

**B.S. Thesis for Research Distinction in Chemical Engineering**

**Photosensitive Drag Reducing Surfactant-Counterion Additives to Achieve Enhanced Heat  
Transfer in Recirculating Systems**

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## **I. Introduction**

The use of additives in drag reducing (DR) fluid transport is a phenomenon that was discovered in 1931 by Forest and Grierson who observed a reduction in energy loss in turbulent transport of wood pulp fiber suspensions in water (Zakin, Lu, & Bewersdorff, 1998). The first commercial success with polymers as drag reducers was in the Alyeska pipeline. The pipeline used 5 to 25 ppm (later lowered to 1 ppm) of high molecular weight polymer additive that increased the flow rates up to 25% which in turn increased the throughput of the pipeline by as much as 500,000 barrels per day (Zakin, Lu, & Bewersdorff, 1998). The drawback to using high molecular weight polymers as drag reducers is that they degrade when subjected to high mechanical shear stress which is common in most pumps (Zakin, Lu, & Bewersdorff, 1998). Therefore, polymers are not useful in recirculating systems because, once these molecules are destroyed, they will not reform.

The application of this project is in district heating and cooling (DHC), recirculating systems that use heated or chilled water to provide heating or cooling to multiple buildings in an urban district. The focus is specifically for use in district cooling applications. Benefits of district cooling in comparison to individual air conditioning (AC) units include: reduction of electrical energy consumption in individual buildings due to centralization of AC which in turn reduces costs and energy consumption overall, centralized maintenance teams which are notably smaller and more responsive than teams responding to individual AC units, and quieter buildings with no bulky equipment on the ground or roof. There are similar advantages in district heating. DHC would benefit from DR additives by decreasing the energy requirements for pumping and thus lowering the operation costs further. Since water constantly recirculates in DHC systems, an

additive which can self-reassemble is desirable. Surfactants, which contain both hydrophobic and hydrophilic portions, can reassemble in a matter of seconds after passing through a region of high shear rate or extension (Zakin, Lu, & Bewersdorff, 1998). The hydrophobic and hydrophilic regions of the surfactant can lead to the formation of large micelle structures which form if the overall Gibbs free energy is minimized. This is achieved in cationic surfactant systems by shielding the hydrophobic portion of the molecule by forming clusters in the center of the micelle with the positively charged hydrophilic heads, dispersed by the negative charge of a counterion, at the surface of the micelles. Micelle structures can be spherical, rod-like, lamellar, or vesicles (Zakin, Lu, & Bewersdorff, 1998). In the presence of appropriate counterions, cationic surfactants form threadlike (rod-like) micelles and these networks of threadlike structures are believed to be a necessary for surfactant solutions to be DR (Zakin, Lu, & Bewersdorff, 1998).

While cationic surfactant and counterion solutions provide efficient DR in pumping, heat transfer in tube-tube heat exchangers is reduced commensurately (Zakin, Lu, & Bewersdorff, 1998). Threadlike micelles dampen the turbulence in the radial direction which in turn reduces heat transfer in the radial direction (Zakin, Lu, & Bewersdorff, 1998). Thus, the use of cationic/counterion solutions for DR in DHC is not beneficial unless high (water-like) heat transfer properties can be momentarily regained while the solution passes through the heat exchanger.

The focus of this research is to overcome this limitation through the use of photosensitive threadlike micelles. When exposed to the right wavelength, such as ultraviolet (UV) irradiation, certain counterions can change from *trans* to *cis* (or vice versa), a phenomenon known as photoisomerization (Shi, et al., 2011). The change in geometric configuration makes the binding



of the counterion to the surfactant less favorable to micelle formation resulting in shorter micelle structures which are not DR (Shi, et al., 2011). Previous research by Dr. Zakin and co-workers has shown the ability to transform a DR fluid with a photosensitive counterion (*trans*-OMCA) from *trans* to *cis* using UV irradiation and achieve increased heat transfer properties (Shi, et al., 2011). A method to switch the counterion back to a DR active mode was not discovered; however, in this research *trans*-ACA was determined to have reversible photoisomerization. UV light irradiation causes the counterion to switch from *trans* to *cis*, and blue light (BL) irradiation causes the counterion to switch from *cis* to *trans*.

The objective of this thesis research is to find a surfactant and counterion system that utilizes the photoisomerization phenomenon to achieve alternating DR active and DR inactive properties for use in DHC. Since the focus of this project will be for district cooling, one goal of this project is to find a system that can be switched between DR active and DR inactive at temperatures of 10-15°C generally used in district cooling systems. The second goal is to find a system which can achieve this switch between DR in a timeframe that will be practical for commercial use. If it takes too long to convert between DR properties, the system will not be commercially favorable.

## II. Experimental Methods

### A. Materials

The chemicals used for this research are shown in Table 1. The surfactants EO12 and EHAC were purified with vacuum filtration to remove isopropyl alcohol and water. Liquid nitrogen was used to trap the alcohol and water in a metal coil. The rest of the chemicals were present in the Koffolt Lab 133, and used throughout the research.

Table 1 - List of Chemicals

Abbreviation	Chemical Name	Purpose	Purity
EO12	bis(hydroxyethyl)methylolammonium chloride	Cationic surfactant	----
EHAC	erucyl bis(2-hydroxyethyl) methyl ammonium chloride	Cationic surfactant	----
NaSal	sodium salicylate	Counterion	99.9%
<i>trans</i> -ACA	<i>trans</i> -azobenzene-4-carboxylic acid	Photosensitive Counterion	~ 99%
NaOH	sodium hydroxide	pH adjustments	----
HCl	Hydrochloric acid	pH adjustments	----
DI H <sub>2</sub> O	distilled water	Solvent	----

### B. Equipment

A list of equipment used during research experiments is listed in Table 2.

Table 2 - List of Equipment

Equipment	Brand	Purpose
Analytical Balance	Adventurer	Measuring mass of powders and samples
pH meter	Oakton	Measure pH
Ultraviolet Lamp	100 W Black-Ray® long wave	Irradiation of solution
Blue Light LED Lamp	LED Wholesales	Irradiation of solution
Homogenizer Motor	Janke & Kunkel	Shearing Solutions
ARES rheometer	TA Instruments	Rheology Measurements

### **C. Preparation of Solutions**

Solutions were prepared by measuring predetermined masses of each surfactant and counterion to make the desired concentrations in a predetermined volume of water. The surfactant was always measured into a beaker that would contain the final solution. This was done to eliminate the difficulty of transferring the thick waxy paste after measurement. DI water was taken from the faucet in Koffolt Labs Room 133. Volumes of water were measured using 100mL graduated cylinders. Once all of the components for the desired solution were obtained, the counterion was placed in the beaker containing the surfactant. The DI water was used to rinse any remaining counterion into the final solution. The desired solution was then placed on a stirring motor with magnetic stir bar and allowed to mix overnight. This ensured a complete homogenous mixture, even though the counterion takes a while to fully dissolve into solution. Typically, a desired pH level was set for each experiment. The pH was adjusted to the desired pH using drops of pre-diluted NaOH solution and HCl solution.

### **D. UV/BL Irradiation**

A Black-Ray® long wave UV lamp, centered at 365nm, and a blue LED lamp, centered at 450 nm, was used to irradiate samples. Irradiation of prepared solutions was done with either 10-15mL samples or 300-500mL samples. The smaller samples were used to determine concentrations of surfactant and counterion that had viscoelastic properties which could be alternated with UV and BL irradiation. Smaller samples were also used to investigate irradiation times. Larger samples were used to explore variables that affected the system including temperature, pH, time, and shear. During irradiation of solutions, all lights in the room were kept off. A cardboard box with a shielded hole on the top was used to block any ambient light still in the room while solutions were irradiated. Solutions were stirred slowly with a magnetic stir bar

during irradiation to ensure even exposure to the light. After irradiation, samples were placed in either 15mL vials or 500mL water bottles wrapped in aluminum foil to shield it from ambient light. It was assumed that any mass loss during irradiation was water. The mass of each sample was taken before and after irradiation and water was added to replace any that was lost to evaporation during irradiation. For larger samples that exceeded the capability of the analytical balance, volume before and after irradiation was used to determine the amount of water lost to evaporation.

### **E. Shearing Solutions**

Some experiments studied the effect of shear on the rheology of the system. Solutions were sheared with a Janke & Kunkel homogenizer at 2500RPM for 60 seconds. 300mL of solution was required to fully submerge the homogenizer. A 500mL plastic water bottle with the top cut off was used to hold the solution during shearing. Sheared solutions were irradiated with UV light; thus, shearing was done with the lights off in the laboratory. The solution was then transferred to a container wrapped in aluminum foil for rheology testing.

### **F. Temperature Control**

Temperatures of the solutions were maintained with an ice bath and a thermometer for low temperature experiments. The heating and chilling plate of the ARES rheometer cone and plate apparatus was also used to maintain the temperature of the solution during rheology measurements. For temperature experiments, it was assumed that the solution had reached the set temperature prior to the start of the measurements. It was determined that the small volume of solution placed on the rheometer took several seconds to reach the temperature of the plate.

## G. Rheology Measurements

An ARES rheometer (TA Instruments) with cone and plate geometry was used to measure first normal stress differences ( $N_1$ ) as a function of shear rate and temperature of the surfactant systems. The cone was 50 mm and had a cone angle of 0.02 rad.  $N_1$  measurements were taken for shear rates of 0-1000RPM. Measurements of  $N_1$  were corrected with equation 1 to account for inertial effects (Shi, et al., 2011).

$$N_1^{corrected} = N_1^{measured} + 0.15\rho\omega^2R^2 \quad (1)$$

Temperature of the solution was controlled with a chilling and heating plate. Typical temperatures ranged from 10 to 40°C. When the sample of interest was loaded onto the plate, all air bubbles were removed by blotting the sample with a paper towel. Any air bubbles in the sample would affect the measurements. Previous studies have indicated that for most DR solutions there is a correlation between large values of  $N_1$  at high shear rates and effective drag reduction (Qi, et al., 2009). Thus, solutions of interest for further testing in DR will have high shear stresses when DR active, and water-like rheology when DR inactive.

### III. Literature Review

#### A. Surfactants

Surfactants are amphipathic molecules which are characterized by a hydrophilic head and a hydrophobic tail (exaggerated in Figure 1). The hydrophobic tail is typically a long alkyl

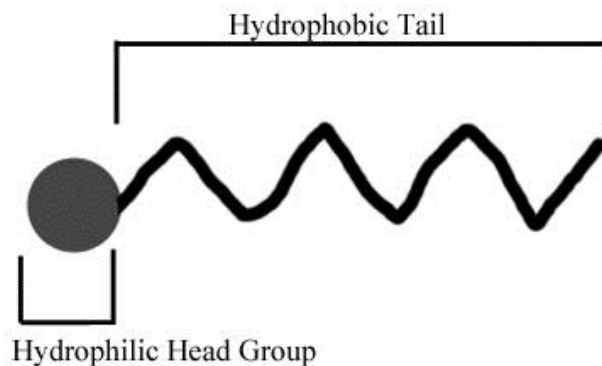


Figure 1 - Exaggerated surfactant molecule

group, and the hydrophilic head is typically an ionizable or polarizable group capable of forming hydrogen bridges (Zakin, Lu, & Bewersdorff, 1998). There are two main classes of surfactants: ionic and nonionic. Ionic surfactants contain the subclasses anionic and cationic. Nonionic surfactants consist of zwitterionic, semipolar, and single bond subclasses. When surfactants are placed in a polar environment, the hydrophobic group favors leaving the polar phase. This can lead to self-association in which micelle structures are formed. The hydrophobic groups move towards the inside of the structure and the hydrophilic groups orient themselves on the outside to shield the hydrophobic tails from the polar solvent. Anionic surfactants are not favorable for use in DHC because of their net negative charge. This negative charge can lead to undesired precipitation of the surfactant with cations such as calcium or magnesium, both of which are present in tap water (Zakin, Lu, & Bewersdorff, 1998). Nonionics do not carry charges, making them better candidates for use in DHC. Nonionics are limited by a narrow effective temperature range (Zakin, Lu, & Bewersdorff, 1998). Zwitterionics have both positive and negative charges

on the same molecule. Their negative charge makes them potentially unfavorable for DHC systems because of the possibility of instability in the presence of other anions or cations. Zwitterionics and nonionics, on the other hand, have the advantage of being rapidly biodegradable and there is a case in Herning, Denmark which reports successful DR with a mixed zwitterionic and nonionic system (Li, Yu, W, & Kawaguchi, 2012). Cationic surfactants are not significantly affected by magnesium or calcium cations. Cationic surfactants also are known to have a wide effective range of temperatures. These characteristics make cationic surfactants the most favorable for the study of drag reducing additives for use in DHC systems. A disadvantage of cationic surfactants is that they are not biodegradable, making their approval for use in DHC difficult. Cationic surfactants are considered toxic to the environment, so an additional separation and recovery system will be needed before the solution can be discharged to the environment (Li, Yu, W, & Kawaguchi, 2012). The use of cationic quaternary ammonium surfactants is not permitted in many countries because they have a strong germicidal effect as well as many unknown environmental effects (Li, Yu, W, & Kawaguchi, 2012).

## B. Micelles

Micelles can be spherical, rod-like (thread-like), lamellar, or vesicles (exaggerated structures shown in Figure 2). It is generally thought that thread-like micelles must be present in

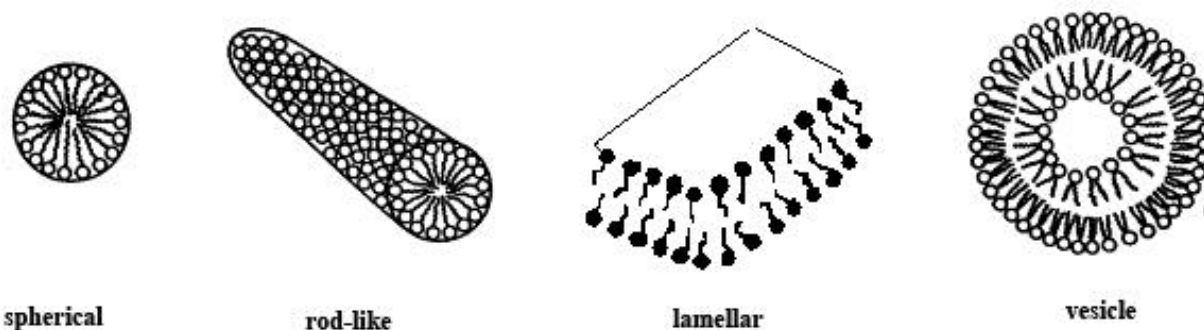


Figure 2 – Exaggerated Micelle Structures (Interfaces, Colloids, and Gels) (12Ma)

order to achieve drag reduction in pipes (Zakin, Lu, & Bewersdorff, 1998). Surfactants form micelles when the concentration of surfactant exceeds the critical micelle concentration (CMC). At concentrations above CMC, the surfactant monomers and micelles exist in a thermodynamic equilibrium in which micelles continuously break and exchange monomers (Michels & Waton, 2000) (Zakin, Lu, & Bewersdorff, 1998). The kraft point of a solution refers to the lowest temperature that micelles will form; below the kraft temperature, the surfactant is gel or crystal-like in solution (Zakin, Lu, & Bewersdorff, 1998). Above this temperature, the surfactant molecules will form micelles if the concentration of the surfactant exceeds CMC. Above CMC, micelles are thought to be spherical. CMCI represents a surfactant concentration for which rod-like micelles form. The presence of these rod or thread-like micelles has been investigated and confirmed through the use of cryo-transmission electron microscopy (cryo-TEM) (Zakin, Lu, & Bewersdorff, 1998). The size and structure of micelles has been observed to be a factor of many variables including: surfactant structure and concentration, counterion structure and concentration, solvent nature, temperature, pH, shear, and irradiation time of photosensitive counterions (Qi, PhD. Dissertation, 2002).

### **C. Photoisomerization**

Photosensitive isomers, photoisomers, are light responsive molecules. When exposed to the right wavelength of light, photoisomers switch between *trans* and *cis* or *cis* to *trans* configurations. The photoisomerization phenomenon is important to the study of alternating DR properties in DHC because it allows for unobstructed fluid flow through the pipe and hence no significant pressure loss. In the presence of appropriate counterions, cationic surfactants form threadlike micelles. A counterion which can be switched between *trans* and *cis* to disrupt the threadlike micelle structures is the desired method to achieve alternation between DR active and



DR inactive properties. For the DR active mode the counterion isomer will form a geometric fit which promotes threadlike micelles. For the DR inactive mode, the alternate isomer will disrupt the binding affinity of the counterion with the cationic surfactant and reduce the size of the micelles. As stated in the introduction, research by Dr. Zakin and co-workers had previously found a way to switch the counterion *trans*-OMCA to *cis* with UV light irradiation and achieve increased heat transfer. A method to switch between *trans* and *cis* isomers has been achieved for *trans*-azobenzene-4-carboxylic acid (*trans*-ACA) and *cis*-azobenzene-4-carboxylic acid (*cis*-ACA) in this study. The chemical structures of *trans* and *cis* ACA are shown in Figure 3 and Figure 4.

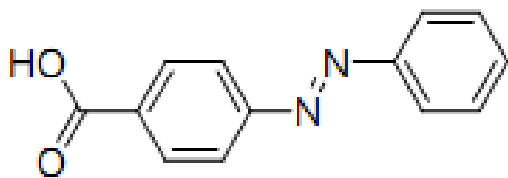


Figure 3 – Chemical Structure of *trans*-ACA

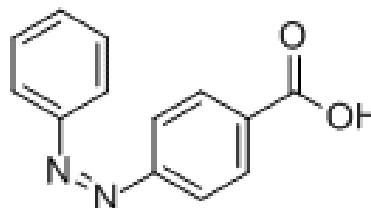


Figure 4 – Chemical Structure of *cis*-ACA

When *trans*-ACA is irradiated with UV light it switches to *cis*-ACA. Following UV irradiation, *cis*-ACA can be converted back to *trans*-ACA with blue light (BL) irradiation. A UV/Vis-spectra for a 0.05mM EO12 + 0.02mM *trans*-ACA solution that has been irradiated with UV and BL is shown in Figure 5. The peak absorbance for *trans*-ACA in the UV spectrum is 321nm and the peak absorbance for the visible light spectrum is 427nm (Figure 6). When exposed to UV light the peak at 321nm drops significantly (Figure 5). This indicates a loss of *trans*-ACA concentration due to photoisomerization to *cis*-ACA. When exposed to BL irradiation the peak on 321nm returns, indicating that the *cis*-ACA has successfully converted back to *trans*-ACA.

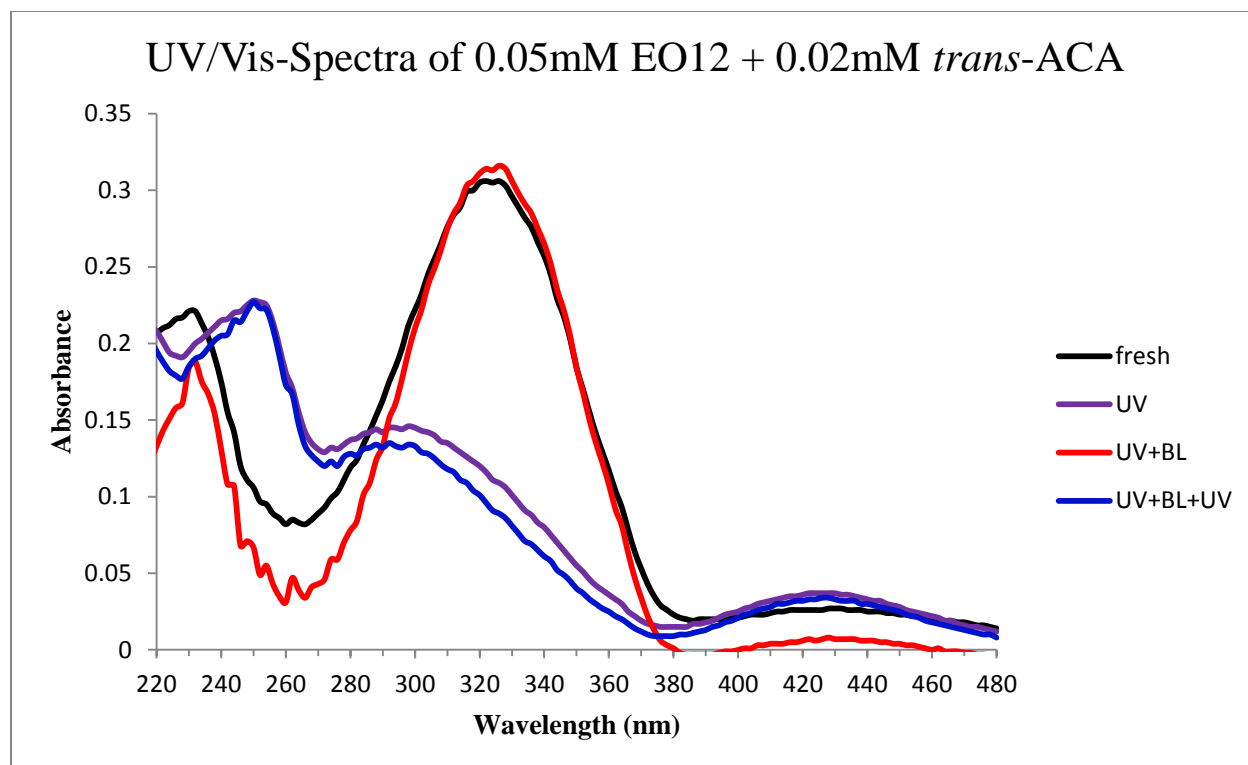


Figure 5 - UV/Vis-Spectra of t-ACA

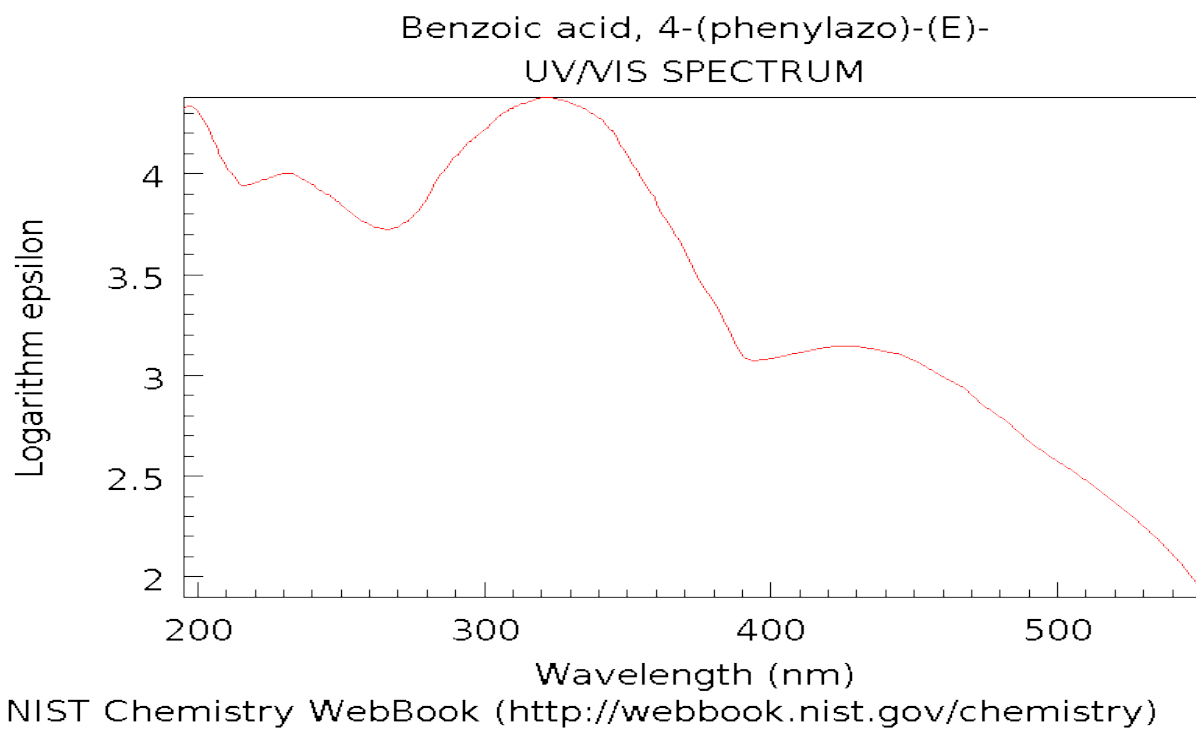


Figure 6 - UV/VIS Spectrum of *trans*-ACA

## D. Viscoelasticity

Viscoelastic fluids are fluids that do not exhibit constant values for the first normal stress ( $N_1$ ) or viscosity. These fluids are referred to as non-Newtonian. When a stress is applied to a viscoelastic fluid there will be an elastic response (recoil) to return to its original state. For example, if a viscoelastic solution is swirled in a vial a reversal in flow can be noticed after the force is removed. Viscoelastic fluids are generally linked to solutions with good drag reduction. Savins and coworkers (1967) recognized that surfactant systems with viscoelastic properties have drag reducing capabilities. They concluded that DR increases with increasing flow rate up to a critical shear stress. After the critical shear stress is reached, increasing the flow rate caused the DR activity to decrease linearly until it reached the turbulence behavior of the surfactant free system. Rheology can be used to measure  $N_1$  and viscosity of solutions to determine if a solution is viscoelastic. Hoffmann and Rehage (1987) concluded that cationic surfactants with cetylpyridium, trimethyl ammonium, or trihydroxy ammonium head groups (Figure 7) form the

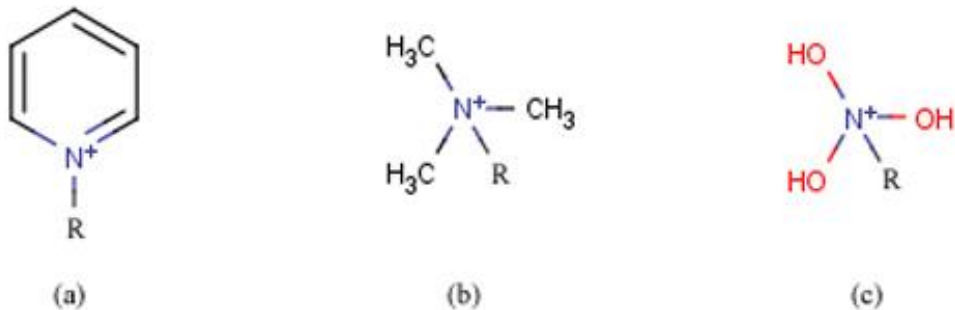


Figure 7 - Surfactant head groups for effective DR (a) cetylpyridium (b) trimethyl ammonium (c) trihydroxy ammonium

most viscoelastic solutions when mixed with the proper counterion. Work by Dr. Zakin and coworkers has determined that at high shear rates, high values of  $N_1$  are correlated to drag reducing fluids (Shi, et al., 2011).

Though it is generally thought that drag reducing fluids are viscoelastic, work done by Lu et. al. (1997) discovered an exceptional system that was drag reducing, but not viscoelastic. A system of 5.0mM Arquad S-50/12.5 mM NaSal was found to be highly drag reducing, but showed constant values of  $N_1$ . Examination of the system with cryo-TEM found that the solution contained a network of thread-like micelles, supporting the belief that this micelle structure is still important to achieve drag reduction. That solution had high extensional viscosity to shear viscosity ratios leading to the conclusion that high extensional viscosity plays an important role in a solutions drag reducing ability but drag reducing fluids aren't always viscoelastic.

## **E. Drag Reduction**

Quaternary ammonium (cationic) surfactants are considered to be the best for drag reduction in DHC because of their low concentration requirement to be excellent drag reducers, their stability in water containing metal cations, and their broad availability. They are also believed to be stable drag reducers that do not show mechanical degradation (Zakin, Lu, & Bewersdorff, 1998). Work by Chou (1991) found that the Ethoquad T/13-50 / NaSal system has stability issues. The system lost drag reducing ability after several days, whereas a previous experiment for the same system ran 11 days without losing drag reduction. A precise conclusion could not be drawn on the loss of drag reduction, but it was hypothesized that the surfactant or NaSal was absorbed by debris in the system or by the walls of the pipes. Research by Rose and Chou et. al. (1989) showed that surfactants of ammonium salts containing bis-hydroxyethyl methyl are more hydrophilic than trimethyl and can provide DR at temperatures down to 2°C.

This research explores two cationic quaternary ammonium surfactants: oleyl bis(hydroxyethyl)methylammonium chloride (EO12) and erucyl bis(2-hydroxyethyl)methylammonium chloride (EHAC). These surfactants are shown in Figure 8 and

Figure 9 below. Their main difference is that EO12 has mainly an 18 carbon alkyl chain while EHAC has mainly a 22 carbon alkyl chain. Research by Chou (1991) found that a system with EO12/NaSal had the best drag reduction at the 1:1.5 ratio at 2°C.

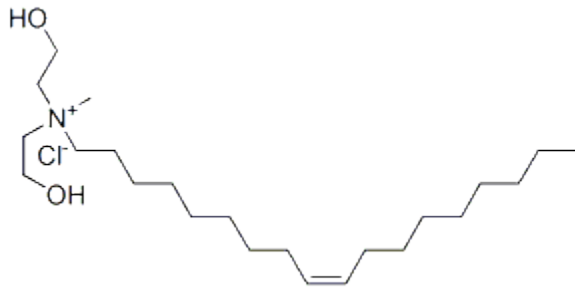


Figure 8 - Chemical Structure of EO12 (18448-65-2)

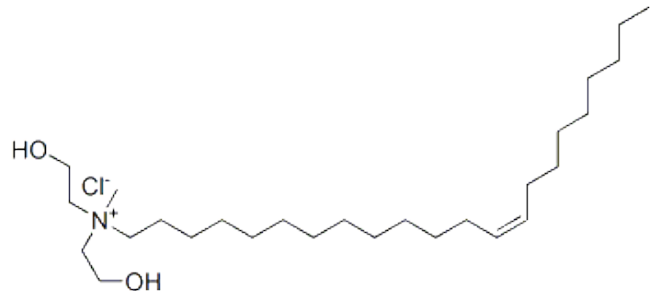


Figure 9 - Chemical structure of EHAC (120086-58-0)

The positive nitrogen head of the surfactant causes repulsion which reduces micelle formation. A negative counterion is necessary to form threadlike micelles because it disperses the positive charges thus allowing for larger growth. Since threadlike micelles are necessary for effective drag reduction, these counterions are necessary for effective drag reduction. The addition of these counterions allows the surfactant concentration for effective DR to be less than 1% (Zakin, Lu, & Bewersdorff, 1998). Research by Wu et. al. (2011) showed that both aromatic counterions as well as salicylate compounds are effective for promoting threadlike micelle formation.

## F. Application in DHC

Several in-flow applications to regain heat transfer temporarily such as fluted-tube heat exchangers, wire meshes, static mixers, metal grids, helical pipes, low-profile vortex generators, and impinging jets have been studied (Shi, et al., 2011). All of these obstruct the flow of fluid and ultimately result in higher energy costs (Shi, et al., 2011). Photosensitive solutions are an

important application for DHC because light can be supplied to the fluid without obstructing the flow in the pipe. An effective surfactant and photosensitive counterion system would reduce the pumping requirements needed in DHC as well as improve the heat transfer in heat exchangers. This in turn will lower pumping and utility costs to operate the facility.

Several successful uses of surfactant additives as drag reducers in DHC have been reported. In the 5.6km hydronic heating system in Herning, Denmark a mixture of zwitterionics and nonionics reduces the power consumption by 4200 MWh per year as well as CO<sub>2</sub> emissions by 3000 t per year (Li, Yu, W, & Kawaguchi, 2012). This mixture of surfactants receives recognition for its low toxicity and high biodegradability (Li, Yu, W, & Kawaguchi, 2012). A central air conditioning system in Kobe, Japan uses a system of EO12/NaSal in combination with LSP-01, a corrosion inhibitor developed by the LSP Cooperation Company, which results in an annual energy savings of 54% (Li, Yu, W, & Kawaguchi, 2012). The test results indicate that LSP-01 is very effective at inhibiting rust formation, but long term DR and corrosion inhibiting effects are unknown (Li, Yu, W, & Kawaguchi, 2012).

## IV. Results and Discussion

### A. EO12/NaSal/*trans*-ACA System

In previous efforts from the spring and summer of 2011, the ability to turn the DR properties of EO12/*trans*-ACA systems on and off was demonstrated; however, it was determined that the irradiation times needed to convert the solution between these two states was too long and the results indicated the system performed better at higher temperatures. From previous studies, it is known that high values for  $N_1$  at high shear rates correspond to fluids with good DR properties. A system of EO12/*trans*-ACA forms a viscoelastic solution. When this solution is irradiated with UV light (*trans*-ACA becomes *cis*-ACA), it becomes non-viscoelastic. The geometric fit of the *cis* counterion is not favorable for promoting threadlike micelles in this system. Figure 10 shows measurements of  $N_1$  at 15°C for samples that were irradiated 30 minutes. At 15°C, the fluid retains some viscoelasticity at high shear rates after 30 minutes of UV irradiation. Comparing  $N_1$  measurements of the fresh solution to UV+BL irradiated solution; viscoelasticity is regained but is reduced. This suggests that for repeated UV and BL irradiation the solution will eventually lose its DR properties. For each trial the volume of fluid irradiated is reduced, and the time to irradiate the solution remained the same. The amount of irradiation time increases with volume. Because the volume decreases for each trial and the irradiation time remains the same, this demonstrates that for multiple radiations, longer irradiation times will be needed. Figure 11 shows the values of  $N_1$  at 25°C for the same solution with the same irradiation times and volumes in Figure 10. Better repeatability in switching on and off DR is achieved at the higher temperature. However, the time required for irradiation is long (30 minutes). The results from this experiment indicated that the irradiation times are too long for the system to be

practical in DHC, and at low temperatures the drag reducing properties start to degrade after multiple irradiations. Ideally the change in DR properties should be a few seconds.

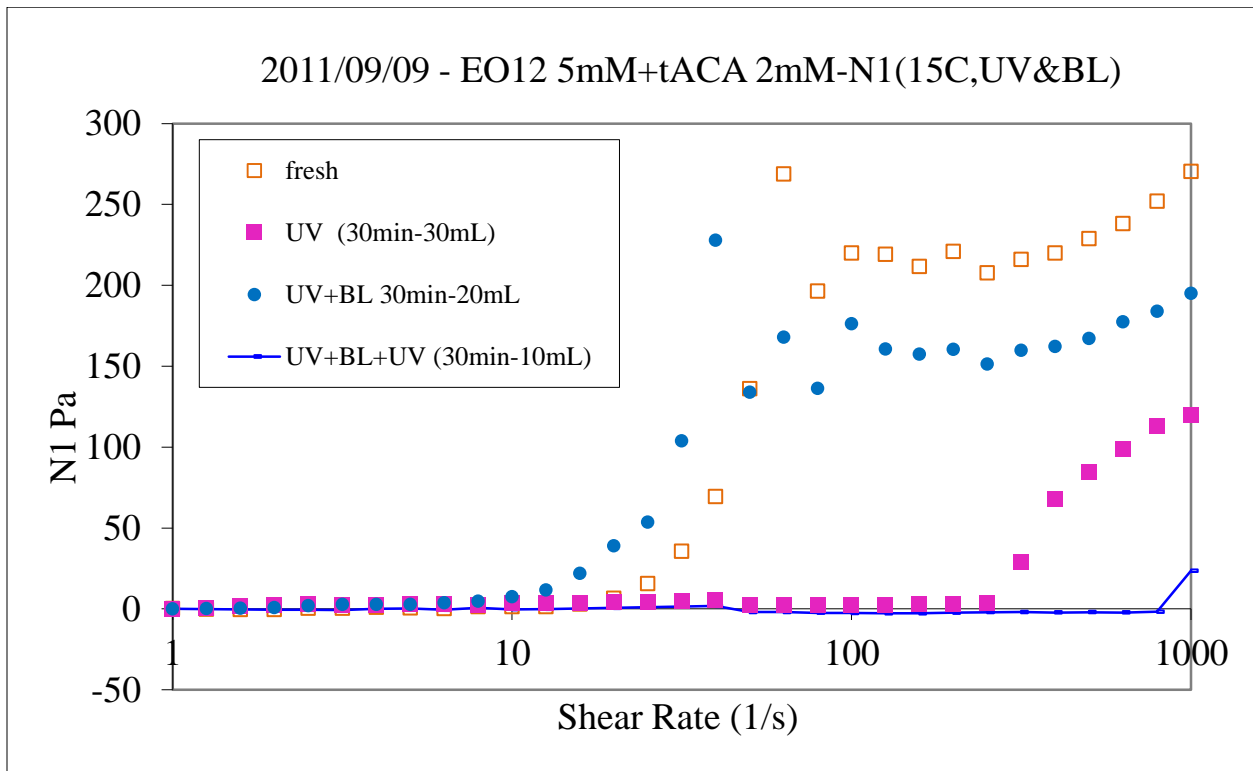


Figure 10 - Rheology of Ultraviolet and Blue Light Irradiated 5mM EO12/2mM trans-ACA at 15C



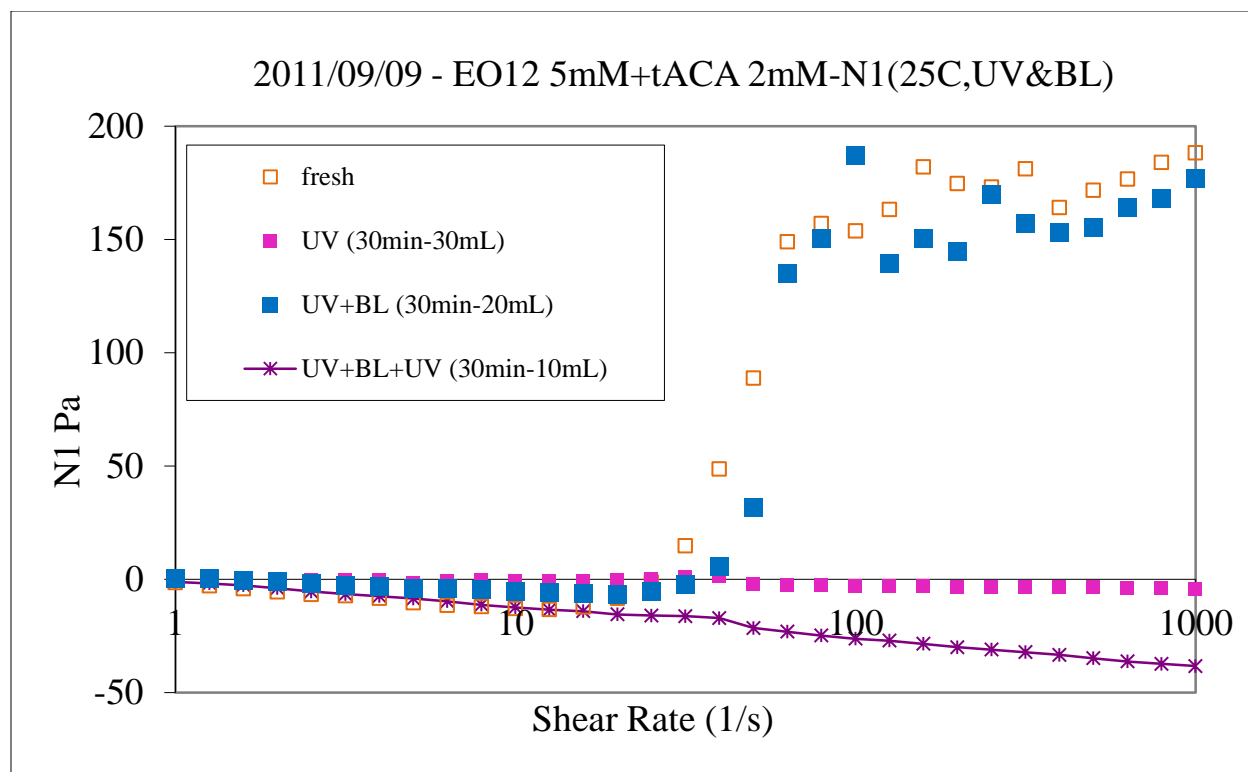


Figure 11 - Rheology of Ultraviolet and Blue Light Irradiated 5mM EO12 / 2mM *trans*-ACA at 25C

The purpose of this thesis investigation is to find a solution of EO12, and *trans*-ACA which can achieve alternating DR and non-DR properties with low concentrations of *trans*-ACA. The target time for complete irradiation of the samples is one minute or less. Lower concentrations of *trans*-ACA will mean less irradiation time should be needed to convert all of the *trans*-ACA to *cis*-ACA. To achieve this, the counterion sodium salicylate (NaSal) has been introduced to the system. Solutions of EO12 and NaSal can form viscoelastic solutions at high pH values. The aim of these experiments is to find a critical concentration of NaSal that is not viscoelastic in a solution of EO12. Next a critical concentration of *trans*-ACA to make the solution viscoelastic must be found. The goal is to have NaSal help contribute to the viscoelasticity of the solution so that only low concentrations of *trans*-ACA are needed. The

solution must be DR inactive when *trans*-ACA is irradiated to *cis*-ACA. Thus, finding a solution of NaSal and EO12 that is non-viscoelastic is important.

The first step to study this new system of EO12, NaSal, and *trans*-ACA was to determine the critical concentration of NaSal for a 5.0mM solution of EO12. This was done by preparing 10mL solutions of 5.0mM EO12, and varying the concentration of NaSal at 10.0mM, 5.0mM, 2.5mM, and 1.25mM. Because viscoelastic materials have an elastic response to an applied stress, the samples were inspected visually for viscoelasticity by swirling them in 15mL vials and checking for recoil. Viscoelastic solutions will reverse the direction they were spinning when swirled after swirling ceases. This is easily identified when air bubbles are present in the solution. The observations using this method indicated that 5.0mM EO12/2.5mM NaSal was viscoelastic, while 5.0mM EO12/1.25mM NaSal was not. The midpoint between these two samples, 5.0mM EO12/ 1.875mM NaSal was prepared and observed for viscoelasticity. This was repeated until a 1.328mM NaSal solution no longer showed an elastic response when swirled, while the previous sample of 1.406mM NaSal did. Thus, the critical concentration of NaSal was determined to be 1.328mM for 5.0mM EO12.

10mL solutions of 5.0mM EO12/1.328mM NaSal were prepared with concentrations of *trans*-ACA at 1.0mM, 0.5mM, 0.25mM, and 0.1mM. pH was adjusted so that it was between 8 and 10 using sodium hydroxide (NaOH). The samples were irradiated with UV light for 2, 4, and 10 minutes. The samples were examined visually for viscoelasticity. The samples all showed signs of viscoelasticity after UV irradiation and it was determined that this system was not satisfactory.

Next a study for a solution of 10.0mM EO12 was initiated. Using the same visual method described previously, the critical concentration for NaSal was found to be 2.75mM,

approximately double the concentration required for the 5.0mM solution of EO12; thus stoichiometric amounts of EO12 and NaSal in this system are required for similar viscoelasticity. Next 10mL solutions of 10.0mM EO12/2.75mM NaSal were prepared with *trans*-ACA concentrations at 0.5mM, 0.1 mM, 0.05mM, and 0.01mM. pH was adjusted so that it was between 8 and 10 using NaOH. The samples were irradiated with UV light for 2, 4, and 10minutes. There was no significant change in viscosity observed when visually comparing the irradiated samples to the non-irradiated samples by swirling them. A 10.0mM EO12/2.75mM NaSal/2.0mM *trans*-ACA solution was prepared and irradiated for 1, 5, and 10 minutes. The values for  $N_1$  were then measured and the results are shown in Figure 12. The samples appeared to have no significant difference in  $N_1$  for all irradiation times. Additionally, 10.0mM EO12/2.75mM NaSal was prepared with no *trans*-ACA, and the measured  $N_1$  values appeared similar to a sample with *trans*-ACA. This indicates a 10.0mM EO12/2.75mM NaSal solution is viscoelastic regardless of whether the *trans*-ACA is present. From these results it was concluded that determining the critical concentrations for viscoelasticity visually is not an accurate method, and all future determinations should be done using the rheometer.

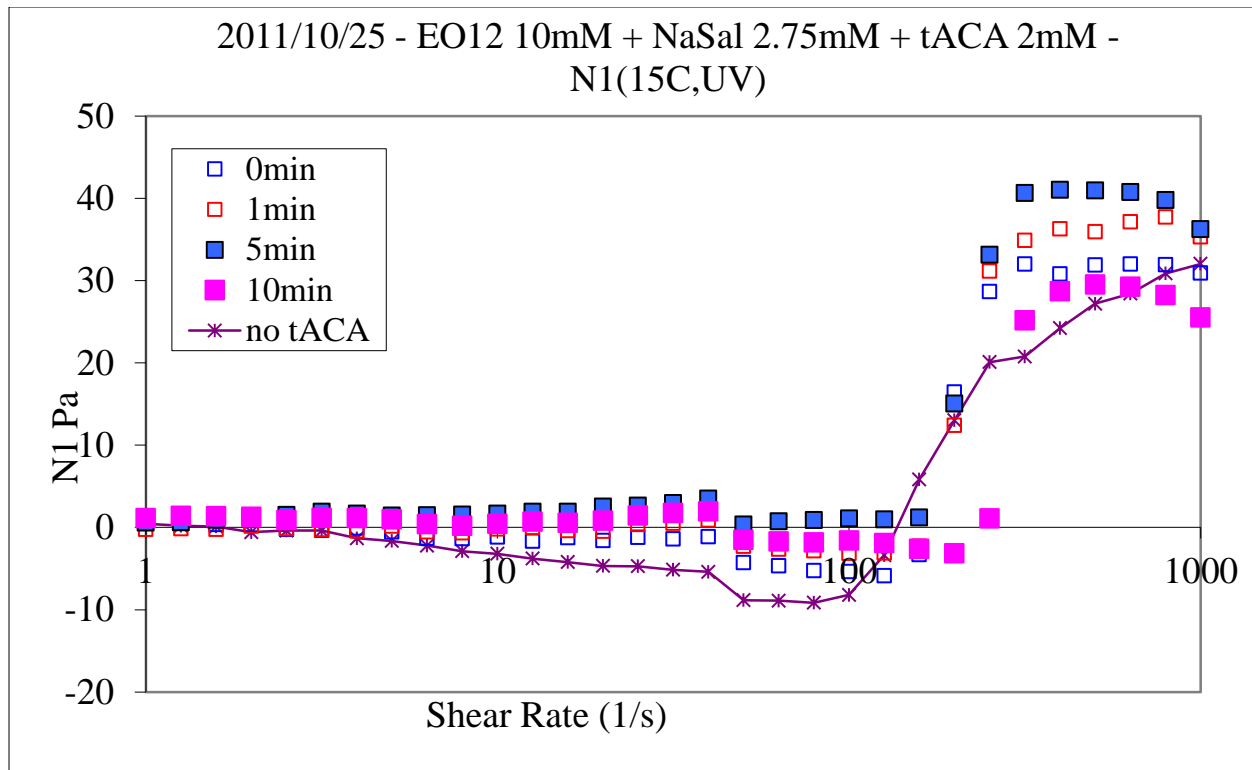


Figure 12 – trans-ACA shows little effect on  $N_1$  values for 10mM EO12 / 2.75mM NaSal

Starting over with an investigation of the critical concentration of NaSal, 10mL solutions of 10.0mM EO12 and NaSal, varied from 2.0mM to 2.5mM, were created and measured with the rheometer. The results from this test are available in Figure 13. The desired critical solution is one that measures close to constant zero  $N_1$  for all shear rates. The results in Figure 13 indicated that the critical concentration of NaSal was 2.25mM for 10.0mM EO12.

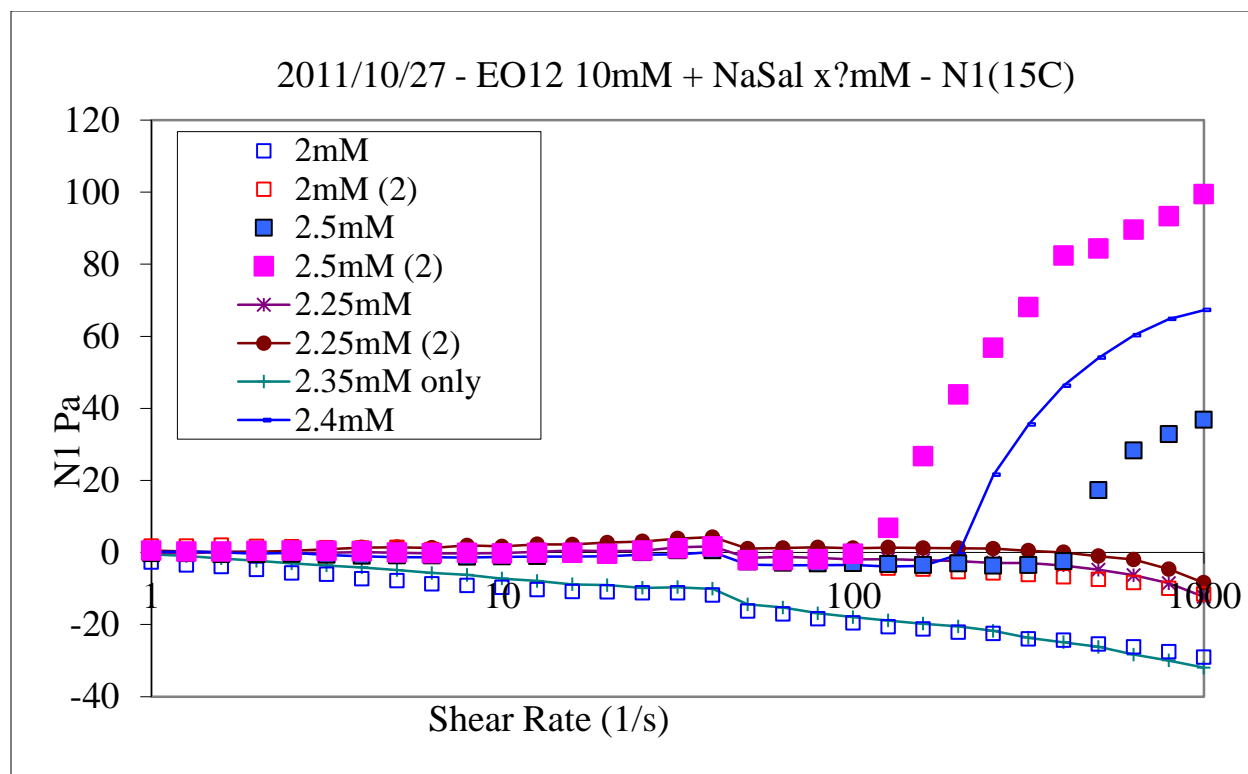


Figure 13 – Determination of Critical Concentration NaSal for 0  $N_1$  for 10.0mM EO12

Next the critical concentration of *trans*-ACA required to make 10.0mM EO12/2.25mM NaSal viscoelastic was found using the rheometer. This was done by preparing 10mL samples of 10mM EO12/2.25mM NaSal with concentrations of *trans*-ACA between 0.1 and 1.0 mM. Figure 14 shows the measured  $N_1$  values for this test. This time, the desired solution should be just barely viscoelastic. The test results indicated that the critical concentration of *trans*-ACA was 0.316mM for 10.0mM EO12/2.25mM NaSal. A 100 mL solution of 10.0mM EO12/2.25mM NaSal/0.316mM *trans*-ACA was prepared for irradiation experiments to be performed the following week.

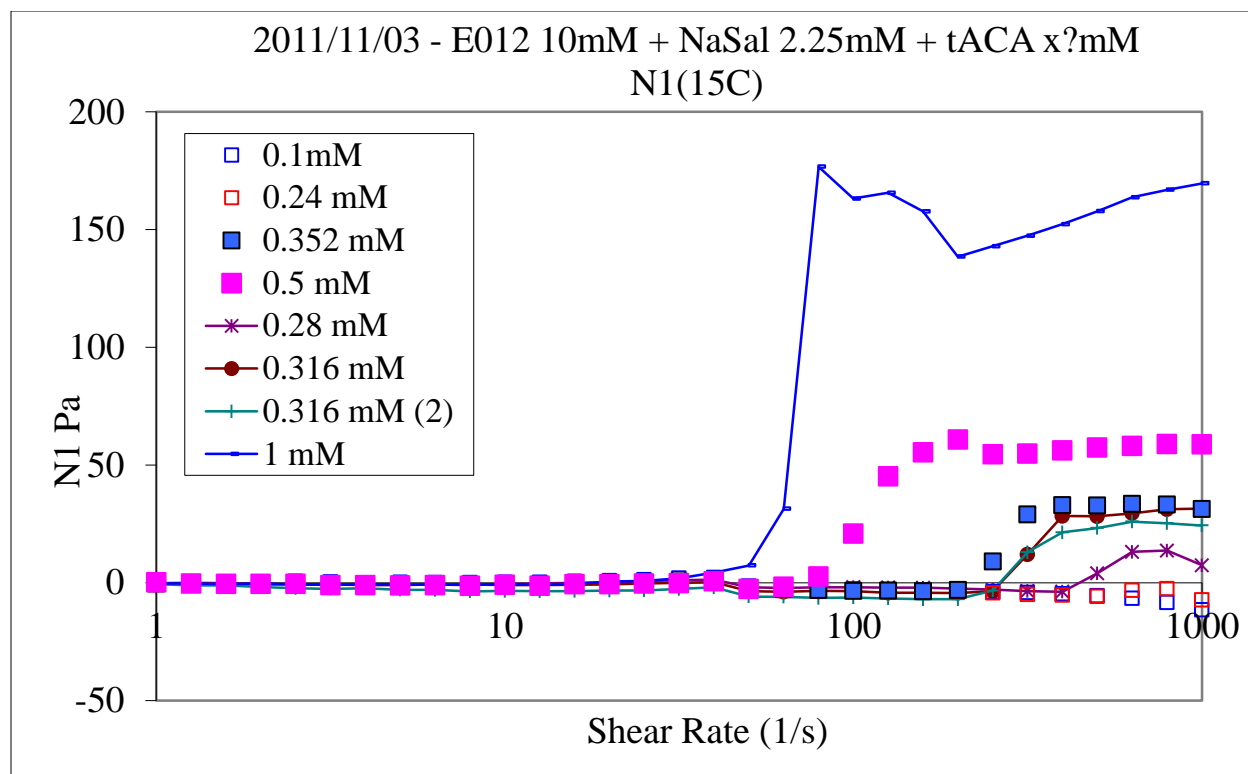


Figure 14 -- Determination of Critical *trans*-ACA Concentration for 10.0mM EO12 / 2.25mM NaSal

The following week, irradiation tests were to be performed for the solution of 10.0mM EO12/2.25mM NaSal/0.316mM *trans*-ACA. However, the rheometer measurements showed that, after sitting one week, the solution was no longer viscoelastic. The pH of the solution had dropped to 6.5, and was adjusted to 9.2 with drops of NaOH. The system remained non-viscoelastic, as determined by the values of  $N_1$ , shown in Figure 15.  $N_1$  became negative at high shear rates. It was hypothesized that at the critical concentration, some of the *trans*-ACA naturally converted to *cis*-ACA over the seven day span, eliminating the viscoelasticity. It is also possible that the system of EO12 and NaSal naturally degrades with time. The work mentioned by Chou (1991) found that a system with an ethoquad and NaSal lost its DR properties after

several days. These findings indicate that systems with critical concentrations of NaSal and *trans*-ACA are not stable over extended periods.

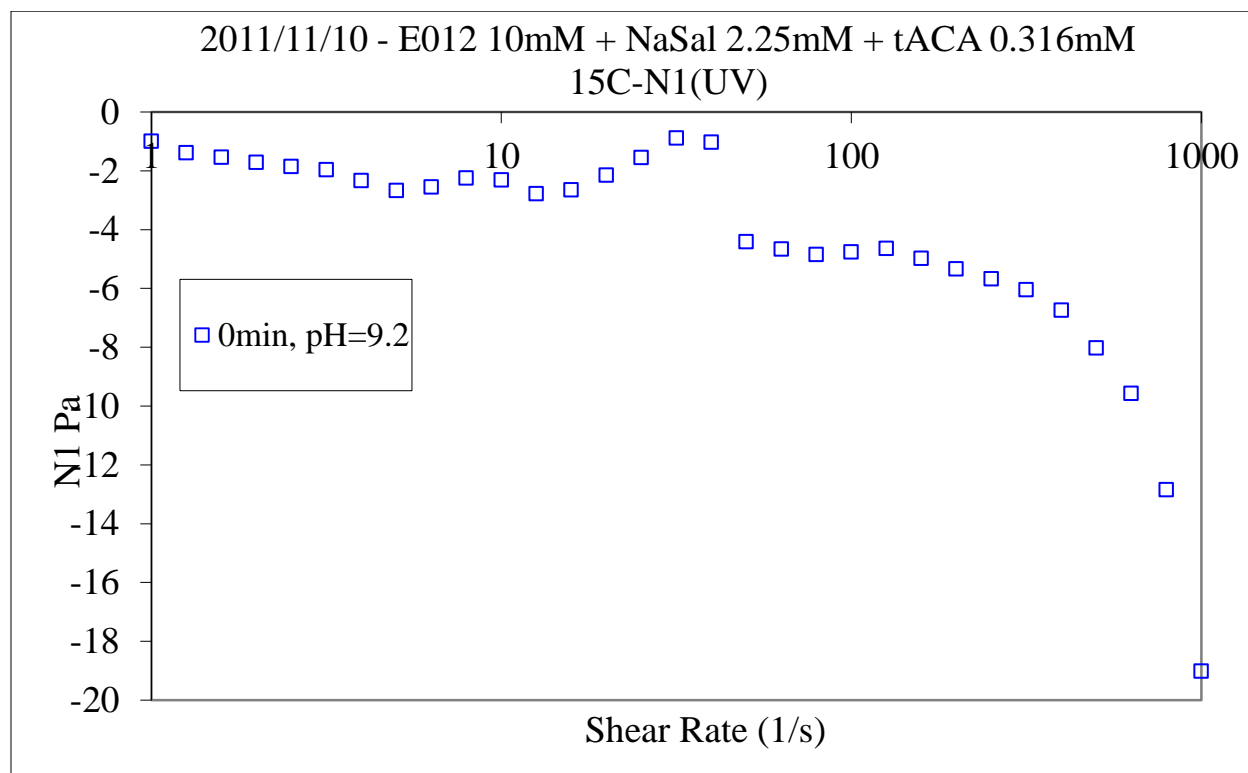


Figure 15 - 10.0mM EO12 / 2.25mM NaSal / 0.316mM *trans*-ACA No UV Irradiation

For the next test the concentration of NaSal was raised to 2.35mM and another investigation of the critical *trans*-ACA concentration was carried out. 10mL samples of 10.0mM EO12, 2.35mM NaSal, and *t*-ACA at 0, 0.2, 0.4, 0.6, 0.8, and 1.0 mM were created and  $N_1$  was measured with the rheometer. The results from this test, shown in Figure 16, indicated that the critical concentration required for viscoelasticity at this NaSal concentration is 0.4 mM *trans*-ACA.

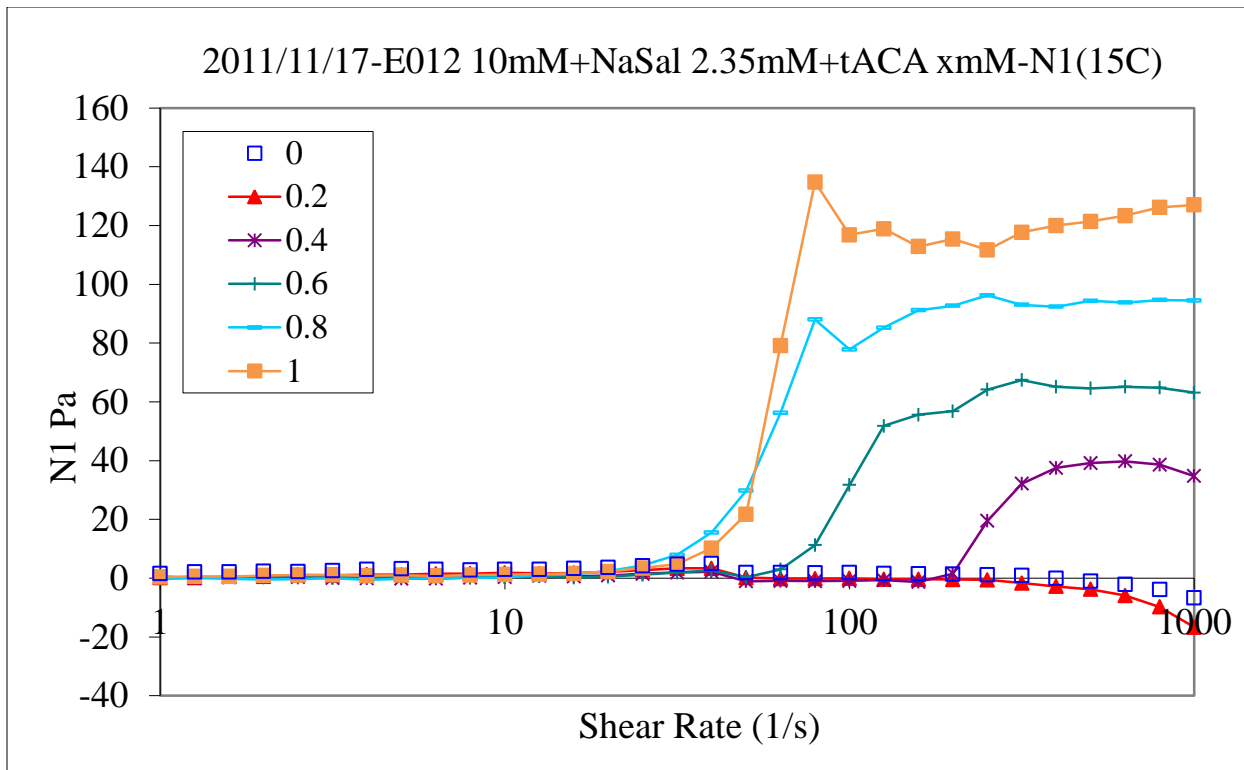


Figure 16 - Determination of Critical *trans*-ACA concentration for 10.0mM EO12 / 2.35mM NaSal

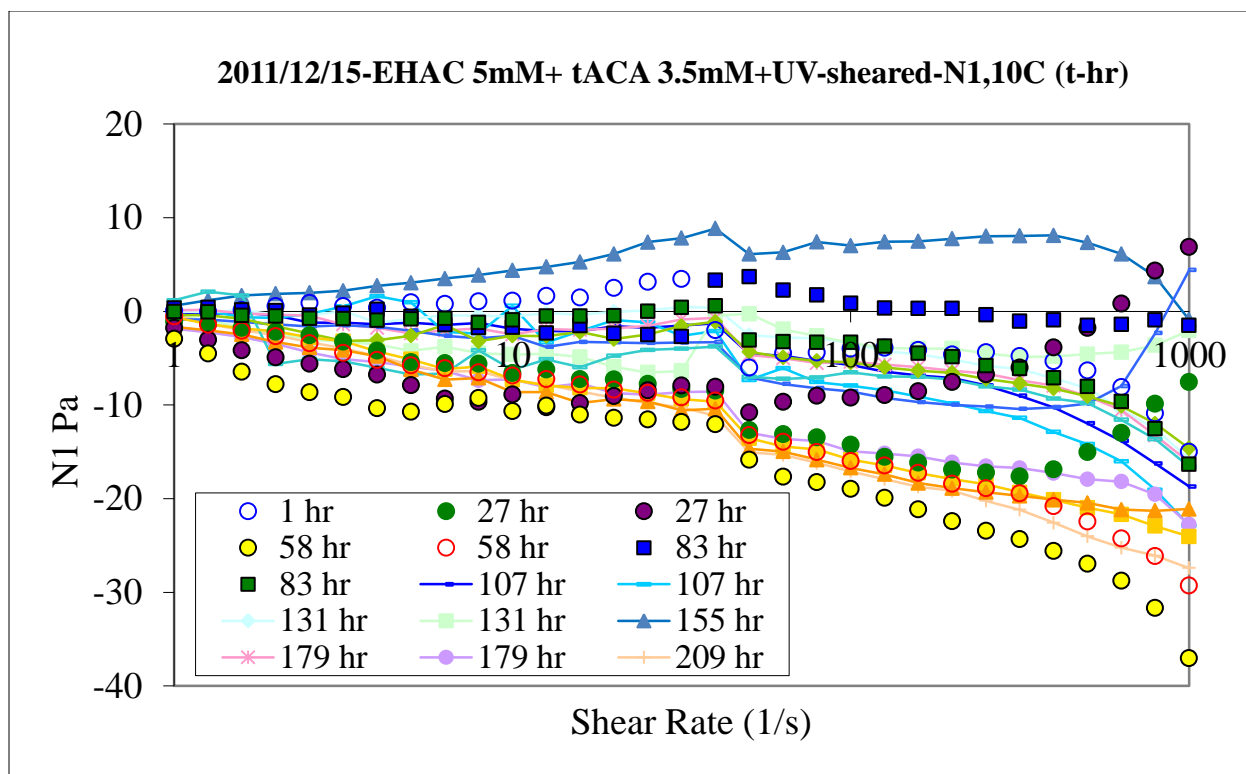
A solution of 10mM EO12/2.35mM NaSal/0.4mM *trans*-ACA is recommended for DR testing. It is expected that this system will lose DR properties after an extended period of time.



## B. EHAC/ *trans*-ACA System

The surfactant erucyl bis(2-hydroxyethyl) methyl ammonium chloride (EHAC) and the counter ion *trans*-azobenzene-4-carboxylic acid (*trans*-ACA) also exhibit the desired properties of a DR alternating system. The counterion *trans*-ACA can be converted to *cis*-azobenzene-4-carboxylic acid (*cis*-ACA) using UV irradiation and then back to *t*-ACA using BL. EHAC and the *cis* isomer of azobenzene-4-carboxylic acid are observed to create a viscoelastic solution. EHAC and *trans*-ACA make a non-viscoelastic solution; however, UV irradiation causes the solution to become viscoelastic. Thus, the configuration of EHAC and *cis*-ACA has the required geometric fit to form drag reducing micelles. Recall that for the previous system of EO12/NaSal, a viscoelastic solution was present with *trans*-ACA. For EHAC, the *cis*-ACA counterion is favored for viscoelasticity. No explanation can be drawn from this research to explain why the opposite configurations of the counterion favor viscoelasticity for EO12 and EHAC. Both surfactants are very similar and additional research will need to be done to explain this phenomenon.

On 12/15/2011, an experiment carried out by Haifeng Shi found that when a solution of 5mM EHAC + 3.5mM *trans*-ACA is sheared at 10°C, it becomes non-viscoelastic. The solution stayed non-viscoelastic for 304 hours as shown in Figure 17. Negative values for  $N_1$  appear in this graph because they have not been adjusted; all values of  $N_1$  should be positive. After shear, the solution regains viscoelasticity when it is heated. Later experiments performed in this thesis study show the effect of shear and temperature on this system of EHAC and *trans*-ACA.



**Figure 17 - Effect of time in hours on UV irradiated and sheared 5mM EHAC/3.5mM trans-ACA at 10C**

On 01/09/2012, a 500mL solution of 5mM EHAC + 3.5mM *trans*-ACA was prepared. On 01/13/2012, this sample was irradiated with UV light for 240 minutes in order to convert the *t*-ACA to *cis*-ACA. The solution was cooled to 15°C. After UV irradiation, the solution was not viscoelastic. The pH was adjusted to 11+ to make the solution viscoelastic. When the solution was sheared with a homogenizer, it didn't appear to lose viscoelasticity. Measurements of  $N_1$  with the ARES rheometer before and after shear (Figure 18) confirmed that  $N_1$  of the solution was not affected by shear. It was hypothesized that at pH of 11+ the solution was viscoelastic despite the effect of shear.

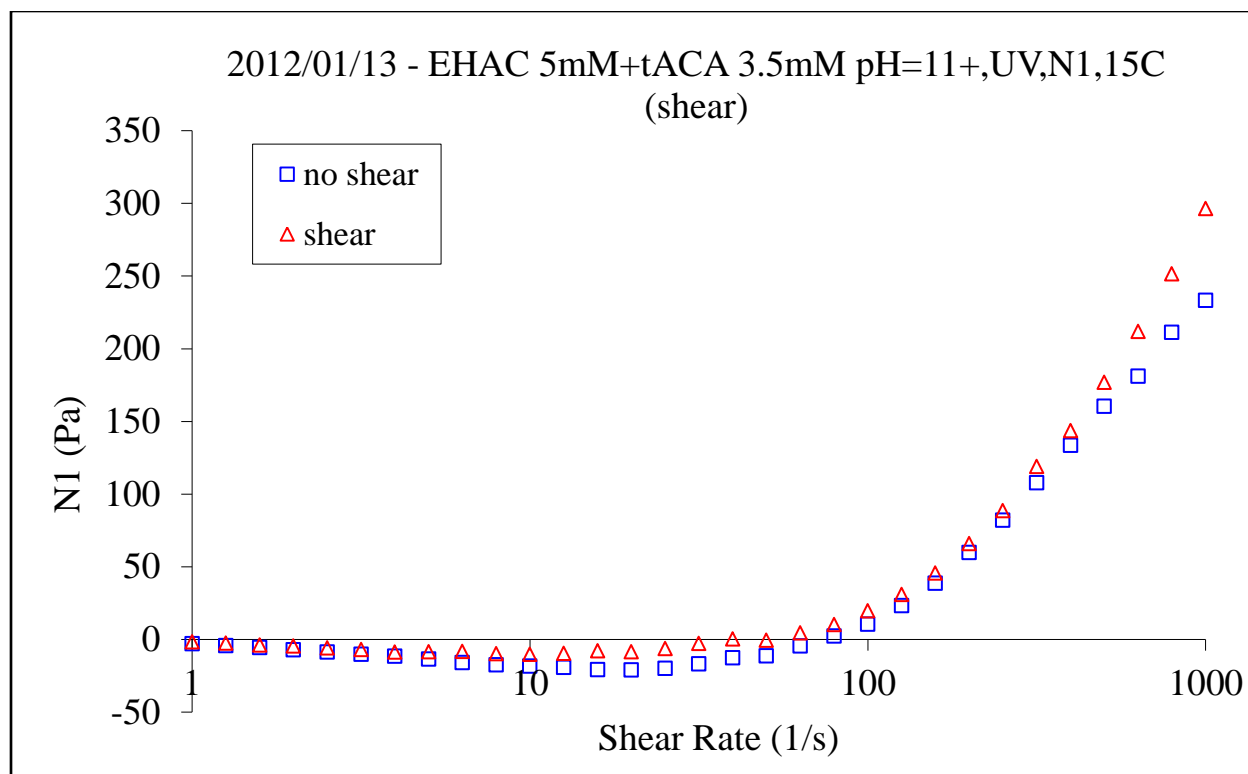


Figure 18 -Effect of shear on 5mM EHAC/3.5mM *trans*-ACA, pH=11+

On 01/23/2012, 10.0mL of 10mM EHAC + 3.5mM *trans*-ACA was adjusted to a pH of 9.0 and irradiated with UV light for 30 minutes. After UV irradiation the solution did not appear viscoelastic when swirled. The pH was adjusted to 11 and the solution regained viscoelasticity as shown by its recoil. When this solution was sheared it did not lose viscoelasticity. Next a 10mL solution of 5mM EHAC + 3.5mM *trans*-ACA was adjusted to a pH of 10.7. The solution appeared viscoelastic when swirled. This solution was then cooled to 10°C and sheared with a vortex mixer. After shear, the solution appeared non-viscoelastic when swirled. This supports the hypothesis that at pH of 10.7+, the EHAC solution's viscoelasticity is independent of the shearing effect.

On 01/25/2012, 250mL of 5mM EHAC + 3.5mM *trans*-ACA with a pH of 10.7 was irradiated with UV for 200 minutes. After irradiation the pH of the solution was 8.89. The

solution was cooled to 10°C. A 10mL sample was drawn and the remaining solution was sheared for 60 seconds. Measurements of  $N_1$  (Figure 19) were taken for the no shear sample at 10°C, and after shear at 10°C, 20°C, 30°C, and 40°C. It should be noted that the plots of  $N_1$  appear jagged. This is likely a result of the neglect to zero the rheometer fixture prior to the measurements. When  $N_1$  for the sheared solution was measured at 10°C, the solution was water-like and non-viscoelastic, the expected result. For each 10°C increase in temperature the solution became more viscoelastic. At 40°C, the sample had similar  $N_1$  behavior as the 10°C sample before shear. This matched the previously observed phenomenon. The data collected indicates that with increase in temperature, viscoelasticity is restored. The solution was frozen and saved for the following week to be tested for repeatability.

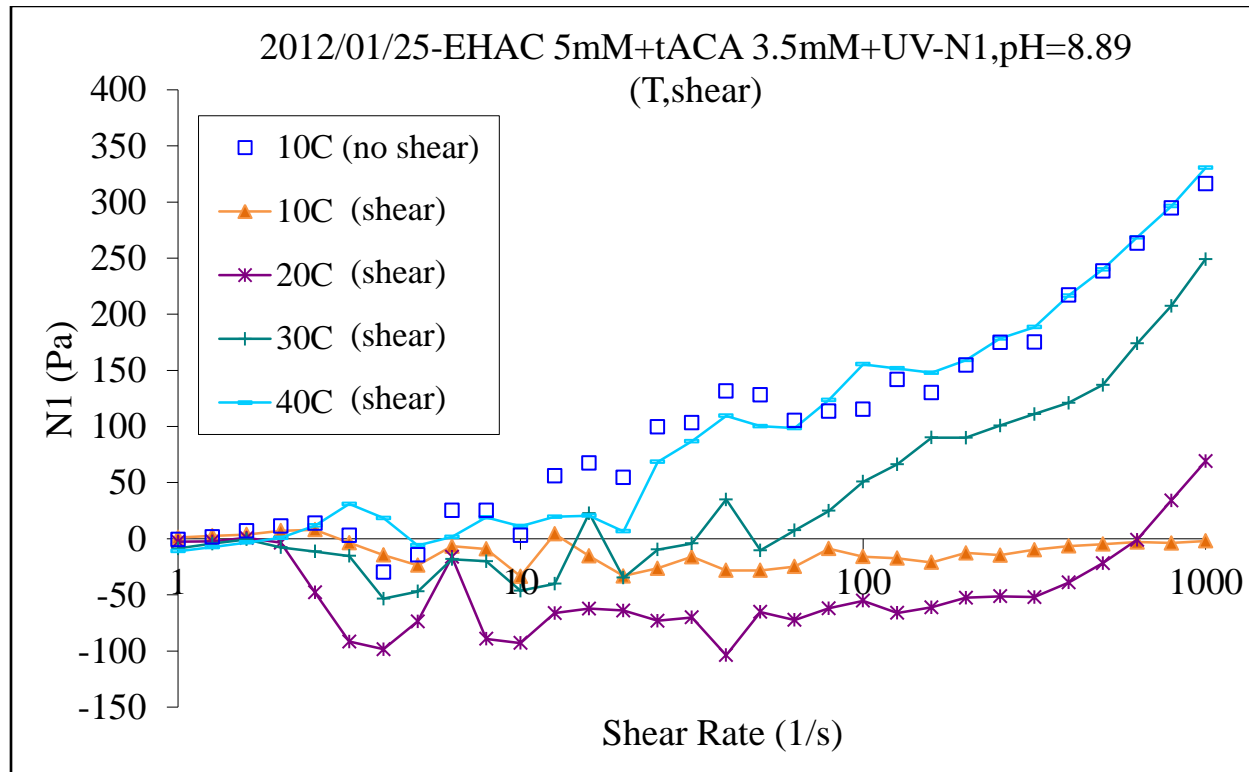


Figure 19 - Effect of temperature on 5mM EHAC/3.5mM trans-ACA after UV irradiation and shear

On 02/03/2012, the 5mM EHAC + 3.5mM *trans*-ACA solution was thawed and appeared to be viscoelastic. The pH was 8.47. The solution was sheared for 60 seconds and appeared non-viscoelastic at 10°C. Measurements of  $N_1$  (Figure 20) were taken with the ARES rheometer for 10°C no shear and 10°C, 20°C, 30°C, 40°C, 10°C three hours after shear. For this experiment the solution was maintained at 10°C with an ice bath during the rheometer measurements. The results for 10°C, 20°C, 30°C, and 40°C after shear showed similar increase in  $N_1$  with increase in temperature. However, an unexpected result was obtained when the sheared sample maintained at 10°C on ice for three hours measured nearly identical  $N_1$  as before the sample was sheared. This conflicts with the results from the 12/15/2012 experiments (Figure 17) in which the solution held at 10°C for over 12 days did not regain  $N_1$ . This suggests that for a 5mM EHAC + 3.5mM *trans*-ACA solution at pH in the range of 8-9, the fluid not only regains viscoelasticity with increase in temperature, but also with increase in time. This is likely due to the destruction of the micelles after shear and the micelles reassembling their geometric fit over time. It was hypothesized that the solution in the pH range 8-9 would regain viscoelasticity with time, and the rate at which the micelles regain would increase with increase in temperature.

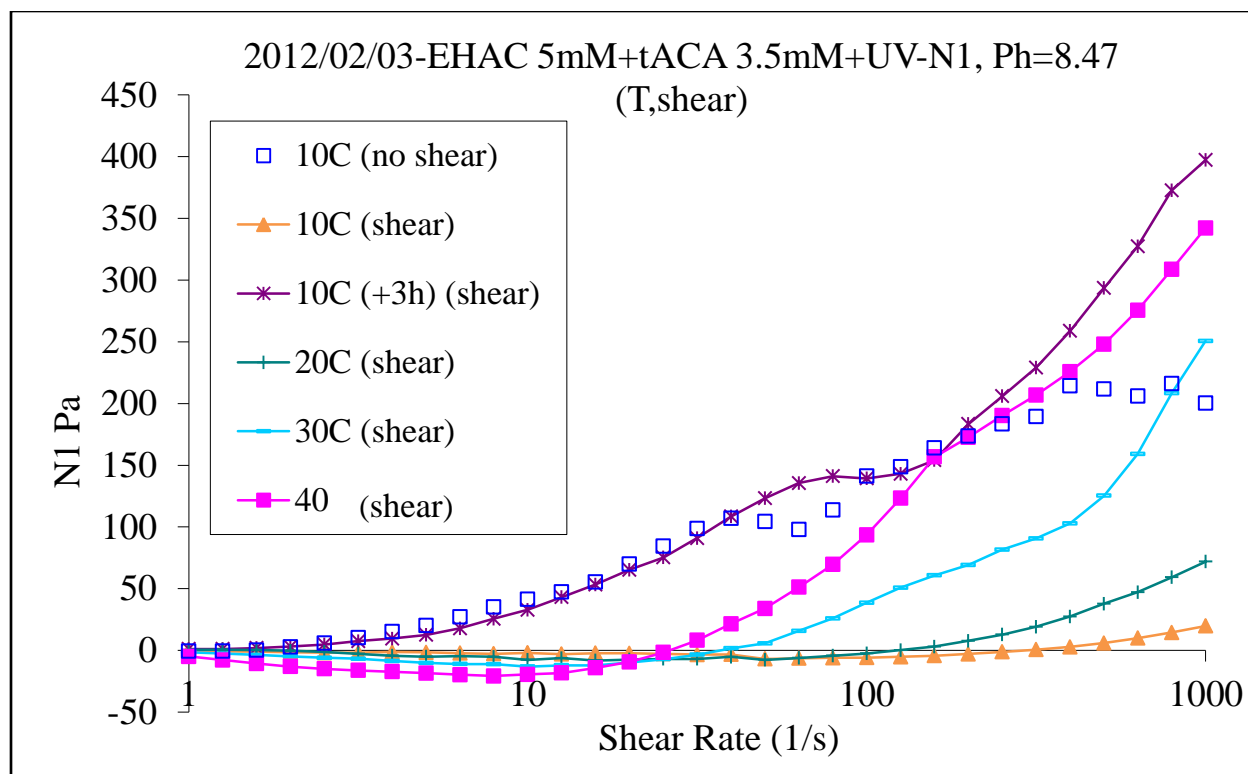


Figure 20 - Effect of temperature on 5mM EHAC/3.5mM trans-ACA after UV irradiation and shear

The proposed hypothesis was tested on 02/08/2012 by shearing UV irradiated 5mM EHAC + 3.5mM *trans*-ACA, pH 8.67, and measuring  $N_1$  every 15 minutes with the rheometer while maintaining the solution at 10°C with an ice bath (Figure 21). Note the trials begin at 8 minutes and not 0 minutes because of the delay between shearing and preparing the sample on the rheometer. The results indicated that after 83 minutes, the solution had fully regained viscoelasticity. This was determined when 3 consecutive measurements of  $N_1$  appeared the same. Not only does the rheometer confirm an increase in  $N_1$  at constant temperature over time, but it is also clearly visible that the solution is becoming thicker and more viscoelastic during each trial preparation. These results support the hypothesis that for a pH in the range of 8-9, the solution regains viscoelasticity over time.

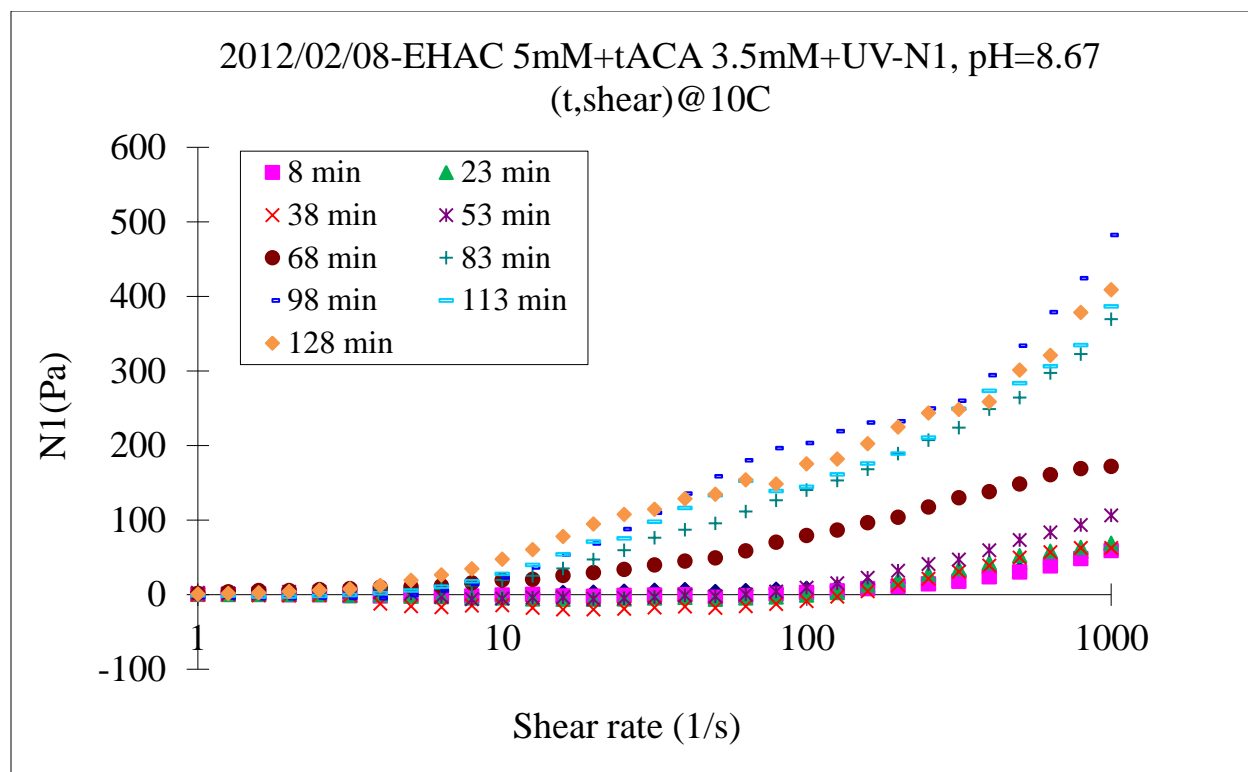


Figure 21 – Effect of time on 5mM EHAC and 3.5mM *t*-ACA solution at 10C and pH 8.67 after UV and shear

The next step was to test the effect of temperature by shearing the UV irradiated 5mM EHAC + 3.5mM *trans*-ACA before each rheometer trial at temperatures of 10°C, 20°C, 30°C, and 40°C. On 02/20/2012 the 5mM EHAC + 3.5mM *trans*-ACA solution was irradiated for 90 minutes and sheared. Shearing resulted in a short time loss of viscoelasticity; it took only a couple minutes to regain. It was hypothesized that this solution, used since 01/23/2012, had been irradiated with UV light too many times and too long causing a large conversion of *trans*-ACA to *cis*-ACA; thus, making the regain in viscoelasticity quicker due to a higher probability of micelle reformation. A fresh 200 mL solution of 5mM EHAC + 3.5mM *trans*-ACA was prepared and the pH was adjusted to 8.9. On 02/22/2012, the solution was adjusted to a pH of 9.0 after 165 minutes of UV irradiation. 10mL of the sample was saved to perform measurements of  $N_1$  before shear at 40°C. The remaining solution was then sheared for 60 seconds each time before measuring  $N_1$  at 10°C, 20°C, 30°C, and 40°C (Figure 22). For 10°C, 20°C, and 30°C, the

$N_1$  measurements show water-like rheology. At 40°C an increase in  $N_1$  was noted, but it did not match the before shear value at 40°C. This indicates that values obtained in Figure 19 and Figure 20 are confounded by the effect of time, which was not expected to be a factor. The 40°C sample was repeated two more times without re-shearing. The third run, approximately 30 minutes after shear, gave  $N_1$  results close to those before shear. Previously, it had been observed that at 10°C, it took 83 minutes to restore viscoelasticity. This indicates that at higher temperature, viscoelasticity is regained quicker.

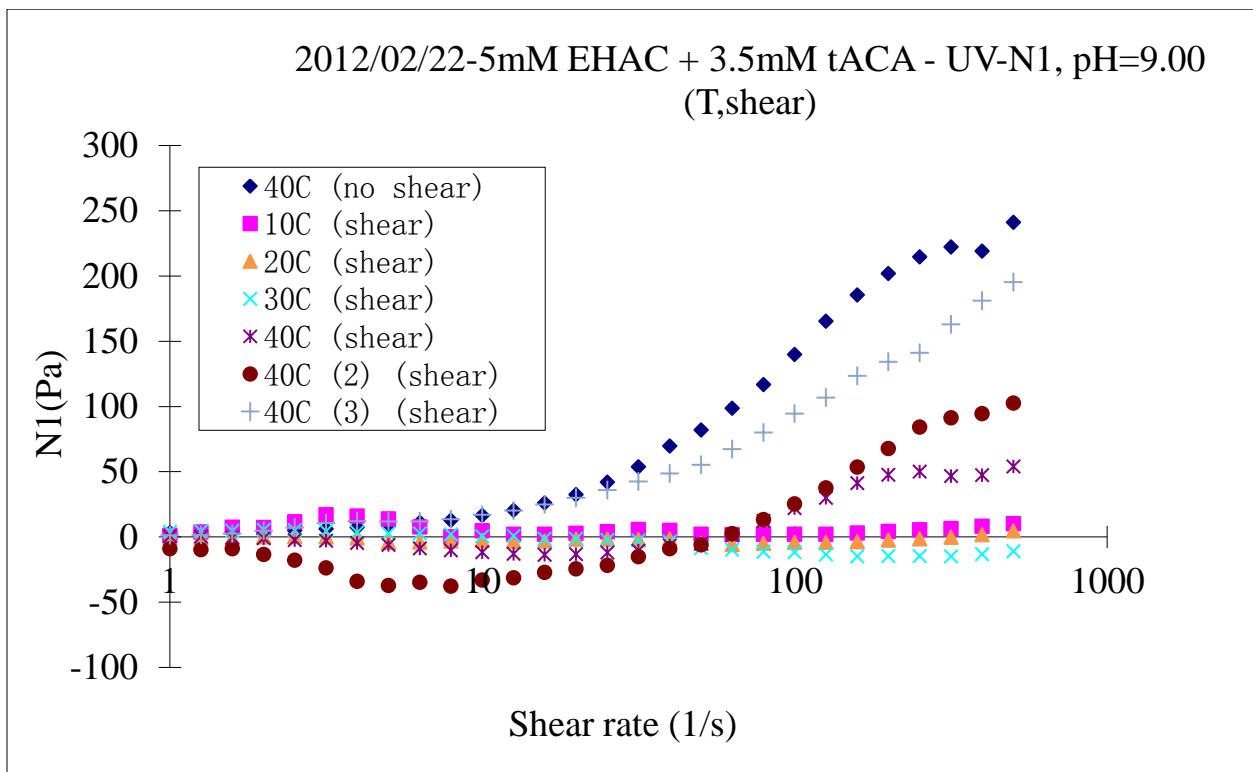


Figure 22 - Effect of temperature on 5mM EHAC and 3.5mM t-ACA solution at 10C and pH 9.00 after UV and shear

Next I investigated the effect of pH on the regain of viscoelasticity. On 02/29/2012, the solution was adjusted to a pH of 7.96 and the test performed on 02/22/2012 was repeated (Figure 23). Similar results were obtained; however, the solution had a larger initial  $N_1$  than the previous trials and the solution appeared to regain  $N_1$  faster than the pH 9.0 trials. This was evident when 20°C, 30°C, and 40°C all showed significant  $N_1$  measurements. It is apparent that pH has an



effect on the rate at which viscoelasticity is regained. It is recommended for future studies that the pH range of this system be further explored to see if a certain pH can prevent viscoelasticity from being regained after shear.

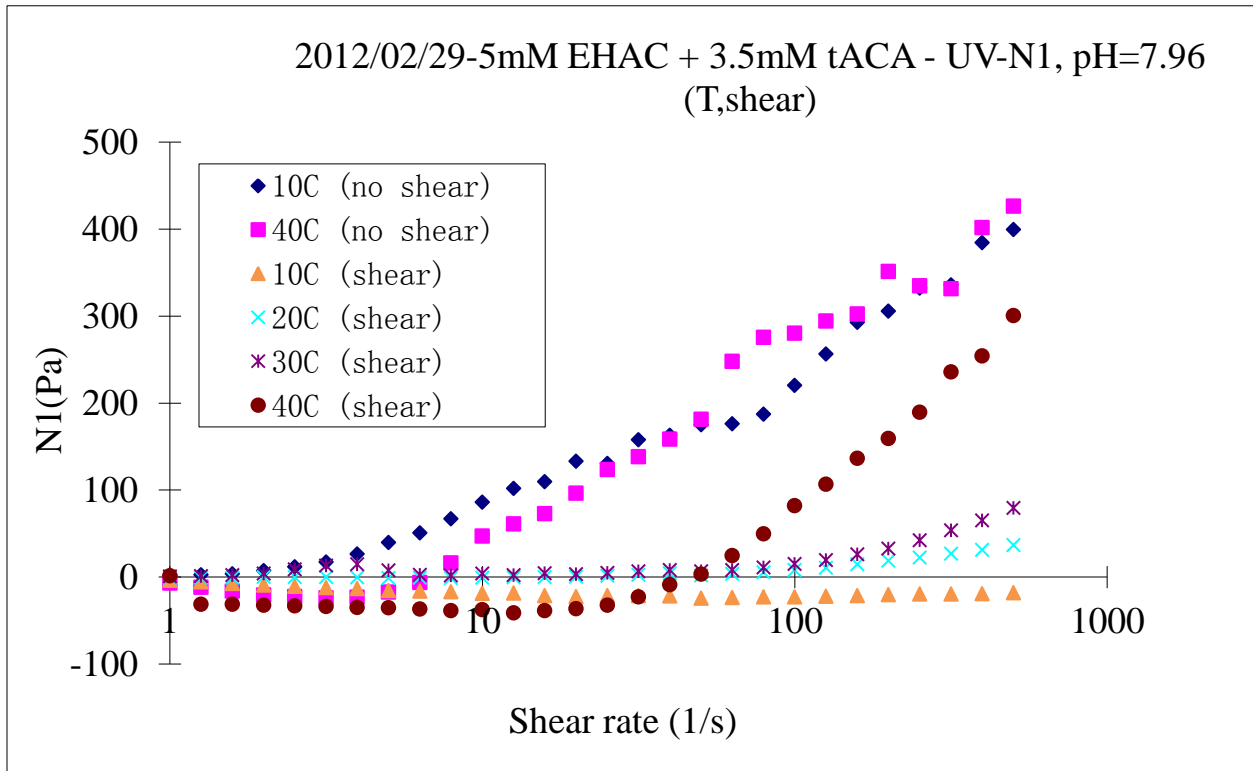


Figure 23 - Effect of temperature on 5mM EHAC and 3.5mM t-ACA solution at 10C and pH 7.96 after UV and shear

## V. Conclusions

The ability to alternate a fluids DR properties has been achieved by the use of the photosensitive counterion *trans*-ACA. A limitation that is present with this phenomenon is the large amount of irradiation time which the fluid requires. By using both NaSal and *trans*-ACA at critical concentrations, a solution that is non-viscoelastic before irradiation and viscoelastic after irradiation has been determined to be 10mM EO12/2.35mM NaSal/0.4mM *trans*-ACA. Results indicate that multiple irradiations lead to longer irradiation times to fully alternate viscoelasticity. It is also apparent that a system of EO12/NaSal/*trans*-ACA loses its viscoelasticity over time.

The study of EHAC/*trans*-ACA revealed that at low temperatures (10°C) shearing the solution caused temporary loss in viscoelasticity. It was determined for a 5mM EHAC/3.5mM *trans*-ACA system that  $N_1$  is a function of shear, temperature, pH, and time. At pH greater than 10.7, this system becomes viscoelastic independent of shearing. Systems with pH between 7.96-10.7 were observed to regain viscoelasticity after shear with time. This effect was accelerated with increase in temperature. Lowering the pH appears to increase the values of  $N_1$  for the solution at high shear rates and also the speed at which viscoelasticity is regained. Further testing will be needed to determine if there is a pH value at which the system will not regain viscoelasticity until heated. Currently, this system has potential use for a case in which the UV irradiated EHAC/*trans*-ACA (DR active) passes through a pump (shearing it and becoming DR inactive) into the heat exchanger, and then is pumped over a long distance, such as in the 5.6km pipeline in Herning, Denmark. The system will regain viscoelasticity with time and thus DR properties will reactivate as it is transported to its destination.

## VI. Recommendations for Future Work

From the work performed on critical concentrations of *trans*-ACA, drag reduction testing is recommended for a 10mM EO12/2.35mM NaSal/0.4mM *trans*-ACA system. Additionally repeatability and irradiation times should be examined. The investigation suggests that critical concentrations of *trans*-ACA may not be stable for long periods of time and it is recommended that the stability of this system be further investigated.

For shear and temperature effects on EHAC/*trans*-ACA it is recommended that a study of the effect of pH be carried out to determine if there is a pH for which viscoelasticity will not be regained until heated. A system that shears (making it DR inactive) the UV irradiated fluid before entering the heat exchanger and then is pumped over long distance (regaining DR active mode over time) is recommended for investigation. It is also recommended that the effect of both BL and shear combined be investigated. Perhaps the use of BL will help to reduce the amount of *cis*-ACA and allow the system to remain non-VE after shear for extended periods. Additionally, a hybrid counterion system with critical concentrations, as performed for EO12/NaSal/*trans*-ACA, is recommended for future study.

It was observed that a EO12/*trans*-ACA system was viscoelastic while a EHAC/*trans*-ACA system was not. Upon UV irradiation the EHAC/*trans*-ACA system became viscoelastic. This indicates that EHAC requires *cis*-ACA to form a viscoelastic solution. EO12 and EHAC have the same headgroup, but EHAC contains a slightly longer alkyl chain. No explanation for EHAC's preference for the *cis*-ACA configuration for viscoelasticity was drawn from the results of this thesis research. It is recommended that this system of EHAC/*trans*-ACA be further studied to provide an explanation for this phenomenon.

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