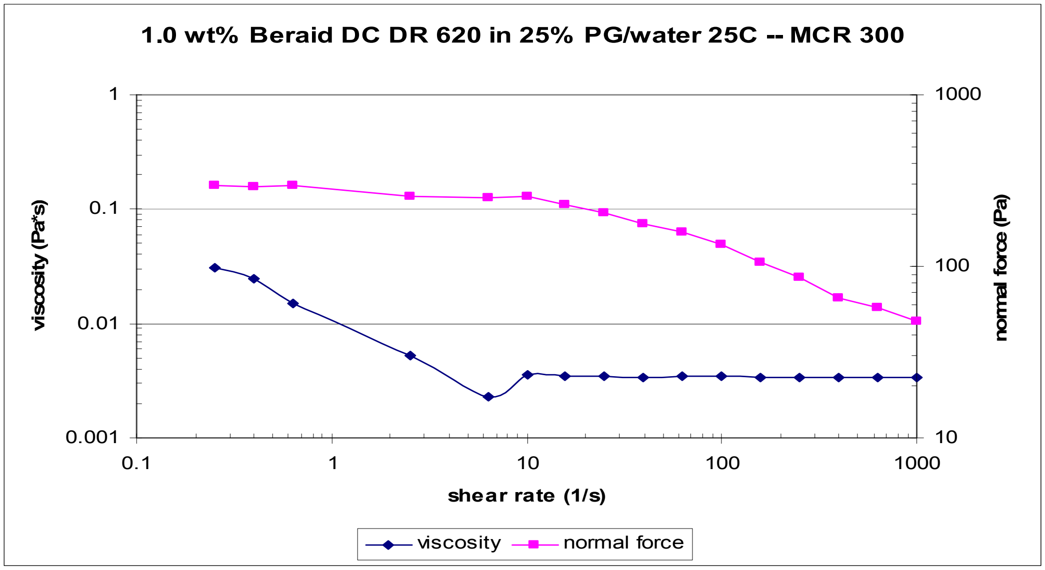

Figure 23: 1.0 wt% Beraid DC DR 620 in 25% PG/water 25°C – MCR 300

The final solution of the Beraid surfactant tested included the previous solvent with the addition of salt. This solution was 1.0 wt% Beraid DC DR 620 + 30mM $NaNO_2$ in 25% PG / water. The results are shown in Figures 24 thru 26. This solution again did not give conclusive evidence as to the presence of SIS in the ARES test. Similar to the previous solution, the tests with the MCR 300 showed apparent SIS behavior at both temperatures and the N_1 in the test at 25 °C decreased at high shear rates.

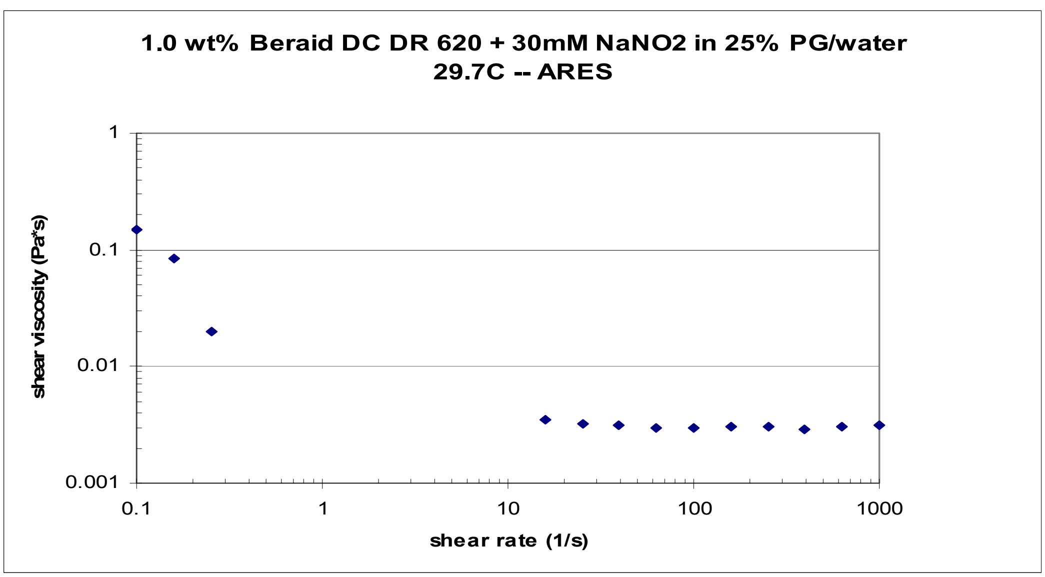

Figure 24: 1.0 wt% Beraid DC DR 620 + 30mM $NaNO_2$ in 25% PG/water 29.7°C – ARES

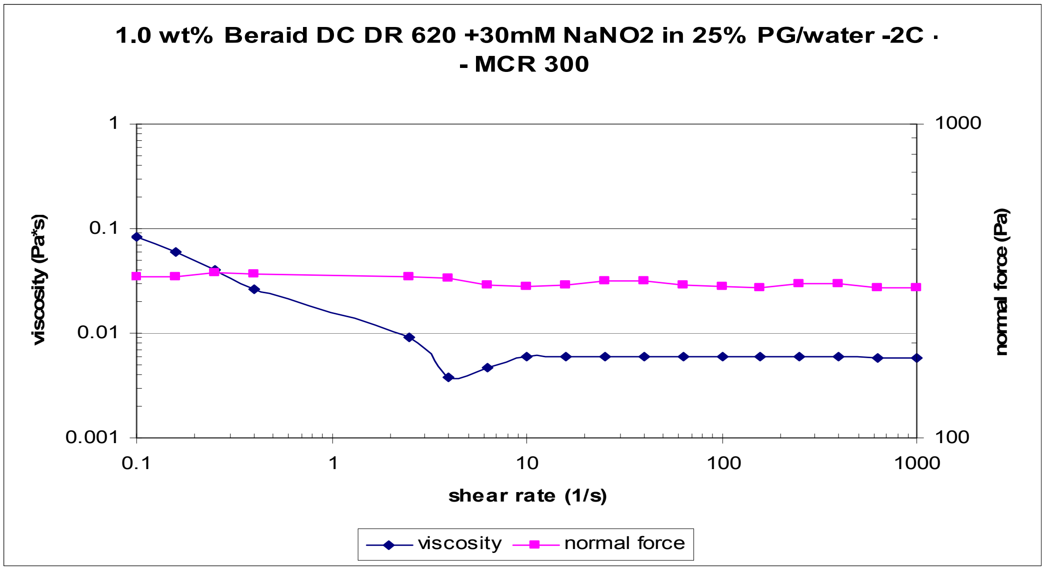

Figure 25: 1.0 wt% Beraid DC DR 620 + 30mM $NaNO_2$ in 25% PG/water -2^{o}C – MCR 300

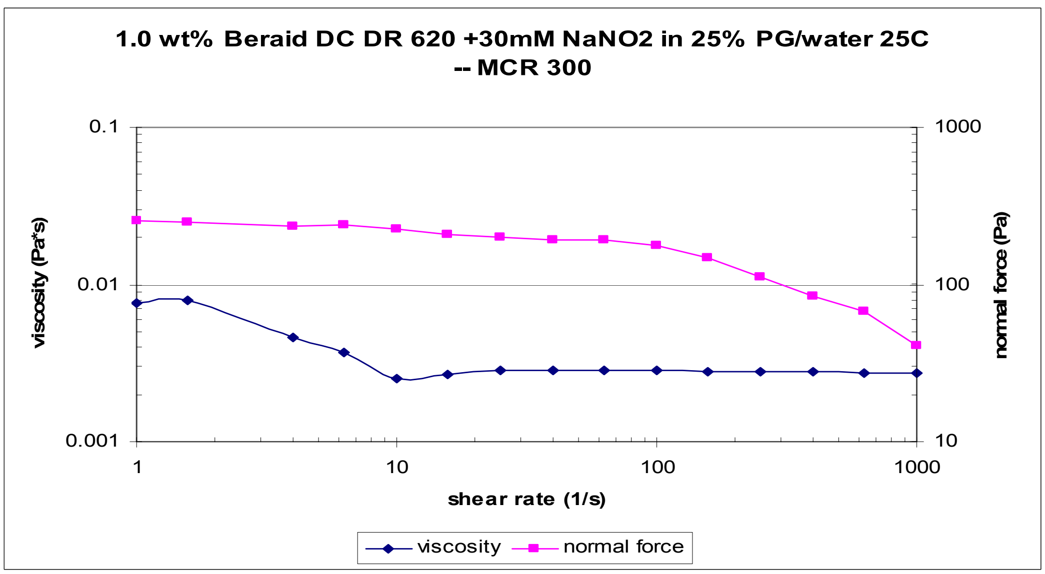

Figure 26: 1.0 wt% Beraid DC DR 620 + 30mM $NaNO_2$ in 25% PG/water 25^{o}C – MCR 300

Overall, the Beraid DC DR 620 surfactant gives good drag reducing results at 0 and 25 ^{o}C for all of the solutions except for the solutions with propylene glycol. The Beraid DC DR 620 typically has one instance of SIS (in a couple cases two) in the shear rate range from 0.1 to 1000 s^{-1}. The first normal stress difference remains constant over the shear rate range for many solutions. If it does not remain constant then, for the tests at low temperatures (-2 ^{o}C), N_1 increases with increasing shear rates and at 25 ^{o}C N_1

decreases with increasing shear. A summary of the results from these tests can be seen in Table 2.

Table 2: Results for Beraid DC DR Solutions

Solution	Rheometer	Temp (°C)	Shear Rate for SIS (peak)	Shear Rate for rise in N_1	Max %DR @ 25 °C	Max %DR @ 0 °C
1.0 wt% Beraid DC DR 620 in water	Ares	27	16	-	~63	~40
	MCR 300	2	2.5	no rise		
	MCR 300	25	2.5	no rise		
1.0 wt% Beraid DC DR 620 + 30mM NaNO2 in water	Ares	26.3	16, 158	-	~63	<40
	MCR 300	2	-	no rise		
	MCR 300	25	10	no rise		
1.0 wt% Beraid DC DR 620 in 20% EG/water	Ares	27.6	16	-	~50	~50
	MCR 300	-2	2.5	251		
	MCR 300	25	2.5	no rise		
1.0 wt% Beraid DC DR 620 + 30mM NaNO2 in 20% EG/water	Ares	26.8	100	-	~50	~40
	MCR 300	-2	10	no rise		
	MCR 300	25	10	no rise		
1.0 wt% Beraid DC DR 620 in 30% glycerin/water	Ares	26.3	16	-	~60	~60
	MCR 300	-2	2.5, 251	63		
	MCR 300	25	10	no rise		
1.0 wt% Beraid DC DR 620 + 30mM NaNO2 in 30% glycerin/water	Ares	29.7	40	-	~60	~60
	MCR 300	-2	2.5, 251	63		
	MCR 300	25	10	no rise		
1.0 wt% Beraid DC DR 620 in 25% PG/water	Ares	30	-	-	~0	~0
	MCR 300	-2	10	no rise		
	MCR 300	25	10	no rise		
1.0 wt% Beraid DC DR 620 + 30mM NaNO2 in 25% PG/water	Ares	29.7	-	-	~0	~0
	MCR 300	-2	10	no rise		
	MCR 300	25	25	no rise		

ii. SPE98300, Trilon A, and Formaldehyde

The surfactant SPE98300 is a zwitterionic surfactant which is pictured in Figure 27. This surfactant was combined with the sequestering agent Trilon A and the biocide formaldehyde. Both of these are shown in Figures 28 and 29.

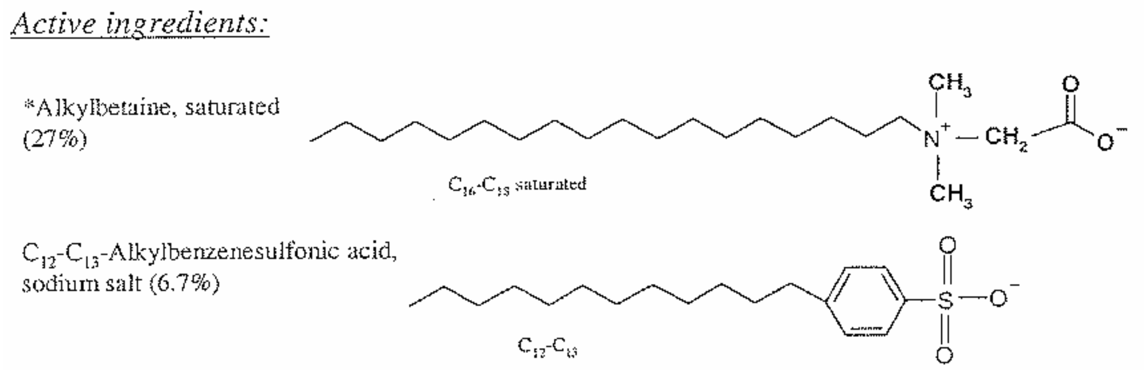

Figure 27: Structure of SPE98300[11]

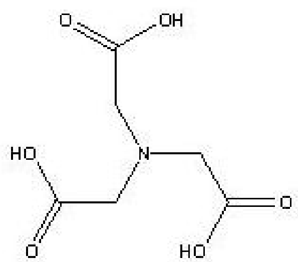

Figure 28: Structure of Trilon A[4]

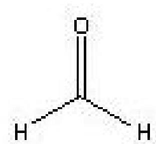

Figure 29: Structure of Formaldehyde[2]

The combination of these three components was tested in a variety of solvents. A summary of the experimental results can be found in Table 3. The first formulation to be tested was 1.5 g/L SPE98300 + 0.5g/L Trilon A + 0.13 g/L formaldehyde in water. The results from this test are shown in Figures 30 thru 32. This solution exhibits SIS behavior in all three tests. Also, there are peaks in N_1 at both 2 and 25 ^{o}C which appear to correspond with a shear rate near the critical SIS shear rate. Such local peaks in N_1 are unusual and should be investigated further.

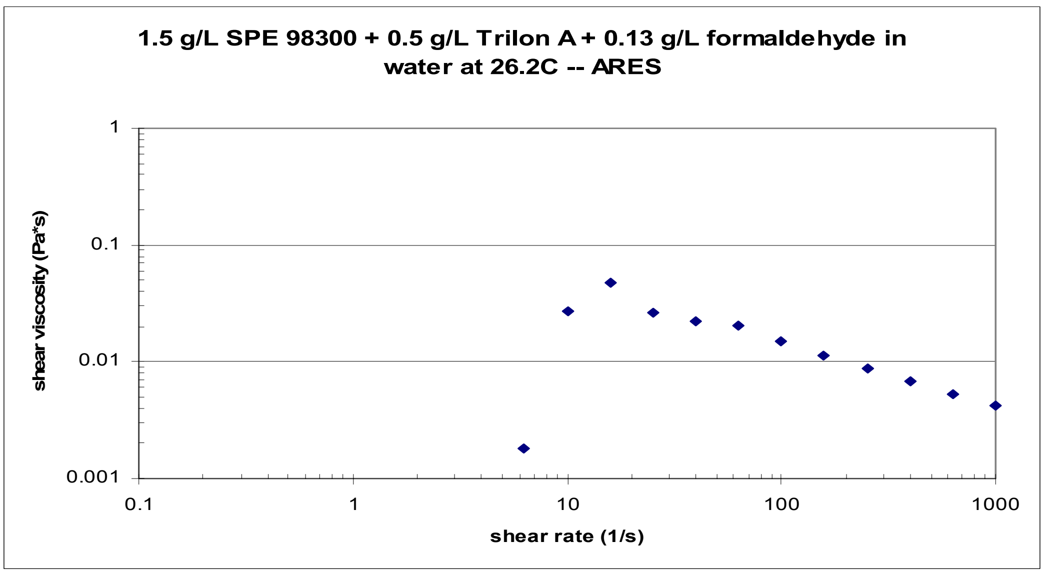

Figure 30: 1.5 g/L SPE98300 + 0.5 g/L Trilon A + 0.13 g/L formaldehyde in water 26.2^{o}C – ARES

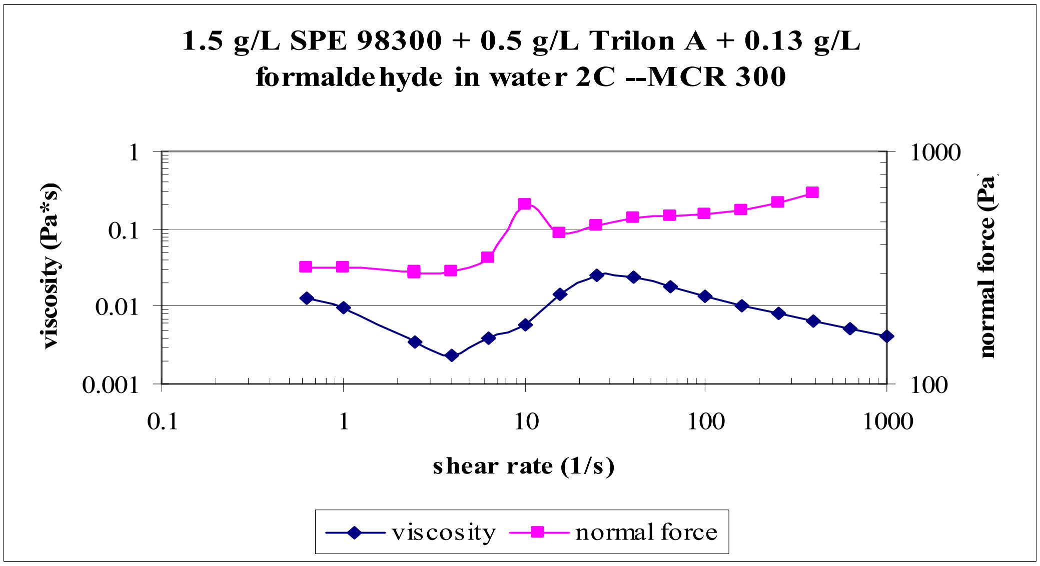

Figure 31: 1.5 g/L SPE98300 + 0.5 g/L Trilon A + 0.13 g/L formaldehyde in water 2 °C – MCR 300

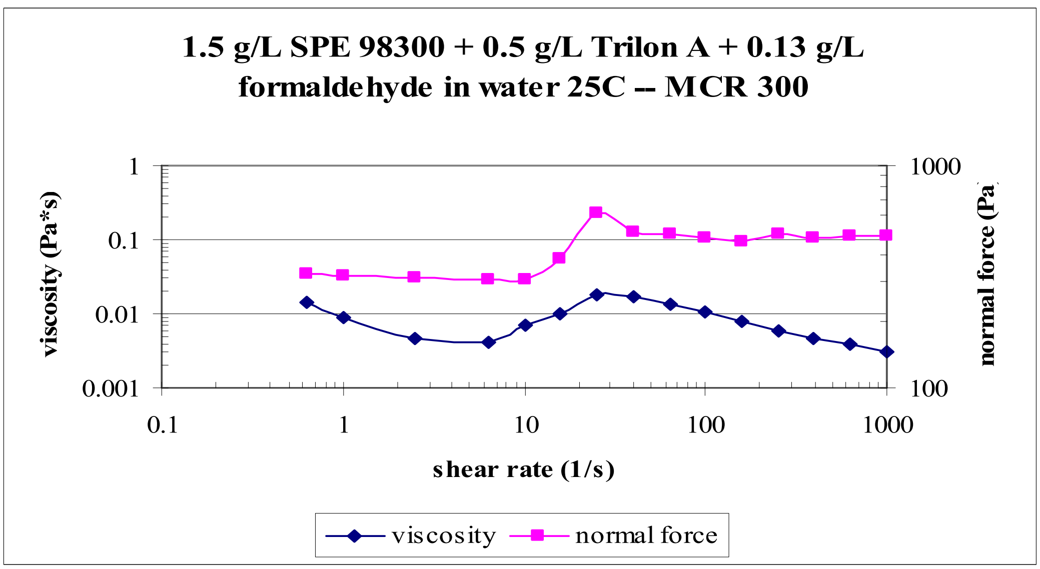

Figure 32: 1.5 g/L SPE98300 + 0.5 g/L Trilon A + 0.13 g/L formaldehyde in water 25 °C – MCR 300

The next solution tested had the same composition as the previous one except it had sodium nitrate. This solution is 1.5 g/L SPE98300 + 0.5g/L Trilon A + 0.13 g/L formaldehyde + 30mM $NaNO_2$ in water. The results from the viscosity and first normal stress difference tests are shown in Figures 33 thru 35. This solution shows SIS behavior for all tests. At 2 °C N_1 experiences a peak around the shear rate corresponding to the peak of SIS. At 25 ^oC the values of N_1 begin to increase around the peak shear rate of SIS.

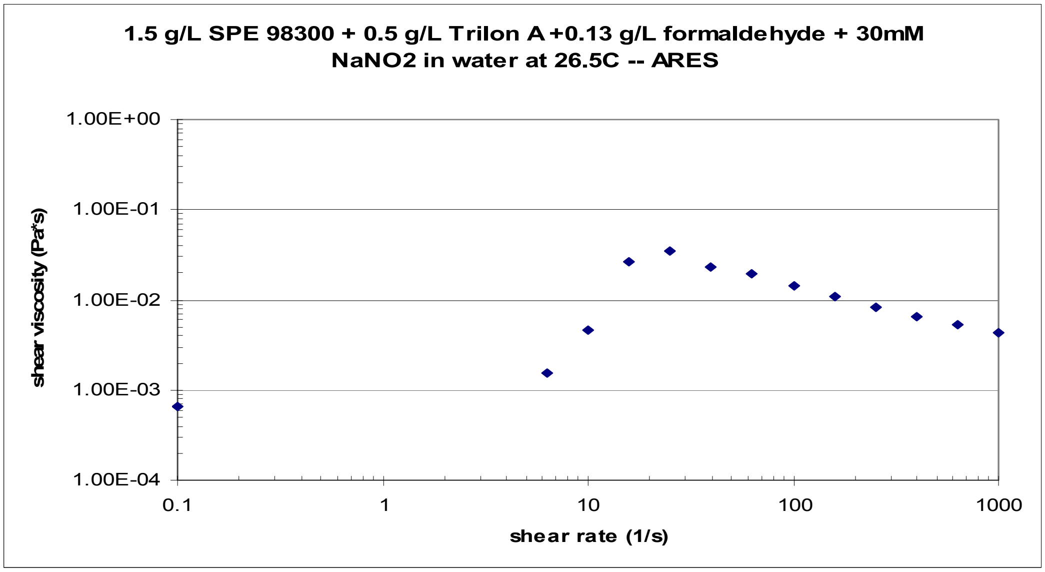

Figure 33: 1.5 g/L SPE98300 + 0.5 g/L Trilon A + 0.13 g/L formaldehyde + 30mM $NaNO_2$ in water 26.5^oC – ARES

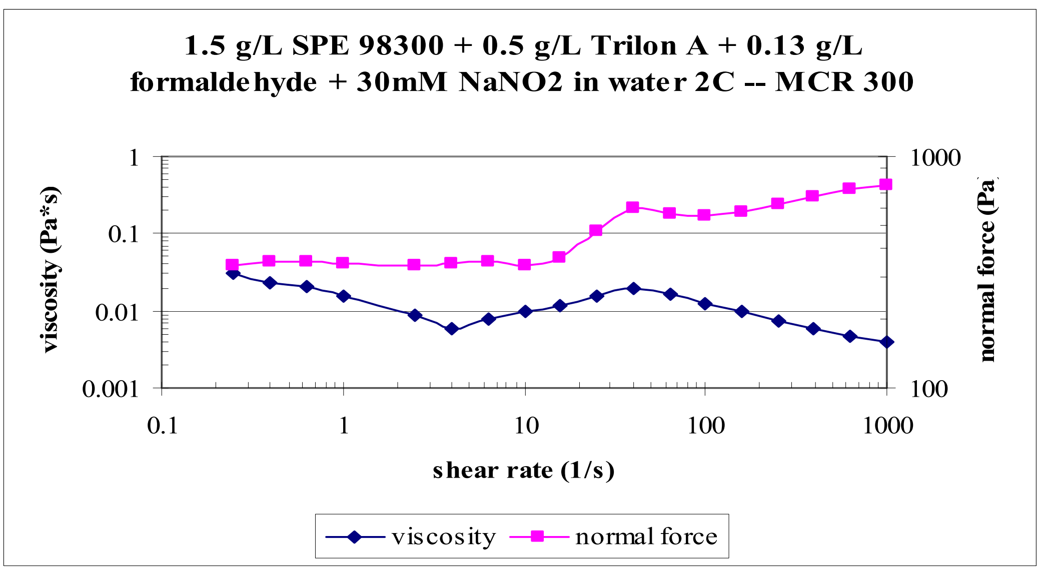

Figure 34: 1.5 g/L SPE98300 + 0.5 g/L Trilon A + 0.13 g/L formaldehyde + 30mM $NaNO_2$ in water 2^oC – MCR 300

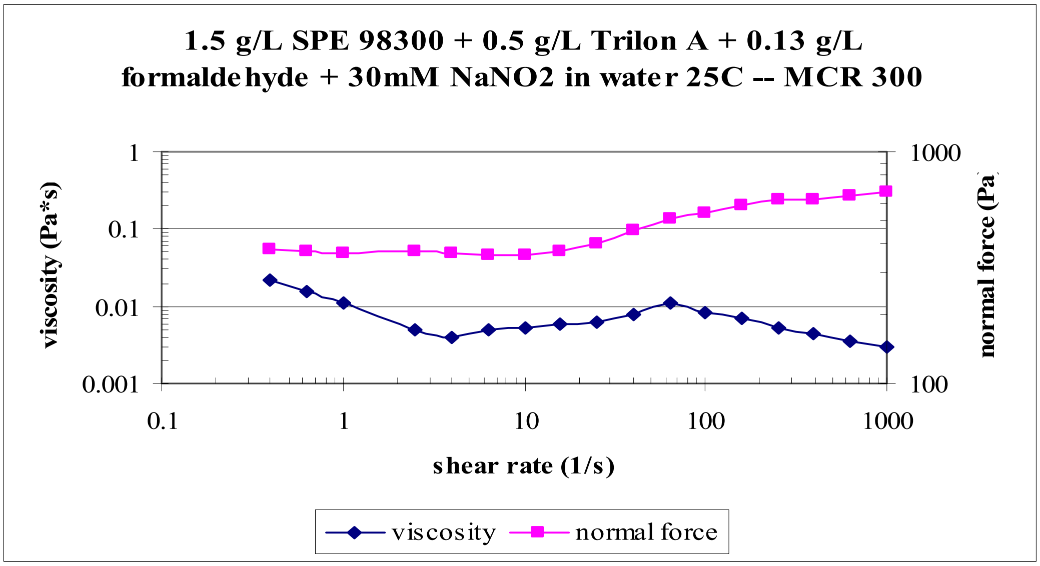

Figure 35: 1.5 g/L SPE98300 + 0.5 g/L Trilon A + 0.13 g/L formaldehyde + 30mM $NaNO_2$ in water 25°C – MCR 300

Next, the solution of 1.5 g/L SPE98300 + 0.5g/L Trilon A + 0.13 g/L formaldehyde in 30% glycerin / water was tested. The plots of the viscosity and of N_1 vs. the shear rate are shown in Figures 36 thru 38. All tests on this solution showed SIS occurring twice in the shear rate range of 0.1 to 1000 s^{-1}. The N_1 data for both -2 and 25 °C shows a direct relationship between the shear rate of the peak viscosity for SIS and the rise in N_1.

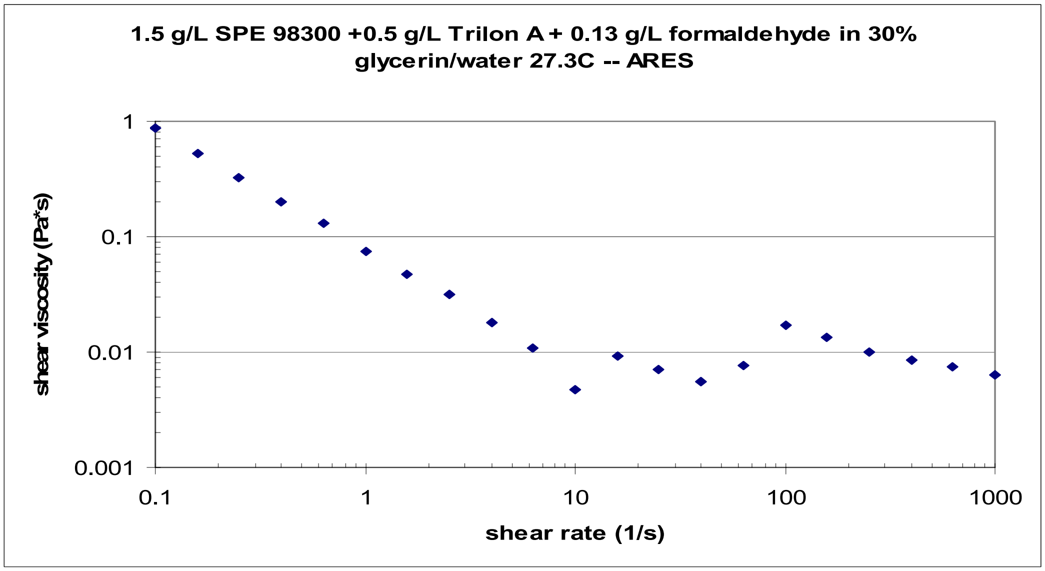

Figure 36: 1.5 g/L SPE98300 + 0.5 g/L Trilon A + 0.13 g/L formaldehyde in 30% glycerin / water 27.3°C – ARES

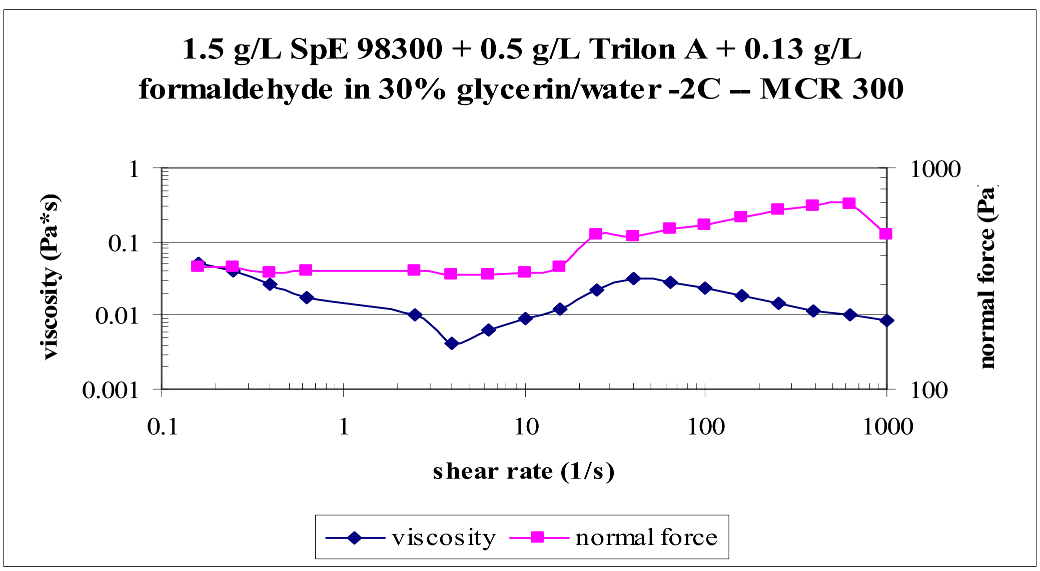

Figure 37: 1.5 g/L SPE98300 + 0.5 g/L Trilon A + 0.13 g/L formaldehyde in 30% glycerin / water -2°C – MCR 300

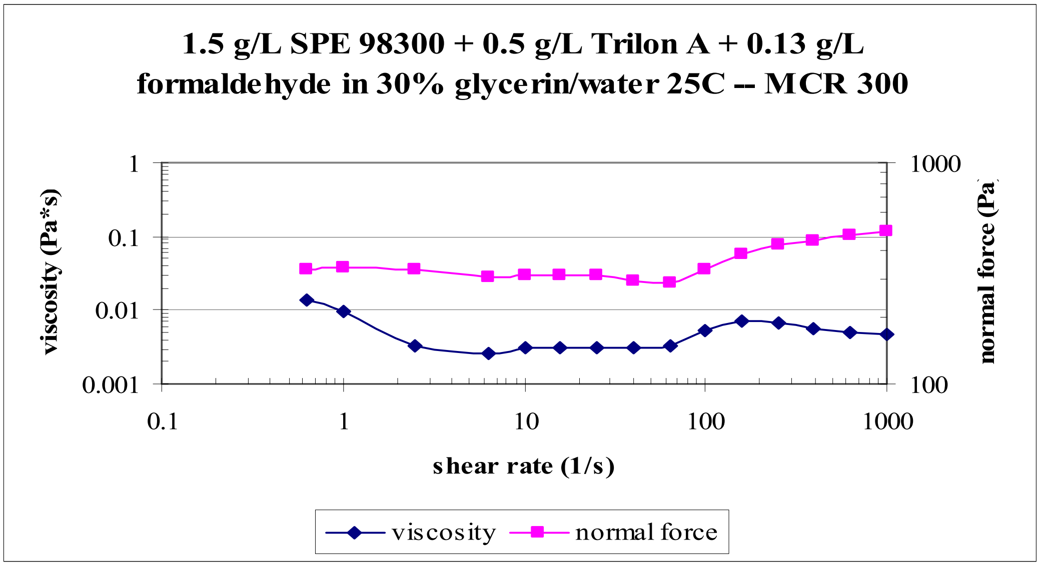

Figure 38: 1.5 g/L SPE98300 + 0.5 g/L Trilon A + 0.13 g/L formaldehyde in 30% glycerin / water 25°C – MCR 300

The final solution tested using the SPE98300 surfactant was a solution of 1.5 g/L SPE98300 + 0.5g/L Trilon A + 0.13 g/L formaldehyde + 30mM $NaNO_2$ in 30% glycerin / water. The experimental results are displayed in Figures 39 thru 41. Like the solution without sodium nitrite, this solution exhibits apparent SIS twice in the shear rate range of 0.1 to 1000 s^{-1}. The first normal stress difference once again rises around the shear rate associated with the peak for the second SIS.

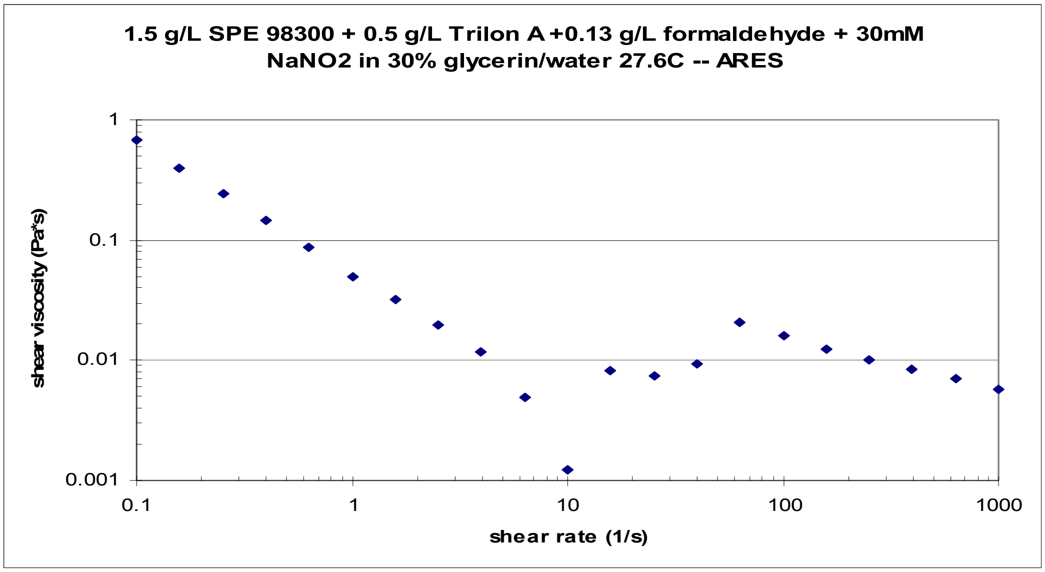

Figure 39: 1.5 g/L SPE98300 + 0.5 g/L Trilon A + 0.13 g/L formaldehyde + 30mM $NaNO_2$ in 30% glycerin / water 27.6°C – ARES

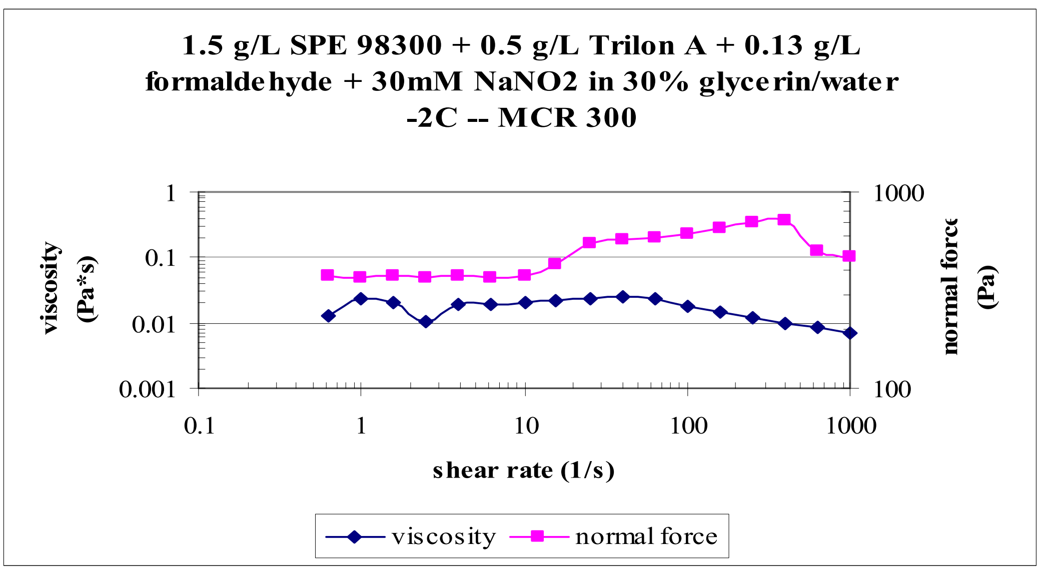

Figure 40: 1.5 g/L SPE98300 + 0.5 g/L Trilon A + 0.13 g/L formaldehyde + 30mM $NaNO_2$ in 30% glycerin / water -2°C – MCR 300

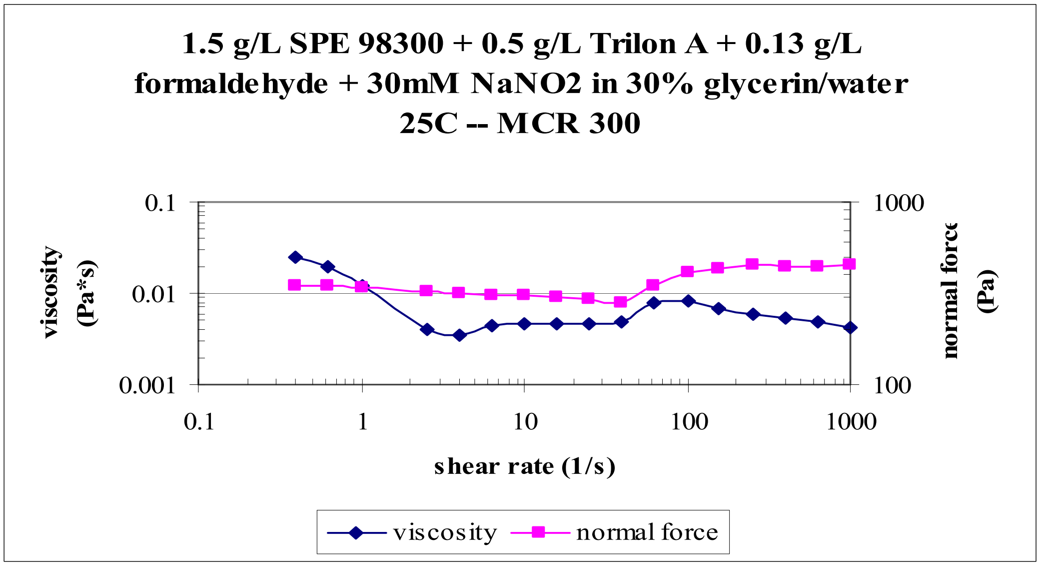

Figure 41: 1.5 g/L SPE98300 + 0.5 g/L Trilon A + 0.13 g/L formaldehyde + 30mM $NaNO_2$ in 30% glycerin / water 25°C – MCR 300

In conclusion, the surfactant formulation of SPE98300, Trilon A, and formaldehyde shows good drag reduction results (%DR > 50) at 25 °C while it has poor drag reducing results at 0 °C. A summary of all of the data obtained from these solutions is presented in Table 3. These solutions exhibit shear-induced structure once or twice in the shear rate range of 0.1 to 1000 s^{-1}. The N_1 values undergo an increase as the shear rate is increased. This increase is always associated with the shear rate at which a rise in viscosity is present as a result of SIS. These surfactant solutions also show the unique behavior of N_1 values forming peaks with increasing shear rate. This behavior occurs more readily at a low temperature than at 25 °C.

Table 3: Results for SPE98300, Trilon A, and Formaldehyde Solutions

Solution	Rheometer	Temp (°C)	Shear Rate for SIS (peak)	Shear Rate for rise in N_1	Max %DR @ 25 °C	Max %DR @ 0 °C
SPE 98300 + Trilon A + formaldehyde in water	Ares	26.2	16	-	~50	<20
	MCR 300	2	25	4		
	MCR 300	25	25	10		
SPE 98300 + Trilon A + formaldehyde + 30mM NaNO2 in water	Ares	26.5	25	-	~60	<10
	MCR 300	2	40	16		
	MCR 300	25	63	16		
SPE 98300 + Trilon A + formaldehyde in 30% glycerin/water	Ares	27.3	16,100	-	~50	<10
	MCR 300	-2	10, 40	16		
	MCR 300	25	10, 160	63		
SPE 98300 + Trilon A + formaldehyde + 30mM NaNO2 in 30% glycerin/water	Ares	27.6	16, 60	-	~57	<20
	MCR 300	-2	4, 40	15		
	MCR 300	25	6, 60	40		

iii. DR0206

The surfactant DR0206 is a mixture of a zwitterionic and an anionic surfactant. The structure of this surfactant is shown in Figure 42.

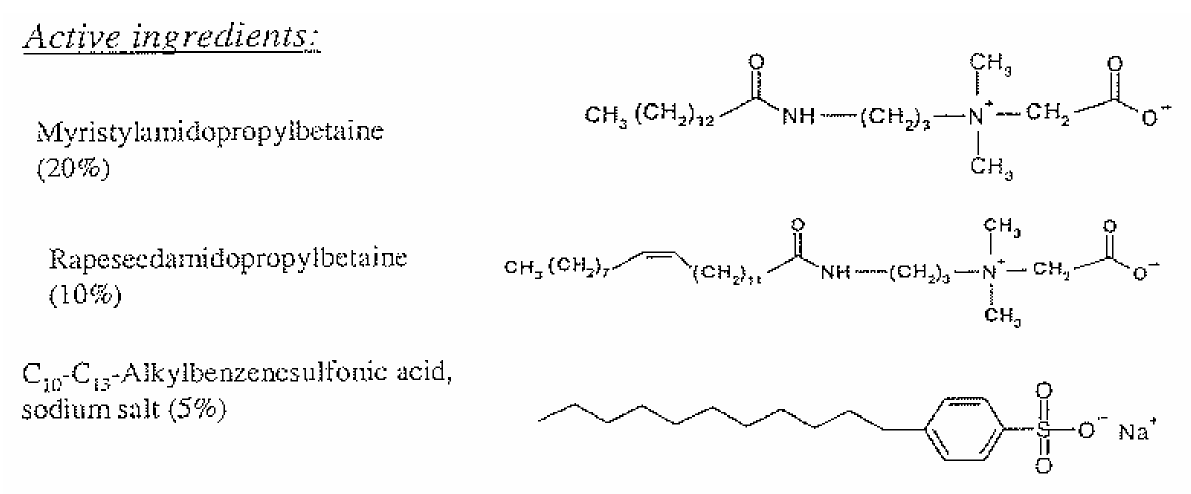

Figure 42: Structure of DR0206[11]

This surfactant was only tested in water (4.0 g/L DR0206) because all other solvents gave poor drag reduction results. The results from this test can be seen in Figures 43 thru 45. For all experiments this solution displayed apparent SIS at one or two different shear rates. The peaks in the N_1 data seemed to correspond with the shear rate at which the viscosity peaked due to SIS.

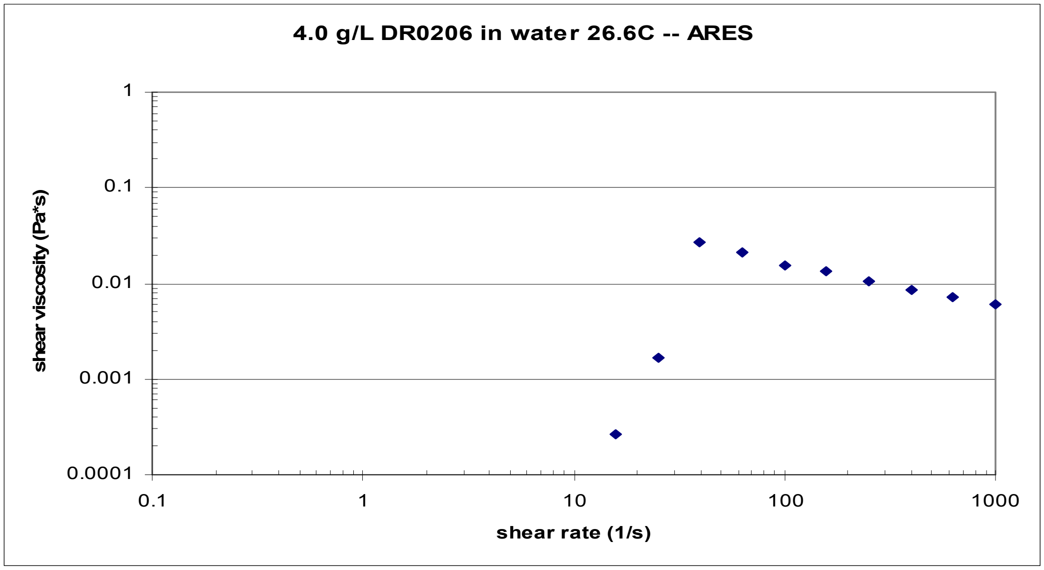

Figure 43: 4.0 g/L DR0206 in water 26.6°C – ARES

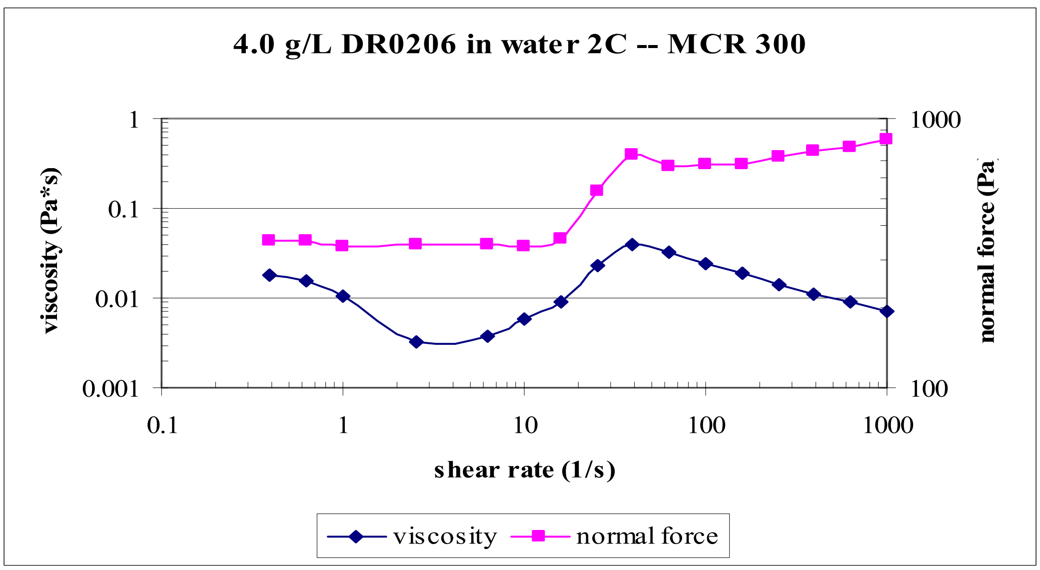

Figure 44: 4.0 g/L DR0206 in water 2°C – MCR 300

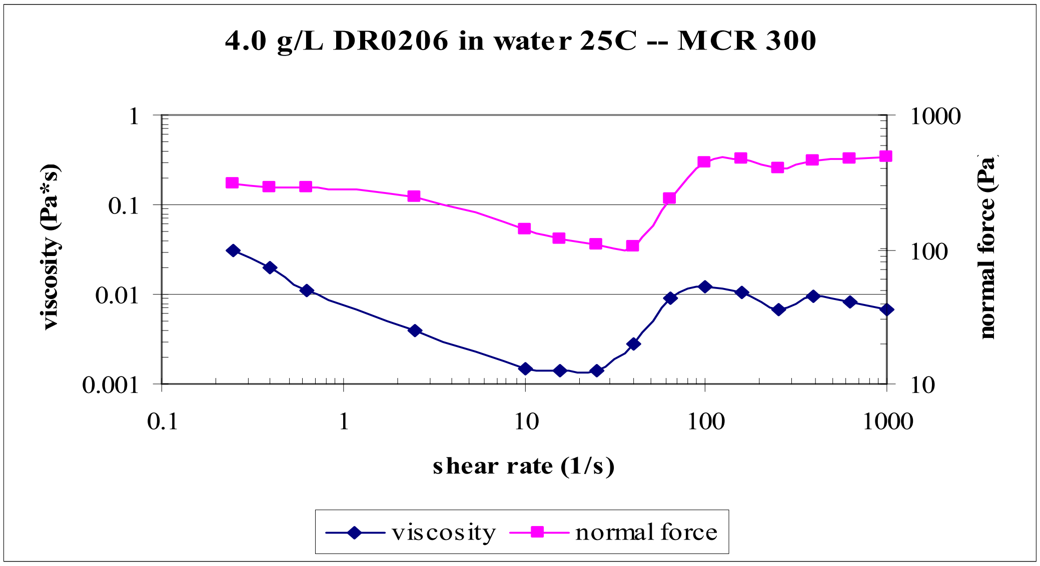

Figure 45: 4.0 g/L DR0206 in water 25°C – MCR 300

The second solution that was tested with this surfactant was 4.0 g/L DR0206 + 30mM $NaNO_2$ in water. The plots of the viscosity and N_1 vs. the shear rate are shown in Figures 46 thru 48. For each test of this solution it has apparent SIS behavior at two different critical shear rates. The N_1 values at both 0 and 25 °C exhibit an increase around the shear rate corresponding to the second SIS although the rise in viscosity may be very small.

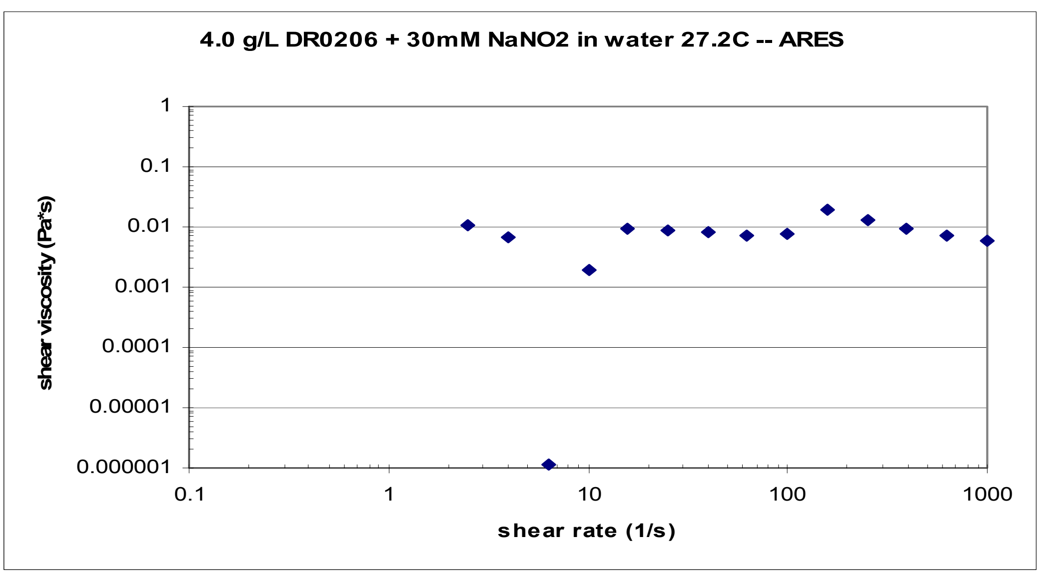

Figure 46: 4.0 g/L DR0206 + 30mM $NaNO_2$ in water 27.2°C – ARES

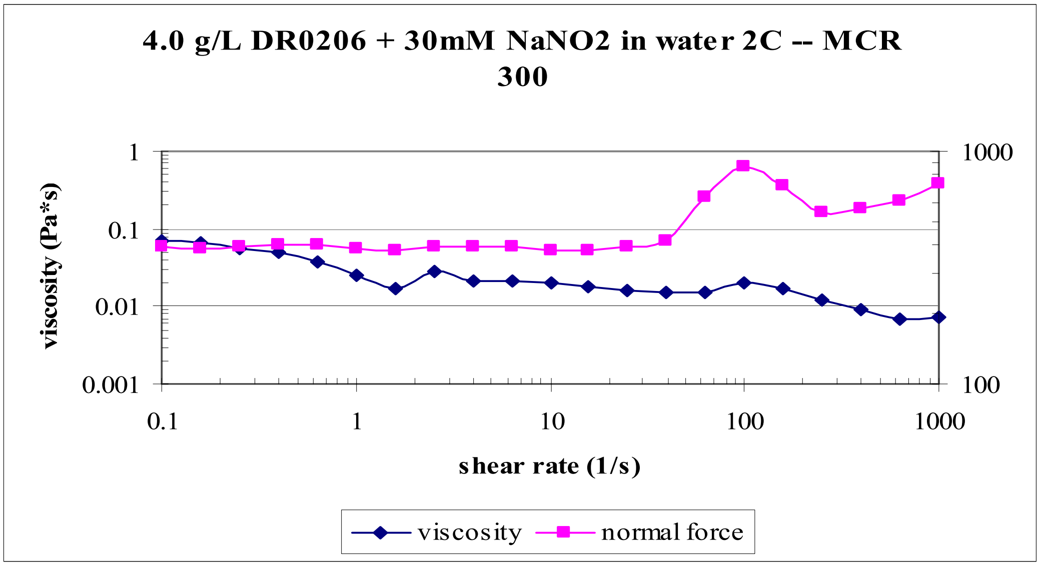

Figure 47: 4.0 g/L DR0206 + 30mM $NaNO_2$ in water 2°C – MCR 300

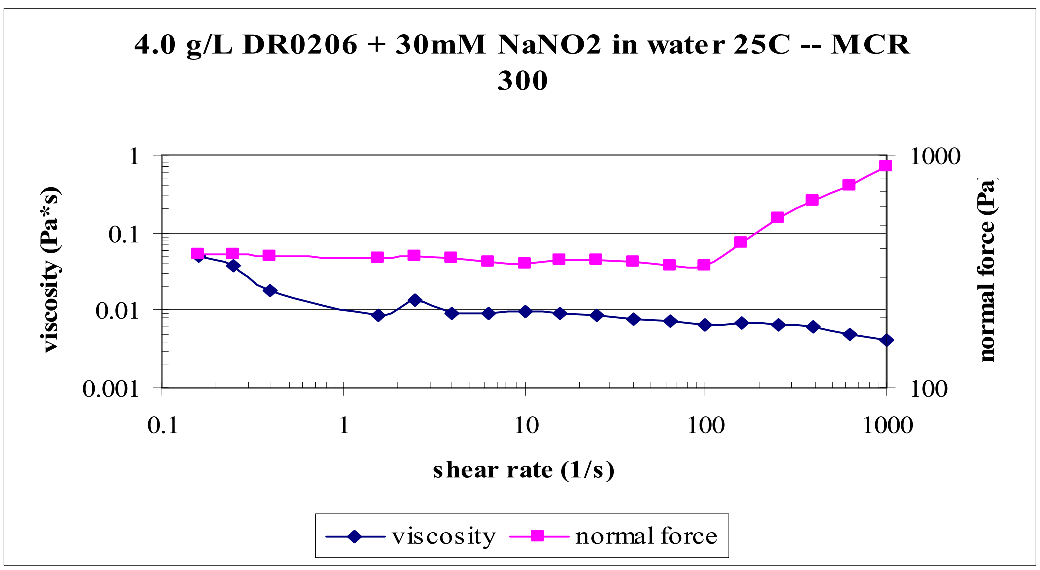

Figure 48: 4.0 g/L DR0206 + 30mM $NaNO_2$ in water 25°C – MCR 300

The DR0206 surfactant systems tested above have good drag reduction at 25 °C, but not at 0 °C. Both of these solutions have SIS behavior in the shear rate range of 0.1 to 1000 s^{-1}. Similar to the SPE98300 solutions, the rise or peak in N_1 is usually associated with a viscosity rise in the solution as a result of SIS. A summary of the results can be found in Table 4.

Table 4: Results for DR0206 Solutions

Solution	Rheometer	Temp (°C)	Shear Rate for SIS (peak)	Shear Rate for rise in N_1	Max %DR @ 25 °C	Max %DR @ 0 °C
DR0206 in water	Ares	26.6	40	-	~55	<20
	MCR 300	2	40	16		
	MCR 300	25	100, 400	40		
DR0206 + 30mM NaNO2 in water	Ares	27.2	16, 160	-	~60	<20
	MCR 300	2	3, 100	40		
	MCR 300	25	3, 160	100		

iv. Oleyl Betaine / SDBS

The surfactant, Oleyl Betaine, is a zwitterionic surfactant which is combined with SDBS, an anionic surfactant. The structure of these surfactants are shown in Figure 49.

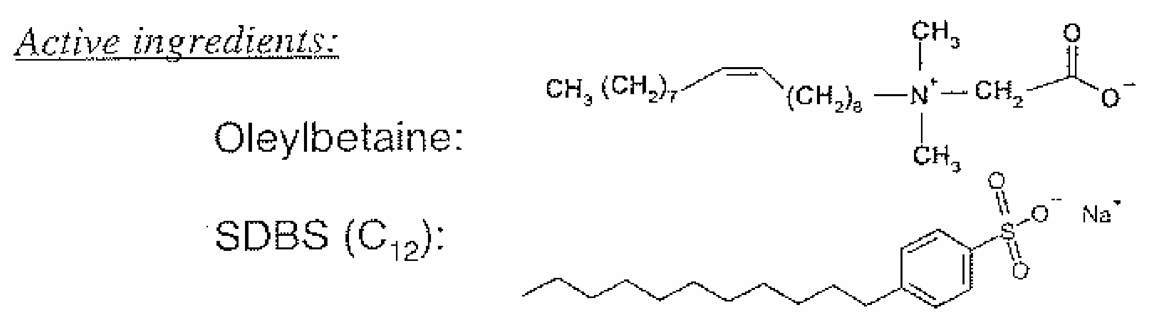

Figure 49: Structure of Oleyl Betaine and SDBS[11]

This surfactant system was tested using several different concentrations of the surfactants and sodium nitrite as well as in different solvents. A summary of the results for these systems is shown in Table 5. The first solution that was tested was 4.8mM Oleyl Betaine + 1.2mM SDBS in water. The plots of the shear viscosity and N1 vs. the shear rate can be seen in Figures 50 thru 52. With this solution, SIS behavior was not detected using the MCR 300. The data from the ARES can not be used to form any conclusions due to the incomplete nature of the results generated by this rheometer for this system. The N1 data at both temperatures tested does not rise at any shear rate but rather decreases as the shear rate increases.

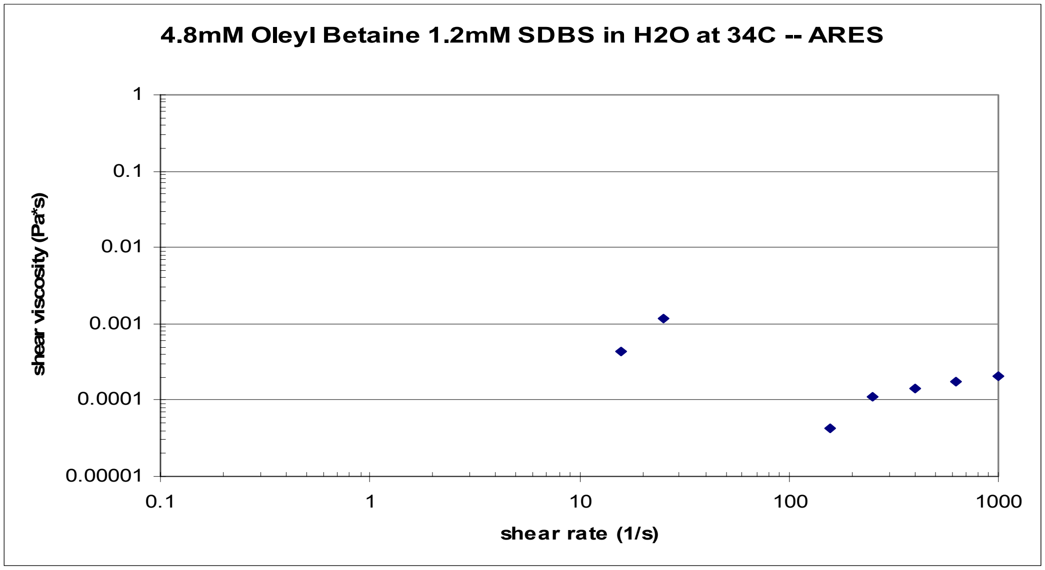

Figure 50: 4.8mM Oleyl Betaine + 1.2 mM SDBS in water 34°C – ARES

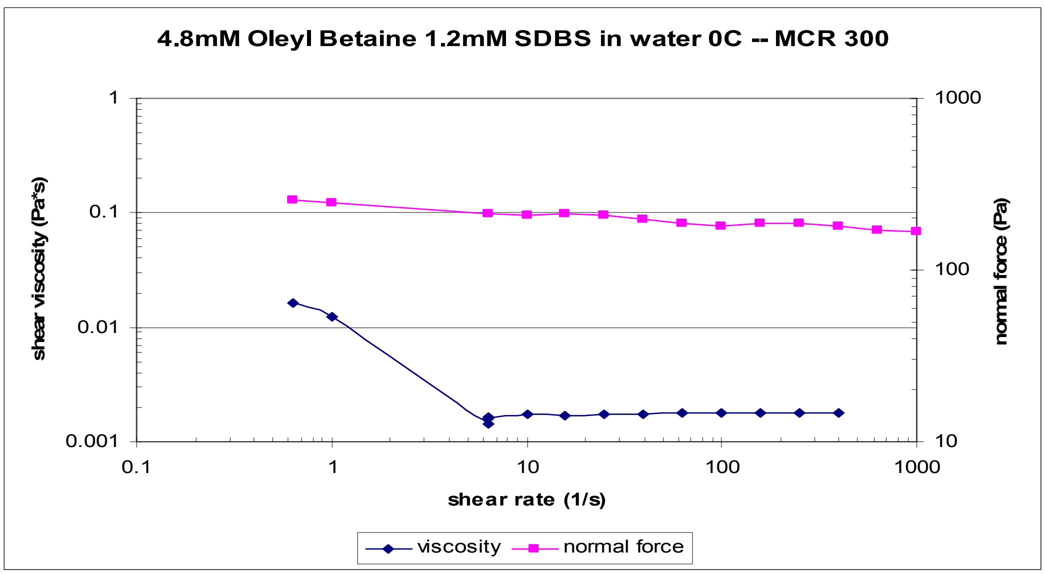

Figure 51: 4.8mM Oleyl Betaine + 1.2 mM SDBS in water 0°C – MCR 300

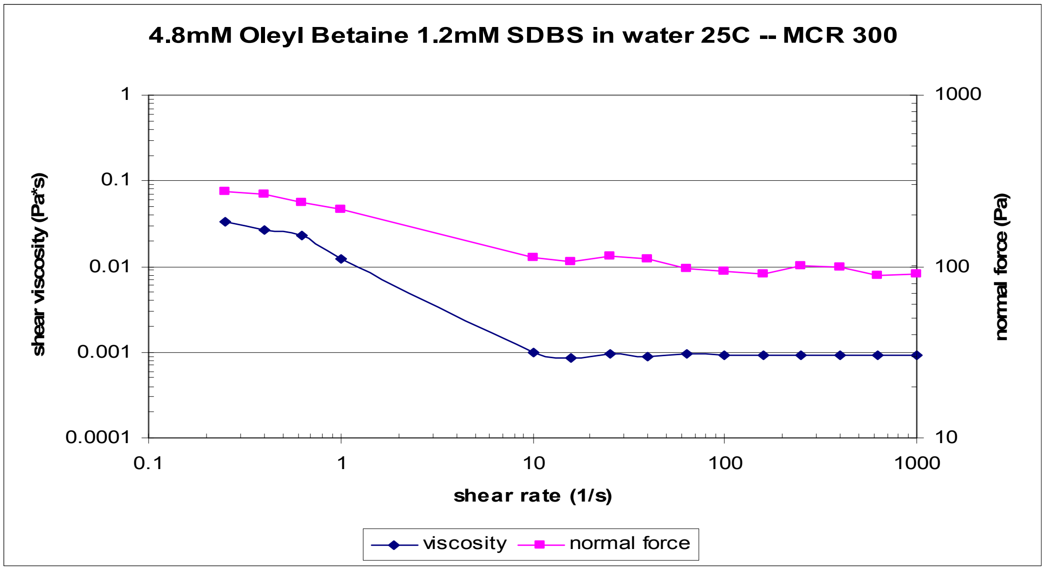

Figure 52: 4.8mM Oleyl Betaine + 1.2 mM SDBS in water 25°C – MCR 300

The next solution that was tested was 4.8mM Oleyl Betaine + 1.2mM SDBS + 6mM $NaNO_2$ in water. The results from these tests can be seen in Figures 53 thru 55. This solution has SIS behavior at all temperatures tested. The N_1 data at 0 °C rises at a shear rate associated with an apparent SIS. At 25 °C the N_1 values increase at the shear rate associated with the second SIS.

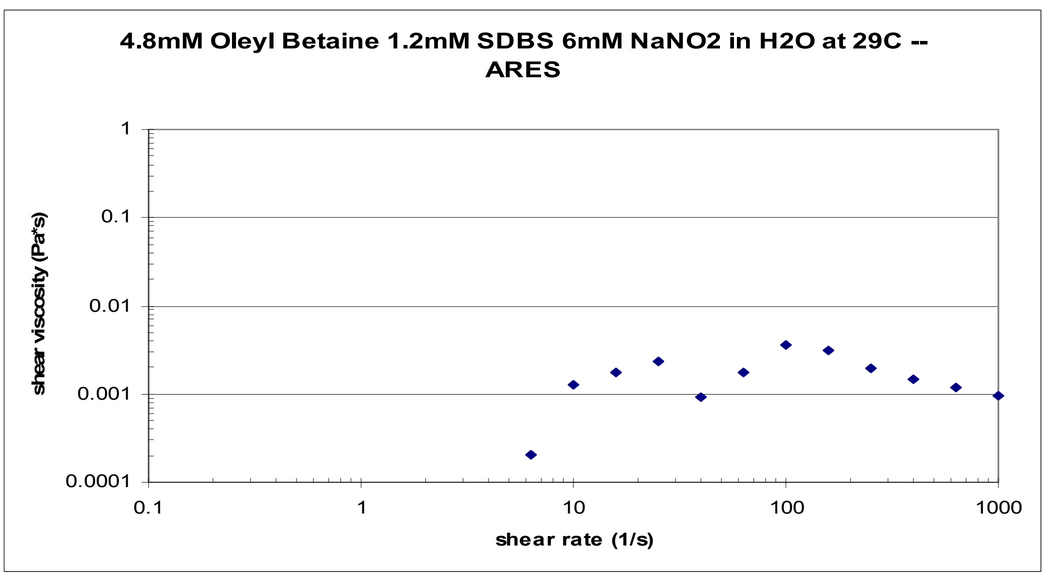

Figure 53: 4.8mM Oleyl Betaine + 1.2 mM SDBS + 6mM $NaNO_2$ in water 29°C – ARES

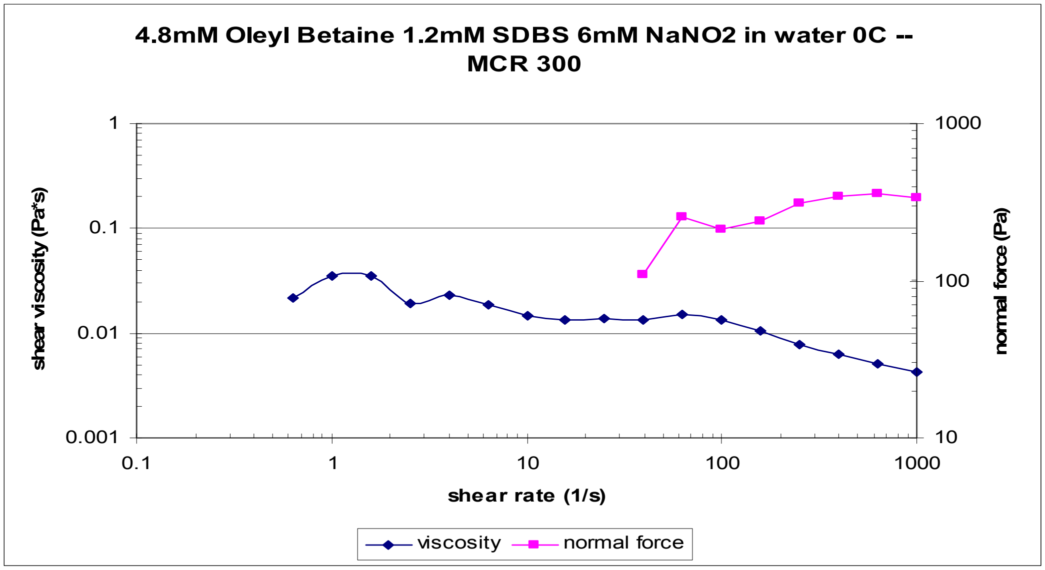

Figure 54: 4.8mM Oleyl Betaine + 1.2 mM SDBS + 6mM $NaNO_2$ in water 0°C – MCR 300

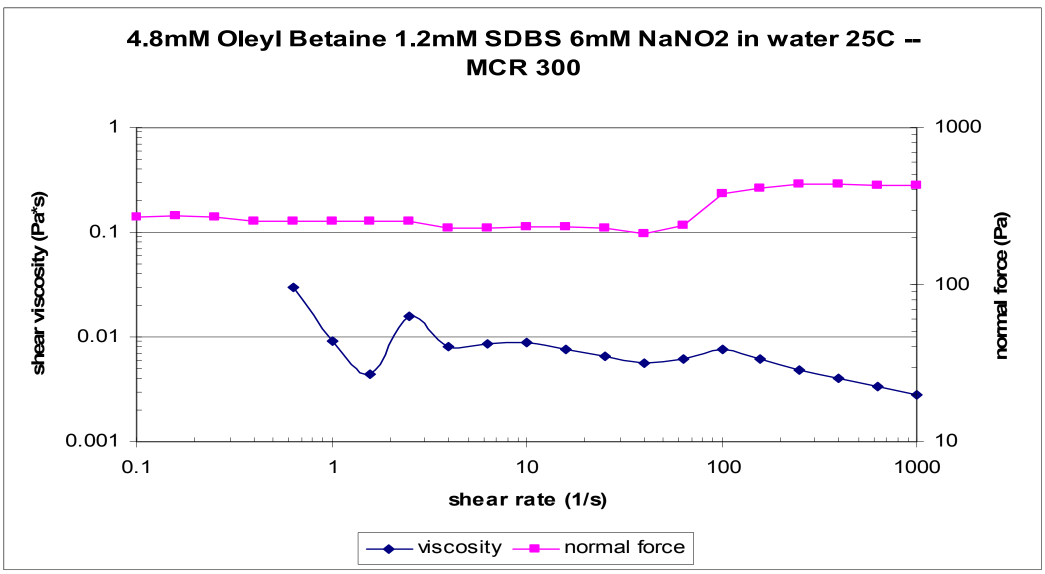

Figure 55: 4.8mM Oleyl Betaine + 1.2 mM SDBS + 6mM $NaNO_2$ in water 25°C – MCR 300

Next, the solution of 4.8mM Oleyl Betaine + 1.2mM SDBS + 30mM $NaNO_2$ in water was tested. The plots of the shear viscosity and N_1 vs. the shear rate can be found in Figures 56 thru 58. This solution again exhibits SIS in all of the tests that were completed. The N_1 also increases, as it did in the previous solutions, in correspondence with the SIS behavior.

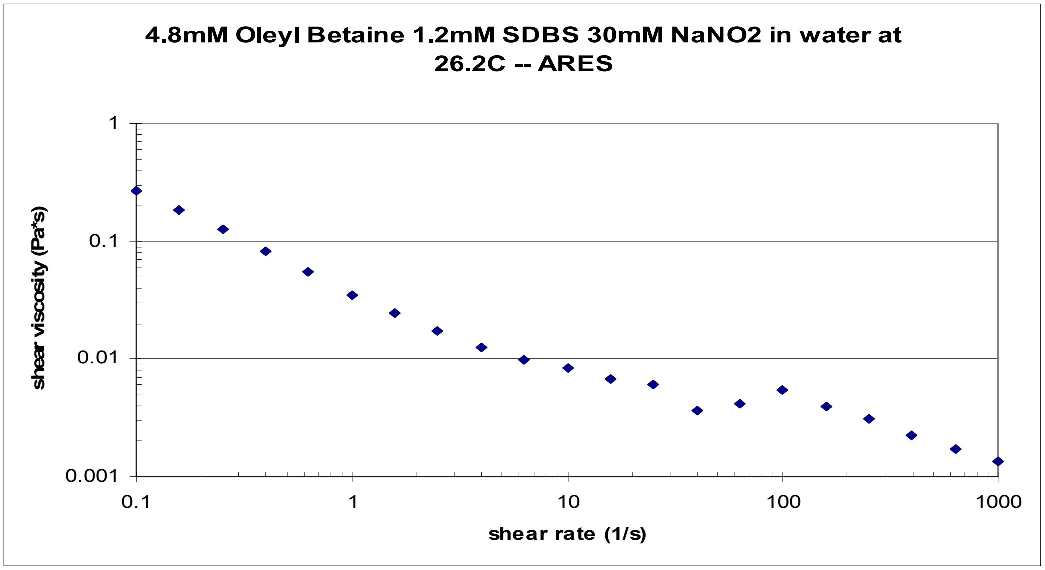

Figure 56: 4.8mM Oleyl Betaine + 1.2 mM SDBS + 30mM $NaNO_2$ in water 26.2°C – ARES

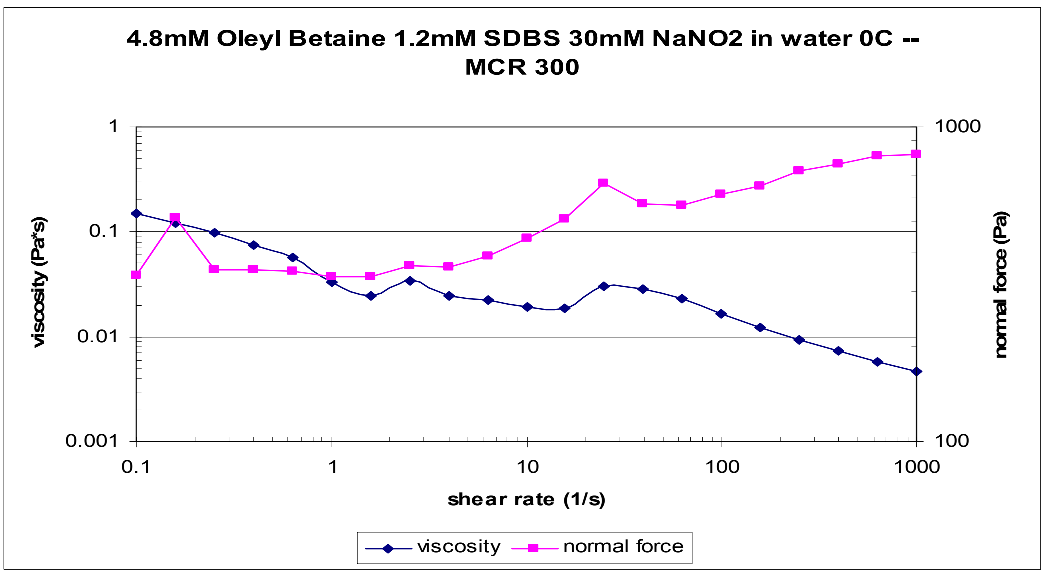

Figure 57: 4.8mM Oleyl Betaine + 1.2 mM SDBS + 30mM $NaNO_2$ in water 0°C – MCR 300

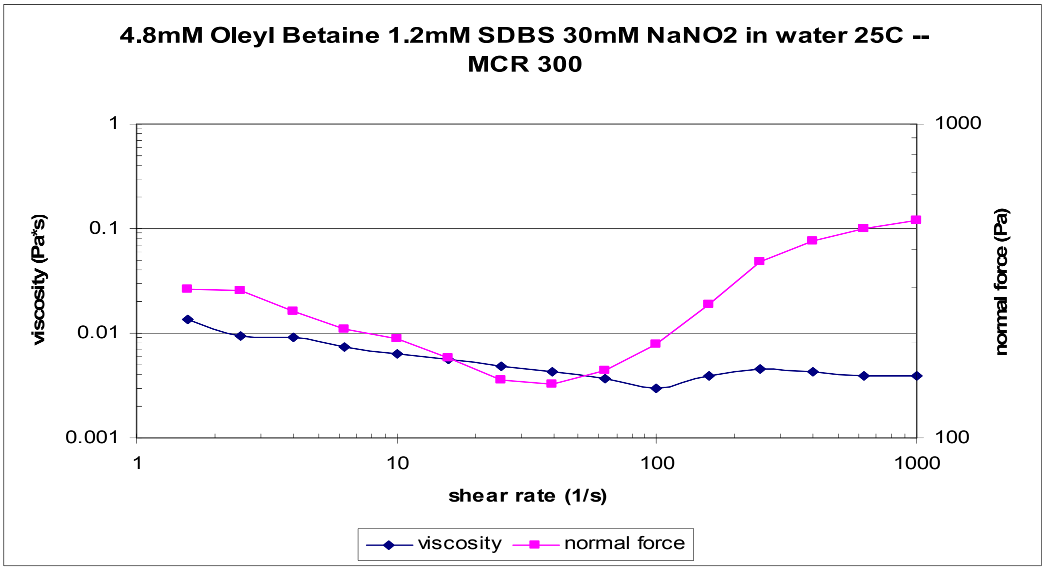

Figure 58: 4.8mM Oleyl Betaine + 1.2 mM SDBS + 30mM $NaNO_2$ in water 25°C – MCR 300

Following the tests of the Oleyl Betaine / SDBS systems in water, these surfactants were then tested in an ethylene glycol / water solution. The first solution tested with ethylene glycol was 4.8mM Oleyl Betaine + 1.2mM SDBS in 20% EG / water. The plots of the data can be found in Figures 59 thru 61. This solution appears to have SIS behavior for the first test using the ARES rheometer at 26.1 °C and the second test using the MCR 300 at 0 °C. The third test, however, using the MCR 300 at 25 °C, does not show any SIS behavior. The first normal stress difference for both tests shows no rise with increasing shear rate. At 25 °C it actually decreases with increasing shear rate.

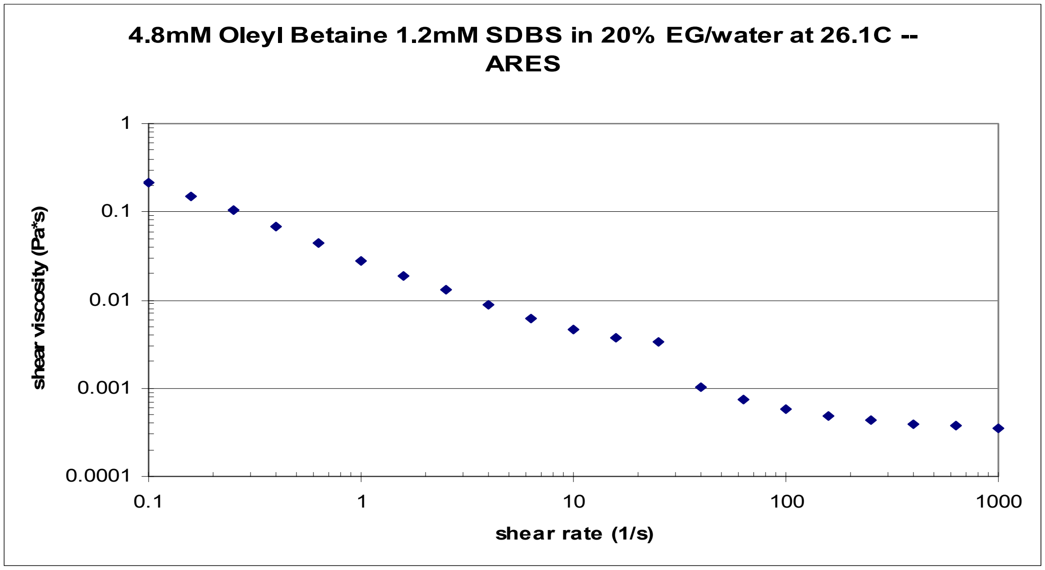

Figure 59: 4.8mM Oleyl Betaine + 1.2 mM SDBS in 20% EG / water 26.1°C – ARES

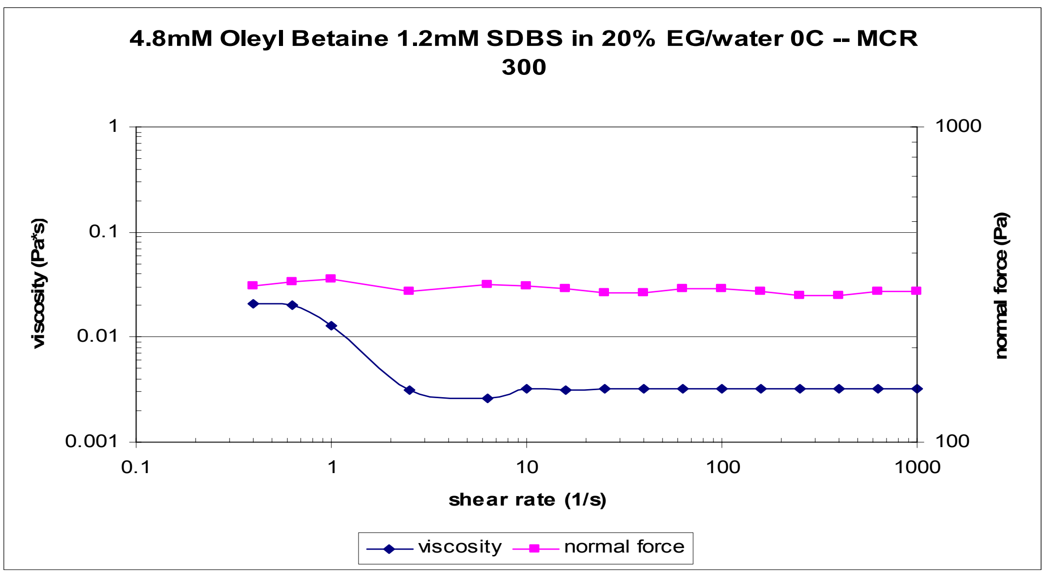

Figure 60: 4.8mM Oleyl Betaine + 1.2 mM SDBS in 20% EG / water 0°C – MCR 300

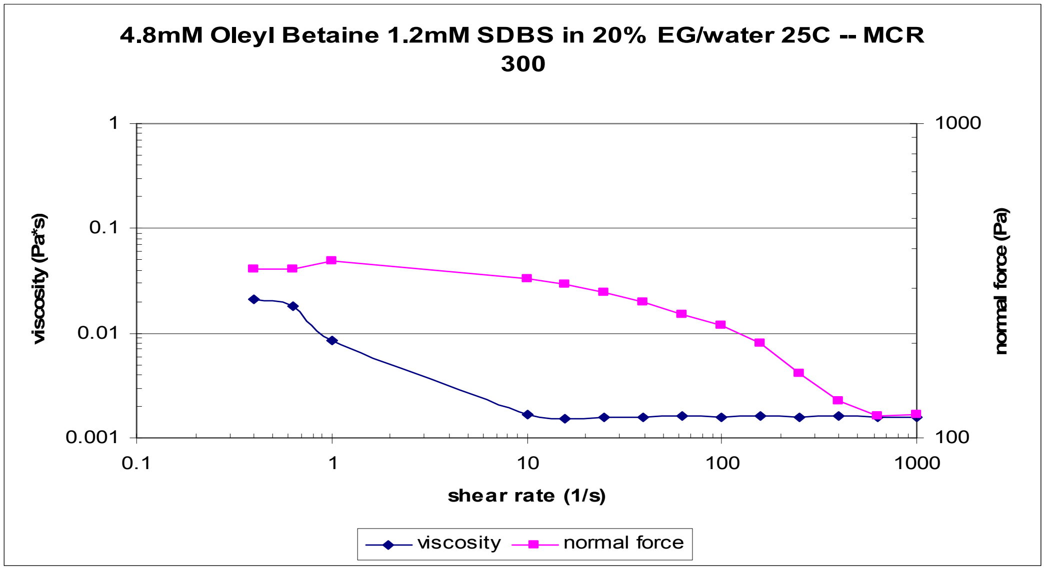

Figure 61: 4.8mM Oleyl Betaine + 1.2 mM SDBS in 20% EG / water 25°C – MCR 300

The next solution tested was 4.8mM Oleyl Betaine + 1.2mM SDBS + 30mM $NaNO_2$ in 20% EG / water. The results of these tests are displayed in Figures 62 thru 64. All three tests run on this solution demonstrate SIS behavior at two different shear rates in the shear rate range of 0.1 to 1000 s^{-1}. The first normal stress difference at both 0 and 25 °C increases around a shear rate corresponding to that of the second SIS although the rise in viscosity is small for both of these.

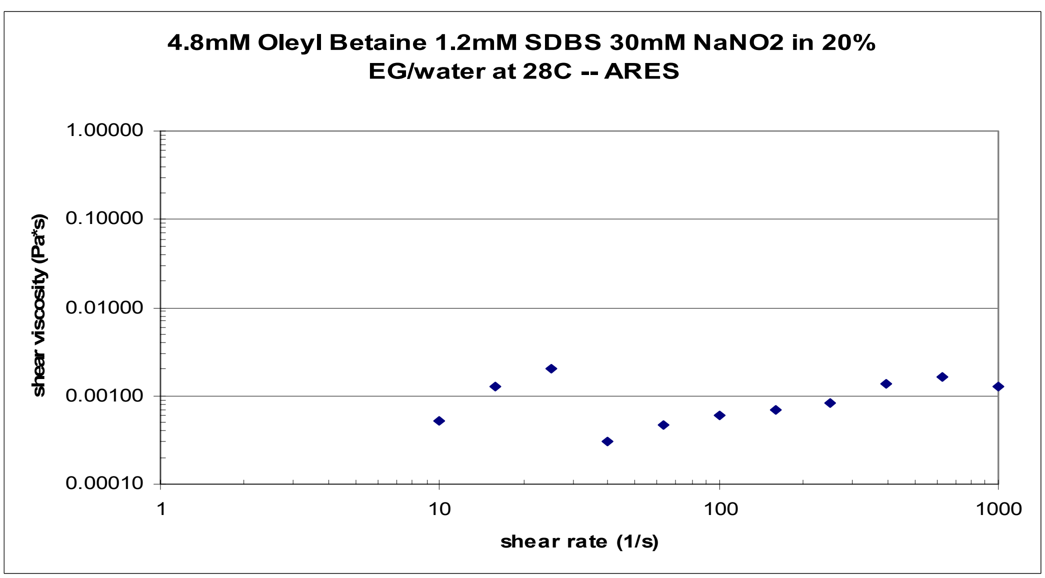

Figure 62: 4.8mM Oleyl Betaine + 1.2 mM SDBS + 30mM $NaNO_2$ in 20% EG / water 28°C – ARES

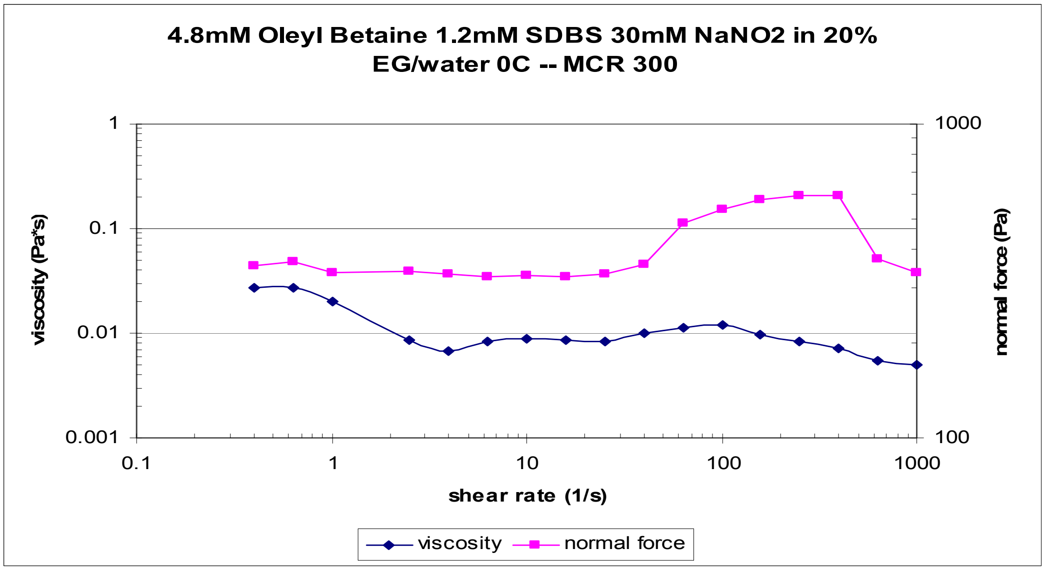

Figure 63: 4.8mM Oleyl Betaine + 1.2 mM SDBS + 30mM $NaNO_2$ in 20% EG / water 0°C – MCR 300

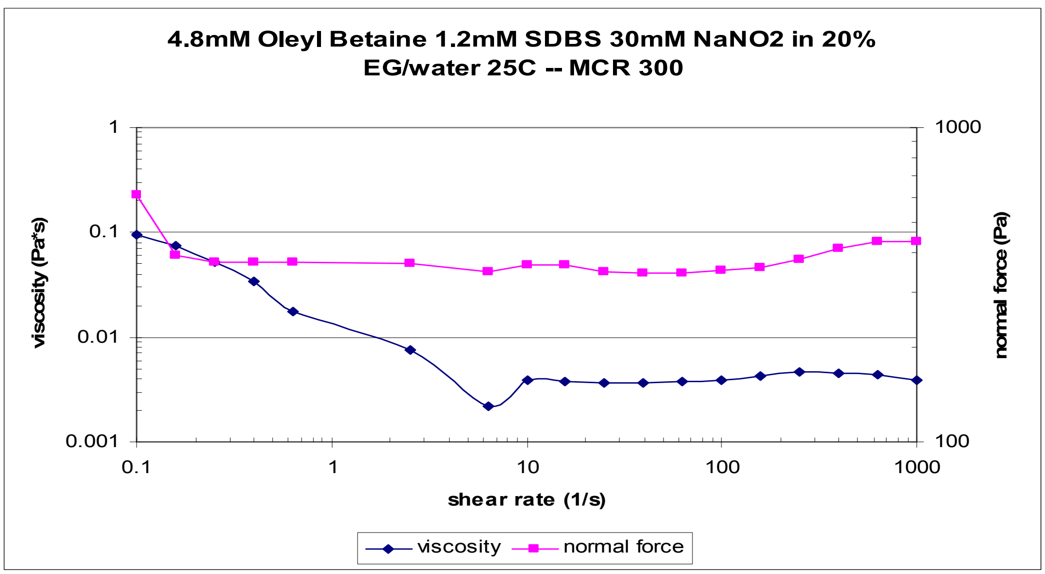

Figure 64: 4.8mM Oleyl Betaine + 1.2 mM SDBS + 30mM $NaNO_2$ in 20% EG / water 25°C – MCR 300

The final solution tested using Oleyl Betaine and SDBS was 8mM Oleyl Betaine + 2mM SDBS + 27mM $NaNO_2$ in 20% EG / water. The plots of the results are displayed in Figures 65 thru 67. All three tests run on this solution exhibit SIS behavior. The N_1 data for this solution at both temperatures shows no correlation with SIS behavior.

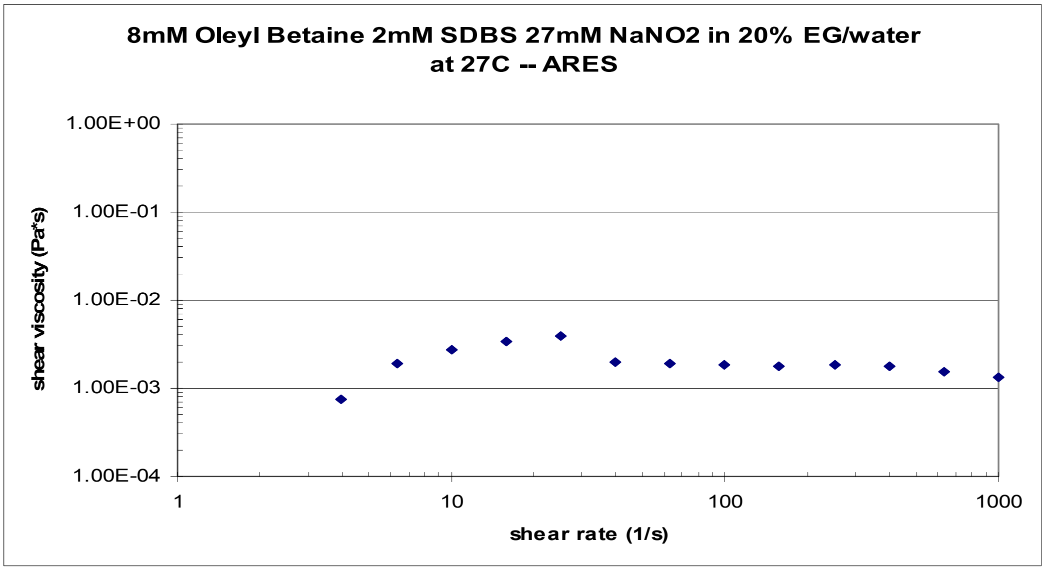

Figure 65: 8mM Oleyl Betaine + 2 mM SDBS + 27mM $NaNO_2$ in 20% EG / water 27°C – ARES

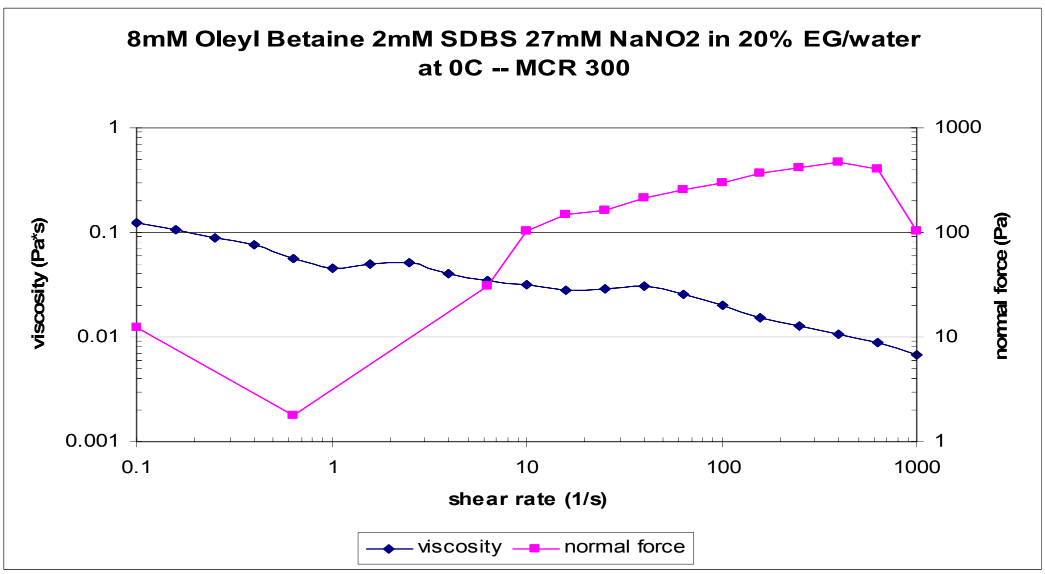

Figure 66: 8mM Oleyl Betaine + 2 mM SDBS + 27mM $NaNO_2$ in 20% EG / water 0°C – MCR 300

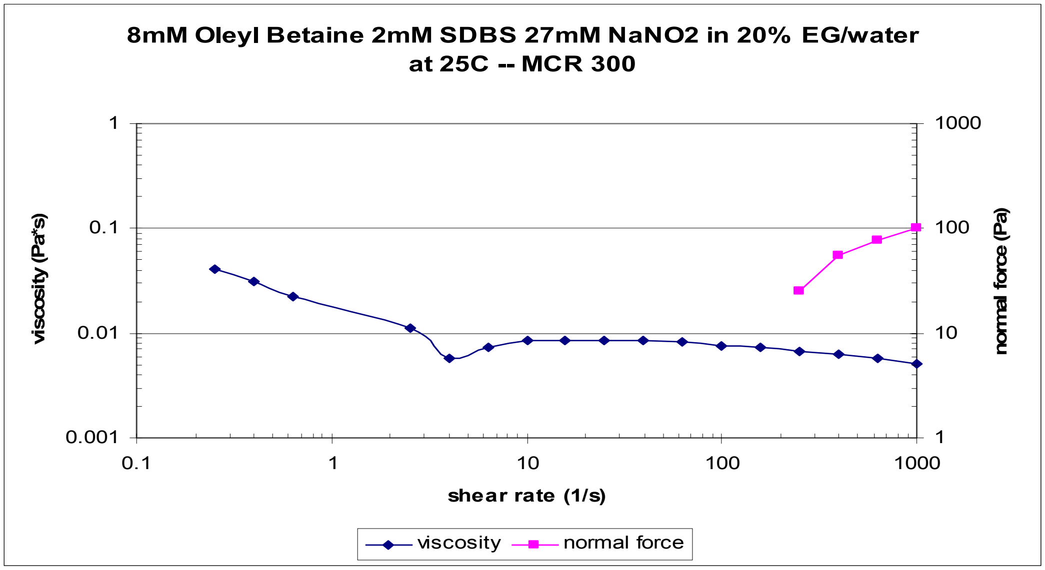

Figure 67: 8mM Oleyl Betaine + 2 mM SDBS + 27mM $NaNO_2$ in 20% EG / water 25°C – MCR 300

The surfactant system of Oleyl Betaine and SDBS generally gives poor drag reduction results. This system does not have significant drag reduction at 0 °C for any of the solutions. The only solutions that exhibit positive drag reduction results are 4.8mM Oleyl Betaine + 1.2mM SDBS + 30mM $NaNO_2$ in water and 8mM Oleyl Betaine + 2mM SDBS + 27mM $NaNO_2$ in 20% EG / water. The Oleyl Betaine / SDBS systems usually exhibit SIS in the range of 0.1 to 1000 s^{-1}. These solutions also have the consistent trend in which N_1 increases or peaks around the critical shear rate for SIS behavior. Again, this surfactant shows the unique ability to form peaks in N_1. This behavior occurs more frequently at the low temperatures tested. A summary of the results for the Oleyl Betaine / SDBS systems can be found in Table 5.

Table 5: Results for Oleyl Betaine / SDBS Solutions

Solution	Rheometer	Temp (°C)	Shear Rate for SIS (peak)	Shear Rate for rise in N_1	Max %DR @ 25 °C	Max %DR @ 0 °C
4.8mM Oleyl Betaine 1.2mM SDBS in water	Ares	34	-	-	~24	~0
	MCR 300	0	10	no rise		
	MCR 300	25	25, 63	no rise		
4.8mM Oleyl Betaine 1.2mM SDBS 6mM NaNO2 in water	Ares	29	25, 100	-	<10	~0
	MCR 300	0	4, 63	N/A		
	MCR 300	25	2.5, 100	40		
4.8mM Oleyl Betaine 1.2mM SDBS 30mM NaNO2 in water	Ares	26.2	100	-	~65	<40
	MCR 300	0	2.5, 25	2		
	MCR 300	25	251	40		
4.8mM Oleyl Betaine 1.2mM SDBS in 20% EG/water	Ares	26.1	25	-	<10	<10
	MCR 300	0	10	no rise		
	MCR 300	25	-	no rise		
4.8mM Oleyl Betaine 1.2mM SDBS 30mM NaNO2 in 20% EG/water	Ares	28	100, 630	-	<10	<10
	MCR 300	0	10, 100	40		
	MCR 300	25	10, 250	160		
8mM Oleyl Betaine 2mM SDBS 27mM NaNO2 in 20% EG/water	Ares	27	10	-	~75	~35
	MCR 300	0	2.5, 40	N/A		
	MCR 300	25	10	N/A		

v. Oleyl Trimethylaminimide

Oleyl Trimethylaminimide is a zwitterionic surfactant. The structure of this surfactant is shown in Figure 68.

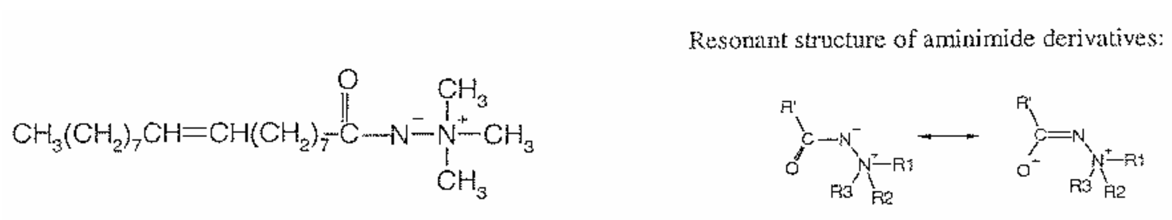

Figure 68: Structure of Oleyl Trimethylaminimide[11]

This surfactant was only tested using the ARES rheometer. Therefore, only shear viscosity data on these surfactant solutions has been generated. Five different solutions with varying surfactant and salt solutions were tested. The results for the shear viscosity vs. the shear rate for the five solutions are displayed in Figures 69 thru 73.

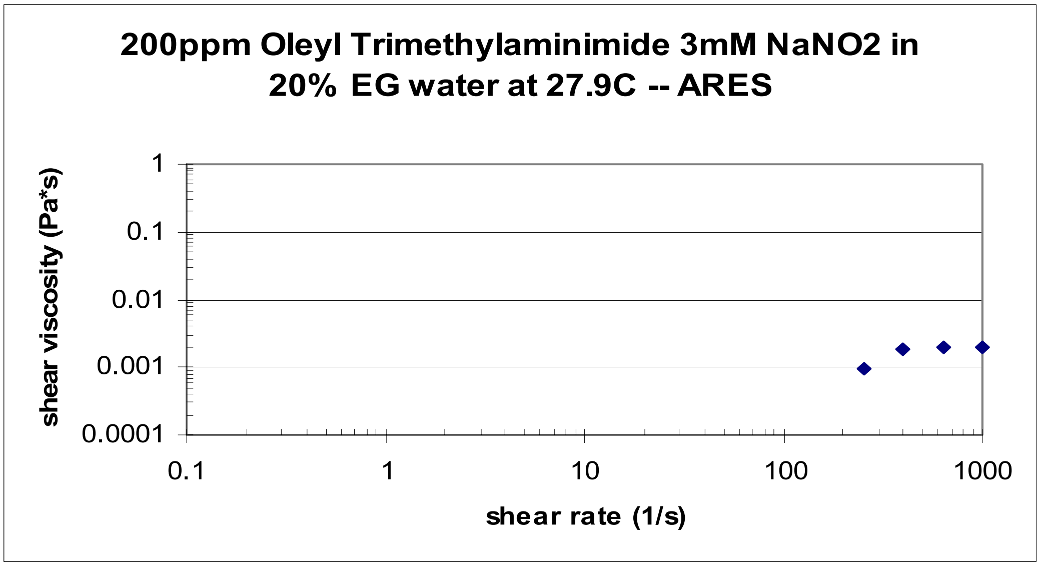

Figure 69: 200 ppm Oleyl Trimethyl aminimide + 3mM NaNO2 in 20% EG/water 27.9°C – ARES

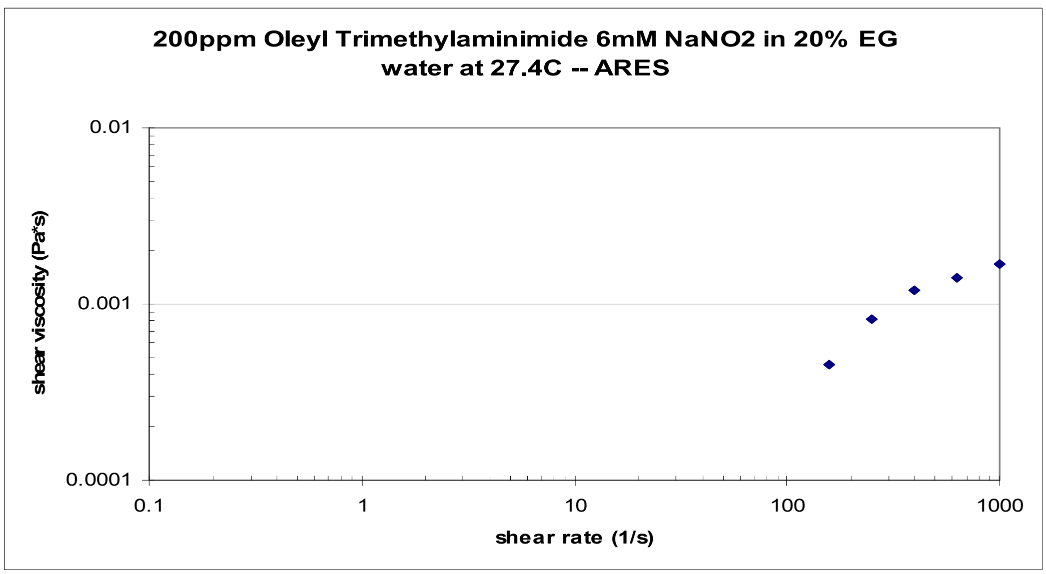

Figure 70: 200 ppm Oleyl Trimethyl aminimide + 6mM NaNO2 in 20% EG/water 27.4°C – ARES

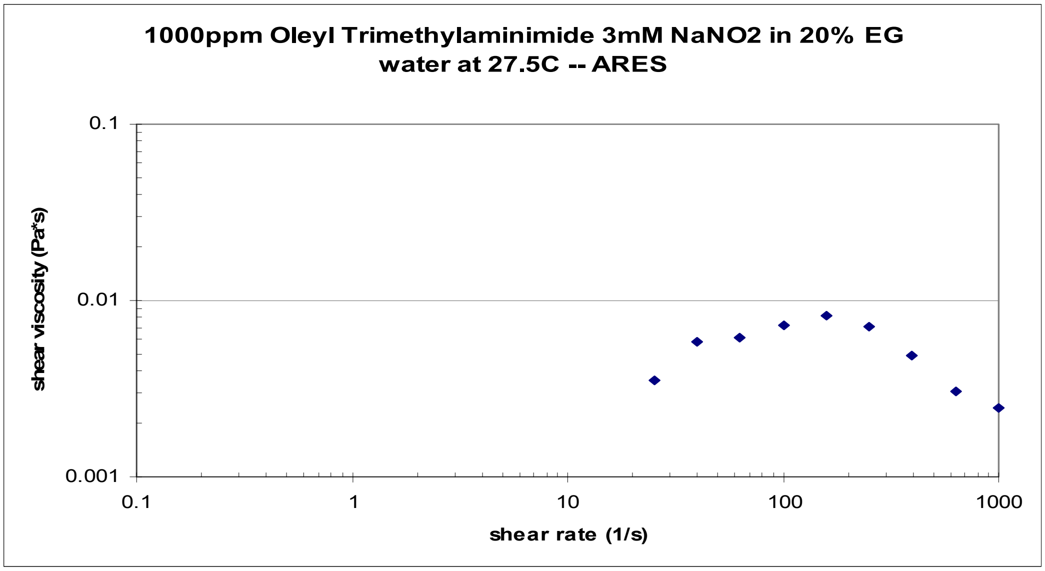

Figure 71: 1000 ppm Oleyl Trimethyl aminimide + 3mM NaNO2 in 20% EG/water 27.5°C – ARES

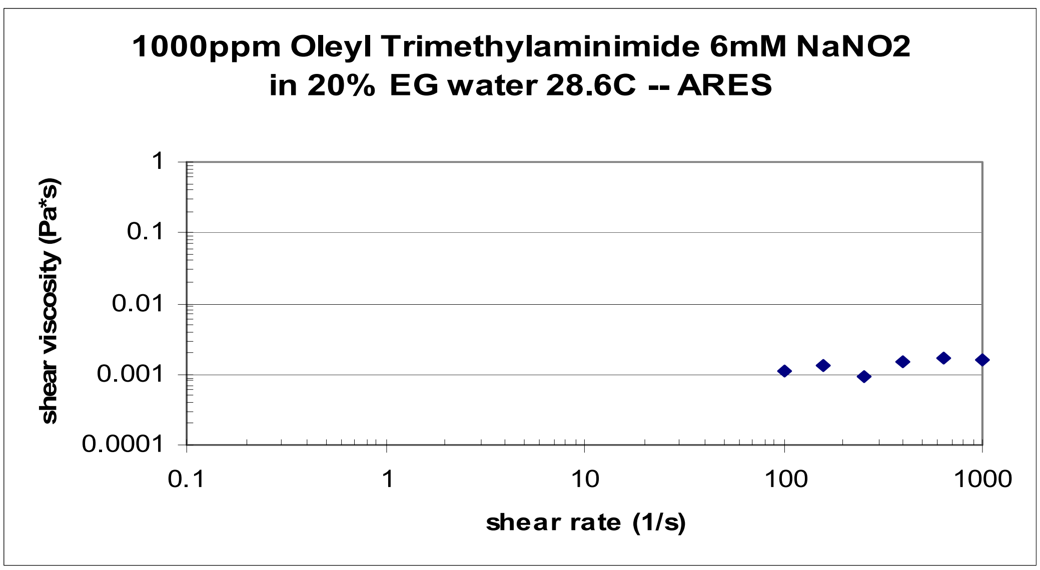

Figure 72: 1000 ppm Oleyl Trimethyl aminimide + 6mM NaNO2 in 20% EG/water 28.6°C – ARES

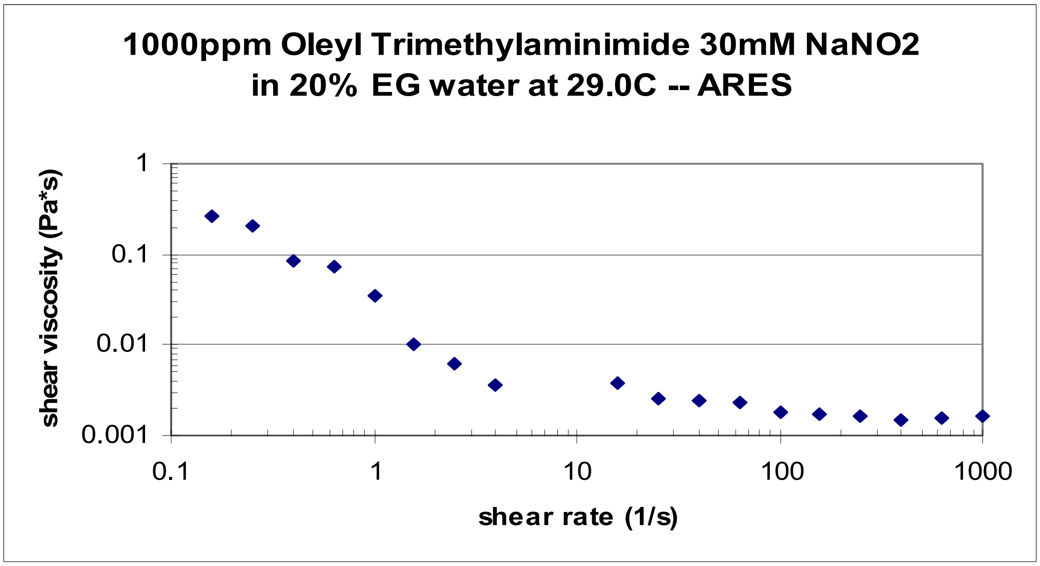

Figure 73: 1000 ppm Oleyl Trimethyl aminimide + 30mM NaNO2 in 20% EG/water 29.0°C – ARES

Three of these solutions have good drag reduction at both 0 and 25 °C. These solutions are: 200 ppm Oleyl Trimethylaminimide + 3mM NaNO2 in 20% EG/water, 1000 ppm Oleyl Trimethylaminimide + 3mM NaNO2 in 20% EG/water, and 1000 ppm Oleyl Trimethylaminimide + 6mM NaNO2 in 20% EG/water. The solution of 200 ppm Oleyl Trimethylaminimide + 6mM NaNO2 in 20% EG/water has good drag reduction at 25 °C, but not at 0 °C while 1000 ppm Oleyl Trimethylaminimide + 30mM NaNO2 in 20% EG/water does not show good drag reduction at either temperature. A summary of these results as well as the results of the viscosity measurements can be found in Table 6.

Most of the viscosity tests that were run on this solution did not give complete results over the shear rate range of 0.1 to 1000 s-1. This is most likely due to sensitivity problems with the rheometer because all of these solutions have relatively low viscosities making it difficult to generate accurate data. It was still possible, however, to detect some SIS behavior in a few of the solutions.

Table 6: Results for Oleyl Trimethylaminimide Solutions

Solution	Rheometer	Temp (°C)	Shear Rate for SIS (peak)	Shear Rate for rise in N_1	Max %DR @ 25 °C	Max %DR @ 0 °C
200 ppm Oleyl Trimethylaminimide + 3mM NaNO2 in 20% EG/water	ARES	27.9	N/A	-	~50	~57
200 ppm Oleyl Trimethylaminimide + 6mM NaNO2 in 20% EG/water	ARES	27.4	N/A	-	~60	~27
1000 ppm Oleyl Trimethylaminimide + 3mM NaNO2 in 20% EG/water	ARES	27.5	158	-	~70	~50
1000 ppm Oleyl Trimethylaminimide + 6mM NaNO2 in 20% EG/water	ARES	28.6	631	-	~58	~52
1000 ppm Oleyl Trimethylaminimide + 30mM NaNO2 in 20% EG/water	ARES	29	16	-	~30	~40

B. Discussion of Viscosity and First Normal Stress Difference Results

By analyzing all of the viscosity and first normal stress difference measurement results, it is possible to draw a few conclusions. First, it is apparent that almost all of these surfactant solutions show SIS behavior. That is, for these solutions a critical shear rate is reached at which the structures of the micelles undergo a change. This phenomenon reverses the normal shear thinning viscosity behavior. This change in structure is often accompanied by a rise in N_1.

Another conclusion that can be drawn, based on the above results is that the critical shear rate at which SIS occurs is dependent upon the concentrations of all components in solution, the temperature, and the geometry used to test the solution. Different solutions, even with small concentration changes, do not have consistent values for the critical shear rate for SIS. Also, when the same solution is tested on the same rheometer at different temperatures the critical shear rates for SIS do not coincide. Finally, the critical shear rates for SIS do not agree when they are tested on the ARES and MCR 300 rheometers at similar temperatures. This is most likely due to the differences in the geometries used to test the samples. The ARES uses Couette geometry while the MCR 300 uses cone and plate geometry.

The final conclusion that can be made from the viscosity and N_1 measurements is that the behavior of N_1 correlates with the SIS behavior in many solutions. For the majority of the solutions tested, with the exception of the Beraid DC DR 620 surfactant solutions, the values of N_1 usually experienced a rise near the shear rate at which the viscosity rises due to SIS behavior. Many of the solutions experienced a peak in N_1 around the same shear rate at which the viscosity peaked. It should be noted that this rise in N_1 always corresponded with the second SIS if the solution had more than one SIS value. From this it can be concluded that N_1 values are generally affected by the occurrence of SIS.

C. Constant Shear Rate Measurements

Two cationic surfactant solutions of Ethoquad O12 were tested at a constant shear rate to determine the time dependent nature of these solutions under shear. The chemical structure of Ethoquad O12 is pictured in Figure 74.

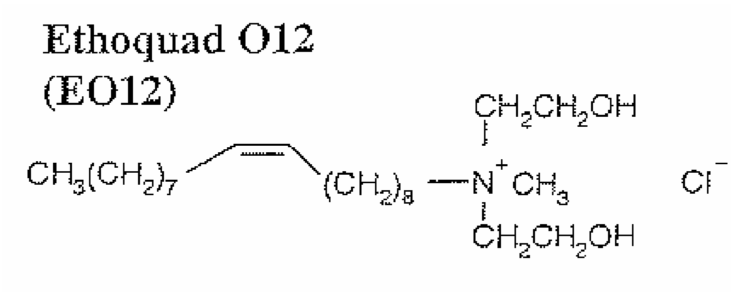

Figure 74: Structure of Ethoquad O12[10]

The two solutions that were tested were 5mM Ethoquad O12 + 12.5mM NaSal in water and 5mM Ethoquad O12 + 12.5mM NaSal in 20% EG / water. These solutions were tested using both the ARES and MCR 300 rheometers at room temperature. The water solution was also tested at 2 ^{o}C.

i. Water Solution – ARES

The 5mM Ethoquad O12 + 12.5mM NaSal solution in water was tested using the ARES rheometer with Couette geometry. The first test run was used to determine the shear viscosity vs. the shear rate to determine the critical shear rate values for SIS. The test results are shown in Figure 75.

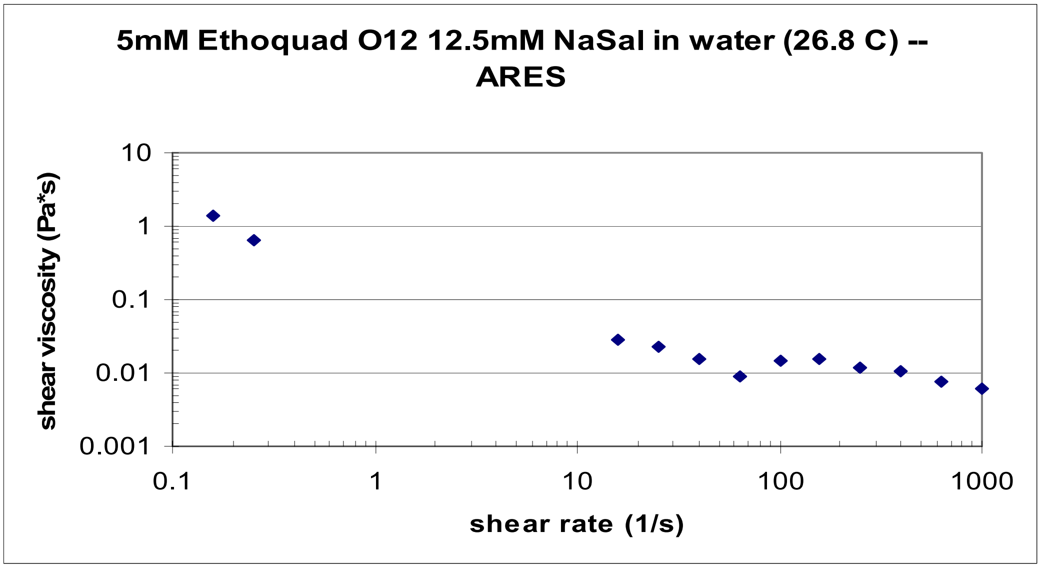

Figure 75: 5mM Ethoquad O12 + 12.5mM NaSal in water 26.8°C -- ARES

From Figure 75 it can be seen that a peak in viscosity due to SIS occurs at about a shear rate of 150 s^{-1}. Using this critical shear rate as a guide, four shear rates were selected to test the sample at constant shear rate over a specified time range. These shear rates were 20, 60, 150, and 400 s^{-1}. The constant shear rates were applied to the solution for either 200 or 400 seconds (specified on each plot) then the shear was abruptly removed to allow the solution to relax. For each shear rate, a plot of the shear stress vs. the time was generated. All of these measurements were performed at room temperature. These plots can be found in Figures 76 thru 79.

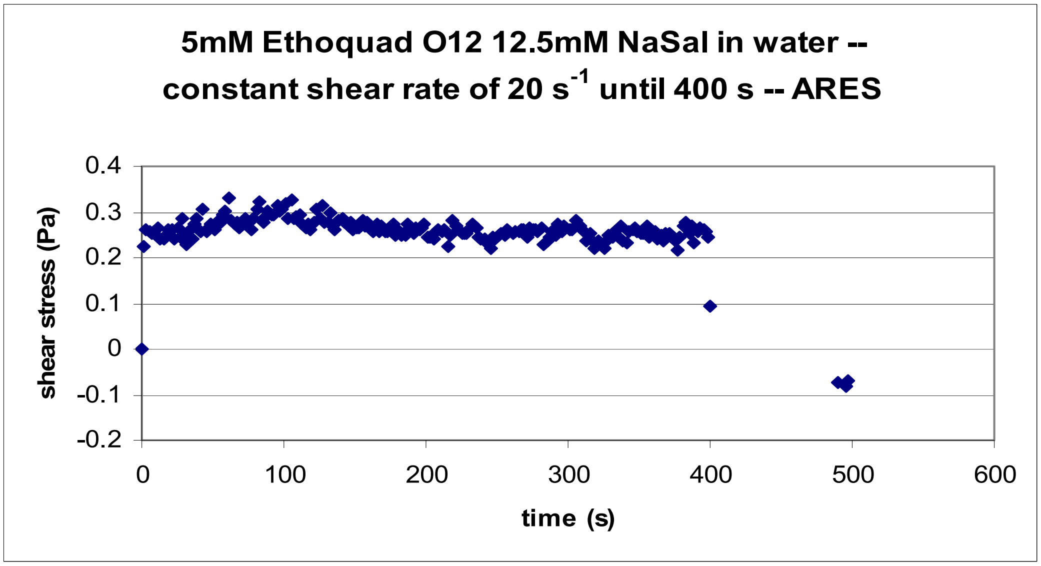

Figure 76: 5mM Ethoquad O12 + 12.5mM NaSal in water (const shear rate of 20 s^{-1}) -- ARES

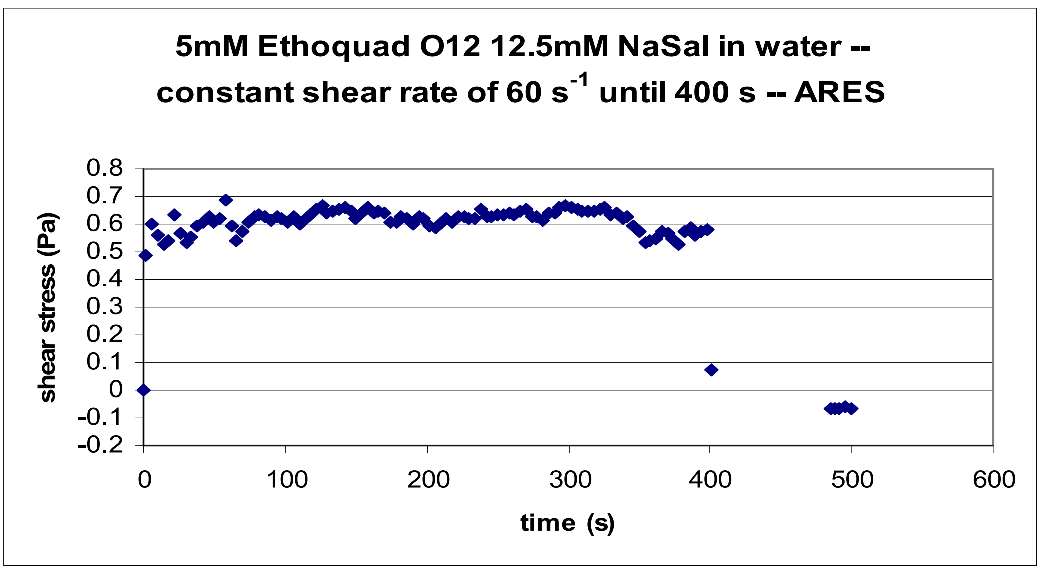

Figure 77: 5mM Ethoquad O12 + 12.5mM NaSal in water (const shear rate of 60 s^{-1}) -- ARES

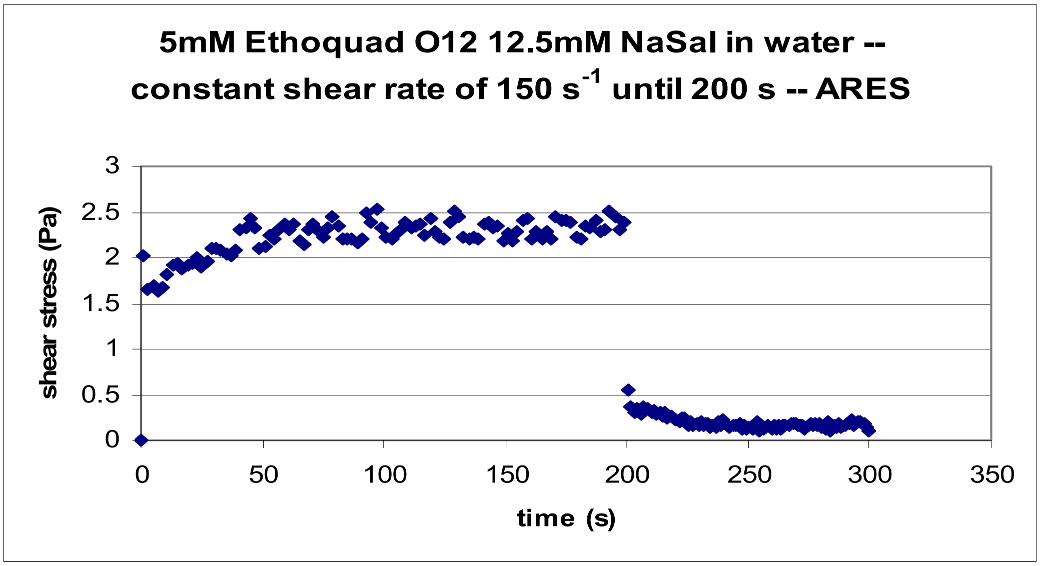

Figure 78: 5mM Ethoquad O12 + 12.5mM NaSal in water (const shear rate of 150 s^{-1}) -- ARES

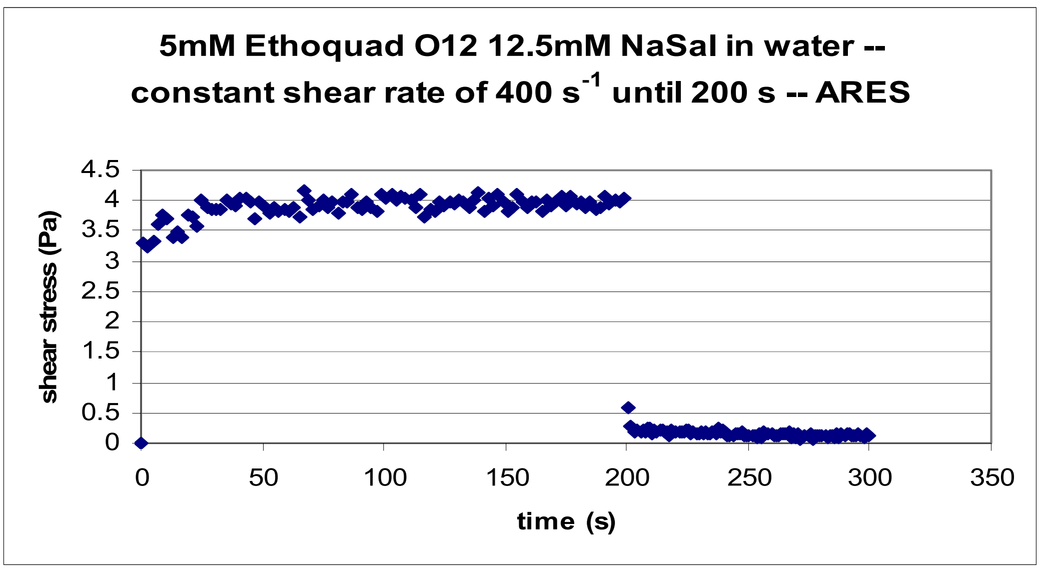

Figure 79: 5mM Ethoquad O12 + 12.5mM NaSal in water (const shear rate of 200 s^{-1}) -- ARES

These solutions do not show any unusual behavior. In general the solutions have a small build up time until they reach a constant value at which they remain for the duration of the test. Also, these tests sometimes give negative values of shear stress upon relaxation. This occurs throughout the remainder of the constant shear rate tests and is most likely due to calibration errors as they should relax to zero shear stress.

ii. Water Solution – MCR 300

The same solution that was tested in the previous section, 5mM Ethoquad O12 + 12.5mM NaSal in water, was also tested using the MCR 300 rheometer. These measurements were done using the cone and plate geometry. This solution was tested at both 2 and 25 ^{o}C. The results at 0 ^{o}C will be presented first.

a. 2 ^{o}C

Again, the first test that was run was to determine the shear viscosity vs. the shear rate of the solution. The result of this test can be found in Figure 80.

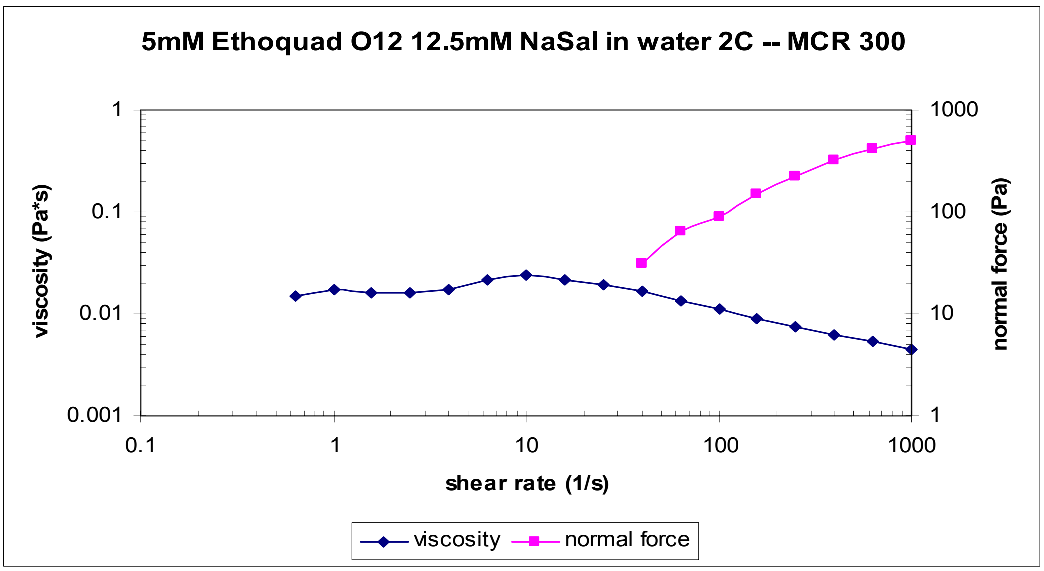

Figure 80: 5mM Ethoquad O12 + 12.5mM NaSal in water 2^{o}C -- MCR 300

A SIS peak was observed at about 10 s^{-1} and so the constant shear rates chosen for testing were 1, 4, 10, 50, 100, and 200 s^{-1}. The results from these tests are shown in Figures 81 thru 86. For each test a constant shear rate was applied for 200 seconds.

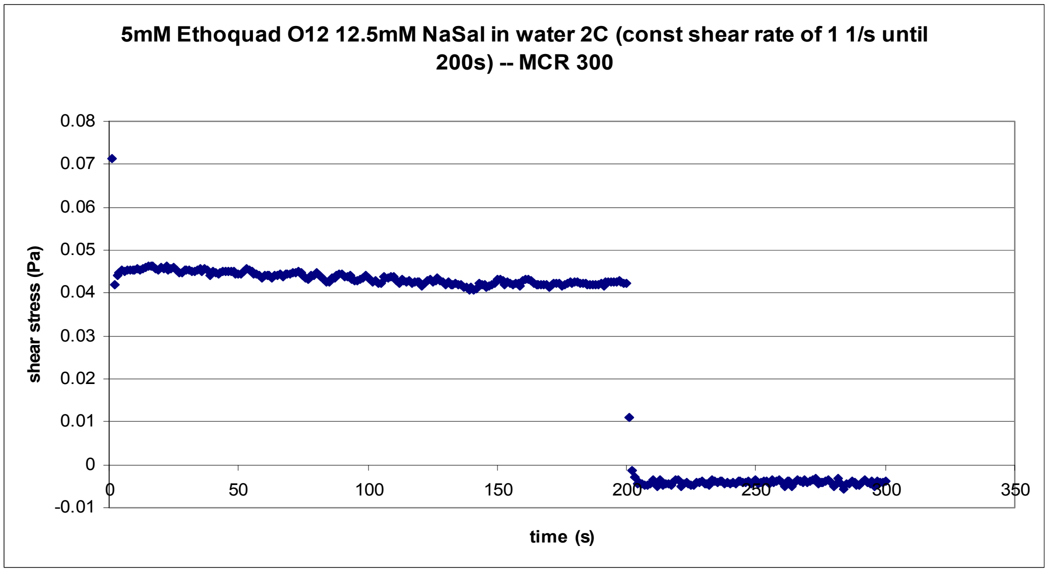

Figure 81: 5mM Ethoquad O12 + 12.5mM NaSal in water 2°C (const shear rate of 1 s^{-1}) – MCR 300

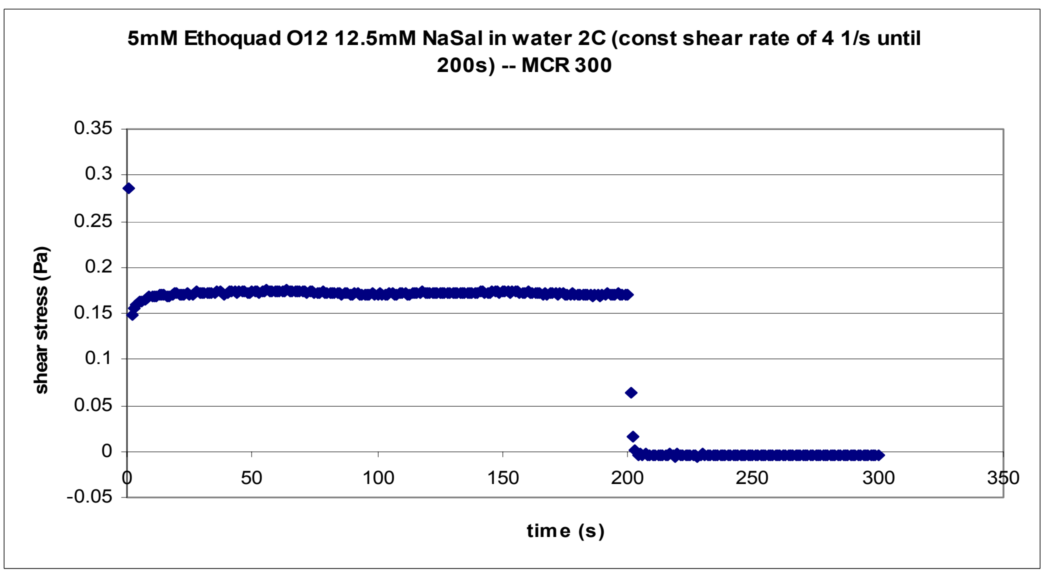

Figure 82: 5mM Ethoquad O12 + 12.5mM NaSal in water 2°C (const shear rate of 4 s^{-1}) – MCR 300

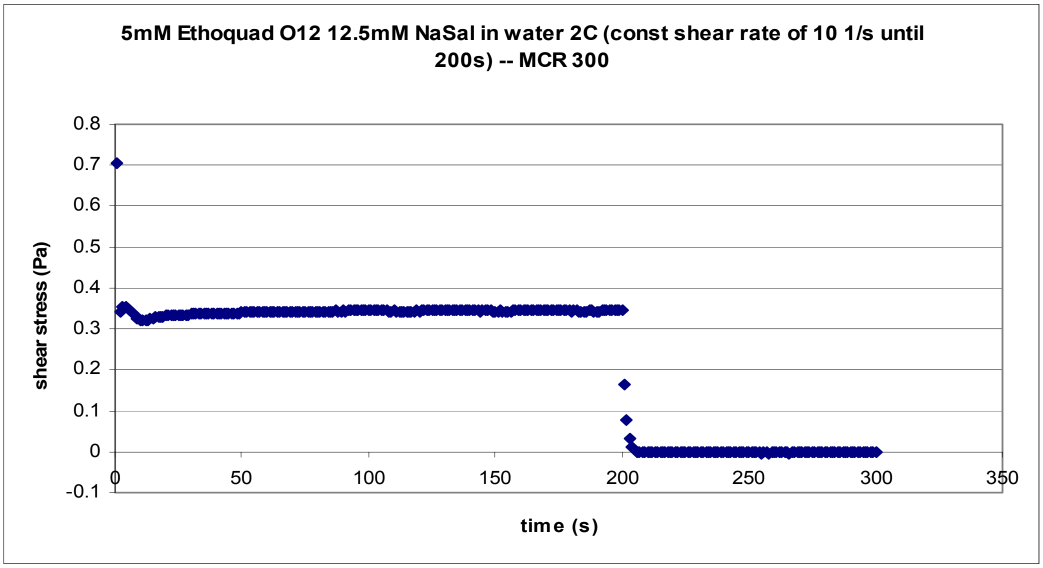

Figure 83: 5mM Ethoquad O12 + 12.5mM NaSal in water 2°C (const shear rate of 10 s^{-1}) – MCR 300

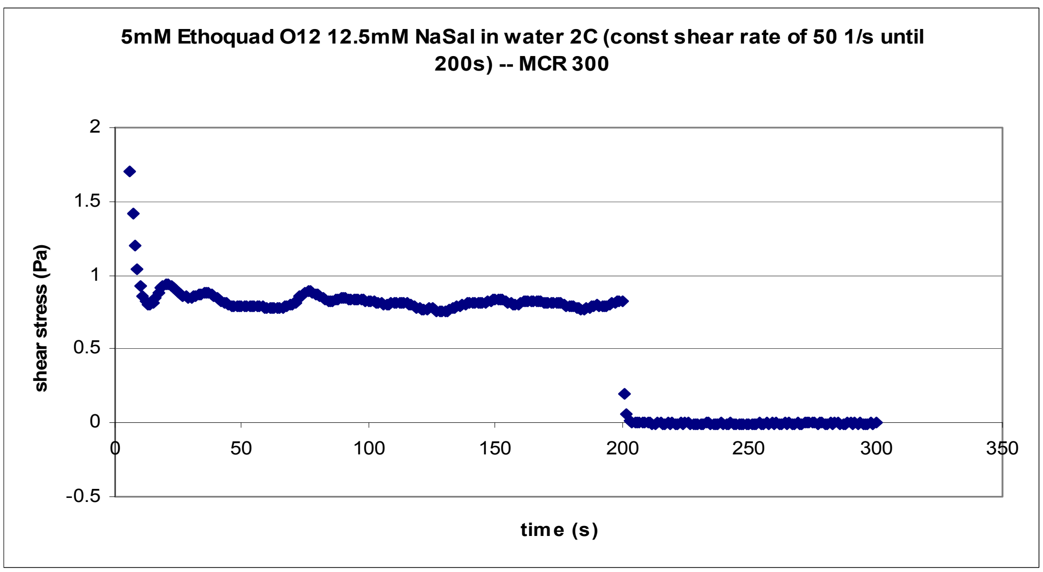

Figure 84: 5mM Ethoquad O12 + 12.5mM NaSal in water 2°C (const shear rate of 50 s^{-1}) – MCR 300

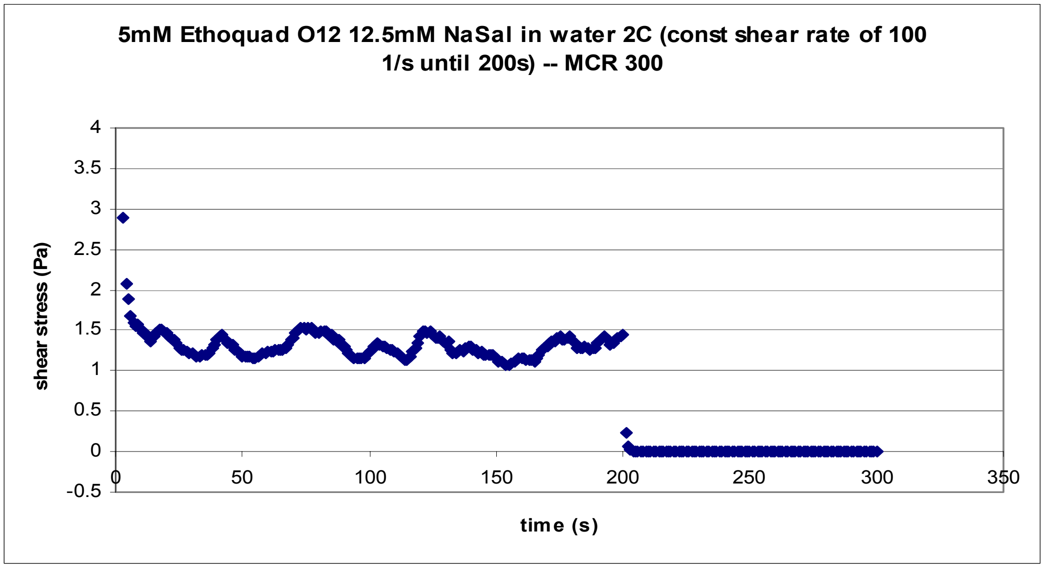

Figure 85: 5mM Ethoquad O12 + 12.5mM NaSal in water 2°C (const shear rate of 100 s^{-1}) – MCR 300

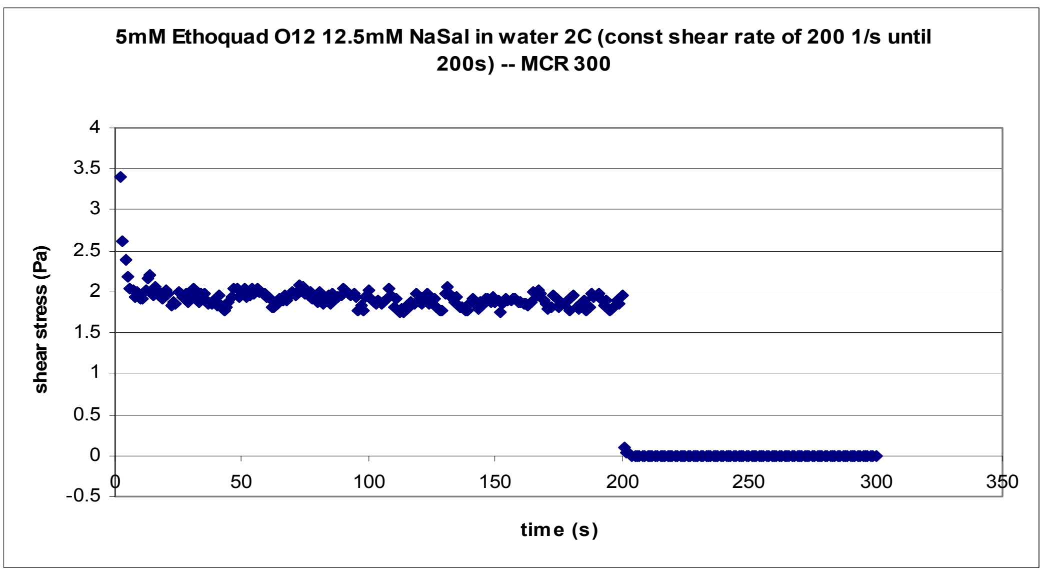

Figure 86: 5mM Ethoquad O12 + 12.5mM NaSal in water 2°C (const shear rate of 200 s^{-1}) – MCR 300

At 2 °C, using cone and plate geometry, the shear stresses of this solution remain fairly constant throughout the duration of these tests at the shear rates of 1, 4, and 10 s^{-1}. At 50, 100, and 200 s^{-1}, strong overshoot is observed followed by reduction in stress to lower values. However, some undulation occurred at these three shear rates.

b. 25 °C

At 25 °C, a shear viscosity vs. the shear rate test was also run. The results from this test are shown in Figure 87.

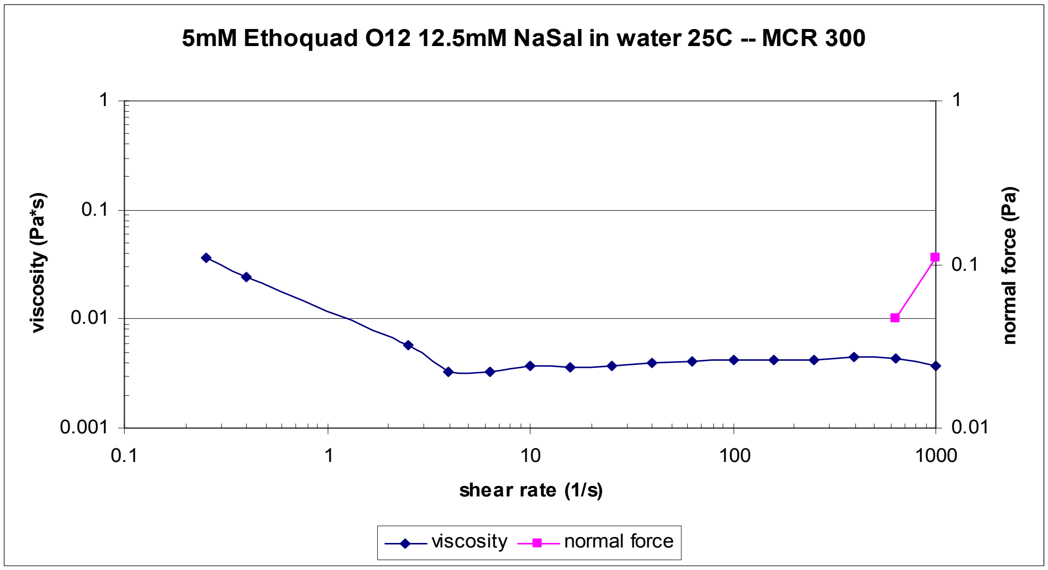

Figure 87: 5mM Ethoquad O12 + 12.5mM NaSal in water 25°C -- MCR 300

From this test it was discerned that the solution undergoes SIS at a shear rate near 10 s^{-1}. The constant shear rates that were chosen to be tested were 0.1, 0.6, 2, 4, 10, and 100 s^{-1}. These tests were run on two separate days. On the first day tests were run on the solution at constant shear rates of 0.1, 0.6, 2, and 10 s^{-1}. These tests gave very interesting results which can be found in Figures 89, 91, 93, and 96. On the second day tests at all of the shear rates mentioned above were run again, but the repeat runs gave very different results from the first day. These results are shown in Figures 90, 92, 94, 95, 97, and 98.

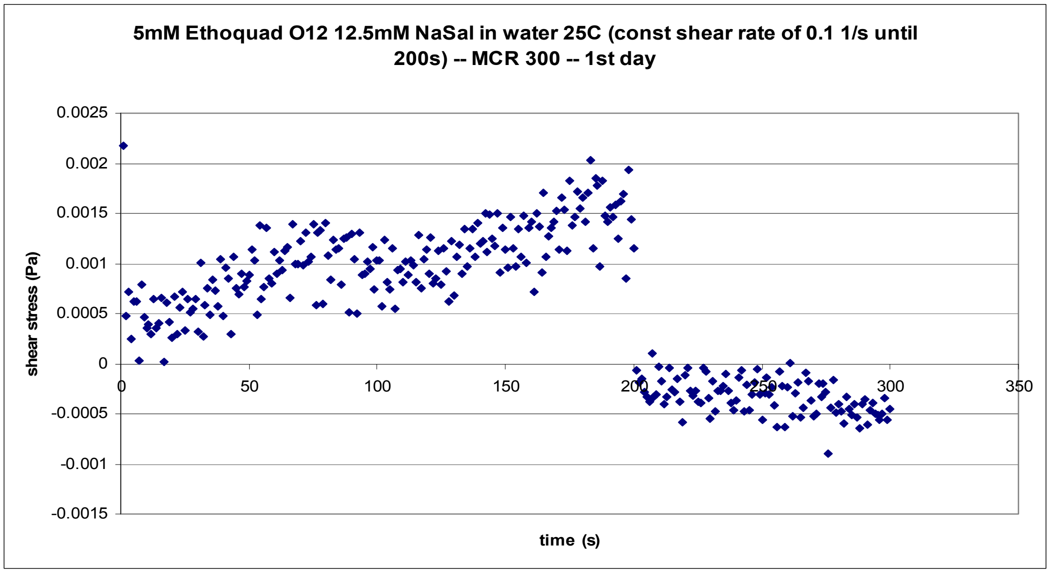

Figure 89: 5mM Ethoquad O12 + 12.5mM NaSal in water 25°C (const shear rate of 0.1 s^{-1}) – MCR 300 – 1st day

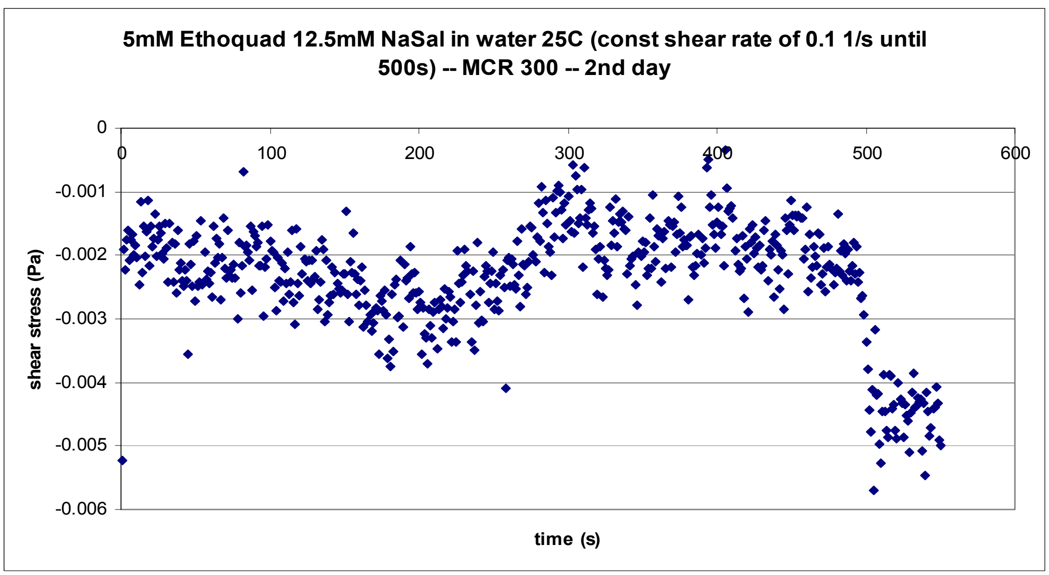

Figure 90: 5mM Ethoquad O12 + 12.5mM NaSal in water 25°C (const shear rate of 0.1 s^{-1}) – MCR 300 – 2nd day

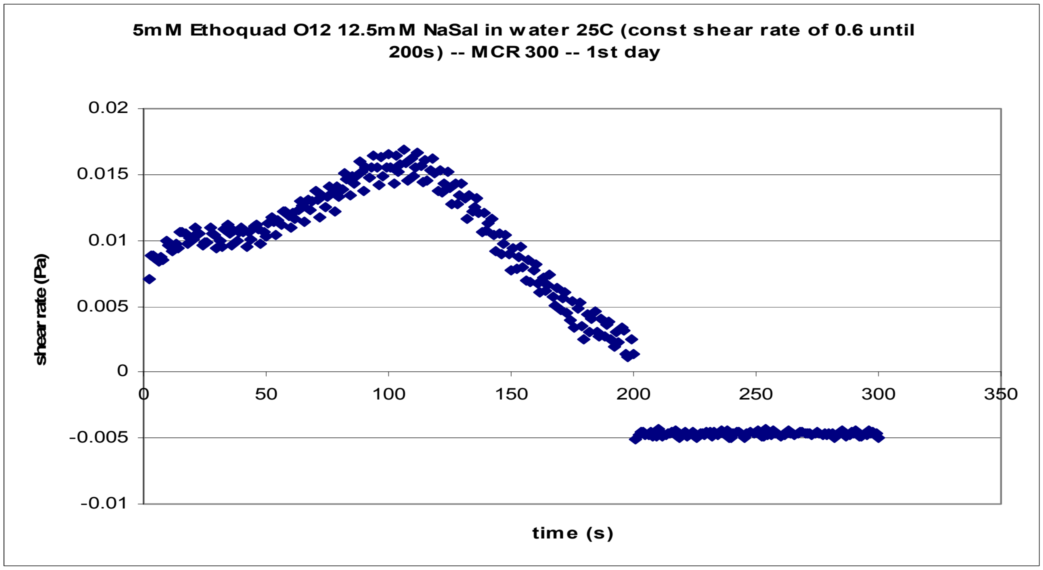

Figure 91: 5mM Ethoquad O12 + 12.5mM NaSal in water 25°C (const shear rate of 0.6 s^{-1}) – MCR 300 – 1st day

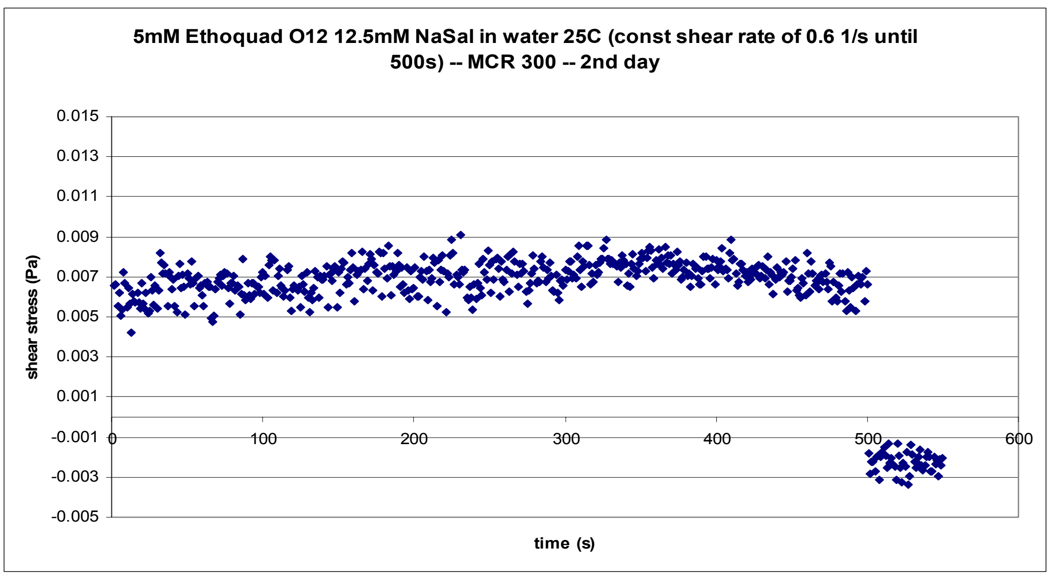

Figure 92: 5mM Ethoquad O12 + 12.5mM NaSal in water 25°C (const shear rate of 0.6 s^{-1}) – MCR 300 – 2nd day

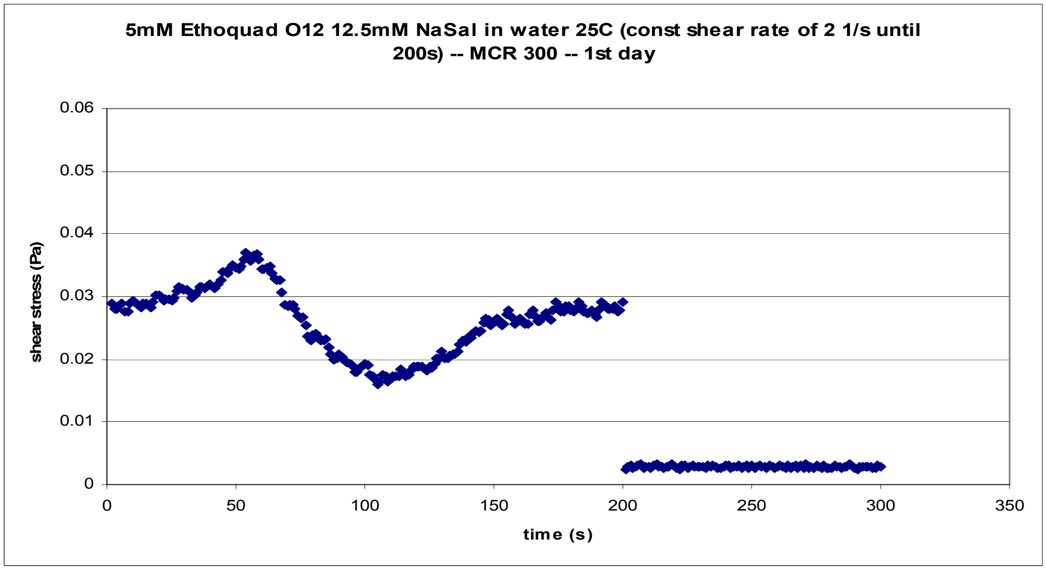

Figure 93: 5mM Ethoquad O12 + 12.5mM NaSal in water 25°C (const shear rate of 2 s^{-1}) – MCR 300 – 1st day

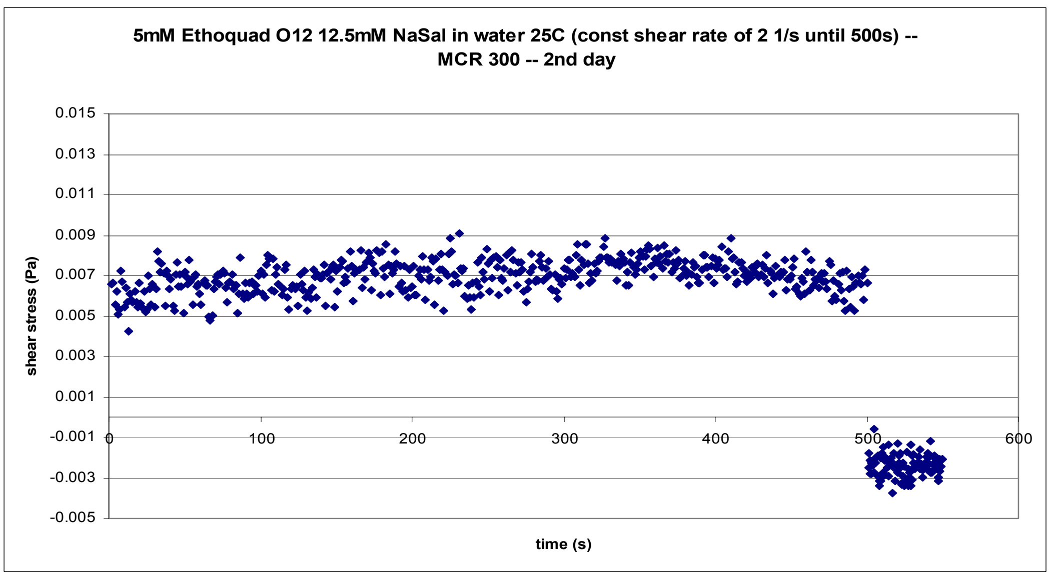

Figure 94: 5mM Ethoquad O12 + 12.5mM NaSal in water 25°C (const shear rate of 2 s^{-1}) – MCR 300 – 2nd day

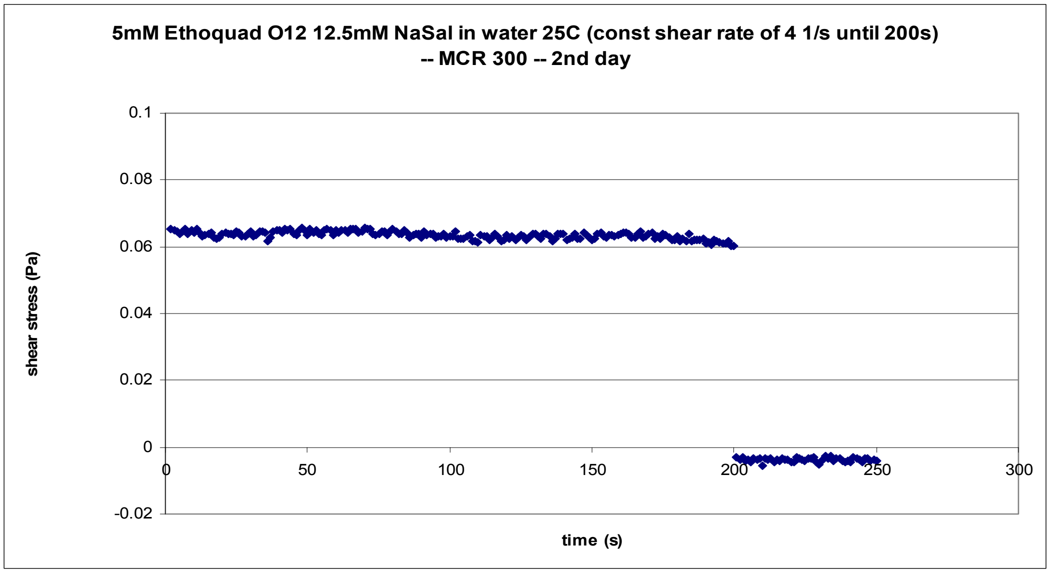

Figure 95: 5mM Ethoquad O12 + 12.5mM NaSal in water 25°C (const shear rate of 4 s^{-1}) – MCR 300 – 2^{nd} day

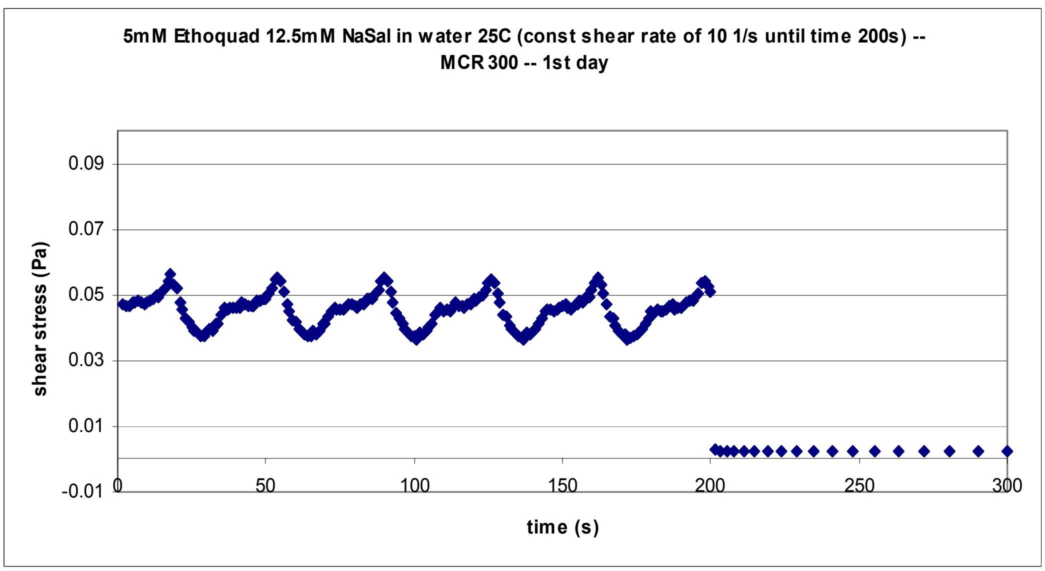

Figure 96: 5mM Ethoquad O12 + 12.5mM NaSal in water 25°C (const shear rate of 10 s^{-1}) – MCR 300 – 1^{st} day

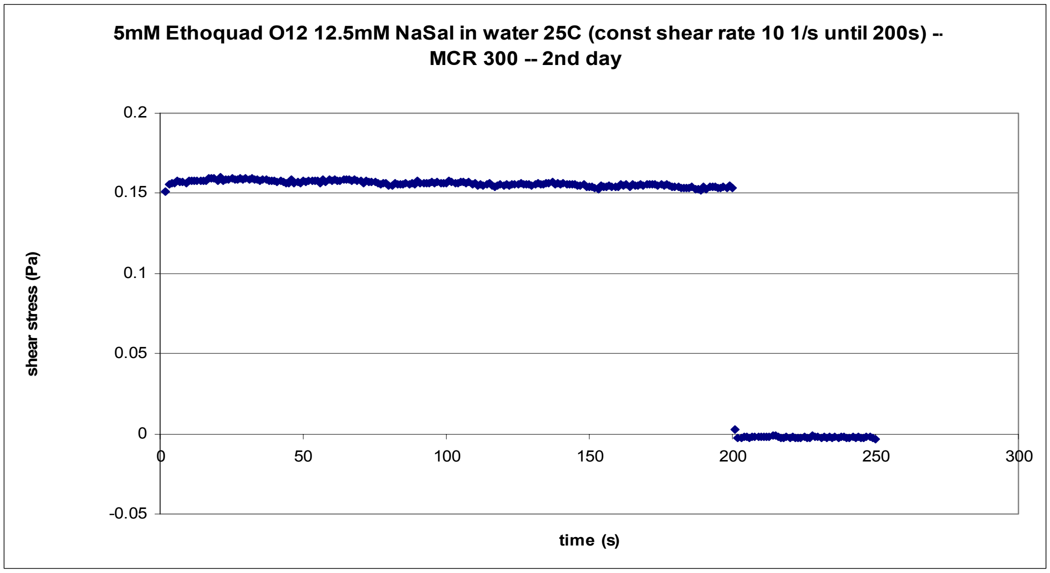

Figure 97: 5mM Ethoquad O12 + 12.5mM NaSal in water 25°C (const shear rate of 10 s^{-1}) – MCR 300 – 2nd day

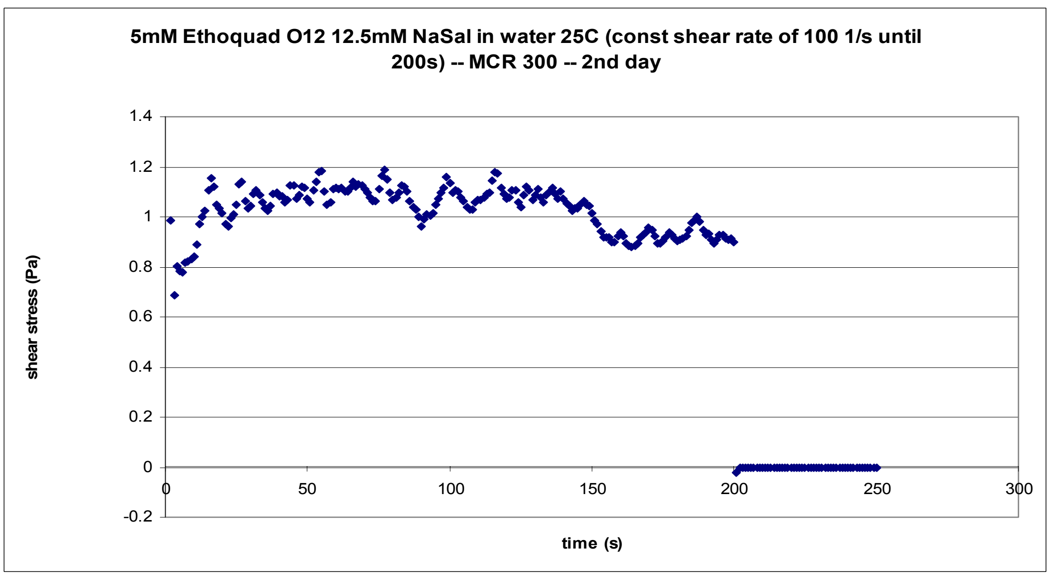

Figure 98: 5mM Ethoquad O12 + 12.5mM NaSal in water 25°C (const shear rate of 100 s^{-1}) – MCR 300 – 2nd day

The samples tested were from the same source on each day of testing. This solution was made in September of 2003, therefore, it is highly unlikely that the composition or microstructure could have changed from one day to the next. The discrepancies in the results seen above cannot be explained.

On the first day of testing the solution showed oscillatory behavior, which was very repeatable. For example, the test run at the shear rate of 10 s^{-1} which is near the SIS (Figure 96) was repeated 4 times. Each time the solution oscillated between the same values of shear stress and had a consistent period of oscillation. Oscillation at this shear rate had the smallest period of the all of the shear rates run on this day. When this test was rerun on the second day, only slight oscillation was seen at very different values of shear stress. This inconsistent behavior cannot be explained and needs to be studied further.

iii. EG / Water Solution – ARES

The second Ethoquad O12 solution tested was 5mM Ethoquad O12 + 12.5mM NaSal in 20% EG / water. This solution was first tested with the ARES rheometer at room temperature using Couette geometry. The first test that was done was to determine the shear viscosity vs. the shear rate and is shown in Figure 99.

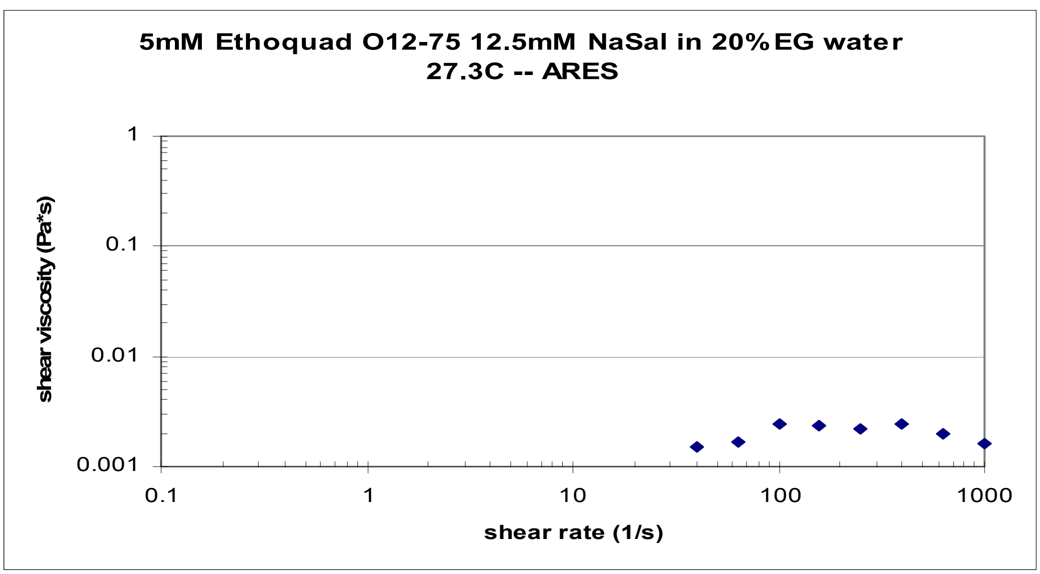

Figure 99: 5mM Ethoquad O12 + 12.5mM NaSal in 20% EG/water 27.3^{o}C -- ARES

From this plot the values of the constant shear rate to be tested were chosen to be 10, 100, 250, and 400 s^{-1}. The plots of the shear stress vs. the time for these tests are displayed in Figures 100 thru 103.

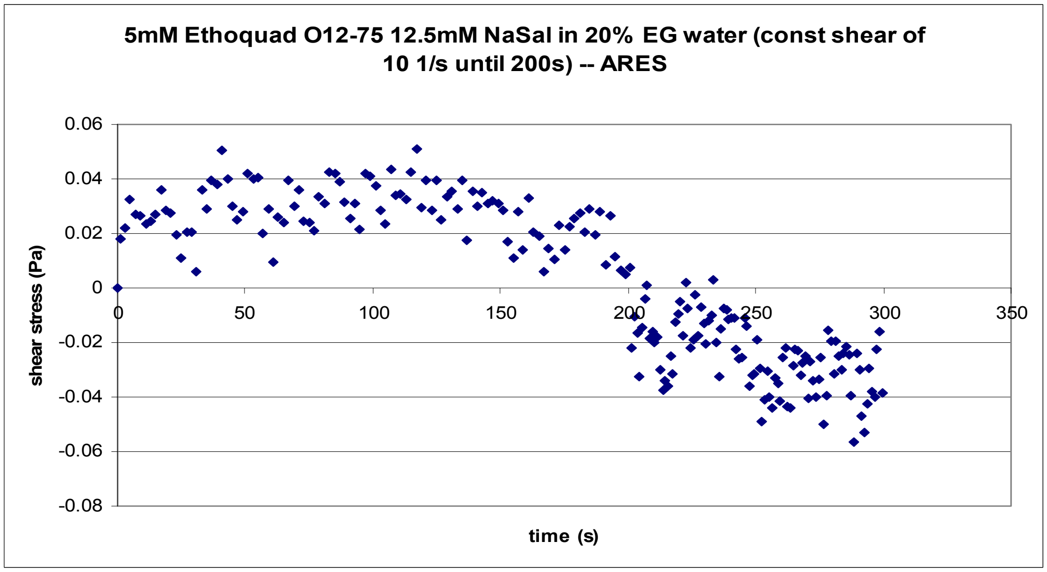

Figure 100: 5mM Ethoquad O12 + 12.5mM NaSal in 20% EG/water (const shear rate of 10 s^{-1}) – ARES

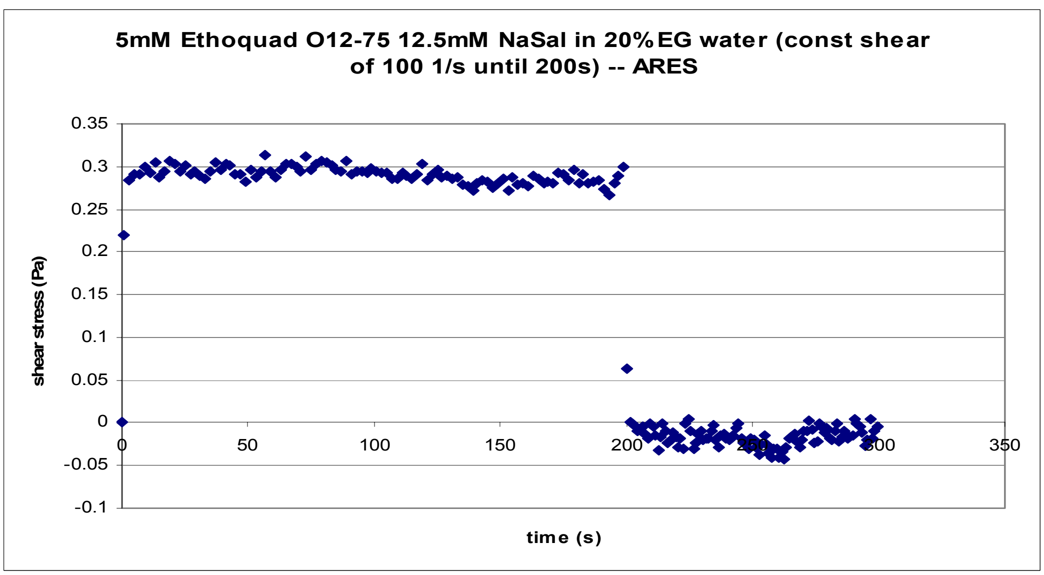

Figure 101: 5mM Ethoquad O12 + 12.5mM NaSal in 20% EG/water (const shear rate of 100 s^{-1}) – ARES

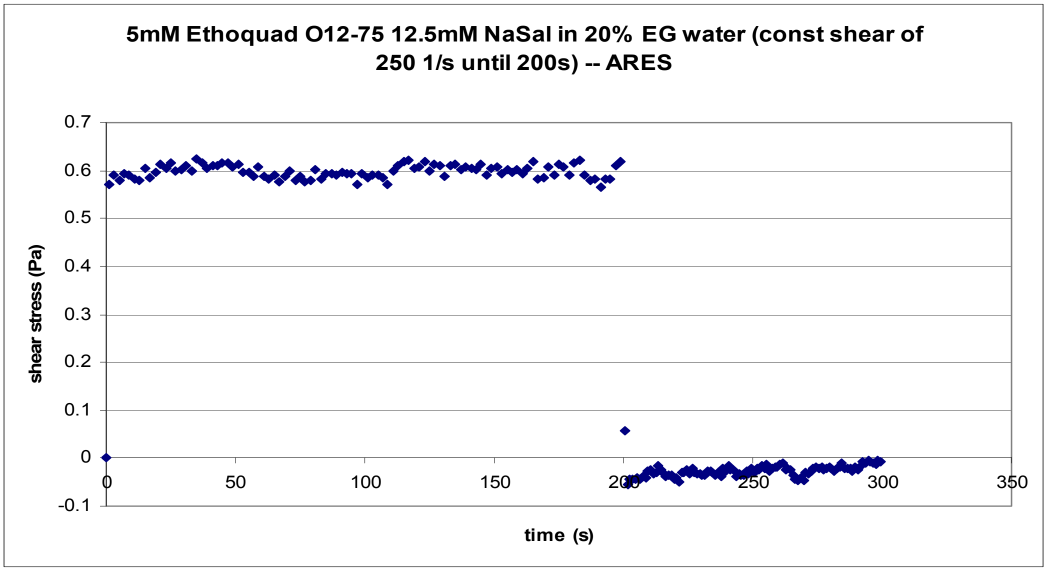

Figure 102: 5mM Ethoquad O12 + 12.5mM NaSal in 20% EG/water (const shear rate of 250 s^{-1}) – ARES

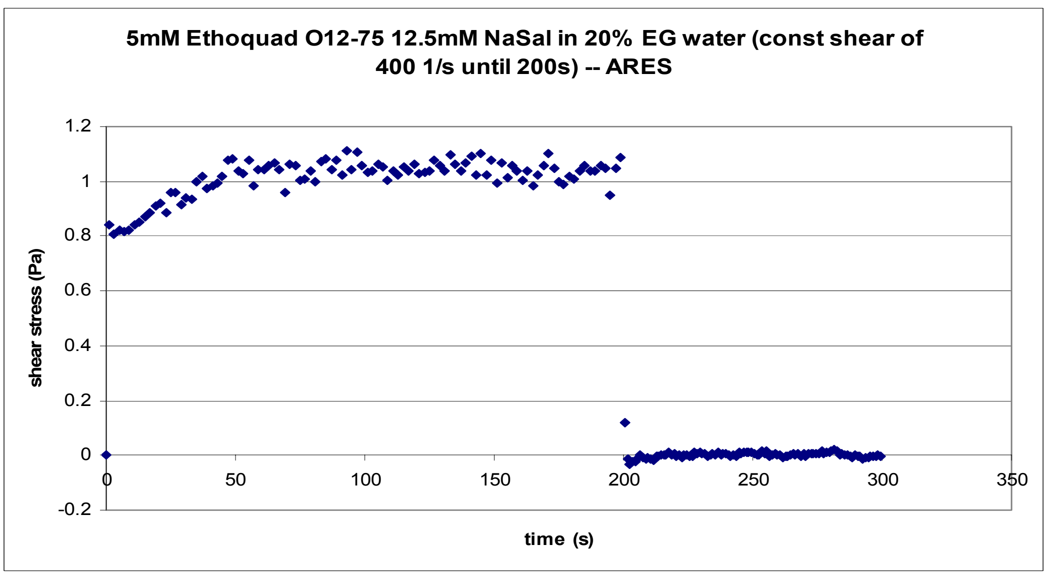

Figure 103: 5mM Ethoquad O12 + 12.5mM NaSal in 20% EG/water (const shear rate of 400 s^{-1}) – ARES

These tests do not reveal any oscillatory behavior. However, similar to the previous results from the ARES rheometer, these results show small build ups of shear stress at the beginning of each run which level out to relatively constant values for the remainder of the run.

iv. EG / Water Solution – MCR 300

The final shear stress measurements were done on the solution of 5mM Ethoquad O12 + 12.5mM NaSal in 20% EG / water using the MCR 300. These tests were done at 25 ^{o}C using cone and plate geometry. First, the shear viscosity vs. the shear rate was found. The plot of this data is shown in Figure 104.

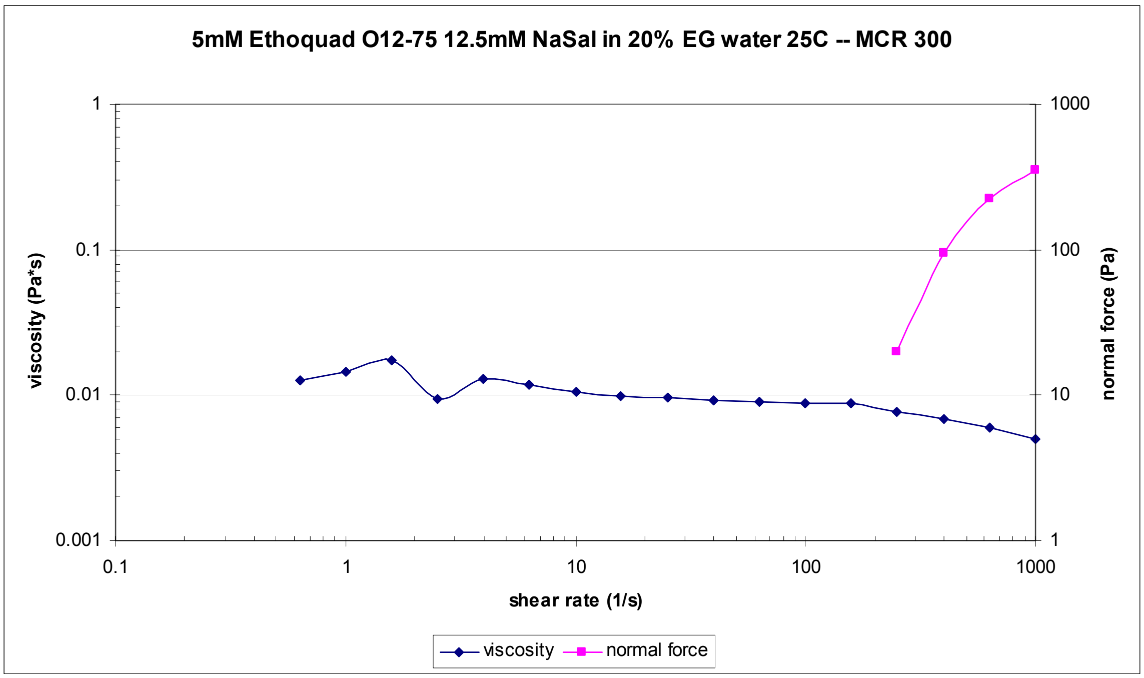

Figure 104: 5mM Ethoquad O12 + 12.5mM NaSal in 20% EG/water 25^{o}C – MCR 300

Since SIS can be observed at a shear rate of about 4 s^{-1}, the shear rate values chosen to test this sample were 1, 2.5, 4, and 100 s^{-1}. The results of these tests are shown in Figures 105 thru 108.

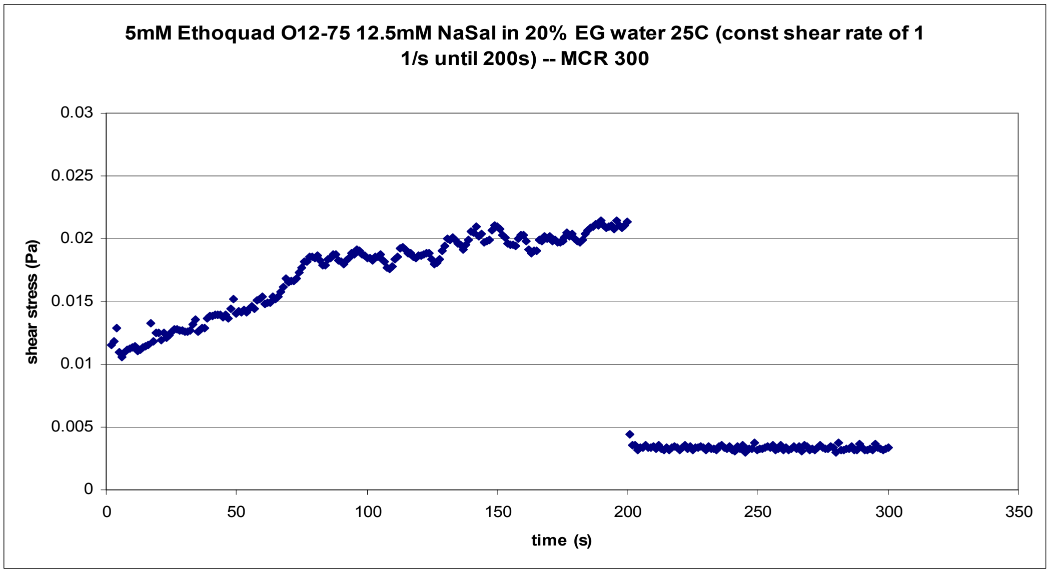

Figure 105: 5mM Ethoquad O12 + 12.5mM NaSal in 20% EG/water (const shear rate of 1 s^{-1}) – MCR 300

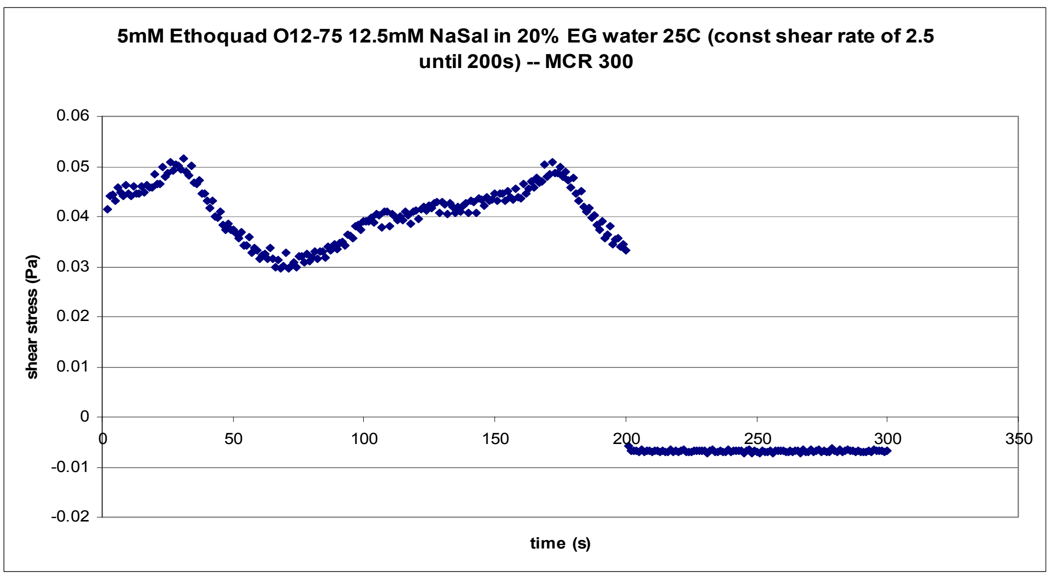

Figure 106: 5mM Ethoquad O12 + 12.5mM NaSal in 20% EG/water (const shear rate of 2.5 s^{-1}) – MCR 300

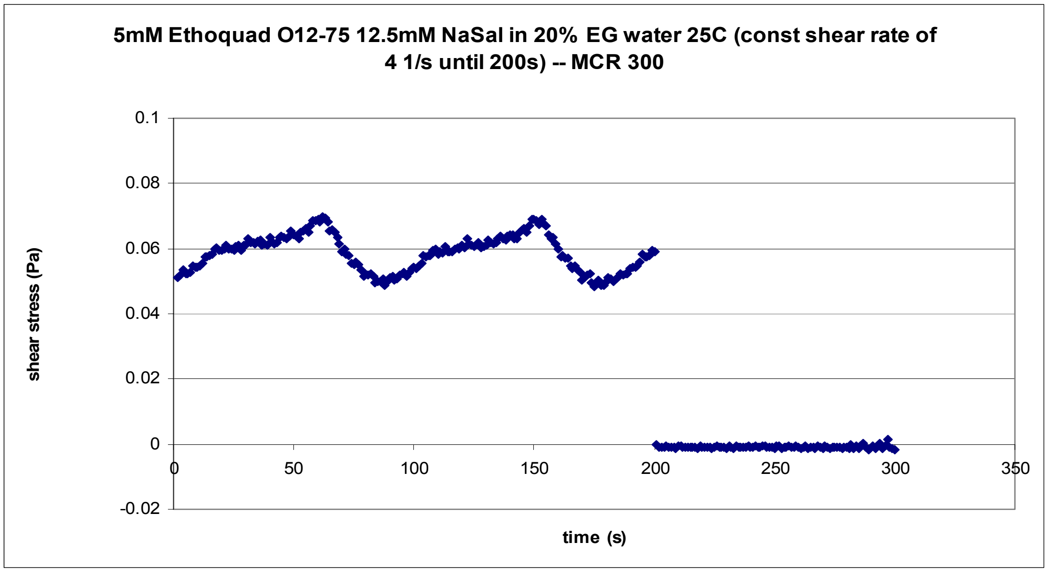

Figure 107: 5mM Ethoquad O12 + 12.5mM NaSal in 20% EG/water (const shear rate of 4 s^{-1}) – MCR 300

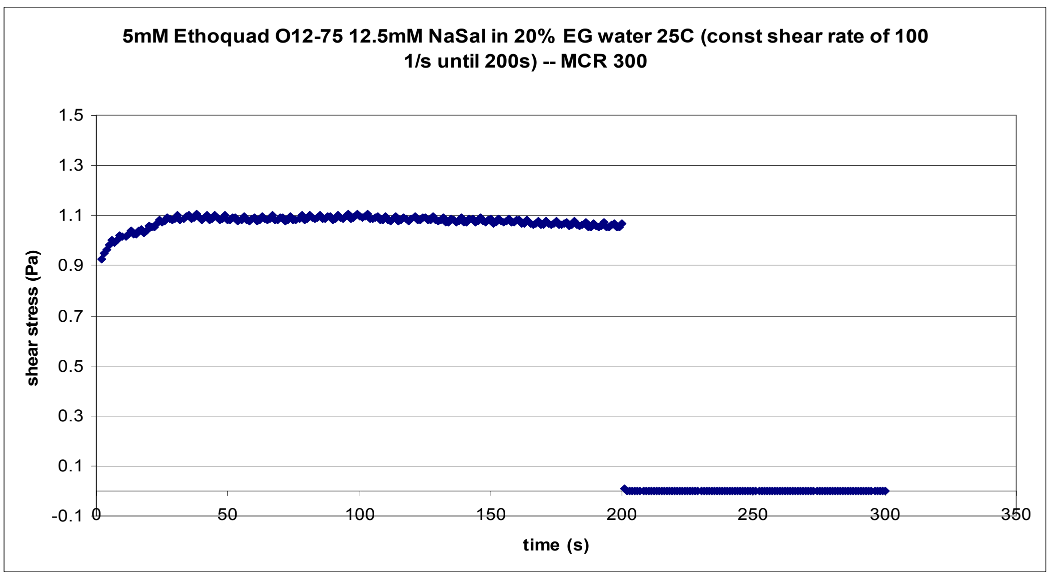

Figure 108: 5mM Ethoquad O12 + 12.5mM NaSal in 20% EG/water (const shear rate of 100 s^{-1}) – MCR 300

From these plots it can be seen that this solution shows oscillatory behavior similar to that seen in the previous solution. The period of oscillation is smallest at the shear rate closest to the peak in viscosity due to SIS.

D. Constant Shear Rate Discussion

Several interesting observations were made during the constant shear rate measurements on the Ethoquad O12 solutions. First, it was observed that the solutions exhibited oscillatory behavior when tested on the MCR 300 (cone and plate) near their SIS, but not when tested with the ARES (Couette). Apparently, this type of behavior can only be observed when a solution is tested using cone and plate geometry as opposed to Couette geometry. Further, the period of the oscillations was the smallest at a constant shear rate close to that of the SIS. The oscillations were also more regular at this shear rate. The second observation was that the tests were not completely repeatable. Tests performed on the same day were repeatable, but upon testing on a second day gave non-repeatable results. These discrepancies require further studies to determine why they occur.

V. Conclusions

1. All of the surfactants studied in this report show the phenomenon of shear induced structure (SIS). This occurs when the structure of the micelles in the solution experience a change at a critical shear rate which causes an increase in viscosity.

2. The critical shear rate at which SIS occurs is dependent on the concentration of surfactant and salt in solution, temperature, and the geometry (cone and plate / Couette) used to measure the viscosity.

3. Typically, values of N_1 are affected by the occurrence of SIS. A rise or peak in N_1 usually coincides with a peak in viscosity due to SIS (with the exception of the Beraid DC DR 20 surfactant solutions).

4. If a solution experiences a rise in N_1 and also has two occurrences of SIS, then the rise in N_1 will always correspond with the SIS which occurs at a higher critical shear rate.

5. At constant shear rate, oscillations in the shear stress as a function of time occur only when a solution is tested using cone and plate geometry as opposed to the Couette geometry. The oscillations are more regular at a shear rate near that of an SIS. They also have a minimum period at that shear rate.

VI. Suggestions for Future Work

1. The ability of some of the surfactant systems to form peaks in N_1 should be investigated further. This should be done to determine why this behavior occurs and also to determine if there are any trends which can be related to the SIS behavior as well as the drag reducing behavior of such systems.

2. It has been suggested that there may be a better correlation between shear stress and SIS behavior than between the shear rate and SIS behavior that was studied in this project. Based on a quick review of this type of data it appears that this may produce a correlation which is independent of the temperature of the system. This correlation should be further studied to determine if this suggestion is valid.

3. The oscillatory behavior in the shear stress that was observed under the application of a constant shear rate should be further investigated. This behavior was only seen using the cone and plate geometry and it produced results that were not always repeatable. Further tests should be run to determine if this is the case for other surfactant systems and to determine if the results can be repeated.

4. The rheological behavior of surfactant systems that do not have positive drag reducing results should be further studied. This would be beneficial because then the rheological behavior of drag reducing systems can be compared to that of systems with no drag reducing ability.

VII. References

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