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CHARACTERIZATION OF DRAG REDUCING SURFACTANT SYSTEMS BY RHEOLOGY AND FLOW BIREFRINGENCE MEASUREMENTS

DISSERTATION

Presented in Partial Fulfillment of the Requirements for the Degree Doctor of Philosophy in the Graduate School of The Ohio State University

By

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1997

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ABSTRACT

Dilute surfactant solutions can be effective in drag reduction and show unique rheological characteristics. Rheological and flow birefringence measurements are performed to characterize these drag reducing surfactant systems. Application studies on separation of surfactants and stability of drag reducing additives are also described.

Counterion structure affects drag reduction and the rheological behavior of surfactant systems. The Arquad 16-50 (5 mM) / 2-Cl-benzoate (12.5 mM) system has no drag reduction, low apparent extensional viscosity, no viscoelasticity and spherical micelles. The 4-Cl-benzoate with the same surfactant has a thread-like micellar network, is drag reducing and viscoelastic, and has high apparent extensional viscosity. The 3-Cl system is similar to the 4-Cl system at 30°C. These differences are caused by the different positions of the chlorine group at the micelle-water interface. A stress induced precipitation phenomenon is observed at 20°C for the 3-Cl system, which may have one of three different microstructures: thread-like micelles, vesicles or precipitation, depending on external forces. A schematic diagram is proposed to describe this phenomenon.
The rheology of drag reducing cationic surfactants also depends on counterion to surfactant ratio, ξ. Experimental results on drag reduction and rheological behavior, including relaxation times, are presented and analyzed in terms of network structure.

Good correlation between drag reduction and high apparent extensional viscosity at 20°C is shown. Also the nonlinear Giesekus model, which can fit data reasonably well for surfactant systems, predicts very high extensional viscosity at high shear rates, even for the non-viscoelastic Arquad S-50 (5 mM) / NaSal (12.5 mM) system. This anomalous system has no N₁, no recoil and no stress overshoot, but has high apparent extensional viscosity and is a good drag reducer, providing strong evidence that extensional viscosity is responsible for drag reduction.

A technique for transient flow birefringence measurements has been established, which enables relaxation of the birefringence and the extinction angle to be correctly measured. The stress-optical rule is not applicable for dilute drag reducing surfactant systems.

Separation methods are evaluated. Drag reduction by cationic surfactant systems may be lost because of adsorption of the cationic surfactant on the wall and on the corrosion byproduct particles, and the presence of copper compounds, but can be overcome. However, these problems are not as serious in large flow systems and thus the practical application of drag reducing cationic surfactant systems is still very promising.
TO MY FAMILY
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Surfactants are a class of chemicals whose molecules contain both a hydrophobic group and a hydrophilic group. When surfactants are dispersed in a polar solvent, the hydrophobic groups prefer to leave the polar environment, while the hydrophilic groups prefer to stay in the polar solvent. These preferences result in some hydrophobic groups associating with nonpolar interfaces, such as a hydrophobic solid surface or a liquid-air interface. If the concentration of the surfactant exceeds a certain critical micelle concentration (CMC), in a polar solvent, the hydrophobic groups form the center of a spherical structure called a micelle, while in a nonpolar solvent, the hydrophobic groups form the surface of the spherical structure which is called a reverse micelle. Under certain conditions, such as at high surfactant concentrations or in the presence of other additives, the spherical micelles will be transformed into rod-like or other shape micelles.

Even though both are macro aggregates, micelles are much different from polymer molecules. Micelles can be spherical, disk-like or rod-like in shape. Though rod-like micelles sometimes can have high length to diameter ratios and hence be similar in shape to the polymer molecules, they are usually smaller than high molecular weight polymer
molecules. Also, the forces holding the surfactant molecules together in micelles are different from the primary chemical bonds of polymer molecules. The former are much weaker than the latter. However, these secondary attractions continue to exist even if the micelle is broken in strong shear fields, and the micelles can reform when the external forces are removed. When polymer molecules are mechanically degraded, the chemical bonds do not reform, i.e., the broken segments of polymer molecules are unlikely to rejoin each other.

Regardless of these differences, both high molecular weight polymers in solution and surfactant solutions (as well as high L/D fibers) can reduce energy losses in turbulent flows (reduce drag) at low concentrations. Drag reduction is a flow phenomenon in which the addition of small amounts of drag reducers to a fluid causes a reduction in the turbulent friction compared with the pure fluid at the same flow rate, or an increase in the flow rate at the same pressure drop. The first observation of drag reduction was made more than sixty years ago in turbulent pipe flow of wood pulp fiber suspensions in water by Forrest and Grierson [1931], though this report of drag reduction went largely unnoticed [Radin, 1974; Nadolink and Haigh, 1995]. The findings by Mysels and his associates [Mysels, 1949; Agoston et al., 1954; Mysels, 1971] and by Toms [1949, 1977] in the 1940's are usually recognized as the first observations of drag reduction.

Polymer solution drag reduction has been studied extensively in both aqueous and hydrocarbon media. Spectacular commercial success was achieved in increasing crude oil
throughput in the Alyeska and other pipelines by injecting concentrated polymer solution into the flowing crude oils at pipeline locations where excessive pressure drops were limiting crude oil flow rates [Burger et al., 1982]. Flow rates were increased by up to 15% increasing the capacity of the 48-inch pipeline by up to 200,000 barrels of crude per day [Burger et al., 1982].

However, application of polymers as drag reducers is limited since, as mentioned above, polymer molecules are permanently degraded in regions of high shear such as in a centrifugal pump. After degradation, the lower molecular weight polymer is not effective as a drag reducer. While surfactants as drag reducers have not received as much attention as polymer solutions, it is generally believed that the existence of rod-like micelles in the surfactant solutions is necessary for drag reduction to occur. A major advantage of surfactant drag reducers is that the micelles are thermodynamically stable and hence they are self-repairable after degradation and so can be used in recirculating systems as they regain their drag reducing ability soon after passing through a pump.

Important recirculation systems are district heating and district cooling systems (DHC). In DHC systems, hot/cold water is pumped from a central station to homes and offices to provide space heating/cooling. In district heating, the station utilizes waste heat from electric power plants or cogeneration plants to heat water. Compared with traditional individual heating or cooling systems in each building, DHC is more efficient, less expensive and reduces air pollution. District heating systems are widely used in northern
Europe and are used in the United States in such cities as Hartford, Trenton, Minneapolis, St. Paul, etc. As the cost of fuel increases, their high efficiency in the use of energy will make them even more attractive. Major costs of DHC systems are the cost of power for pumping the fluid and the capital expenses for pipes, fittings and pumps. For existing systems, the operating power costs can be reduced by the use of drag reducing additives. For new systems, the capital costs of pipes, fittings and pumps can be reduced because drag reduction allows greater throughput for fixed pumping power. As discussed above, polymer drag reducers are susceptible to permanent degradation when subjected to high shear so they are not suitable for circulation systems, such as DHC systems, while surfactants are suitable for DHC systems because of their ability to repair themselves after degradation.

However, while surfactants are potentially applicable in recirculation flow systems, only a few systems have been investigated and those tested so far are far have not been optimized for effectiveness. Complete studies of the influence of the chemical structures of surfactants and counterions, their molar ratios and concentration for maximum effectiveness and their stability, etc., have not been made. Determination of the effects of these variables on rheological and flow birefringence behaviors, on surfactant microstructures and their effects on drag reduction efficiency are needed to develop more effective surfactant systems.
This work focuses on research on molecular variables affecting characteristics and performance of cationic surfactant drag reducers. The research includes two parts: characterization of surfactant solutions and studies on the practical application of surfactant drag reducers.

The objectives of the characterization part of the research are to characterize cationic surfactant solutions, to identify key rheological properties which correlate with drag reduction, and to develop a rheological model for these drag reducing surfactant systems as well as to determine the effect of variations in the chemical structures of nonionic and cationic surfactants and counterions on the microstructures of micellar solutions and on their rheological and flow birefringence properties and drag reduction behavior. Wherever possible, chemical structures will be varied such that only one variable is changing at a time, for example, alkyl chain length and counterion effect (location and nature of polar and non-polar groups on counterions) in cationic surfactants. The surfactant/counterion ratios and total concentrations are also varied. The former will affect the micellar charge and the latter the degree of overlap of micellar pervaded volumes. Also, to have a better understanding of the effect of chemical structure on flow birefringence, transient flow birefringence measurements are to be established. Cryo-TEM images obtained from collaborative laboratories are examined against rheological and drag reduction data.
The mechanism of drag reduction remains unknown even though numerous researchers have studied this subject. For surfactant drag reduction, Savins [1967] was the first to recognize that drag-reducing surfactant solutions show viscoelastic flow behavior. Later, extensive studies on drag reducing surfactant systems led to a general belief that viscoelastic rheological properties of the surfactant solutions are responsible for the occurrence of drag reduction. For surfactant solutions, the presence of rod-like (or thread-like) micelles and shear-induced structures (SIS) were reported to be responsible for the viscoelasticity and thus for drag reduction [Ohlendorf et al., 1986a, b; Rehage et al., 1986; Bewersdorff and Ohlendorf, 1988; Chou, 1991b; Bewersdorff and Thiel, 1993]. These researchers proposed that smaller ordered clusters damp the turbulent eddies in the near-wall region, while in the core region, the SIS damps the large scale turbulence.

High extensional viscosity has been suggested as the cause of drag reduction by polymer additives [Landahl, 1977; Durst et al., 1982; Hoyt, 1986; Bewersdorff and Thiel, 1993]. These researchers stated that the extensional viscosity of dilute polymer solutions can be large compared to that of the Newtonian solvent. This results in an additional resistance against vortex stretching and turbulent eddy growth, and leads to reduction of energy dissipation or drag reduction. However, there are only a limited number of reports in the literature on extensional rheology for surfactant systems.

While clarifying the drag reduction mechanism would be of great importance, it is not expected that this research will provide a detailed mechanism for the phenomenon.
However, rheological measurements can help clarify which properties correlate with drag reduction. Extensional viscosity results along with relaxation times from flow birefringence, dynamic viscoelasticity measurements, normal stress and shear stress will be examined and correlated with drag reduction results. Models for the rheological behavior of cationic surfactant solutions will be tested.

Problems related to practical applications of drag reducing surfactant solutions in flow systems have also been investigated. One concern is the toxic effects of the cationic surfactants. Solutions in large scale applications can not be discharged unless surfactant and counterions are separated from the solution. Thus, separation methods need to be developed and tested. Also, the drag reduction effectiveness of nonionic surfactant systems, which have lower toxicity and faster biodegradability, is evaluated. Another concern in practical applications is the chemical stability of surfactant solutions. Repeated laboratory experiments found and confirmed that two commercial surfactants, Habon G and Ethoquad T/13-50/NaSal, lose their drag reduction effectiveness after three or more days although Habon G in field tests was effective for months and Ethoquad T/13-50 / NaSal was effective for longer periods on other laboratory tests. Chemical tests made to determine the causes of the loss of drag reduction found that adsorption of surfactant on rust particles and copper hydroxide particles are the main causes of the loss of drag reduction. Chemical additives which inactivate the metal corrosion products have been found which can be used to restore drag reduction.
In Chapter 2, a literature review on drag reduction, rheology and flow birefringence studies on surfactant solutions is provided. This chapter is to provide readers with the current status of research as well as background knowledge in this field. Chapter 3 describes experimental methods as well as the related theoretical backgrounds. Chapter 4 provides results and discussion on flow birefringence results, mainly on transient data. Chapter 5 addresses results and discussion on drag reduction and rheological data. Constitutive models are tested for drag reducing surfactant systems and a stress induced precipitation phenomenon is introduced in Chapter 5 as well. Chapter 6 focuses on results and discussion of application studies including separation and stability studies. Chapter 7 summarizes important findings in this research. Chapter 8 lists important future proposed work in this field.
2.1 Surfactant Solutions

2.1.1 Characteristics of Surfactant Solutions

Surfactants are characterized by the coexistence of a hydrophobic "tail" and a hydrophilic head group in one molecule and are referred to as amphiphilic compounds. The hydrophobic tail is generally a long chain alkyl group, whereas the hydrophilic head of the molecule is ionizable, polar, polarizable and is often suitable for forming hydrogen bridges. For surfactants in an aqueous environment, the hydrophilic groups like to reside in the water phase and the hydrophobic groups try to leave the water phase. There are two ways to avoid the unfavorable hydrophobic group-water contact. One way is for the hydrophobic groups to orientate themselves into a nonpolar phase, such as a gas phase, a non-polar solid or a hydrophobic liquid phase. Another choice is self association, that is, for surfactant molecules to form assemblies called micelles in which the non-polar portions concentrate in the center while the polar ends lie on the surface in contact with water. Micellization is a feature of surfactant solutions above their Critical Micelle
Concentration (CMC). Above the CMC the micelles are always in thermodynamic equilibrium with the monomer molecules.

A simplified phase diagram for aqueous surfactant solutions is shown in Fig. 2.1. When the temperature is lower than the so-called Kraft point, the surfactant is partially in crystal or gel form in the solution. For temperatures higher than this point, surfactant molecules aggregate together to form spherical micelles when the concentration exceeds the CMC, and rod-like micelles are formed when the concentration further increases to exceed the CMC\textsubscript{H}. One can see from Fig. 2.1 that the CMC is almost independent of temperature, while the CMC\textsubscript{H} increases with temperature.

Surfactants can be grouped into two broad classes by their hydrophilic or polar groups: ionics and nonionics. Ionics can be further divided into two subclasses namely, anionics and cationics, and nonionics have three subclasses: zwitterionic, semipolar and single-bond subclasses [Laughlin, 1991].

2.1.2 Micellization

When the surfactant concentration exceeds a certain value, the so-called critical micelle concentration or CMC, surfactant molecules begin to aggregate to form micelles (see Fig. 2.1). There are two models to explain micelle formation [Wennerstrom and Lindman, 1979]. One is the pseudo-phase separation model, which considers micelle formation as a phase separation. That is, upon formation, micelles are separated from the monomeric
Figure 2.1  Schematic phase diagram for surfactant solutions.
phase to a pseudo-phase. The CMC is then the saturation concentration of the amphiphile in the monomeric state. Another model, the *mass action model*, assumes that the micelles can be described by an aggregate $M_m$ with a single aggregation number, $m$. This model treats micelle formation as a chemical equilibrium. Both models are sufficiently accurate to account for the concentration dependence of molecular properties [Wennerstrom and Lindman, 1979].

At concentrations above the CMC, monomers and micelles coexist in the solution, and the concentration of monomers stays the same while the concentration of aggregates increases with the total concentration [Wennerstrom and Lindman, 1979]. Ohlendorf et al. [1986a] and Rehage and Hoffmann [1991] suggested that there is a real thermodynamic equilibrium between the free monomers and the monomers forming the micelles. In a given time interval a certain number of monomers leave the micelle by diffusion processes, but at the same time other molecules enter the micelles. At equilibrium, the net exchange is zero. In their view, micelles are fragile, dynamic objects, and there is a limited life time for micelles.

Upon micellization, many properties of the system, such as equivalent conductivity, surface tension, osmotic pressure, etc., undergo abrupt changes in their rate of change with concentration (Fig. 2.2) [Wennerstrom and Lindman, 1979; Lindman and Wennerstrom, 1980; Rosen, 1989]. These changes enable the measurement of CMC to be
Figure 2.2 Physical property changes upon micellization.
made. Values of CMC of a number of surfactants were tabulated by Wennerstrom and Lindman [1979], Lindman and Wennerstrom [1980] and Rosen [1989].

2.1.3 CMC

The critical micelle concentration (CMC) depends on many factors, including the surfactant hydrocarbon chain length, surfactant headgroup, counterion, added salts and temperature [Wennerstrom and Lindman, 1979; Rosen, 1989].

Temperature may have only a weak effect on CMC (see Fig. 2.1) [Ohlendorf and Interthal, 1986b; Rosen, 1989]. However, this effect is complex. The CMC value first decreases with temperature to a minimum point and then increases with further increase in temperature [Rosen, 1989].

In aqueous solution, the CMC decreases as the length of the surfactant hydrocarbon chain increases up to 16 carbon atoms. There is a general rule for ionic surfactants which says that the CMC is halved by the addition of one methylene group to a straight-chain hydrocarbon chain [Rosen, 1989]. When the chain length exceeds 16, the decreases in CMC are slowed down and when the chain exceeds 18 carbons, the CMC may remain unchanged with further increase in the chain length [Rosen, 1989]. The presence of a branch on the hydrocarbon chain will decrease the CMC. The CMC of those surfactants with double bonds in the hydrocarbon chain is higher than the corresponding saturated surfactants [Rosen, 1989].
For homologous straight-chain ionic surfactants in aqueous solutions, Klevens [1953] established a relation between the CMC and the number of carbon atoms, N, in the hydrophobic chain:

\[ \log CMC = A - BN \]  

(2.1)

where A and B are two positive constants for a particular ionic head and given temperature. This equation predicts decrease in CMC with increase in N. Values of A and B for some surfactants are tabulated by Rosen [1989] based on many researchers’ results. It is interesting to note that the value of B is close to 0.3 or \(\log 2\) for different ionic surfactants, which is consistent with the CMC being halved for each increase in N [Rosen, 1989].

It was found that ionic surfactants have much higher CMCs than nonionic surfactants with equivalent hydrophobic groups [Rosen, 1989]. This may be the result of the electrical repulsion of head groups with the same charge. It has been noted that the CMC is higher when the charge on the head group is closer to the \(\alpha\)-carbon atom of the alkyl chain [Stigter, 1974].

In the presence of additional electrolyte, the CMC is depressed due to the decrease in the thickness of the ionic atmosphere surrounding the ionic head groups, and consequently the decrease of the repulsion between headgroups in the micelle [Rosen, 1989]. The effect of adding inorganic salts on CMC has been extensively studied by Anacker and Ghose
[1963] using light scattering measurements. They found that the ability of the anions to depress the CMC of dodecyltrimethylammonium bromide is in the order:

\[
NO_3^- > Br^- > BrO_3^- > Cl^- > IO_3^- > CHO_3^- > F^-
\]

This order only roughly follows the lyotropic series for anions [Anacker and Ghose, 1963]. Rosen [1989] reported the following order of effectiveness in decreasing of CMC for a different group of anions. For several anions, they didn’t agree.

\[
SO_4^{2-} > F^- > BrO_3^{-} > Cl^- > Br^- > NO_3^- > I^- > CNS^-
\]

For cations, Rosen [1989] reported:

\[
NH_4^+ > K^+ > Na^+ > Li^+ > Ca^{2+}
\]

and

\[
(CH_3)_4N^+ > (C_2H_5)_4N^+ > (C_3H_7)_4N^+
\]

He believed that the effectiveness of the electrolyte depends on the radius of the hydrated ion: the smaller the radius of the hydrated ion, the greater the effect.

For cationic surfactants, it has been shown that increase in hydrophobicity of the organic counter-ion causes a decrease in CMC [Underwood and Anacker, 1987]. Aromatic acid counterions, such as benzoates, benzenesulfonates, p-methyl-benzoates and p-methyl-benzenesulfonates, have been shown to reduce the CMC an order of magnitude lower than inorganic and aliphatic counter-ions [Gravsholt, 1976; Underwood and Anacker, 1987].
Rosen [1989] divided organic additives to surfactants into two classes. Class I materials affect the CMC by being incorporated into the micelle, while Class II materials change the CMC by modifying solvent-micelle or solvent-surfactant interactions. Rosen [1989] suggested that the short chain Class I molecules are adsorbed mainly in the outer portion of the micelle, and the long chain Class I molecules are probably adsorbed mainly in the outer portion of the core, between the surfactant molecules. Adsorption of these materials decreases the CMC of surfactant.

The Class II organic additives include urea, formamide, N-methylacetamide, guanidinium salts, short-chain alcohols, water-soluble esters, dioxane, ethylene glycol and other polyhydric alcohols [Rosen, 1989]. Xylose and fructose decrease the CMC, while other Class II organic additives may increase the CMC [Rosen, 1989]. Almgren and Swarup [1984] studied the sodium dodecyl sulfate (SDS) system. They found that with the addition of different alcohols, the size of SDS micelles decreases with alcohol concentration to a minimum and then increases with further increase in alcohol concentration. The minima in micelle sizes occur at the same alcohol concentrations where minimum CMC values were reported. Solvents also play an important role in affecting the CMC and micelle size.

Some researchers defined the sphere-rod transition concentration as the second critical concentration, $\text{CMC}_n$ [Porte et al., 1984; Hoffmann et al., 1984a]. It was noticed that the $\text{CMC}_n$ can lie anywhere between the CMC and very high concentration (see Fig. 2.1).
Ohlendorf et al. [1986a, 1986b] found the CMC increases very rapidly with temperature. Salt concentration can dramatically change the CMC. For example, the CMC of cetyltrimethylammonium bromide (CTAB) is 0.2-0.3M [Lindman and Wennerstrom, 1980]. However, in the presence of 0.2 M NaBr, rod-like micelles several hundred nanometers long were detected by dynamic light scattering measurements in 0.004M CTAB solution [Nicoli et al., 1981].

2.1.4 Micelle Shape

The major types of micelles are (1) spherical; (2) rod-like; (3) lamellar; (4) vesicles [Rosen, 1989]. Micelles are believed to be of spherical or roughly spherical shape at the CMC. Tanford [1972] proposed that small micelles are ellipsoidal rather than spherical in shape. He believed that the ellipsoidal shape can incorporate a larger number of hydrocarbon chains in a micelle and he provided a calculation for the shape of ellipsoids necessary for aggregation numbers up to 570. He suggested that amphiphiles with a single hydrocarbon chain per polar head group form micelles with ellipsoidal or spherical shapes.

Regardless of the shape of the micelle at the CMC, when the concentration is increased to CMC n, rod-like micelles are formed in the solution. Evidence to support the existence of rod-like or elongated micelles has been provided by a number of investigators using different experimental techniques over the years [Debye and Anacker, 1951; Young et al., 1978; Porte et al., 1980; Ikeda et al., 1981; Lindner et al., 1990]. Debye and Anacker
[1951] studied the cetyltrimethyl ammonium bromide/potassium bromide (CTAB/KBr) system using static light scattering and found that the micelles are not spherical or disk-like in shape, and the data indicate they are rod-like. Porte et al. [1980] combined results from magnetic birefringence, quasi-elastic light-scattering spectra and NMR measurements on 6 mM cetylpyridinium bromide with various amounts of NaBr and NaCl (0-0.8M), and concluded that the micelles in that solution are semiflexible rods. Young et al. [1978] studied a 2g/L aqueous solution of sodium dodecyl sulfate (SDS) in 0.6 M NaCl using light scattering and concluded that the micelles in this solution were rod-shaped. The angular dependence of light scattering, observed by Ikeda et al. [1981], indicated that the large micelles formed in sodium dodecyl sulfate (SDS) with sodium halide solutions are rod-like. Experimental results from NMR also indicated that CTASal micelles are rod-like in shape [Olsson et al., 1986]. More recently, Lindner et al. [1990] detected rod-like micelles of average length 249 nm in a 2.4 mM tetradecyltrimethyl ammonium salicylate (C_{14}TASal) in heavy water (D_{2}O) system by small angle neutron scattering and light scattering methods.

Recent developments in cryo-transmission electron microscopy (cryo-TEM) techniques have made it possible for researchers to get direct images of micellar structures without altering the structures in sample preparation. Rod-like or worm-like micelles have been observed in various surfactant/salt systems [Bellare et al., 1988; Vinson and Talmon, 1989; Walter et al., 1991; Clausen et al., 1992; Cochin et al., 1992].
The addition of salts, co-surfactants or counterions can also induce the formation of rod-like micelles [Ohlendorf et al., 1986a]. All of these additives can neutralize or disperse the electrostatic repulsion between the ionic headgroups, stabilize the micelle and promote formation of large micelles.

Israelachvili et al. [1976] developed a theory of micellar structure. Considering a surfactant with an alkyl chain length, \( l \), a volume of alkyl chain in the micelle core per molecule, \( V \), and a cross sectional area of headgroup per molecule, \( a \), the value \( \frac{V}{la} \), the packing parameter, determines the shape of the micelles (Table 2.1).

<table>
<thead>
<tr>
<th>Value of ( \frac{V}{la} )</th>
<th>Shape of the Micelle</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-1/3</td>
<td>Spherical</td>
</tr>
<tr>
<td>1/3-1/2</td>
<td>Rod-like</td>
</tr>
<tr>
<td>1/2-1</td>
<td>Lamellar</td>
</tr>
<tr>
<td>&gt;1</td>
<td>Reversed micelles in nonpolar media</td>
</tr>
</tbody>
</table>

Table 2.1 Micelle shape for different \( \frac{V}{la} \).

Tanford [1972] established the equations to calculate volume occupied by an alkyl chain of \( N \) carbon atoms embedded in the hydrocarbon core, \( V \), and the maximum possible extension of a hydrocarbon chain, \( l_{max} \):

\[
V = 27.4 + 26.9N \left( \, \text{Å}^3 \right)
\]

\[
l_{max} = 1.5 + 1.265N \left( \, \text{Å} \right)
\]
For spherical micelles, the maximum micelle aggregation number can be uniquely determined from these two equations [Tanford, 1972].

Tanford [1972] and Israelachvili et al. [1976] pointed out that regardless of the shape of the micelles, no point within the micelle can be farther from the hydrocarbon-water interface than $l_{\text{max}}$. This is equivalent to saying that at least one of the three dimensions of the micelles must not exceed $2l$ to ensure an aqueous environment for the polar heads. Thus, the radius of the spherical micelles is approximately equal to $l_{\text{max}}$. For rod-like micelles, the radius of the rod should also be approximately $l_{\text{max}}$. However, Shikata et al. [1987b] took electron micrographs of 1 mM CTAB/SA (salicylic acid) solution simply by drying a drop before taking the picture, and observed very long rigid rod-like micelles with a diameter of 10-12 nm. From Eq. 2.3, $l$ can not be larger than 21.74 Å (for $N = 16$), or the diameter of rod-like micelles should not be larger than 5 nm, which is contrary to the results of Shikata et al. [1987b]. Vinson and Talmon [1989] argued that the results of Shikata et al. [1987b] didn't represent the physical structure which existed in the solution and that there was probably a structure change during the drying process.

2.1.5 Micelle Size

The size of the micelle depends on many factors, including the chain structure of the surfactant, the head group of the surfactant, counterions, added salts and temperature, etc. From geometric considerations, one can expect that the aggregation number of spherical micelles will increase with the hydrocarbon chain length of the surfactant and decrease...
with increase in the hydrophilic head group size [Rosen, 1989] and, it has been observed that the micelle aggregation number increases rapidly with increase of hydrocarbon chain length and decreases with increasing cross-sectional area of the headgroup [Wennnerstrom and Lindman, 1979]. Geer et al. [1971] found in their light scattering studies that decylammonium bromide gives the largest micelle weight while decyltriethylammonium bromide gives the lowest micelle weight. They suggested that larger headgroups tend to keep the counter-ions from approaching the charge center and thus are not favorable for micellar growth. Rehage and Hoffmann [1991] explained the headgroup effects on micelle shape based on geometrical considerations. If the hydrophilic head group requires an area larger than the corresponding cross section of the hydrocarbon chain, the system will tend to form aggregates with convex curvatures. If both sizes are the same, planar structures are favored. If the head group needs an area less than that of the hydrocarbon chain, inverse micelles will be formed.

The length of rod-like micelles has been shown to increase with increase in surfactant concentration and decrease in temperature [Missel et al., 1980, 1983; Elson and Garside, 1983; Hoffmann et al., 1985b; Myska et al., 1996]. Missel et al. [1980, 1983] measured rapid increases of the aggregation number and the hydrodynamic radius of micelles with increasing surfactant concentration. Based on their measurements of drag reduction and swirl decay time (SDT) on cationic surfactant/1-naphthol systems, Elson and Garside [1983] suggested that the rod-like micelles are longest and strongest around the surfactant Kraft point. Hoffmann et al. [1985b] found the rod length increases linearly with
increasing concentration to a peak and then begins to decrease. The concentration for the maximum rod length is noted as \( c^* \). It was believed that at \( c^* \), the length approaches the mean distance between the rods. It should be mentioned that \( c^* \) increases with decreasing length of the alkyl chain length. The aggregation number may be very large at some moderate concentration. Strivens [1989] calculated the aggregation number for 0.1 M CTAB-SA (salicylic acid) solution to be about 5000 at 25°C from rheological measurement results. This is equivalent to a micellar weight of 2,000,000. Myska et al. [1996] found in their light scattering studies on cationic surfactant drag reducing solutions that the micelle size increases with the concentrations of surfactant and of counterion. They also found that the length of rod-like micelles in Habon G \([C_{16}H_{33}-N(CH_3)_2 (C_2H_4OH)(3-OH-2-naphthoate)]\) solutions are about four times those of Ethoquad T/13-50 (Tallow-\(N(C_2H_4OH)_3Ac\)) and Arquad 16-50 \((C_{16}H_{33}-N(CH_3)_3Cl)\) solutions at 5 mM concentration.

Salts play an important role in affecting the micellar growth. This is because the micelle formation is strongly controlled by the positive charges on cationic surfactant headgroups. Salts with greater ability to neutralize these charges will certainly favor both micellar formation and growth [Rosen, 1989].

Ohlendorf et al. [1986b] studied the effect of the addition of salts on the length of the rod-like micelles for cationic surfactants. Their results showed that the length first increases with salt concentration reaching a peak and then decreases. They found that the higher the
valence of the anionic ions, the more effective are the salts. Bewersdorff and Ohlendorf [1988] and Myska et al. [1996] found that the rod-like micelles are longer in tap water than those in deionized water, which they interpreted as an effect of the salts in the tap water.

In general, the effectiveness of salt on the aggregation number of rod-like micelles increases with increasing lyotropic number of the anion. Anacker and Ghose [1963, 1968] reported the order of effectiveness in increasing the aggregation number for dodecyltrimethyl-ammonium micelles is:

$$IO_3^- < CHO_2^- < BrO_3^- < F^- < Cl^- < NO_3^- < Br^- < ClO_3^- < SCN^-$$

and for cetylpyridinium micelles:

$$IO_3^- < F^- < Cl^- , BrO_3^- << Br^- < NO_3^- < ClO_3^- << SCN^-, ClO_4^-, I^-$$

These are different from the order for reducing CMC reported by the same authors and cited in section 2.1.3.

Ford et al. [1966] studied the dodecylpyridinium system by light scattering and concluded that the micellar size increases as the counterion is changed in the order Cl^-, Br^-, I^-.

Bartet et al. [1980] used ionic exchange theory combined with spectrophotometric measurements, and showed that the binding ability of different anions on cetyltrimethyl ammonium (CTA) micelles increased in the order:

$$F^- < OH^- < CO_3^{2-} < B_4O_7^{2-} < HPO_4^{2-} < Cl^- < SO_4^{2-} < Br^- < NO_3^-$$
Using the same ionic exchange model but combined with ultrafiltration measurements, Gamboa et al. [1981] obtained an order the same as above except without OH\(^-\) and CO\(_3\)^{2-}\) in the series.

For aromatic acid anions, Rehage and Hoffmann [1991] concluded from their studies of the effects of benzoate with different counterions on the viscosity of the solution that the micellar growth is induced by two different processes: a change in the packing parameters (area/volume ratio) and a reduction of the surface charge. Aromatic acid anions are known to be absorbed at the micellar interface. The degree of penetration depends on the nature and position of the substituent groups on the phenyl ring. With different degrees of penetration, the degree of change in the packing parameters and the reduction of the surface charges are different.

Shikata et al. [1990] studied the CTAB system with the addition of salicylic acid and of sodium salicylate. They found that when the molar concentration of the salicylic acid reaches 50% of the concentration of CTAB, the degree of dissociation of Br\(^-\) is 100%, which means the CTAB:HSal micelles possess a net positive charge. However, with the addition of sodium salicylate, the concentration of sodium salicylate has to equal that of the surfactant to dissociate all the Br\(^-\) from the CTAB. Their results show that salicylic ion has a much stronger binding ability with the surfactant than the Br\(^-\).
Gravsholt [1976] suggested that the counterions of great importance are salicylate, m-chlorobenzoate and p-chlorobenzoate, which give rise to viscoelasticity, while o-chlorobenzoate, m-hydroxybenzoate and p-hydroxybenzoate have no effect on micelle structure. With the presence of a few millimoles per liter of salicylate, rod-like micelles of several hundred angstroms in length were detected at a few millimoles per liter of cationic surfactant solution [Hoffmann et al., 1984a; 1985a; Lindner et al., 1990]. Rehage and Hoffmann [1991] found that while p-toluic acid (4-methyl-benzoate) can greatly increase the solution viscosity, the o-toluic acid has no effect on the viscosity, and the m-toluic acid has an intermediate effect. They concluded that the viscoelasticity not only relates to the binding, but also to the specific orientation of the added compounds. By their FT-NMR studies on cationic surfactants with hydroxy-benzoate, chloro-benzoate and hydroxy-naphthoate counterions, Smith et al. [1994a] found that the counterion molecules orientate their polar portion toward the water, while the nonpolar portion is oriented into the micelle when their structure permits. The positions of the substituents on the benzene ring have to be right for these surfactant systems to orientate in this way and when their structure is right they are also good drag reducers. It is generally agreed that drag reduction ability is related to the existence and the size of rod-like micelles. Thus, the results by Smith et al. [1994a] also imply a relation between the orientation of counterions and the micellar size, a result confirmed by line broadening in the NMR data.

There is some experimental evidence to show that the micelles are polydisperse. Missel et al [1980] measured a strong increase in the polydispersity of SDS micelles as the
surfactant concentration increased. Strivens [1989] concluded from a broad $G''$ peak in
dynamic viscosity measurements and lower slopes for viscosity-shear rate plots of a
0.01M CTAB-SA solution that the micelles were polydisperse but he believed the micelle
size is very uniform for 0.1 M CTAB-SA solutions. Hoffmann et al. [1984b] found from
electric birefringence measurements that there is a size distribution but it is narrow.

Several theoretical approaches were developed to treat the polydispersity in micelle size.
Most of these models are based on the multiple equilibrium between single molecules and
micelles [Mukerjee, 1972; Missel et al., 1980; Porte and Appell, 1981; Ikeda, 1984].
Mukerjee [1972] defined a size distribution index as the ratio of the weight average
degree of association to the number average degree of association. He found the size
distribution index is close to unity for spherical or spheroidal micelles. He developed a
step-wise self-association model, which showed that the index value is 2.0 for elongated
micelles. Ikeda et al. [1981] found experimentally that the index increases with
concentration to a maximum, which is about 1.8, and then decreases. Their results are in
agreement with the theory by Mukerjee [1972].

2.1.6 The Flexibility of Rod-Like Micelles

Nagarajan [1982] suggested that rod-like micelles should be rigid. Because the average
micelle size of the polydisperse micelles is proportional to the square root of the micelle
concentration [Mukerjee, 1972], the intrinsic viscosity of the micellar solution should
also depend on the concentration of micelles. He found the experimental results for
intrinsic viscosity are in good agreement with the theoretical results if rigid micelles are assumed. Hoffmann et al. [1984b] also claimed the rod-like micelles in their CPySal system are stiff by comparing the experimental and theoretical results for the micelle length.

On the other hand, results by other researchers suggested that the rod-like micelles should be flexible. Porte et al. [1980] performed magnetic birefringence measurements on CPyBr solution. They believed that if the micelles were rigid, the so-called Cotton-Mouton constant $C_{CM} = \Delta n/H^2$, where $\Delta n$ is the birefringence and $H$ is the strength of the magnetic field, should be proportional to the micelle length, $L$. However, they didn't observe such a proportionality in their experimental measurements. Thus they concluded the micelles must be flexible. Appell and Porte [1981], using quasi-elastic light scattering spectroscopy, measured the mean hydrodynamic radius and the mean gyration radius, and they concluded that for large micelles, the micelles should be flexible. There was some uncertainty about this conclusion, however, due to the experimental bias introduced by the micellar polydispersity [Appell and Porte, 1981]. Appell et al. [1982] reinterpreted their old data [Porte et al., 1980; Appell and Porte, 1981] taking into account the polydispersity and reached the same conclusion about the flexibility. Ikeda et al. [1980] defined a molecular pitch as the ratio of micellar length to aggregation number. They believed the pitch should be constant for rigid micelles. However, in their experiments, they found that the molecular pitch decreases with the aggregation number. Thus they concluded the micelles should be flexible. Olsson et al. [1986] suggested that the
flexibility of micelles strongly depends on the degree of counter-ion binding. Based on their NMR measurements, they proposed that when the counterion binding increases with the concentration, the flexibility of the micelles also increases. Shikata et al. [1987a] studied 0.1 M CTAB with different amounts of NaSal. In contrast to the previous authors, they believed that when the ratio of NaSal to CTAB is increased from 0 to 1.0, the rigidity of the threadlike micelles increases. The rheological behavior of the solutions such as the shape of the $G'$ and $G''$ curves doesn't match that of a rigid-rod model, however. Thus, the rod-like micelles in their solutions had to be flexible. Recent cryo-TEM results showed that the micelles are rod-like and flexible [Bellare et al., 1988; Vinson and Talmon, 1989; Walter et al., 1991; Clausen et al., 1992; Cochin et al., 1992].

Thus, it appears that the flexibility of rod-like micelles depends on a number of factors such as ionic strength, micelle charge density, interfacial tension, nature and concentration of counterions and the chain length of the surfactant, as suggested by Hoffmann et al. [1984b]. They suggested that under different conditions, even the same surfactant system can have different degrees of flexibility.

### 2.2. Drag Reduction

Drag reduction by additives is a flow phenomenon in which the presence of small amounts of an additive in a carrier fluid causes a reduction in the turbulent friction compared with the pure fluid at the same flow rate. The drag reduced flow is still
turbulent, however, with a modified structure of turbulence and the additives normally do not cause relaminarization.

A reduction in energy loss in turbulent pipe flow of wood pulp fiber suspensions in water was reported by Forrest and Grierson [1931] more than sixty years ago. This first report of drag reduction went largely unnotice [Radin, 1974; Nadolink and Haigh, 1995]. Mysels and his associates [Mysels, 1949; Agoston et al., 1954; Mysels, 1971] found that the pressure drop in pipe flow for gasoline thickened by aluminum disoaps was less than that of pure gasoline under the same flow rate. This was the first drag reduction result widely recognized. Their results were not published until 1949 due to the Second World War. At the First International Rheological Congress (1948), Toms [1949, 1977] reported drag reduction results on dilute solutions of high molecular weight poly(methyl methacrylate) in monochlorobenzene. He observed that at constant pressure gradient, the flow rate could be increased by the addition of the polymer. Drag reduction is sometimes called the "Toms Effect".

Since the first reports of drag reduction, a great number of researchers have worked in this area. Nadolink and Haigh [1995] compiled a bibliography on drag reduction by polymers and other additives. There are over 4,900 references dating from 1931 to 1994.

There are three different kinds of drag reducers: fibers, polymers and surfactants. Polymer solutions have received a great deal of attention. Until recent years, only a few studies
were done on surfactant drag reducers. In the following sections, drag reduction by each of these three types of drag reducers will be reviewed with an emphasis on surfactant drag reduction.

2.2.1 Drag Reduction of Fiber Suspensions

Fibers are effective in drag reduction by damping turbulence and reducing energy dissipated by viscous shear to below that of the suspending medium under the same conditions [Lee and Duffy, 1976]. Drag reduction was observed in solutions with fibrous additives of aspect ratio \((\lambda/d)\) of 25-35, as long as the concentration of fibers was sufficiently high [Radin, 1974; Radin et al., 1975]. It was found that the effectiveness of fibers increases with increasing aspect ratio and decreasing fiber diameter [Radin, 1974; Radin et al., 1975; Lee and Duffy, 1976]. Lee et al. [1974] and Kale and Metzner [1974] reported that mixed fibers with polymers systems gave drag reduction up to 95%, which is higher than that for polymer or fiber alone. The sensitivity of polymer to degradation was decreased as well.

Fibers in aqueous solutions are stable to environmental factors. Choi et al. [1988] pointed out that the fibers are insensitive to water chemistry, piping materials and temperature so that they can be effective over a wide temperature range. Another feature of fibers as drag reducers is that their separation from the suspension is easy to accomplish and they are mechanically stable [Radin, 1974; Shenoy, 1984].
Lee and Duffy [1976] tried to find the mechanism for drag reduction by fibers. By measuring the local velocity profile, they found that the wall layer appears to be unaffected by the addition of fibers. They concluded that drag reduction by fibers could be attributed to the turbulent core region. This mechanism, however, contrasts with that of polymer solutions. According to Virk [1975a], the mechanism for polymer drag reduction occurs near the wall.

One critical disadvantage to their use in flow systems is that fibers can cause plugging problems in pipelines due to the high concentration required for drag reduction (as high as a few percent [Radin, 1974]).

2.2.2 Drag Reduction of Dilute Polymer Solutions

High polymers are the most efficient drag reducers as they require much lower concentrations for effective drag reduction compared with the other two kinds of additives. In a 6 mm diameter pipe, as little as 0.02 ppm polyacrylamide solution gave 5% drag reduction [Oliver and Bakhtiyarov, 1983]. Usually, concentration in the tens or hundreds of ppm are needed to achieve the maximum drag reduction [Hoyt, 1986].

Polymer solution drag reduction has been studied extensively in both aqueous and hydrocarbon media and a number of excellent reviews on the subject are available [Lumley, 1969; Patterson et al., 1969; Virk, 1975a; White and Hemmings, 1976; Frenkiel et al., 1977; Berman, 1978; Sellin et al., 1982a, b; Sellin, 1984; Shenoy, 1984; Giesekus
et al., 1985; Hoyt, 1985; Giesekus and Hibberd, 1987; Kulicke et al., 1989; Gyr and Bewersdorff, 1995]. The state of the art is also documented in conference proceedings, Sellin and Moses [1984], Gampert [1985], Rabin [1985], Sellin and Moses [1989], Gyr [1990] and ASME [1996]. In the following sections, a simple review of polymer drag reduction will be provided. Readers who need more details are referred to the above reviews.

Hershey and Zakin [1967b] pointed out that there are two types of drag reduction. In one type drag reduction occurs after the wall shear rate or shear stress exceed a critical onset value. In the second type drag reduction occurs as an extension of the laminar flow region such that the friction factor of the flow is less than that of turbulent flow at the same flow rate. Extension of the laminar flow region occurs because the presence of a sufficient concentration of polymer molecules increases the flow stability [Hershey and Zakin, 1967b]. Savins [1969], however, proposed four types of drag reduction for polymeric solutions. Based on the two types mentioned above, he further classified the drag reduction data in terms of the existence of the transition region. However, his classification didn't change the nature of the two basic types. Thus, people generally agree that there are only two types of drag reduction for polymeric solutions [Virk and Wagger, 1989].

The onset point of the first type of polymer drag reduction is the point at which drag reduction begins. The onset stress is the wall shear stress when this occurs. Below this
point there is no drag reduction. The same holds for the onset shear rate. For the type of
drag reduction in which there is an extension of the laminar flow region, the onset points
are not observed. In type one, there is always a definite set of flow conditions that must be
exceeded before drag reduction begins [Hunston and Zakin, 1980]. Virk et al. [1967] and
Hansen and Little [1971] found that the onset shear stress decreases with increasing
polymer molecular weight. Hershey [1965], White [1966] and Virk et al. [1967] found
the onset shear rate or shear stress to be independent of pipe diameter. Introducing the
Blasius law [White, 1966], one can predict that the onset Reynolds number is
proportional to the 8/7th power of the pipe diameter. However, Hansen and Little [1971]
observed a decrease in onset shear stress with tube diameter for which they provided a
qualitative explanation. Virk and Baher [1970a] and Virk [1975a] found that the onset
wall shear stress was independent of polymer concentration. However, the results from
other researchers have shown a decrease of the onset shear stress and onset shear rate
with increasing concentration [Hershey, 1965; Paterson and Abernathy, 1970; Hansen and
Little, 1971].

Three different models have been proposed to predict the onset phenomenon, namely,
length scale [Virk and Merrill, 1969], time scale [Fabula et al., 1966; Hershey, 1965;
Hershey and Zakin, 1967a], and strain energy storage models [Walsh, 1967]. Details will
be given in Section 2.2.6.
After onset, drag reduction of polymer solutions usually increases with the flow rate [Virk, 1975a]. With further increase in flow rate, the drag reduction reaches a peak and then decreases [Sellin, et. al., 1982a].

The effectiveness of polymer solutions in drag reduction seems to depend on the stretching of individual molecules by the stresses in the flow. Sellin et al. [1982a] and Hoyt [1986] claimed that linear, unbranched polymers give the best drag reduction performance. For coiled molecules in hydrocarbon solvents, Liaw [1968] found that more flexible polymer molecules show better drag reduction than less flexible molecules. Good solvents allow polymer molecules to stretch more freely in the solution and polymers in good solvents are better drag reducers. Hershey and Zakin [1967a] found that the drag reducing ability of polyisobutylene was improved when the solvent was switched from benzene (a poor solvent) to cyclohexane (a good solvent). Hunston and Zakin [1980], in their study of drag reduction of polystyrene in good solvents (benzene and toluene) and in poor solvents (mixtures of toluene and isooctane), found that the onset occurred earlier in the former case. Poor solvents also affect the mechanical degradation rates of polymers. Zakin and Hunston [1977] found that in a poor solvent mechanical degradation is more rapid than in a good solvent. Thus, they noted that both drag reducing efficiency and mechanical stability are greater in good solvents [Zakin and Hunston. 1977]. In aqueous systems, solvent goodness can also be altered by changing the electrolyte concentration. Sellin and Loeffler [1977] found that magnesium chloride caused a sharp drop in the drag reduction of PAA. As salt is added, the polymer molecules shifted from rod-like shapes
stiffened by repulsive charges on the chain to coiled shapes which show lower drag reduction efficiency.

Polymer concentration is another factor of importance. In general, effectiveness of drag reduction increases with concentration until a certain concentration. Beyond this concentration, further increase in concentration leads to a leveling off [Hoyt, 1984; Hoyt, 1986]. Paterson and Abernathy [1970] even suggested that unless tests are conducted on narrow molecular weight distributions, there is little possibility to establish the true dependence of drag reduction on concentration, even though all their data showed increasing drag reduction effectiveness with increasing polymer concentration. Virk and Baher [1970a] observed that drag reducing polymer solutions obey a linear relationship on semilogarithmic Prandtl-von Karman coordinates \( \frac{1}{\sqrt{f}} \) vs. \( \text{Re}\sqrt{f} \). The slope of that plot is proportional to the square root of the concentration.

Polymers with molecular weight below 100,000 seem to be ineffective [Hoyt, 1986]. The higher the average molecular weight, the greater the drag reduction for a given concentration and Reynolds number. Shenoy [1984] concluded after his review of previous works that any macromolecular molecule with a linear structure and a molecular weight of 500,000 or more is a good drag reducer. However, Paterson and Abernathy [1970] concluded from the lack of correlation between intrinsic viscosity and drag reduction that the average molecular weight may have little relevance to the actual drag reduction behavior. Patterson et al. [1966], Paterson and Abernathy [1970], Hunston and
Reischman [1975] and Hoyt [1986] pointed out that drag reducing effectiveness depends strongly on the highest molecular weight components of a given molecular weight distribution, which does not necessarily correlate with intrinsic viscosity. Liaw [Liaw, 1968; Liaw et al. 1971] defined the entanglement capacity, m', as the ratio of polymer molecular weight to the critical molecular weight for entanglement. Good drag reduction is obtained if the m' value of the polymer is greater than 50. Liaw pointed out that polymers such as polyethylene oxide and polydimethyl siloxane with flexible chains are more efficient drag reducers than more rigid molecules such as polystyrene and polymethyl methacrylate. While for polymers with an m' value of only 15, poor drag reduction was found no matter what the flexibility.

It has been shown that polymer drag reduction is pipe diameter dependent. White [1966] found that drag reduction is greater in a smaller pipe for the same concentration and Reynolds number. Paterson and Abernathy [1970] pointed out that the extent of drag reduction is independent of pipe diameter for the same solvent wall shear stress.

The disadvantage to polymer drag reducers is their mechanical degradation in service [Sellin, et. al., 1982a, Shenoy, 1984]. The high molecular weight polymers, which seem to be the best drag reducers, are the most susceptible to degradation [Patterson et al., 1969]. Zakin and Hunston [1977] found that the rate of mechanical degradation of polystyrene solutions increases with increasing molecular weight. White [1966] found that guar gum can be pumped for one hour before any degradation happens. He believed
that guar gum is very stable with respect to mechanical shear but no reason was provided. Choi et al. [1992] studied two commercial polymer drag reducers: Polyox WSR-301 (polyethylene oxide, Union Carbide) and Separan AP-273 (partially hydrolyzed polyacrylamide, Dow Chemical), in a recirculatory system. They found that Polyox degraded completely in less than 24 hours but the Separan solution partially degraded initially but was able to maintain 25% drag reduction for up to 730 hours. They believed that Separan AP-273 may be an acceptable polymer drag reducer for recirculation systems.

The loss of the drag reduction ability of polymer drag reducers may not be completely attributable to degradation of the polymer. Recently, Kim et. al. [1993] observed that when a stable interchain association is formed under high shear flow, drag reduction of poly (acrylic acid) sharply decreases. Upon addition of a minute amount of salt, drag reduction is recovered because of the breaking of the interchain association by the salt. They believed H-bonding connects polymer chains to form a superstructure. Their conclusion is that the superstructure doesn’t favor drag reduction.

2.2.3 Drag Reduction of Surfactant Solutions

Three classes of surfactants have been investigated for drag reduction, namely anionic, cationic and nonionic. Anionic surfactants have proven to be good drag reducers and mechanically stable [Savins, 1967]. However, their applications are limited due to precipitation of the salts formed with calcium and magnesium ions normally present in
tap and sea water [Zakin et al., 1971]. Other problems may arise due to their strong tendency to form foams with air. Nonionic and cationic surfactants are both less sensitive to cations. However, nonionic surfactants are effective as drag reducers only in a narrow temperature range around the cloud point of the surfactant [Zakin and Lui, 1983]. Cationic surfactants, on the other hand, show much broader effective temperature ranges [Chou, 1991b] and thus may have more potential applications. In the following sections, these three kinds of surfactant drag reducers will be reviewed.

2.2.3.1 Drag Reduction of Anionic Surfactant Solutions

Savins [1967; 1968a, b; 1969] obtained more than 80% drag reduction using 0.2% sodium oleate in water with KCl. Increasing KCl concentration from 3.5 to 10% increased drag reduction from 45% to 82%. He suggested that with increasing electrolyte concentration, spherical micelles were probably rearranged into cylindrical micelles which formed a network of interlaced rod-like elements.

Savins also noted that when the wall shear stress exceeded a critical stress, drag reduction dropped to zero, but the process was reversible, i.e., drag reduction was regained when the shear stress was lowered. The loss of drag reduction was presumably caused by break-up of the micelle microstructure due to high shear stresses. The rate of break-up was faster than the rate of reformation. The recovery of drag reduction when the flow rate was lowered showed that the micelle microstructure reformation rate exceeded the rate of break-up. No permanent degradation was noticed after 88 hours of continuous shear
above the critical wall shear stress. These findings are important for surfactant drag reduction applications and were also observed for cationic surfactants. The problem with anionic surfactants is their sensitivity to \( \text{Ca}^{2+} \) and \( \text{Mg}^{2+} \) normally found in tap water and sea water which cause precipitation.

### 2.2.3.2 Drag Reduction of Nonionic Surfactant Solutions

Nonionic surfactant molecules don’t carry charges and thus they are less affected by other ions. This property is an advantage for nonionic surfactants as drag reducers as they will not be inordinately affected by calcium and magnesium ions normally present in tap water. Nonionic surfactants also have unique upper coacervation temperatures or cloud points at and above which the surfactant-water systems separate into two phases.

Zakin and coworkers were pioneers in investigating the drag reduction effectiveness of nonionic surfactants [Zakin and Chiang, 1972; Zakin and Lui, 1983; Chang and Zakin, 1985; DeRoussel, 1993]. They observed that nonionic surfactants with straight chain alkyl groups \(( \text{C}_x \text{H}_y-(\text{OCH}_2\text{CH}_2)_z-\text{OH})\), where \(x\) is 12 to 18, \(y\) is \(2x+1\) or \(2x-1\) and \(z\) is about 0.5\(x\) were effective while alkyl phenyl surfactants were not. Chang and Zakin [1985] discovered that some mixtures of nonionic surfactants at 1% concentration with the chemical structure of \( \text{C}_{18}\text{H}_{35}(\text{OCH}_2\text{CH}_2)_n-\text{OH} \) were effective drag reducers at temperatures just below and above their cloud point temperatures. They found that the addition of sodium sulfate or of phenol lowered the cloud point and increased the relative viscosity. Thus the drag reducing ability at temperatures below the normal cloud point is
enhanced upon the addition of the salt or phenol as the cloud point was lowered to approach the measurement temperature [Chang and Zakin, 1985]. Their surfactant systems appeared to be mechanically stable. Mechanically degraded solutions quickly regained their reducing ability upon entering a low shear region, i.e. after passing through a pump [Zakin and Lui, 1983].

DeRoussel [1993] performed drag reduction measurements on a number of nonionic surfactants containing saturated and unsaturated C<sub>12</sub> to C<sub>18</sub> alkyl groups with 4 to 23 ethylene oxide groups at 1% concentration. The conclusions he reached are that the temperature at which maximum drag reduction is observed is close to the cloud point (coacervation temperature) of the surfactant solution. At least 20% drag reduction was observed at temperatures 10 to 25°C above and below the cloud point temperature. Increase of the length of the alkyl group and decrease in the number of ethylene oxides both decreased the cloud point and the effective temperature range for drag reduction. Further, mixed surfactants have cloud points intermediate between those of the pure surfactants. Thus, selection of the length of the alkyl chain, the number of ethylene oxide groups, and the constituents and concentrations of mixed surfactant systems can be used to affect the cloud point and hence the potential temperature range in which a surfactant system would be effective for drag reduction. This does not guarantee the surfactant system selected will be effective in the temperature range, but it does provide a guide for rapid screening of possible additives for a particular application with a defined temperature range. Minor adjustments can also be made by considering the saturation or unsaturation of the alkyl group. Unsaturation will shift the cloud point to a higher
temperature compared with a saturated alkyl group. A measurement on a mixture of nonionic and cationic surfactants was also carried out in the same study. However, the level of drag reduction was below that of the nonionic surfactant alone.

Hellsten and Harwigsson [1994] tested a nonionic surfactant for drag reduction effectiveness. The surfactant is ethoxylated fatty acid ethanolamide, $C_nH_{2n-1}CONHC_2H_4(OC_2H_4)_mOH$. Two main groups, RMA-m ($n=22$, from rapeseed monoethanolamide) and OMA-m ($n=18$, from oleic acid monoethanolamide), were investigated. They found that RMA-3, RMA-6, RMA-8 or their mixtures and OMA-5 were effective in different parts of the temperature range from 43-95 °F. The RMA's were effective at the high end of the range and OMA was effective at the low end. Lu et al. [1997b] reported that OMA-3/4 was effective from 1°C to 15°C (see also Section 5.1.5). The concentrations used in these studies ranged from 2000 ppm to 6000 ppm. Biodegradability and toxicity data were also provided to show that this kind of surfactant is rapidly biodegradable and has low toxicity against marine organisms [Hellsten and Harwigsson, 1994]. They suggested that this kind of surfactant may be a good candidate for applications in district cooling systems which operate at 5 to 15 °C.

Zwitterionic surfactants have both positive and negative charges in one surfactant molecule and thus form a special kind of nonionic surfactant [Laughlin, 1991]. Most recently, Hellsten et al. [1996] studied a zwitterionic surfactant, N-alkylbetaines ($CH_3(CH_2)_n - N^+(CH_3)_2CH_2COO^-$, $n = 15$ or $17$) with 5-15% (mol.) of sodium dodecyl benzene sulphonate (Na-LAS). They found that the $C_{16}$-betaine (2.5 mM) / Na-LAS (0.5
mM) system is drag reducing between 8 and 50 °C and the C\textsubscript{18}-betaine (2.5 mM) / Na-LAS (0.5 mM) system between 30 and 85 °C. They also studied the effect of this kind of surfactant system on heat transfer. A reduction up to 21% was measured for overall heat transfer in a plate heat exchanger. The betaines are considered readily biodegradable and less toxic to marine organisms than cationic surfactants. However, since zwitterionic surfactants have both positive and negative charges in a single surfactant molecule, they may be sensitive to ions existing in water or present in the flow system. Thus, their stability in the presence of anions and cations needs to be investigated.

2.2.3.3 Drag Reduction of Cationic Surfactant Solutions

The narrow temperature range for effective drag reduction limits the usefulness of nonionic surfactants as drag reducers, and precipitation caused by calcium and magnesium ions found in tap water limits the applications of anionic surfactants. Cationic surfactants generally have wider temperature ranges and are not very sensitive to calcium or magnesium ions. Because of their potential for applications, extensive research on cationic surfactant drag reducing additives has been carried out over the last ten years. Research in this area will be reviewed in a systematic manner in the following sections.

2.2.3.3.1 Surfactant Structure Effects

Quaternary ammonium surfactants and those with related structure (cetyl pyridinium salicylate or CPySal) have excellent drag reduction ability. Cetyl trimethyl ammonium bromide (CTAB) was the first cationic surfactant to receive attention in drag reduction studies [White, 1967; Zakin et al., 1971]. White [1967] studied a 508 ppm CTAB with
equi-molar 1-naphthol. No onset phenomenon was observed but rather a gradual departure from the laminar line. He found that drag reduction terminates at a fixed wall shear stress which was independent of diameter. He called that stress the critical wall shear stress. Zakin et al. [1971] studied 1500 ppm CTAB with varying amounts of 1-naphthol. They found that drag reduction increased with the Reynolds number to a maximum of about 70% and then decreased to zero when the wall shear stress exceeded the critical shear stress. They suggested that at this point, the forces causing the soap to aggregate are overcome by the shear stress so the aggregates are broken down to small particles which have little drag reduction ability; similar to Savins' proposal for anionic surfactant aggregates.

Chou et al. [1987, 1988] reported drag reduction results on three cationic surfactant systems: Arquad 16-50 (C16TAC or CTAC, C16H33-N(CH3)3Cl), Arquad 18-50 (C18TAC, C18H37-N(CH3)3Cl) and Kemamine Q-2983C (C22TAC or ETAC, C22H43-N(CH3)3Cl). All surfactants were at 2000 ppm with 2000 ppm sodium salicylate as counterion. They reported the effective drag reduction temperature ranges are 30 to 60°C, 30 to 90°C and 60 to 110°C for the C16TAC/NaSal, the C18TAC/NaSal and the C22TAC/NaSal systems, respectively, independent of tube diameters in 0.106-inch, 0.243-inch and 0.824-inch pipes. Effective drag reduction at 80, 93 and 107 °C was also observed for the C22TAC (ETAC) system in a 6-inch pipe. Thus, they concluded that there is an upper temperature limit for effective drag reduction which is dependent on the alkyl chain length [Chou et al., 1988]. Rose et al. [1984, 1989] also reached the same conclusion. Above the
maximum critical temperature, the solutions lose their effectiveness, but regain it when cooled below the critical temperature. These conclusions were confirmed in later studies on other alkyl trimethyl ammonium chlorides, alkyl bis-hydroxyethyl methyl ammonium chloride and alkyl tris-hydroxyethyl methyl ammonium acetate surfactants with different alkyl chain lengths [Chou et al., 1989a; Chou, 1991b].

Rose et al. [1984, 1989] and Chou et al. [1989a] also found that the lower temperature limit depends on solubility of the surfactant. Surfactants containing alkyl bis-hydroxyethyl methyl are more hydrophilic than those with alkyl trimethyl and thus the former can provide drag reduction down to lower temperatures, such as 2°C (the lowest temperature they tested). Unsaturation of the alkyl chain also improves the solubility of long chain surfactants and thus provides the possibilities for them to be drag reducing at low temperature [Rose et al., 1984, 1989; Chou et al., 1989b].

Chou and Zakin [1991a] also studied the drag reduction effectiveness of mixed cation and mixed counterion cationic surfactant systems. The mixed surfactants are dodecyl (C12) trimethyl ammonium chloride / erucyl (C22) trimethyl ammonium chloride (DTAC/ETAC), and dodecyl trimethyl ammonium chloride / cetyl (C16) trimethyl ammonium chloride (DTAC/CTAC). They noted that the effective drag reduction temperature range for long chain cationic surfactants usually extends to high temperatures and the short chains are only effective at low temperatures. However, when a long chain surfactant was mixed with a short chain surfactant, the temperature range was extended.
The addition of a small amount of short chain surfactant greatly depressed the lower temperature limit of the long chain surfactant, while its upper temperature limit could be maintained at a high level. Thus, it is possible to have cationic surfactant systems with a temperature range wide enough to cover temperatures involved in both district cooling and district heating systems. In the same study, they also explored the effect of mixed counterions. In general, the results were similar but the effect was smaller.

### 2.2.3.3.2 Counterion Effects

Generally, without counterions, cationic surfactants would not form the rod-like micelles necessary for drag reduction at low concentrations such as less than 1%. Thus, it is necessary to add certain kinds of counterions to cationic surfactant solutions for drag reduction.

The first counterion to receive wide attention was 1-naphthol. After White's [1967] research, several other researchers investigated the cationic surfactant/1-naphthol system. Zakin et al. [1971] studied 0.15% CTAB with varying amounts of 1-naphthol. They found that the highest critical shear stress (maximum shear stability) occurred when the weight ratio of CTAB to 1-naphthol was 2.1 to 1 (1:1 molar ratio).

Various alkyl trimethyl ammonium halides with 1-naphthol were studied by Elson and Garside [1983]. They investigated the 1-naphthol counterion concentration effect. They believed that, due to the solubility of the counterion, at low concentrations the counterion
has to be more than equimolar with the surfactant in order to offset part of the 1-naphthol which was dissolved in the water. At high surfactant concentrations, however, the effect is small. Thus, the optimum ratio of counterion to surfactant will be one to one for high concentrations, while it should be higher than one to one for low concentrations of surfactant.

Extensive drag reduction tests with sodium salicylate as counterion were performed [Chou et al., 1987, 1988, 1989a, 1989b, 1991a, 1991b; Gasljevic, 1995a]. Chou et al. [1989b; 1991b] studied the 5 mM Ethoquad O-12 (oleyl bishydroxymethyl ammonium chloride) system with various amounts of sodium salicylate. They found that at 2 °C with a 1.5:1 ratio of counterion, the surfactant system showed the highest critical wall stress, i.e., the most effective drag reduction system at this ratio. Rose et al. [1984, 1989] found that excess quantities of salicylate give a higher critical temperature and higher critical Reynolds number for loss of drag reduction for the CTASal system. They found that a CTASal solution with excess salicylate maintained effective drag reduction activity for 10 weeks in their district heating study at temperatures between 40 and 90 °C. For hydroxynaphthoates as counterions, however, excess counterion reduces the drag reduction efficiency [Chou, 1991b]. He suggested that the rod-like micelles become more rigid in this case.

Chou et al. [1989a] proposed that while salicylate is the most widely used counterion, other counterions may also be very effective. The existence of a hydrophobic substituent
group on benzoate or naphthoate compounds may promote more effective drag reduction systems as long as they are separated from other hydrophilic substituent groups on the same ring. Later, through NMR studies, Smith et al. [1994a] confirmed that the position of substituent groups on the benzoate and naphthoate rings can affect the orientation of counterion molecules at the micelle-water interface. If a hydrophobic group adjacent to the carboxylate must reside in the water phase, then no stable rod-like micelles can be formed and correspondingly, no drag reduction occurs.

An intriguing phenomenon observed in surfactant drag reduction is the so-called "gap phenomena" [Chou, 1991b; Kleuker et al., 1991]. When Chou [1991b] measured drag reduction for a 2.85 mM Habon (hexadecyl trimethyl ammonium-3-hydroxy-2-naphthoate) plus 9.375 mM NaSal, he found no drag reduction at 50 °C, while at 30, 40, 60 and up to 100 °C this system showed good drag reducing ability. A similar observation was reported by Kleuker et al. [1991] when they studied the drag reduction of a Dobon-G (docosyl dimethyl hydroxyethyl ammonium-3-hydroxy-2-naphthoate) plus NaSal solution in a large scale system. They found the drag reduction effect was lost in a middle temperature range (from 60 to 80 °C) after a few days of operation, while the solution was effective from 40 to 130 °C in laboratory tests (the details were not reported). They explained this as due to biological contamination by protein. Both surfactant systems involved here have 3-hydroxy-2-naphthoate as counterion plus excess sodium salicylate. Chou [1991b] explained the "gap" phenomenon as the result of the competition between the 3-hydroxy-2-naphthoate and the salicylate. He postulated that at certain temperatures,
they canceled each other's effectiveness. Kleuker et al. [1991] also mentioned that Dobon-G normally features a quite narrow temperature span in drag reduction from 100 to 140°C. The addition of the NaSal shifted the effective temperature range to 40 to 130°C. They suggested that the salicylate counterions probably replaced the naphthoate counterions at the surface of the micelles at lower temperatures. However, as noted above, in their laboratory tests, no gap phenomenon was observed. These anomalous results have not been further studied.

2.2.3.3.3 Diameter Effects

For Newtonian fluid turbulent flow, the Reynolds number accounts for the effect of pipe diameter, i.e., the turbulent flow of Newtonian fluids will follow a single friction factor-Reynolds number curve for different size pipes. However, for drag reducing fluids, this is not the case. The friction factor is a function of both $N_{Re}$ and pipe diameter. Since most practical flow systems use larger pipe sizes than those in the laboratory, it is important to be able to scale up to predict drag reduction performance in large pipes from small diameter measurements. Some research has been done with polymer drag reduction scale-up. However, only a limited number of efforts have been made on surfactant drag reducers. These researchers tried to extend rules appropriate for drag reducing polymers to surfactants.

During his drag reduction study on a 508 ppm CTAB with equi-molar 1-naphthol system, White [1967] found drag reduction terminates at a fixed wall shear stress which was
found to be independent of diameter. This was confirmed later by several researchers [Savins, 1969; Elson and Garside, 1983; Ohlendorf et al., 1984; Rose et al., 1984, 1989].

Hoyt and Sellin [1991] developed a technique for scale-up of polymer drag reduction. He assumed that the negative roughness, $\Delta B$, is independent of diameter at a given friction velocity and the velocity profile for polymer drag reduction is shifted by $\Delta B$ from that of Newtonian flow. The scaling process is relatively simple using this method and no iteration or graphical techniques are needed. This method is quite successful in pipe sizes larger than 10 mm. The reason for failure of the method for pipes smaller than 10 mm is believed to be the relatively larger extent of the viscous sublayer in small tubes than in large tubes [Hoyt and Sellin, 1993].

Gaslijevic and Matthys [1995b] studied drag reduction of Ethoquad T/13-50 (2300 ppm) / NaSal (2000 ppm) solutions in four tubes of 2 mm, 10 mm, 20 mm and 52 mm. They found that with the exception of the 2 mm tube, drag reduction in the subcritical region (shear stress lower than critical shear stress) is a function of bulk fluid velocity and is independent of pipe diameter. The deviation is smaller than 7% over the pipe diameter range and velocity range of 0.5 to 10 m/s they studied. They also suggested that in the supercritical region (where drag reduction decreases with increase in velocity) the shear stress may be a better parameter.
Pollert et al. [1996] reported that drag reduction is increased with increasing pipe diameter for the 500 ppm Habon G system at diameters above 4 mm. They also investigated drag reduction in a 4 mm pipe in parallel with a 10 mm pipe as a simulation of a pipe network in real flow systems. They found that drag reduction in the 4 mm pipe of that network has a higher critical shear stress than that in a single 4 mm pipe. This held only if the diameter ratio of the parallel pipes was larger than 2.5:1. They were not able to explain this phenomenon.

Park et al. [1996] investigated drag reduction of CTAC/NaSal, STAC (stearyltrimethyl ammonium chloride) /NaSal and Habon G systems at low concentrations, 100, 250 and 500 ppm. They found that drag reduction increased with increasing concentration and with increasing pipe size (4.65 mm and 10.85 mm).

2.2.3.4 Stability of Surfactant Drag Reduction

It is generally believed that cationic surfactant drag reducers are stable. Early studies on cationic surfactant drag reduction found that cationic surfactants show no mechanical degradation although the 1-naphthol systems were chemically unstable and deteriorated in days [White, 1967; Zakin et al., 1971]. Rose et al. [1984, 1989] found that a 0.2% CTASal drag reducing solution was stable over a time period of 2.5 months.

However, recent research has shown that a cationic surfactant, Ethoquad T/13-50 / NaSal, may not be stable with time [Lu et al., 1995b; Gasljevic, 1995a], which will be discussed
in more detail in Chapter 6. Drag reduction was completely lost after several days. However, earlier data by Chou [1991b] on the same surfactant system showed no loss of drag reduction after 11 days. This degradation may have been due to interactions of the surfactant molecules with different materials in the flow system and/or adsorption of the surfactant molecules on the inside wall of the flow system [Lu et al., 1995b]. However, a definite conclusion can not be drawn.

2.2.4 Heat Transfer Reduction in Drag Reducing Flows

Drag reduction is accompanied by a reduction in the heat transfer coefficient in a tube-tube exchanger [White, 1970; Monti, 1972; Debrule and Sabersky, 1974; Dimant and Poreh, 1976; Rose et. al., 1984; Matthys, 1985; Christensen and Zakin, 1991; Matthys, 1991]. It is believed that the increased thickness of the viscous boundary near the wall which accompanies drag reduction causes an increase in the thermal resistance between the wall and the bulk fluid and therefore a reduction in the rate of heat transfer [Sellin et al., 1982a].

White [1970] measured the overall heat transfer coefficient for drag reducing polyethylene oxide and found it decreased with increasing Reynolds number and is only 10% of that of water at a Reynolds number of 10,000. Their results showed that drag reduction and heat transfer reduction occur at the same Reynolds numbers. Monti [1972] found a commercial drag reducer, ET-597 (a high molecular weight partially hydrolyzed polyacrylamide from DOW) greatly reduced the heat transfer in pipe flow in the region at
which it is effective in drag reduction. They also found that the addition of NaCl or FeCl₃ can reduce the drag reduction and heat transfer reduction of the polymer up to 95%, i.e., the solutions with salt behave like water.

Debrule and Sabersky [1974] studied 10 ppm and 50 ppm polyethylene oxide solutions. They found that the 50 ppm solution provided as much as 72% drag reduction in smooth pipe, while at the same time the heat transfer coefficient was reduced to 20% of that of water. Thus the heat transfer reduction is greater than the drag reduction. For rough pipe, the heat transfer was reduced even more drastically. They also noticed that when drag reduction began to be lost, the heat transfer coefficient also approached that of water.

Dimant and Poreh [1976] studied heat transfer in drag reducing pipe flow. They found that there are large differences between the two heat transfer modes: constant wall temperature and constant heat flux. The thermal entrance lengths were longer than those of water, and the fluid properties are more temperature dependent than water. They concluded that when drag reduction occurs, heat transfer can be characterized by laminar heat transfer. From this conclusion, all three abnormal phenomena could be explained.

Rose et al. [1984] observed that viscoelastic surfactant solutions simultaneously lower the pipe flow friction and the heat transfer coefficient. However, unlike polymers, surfactants have a critical temperature and a critical shear stress at which drag reduction is lost and the heat transfer coefficients return to those of water. They suggested that heat exchangers
should be designed to take advantage of this characteristic as a solution to the problem of the low heat transfer coefficients of drag reducing surfactant solutions.

More recently, Matthys [1985, 1991] found the Reynolds analogy is not valid for polymer drag reducing fluids, which means that heat transfer and momentum transfer of drag reducing fluids are not affected by the properties of the fluid to the same extent. He suggested this discrepancy is responsible for the reported very long (up to hundreds of diameters) thermal entrance region for drag reducing flow. He also suggested that studying heat transfer may provide back-door access to the mechanism of drag reduction.

Plate heat exchangers are very efficient in heat exchange. They rely on tortuous paths along parallel plates which lie close to each other. Christensen and Zakin [1991] investigated drag reduction and heat transfer reduction of the erucyltrimethylammonium / NaSal system both for a tube in tube heat exchanger and a plate heat exchanger. They measured heat transfer reduction in the latter from 10% at high flow rates to 65% at low flow rates, while the heat transfer reduction for a tube in tube heat exchanger was as high as 90%. Pollert et al. [1996] studied heat transfer to a drag reducing fluid in a plate heat exchanger. In their experiments, overall heat transfer reduction increased with surfactant concentration up to 25%. Thus, an additional benefit of the use of plate heat exchangers for drag reduction flow systems is that the heat transfer reduction is smaller. Suggested causes for the modest decreases in heat transfer coefficient are the destruction of the secondary structure by a high shear region at the entrance to the exchanger, or high shear
stresses in the flow through the narrow and irregular channels of the plates. However, a simple calculation discloses that the shear stress in the channels is much lower than the critical shear stress for loss of drag reduction. Another possible reason is that the fluid flowing in the channels changes directions so often that the boundary layer is destroyed before it is fully developed, resulting in higher heat transfer coefficients compared with pipe flow [Christensen and Zakin, 1991].

For transport of heating or cooling water, over long distances, the lower heat transfer coefficients are advantageous in reducing heat loss. For a liquid to air tube-tube heat exchanger, the air side resistance is dominant and the increased resistance of the drag reducing fluid is not a major effect. But for liquid-liquid tube-tube heat transfer the problem is serious. Gasljevic [1995a] attempted to introduce a high shear obstacle at the entrance to the exchanger to temporarily destroy the micellar structure. Surprisingly in field tests at Völklingen, Germany [Kleuker et al., 1991] and at Kladno-Krocehlavy, Czech Republic [Pollert et al., 1994] no significant reductions in overall heat transfer coefficients were observed, possibly because the exchangers are old and corroded with high resistance in the corroded metal pipes or they were overdesigned.

2.2.5 Maximum Drag Reduction Asymptote

It was found there is a maximum drag reduction asymptote for polymer drag reducers [Castro and Squire, 1967; Giles and Pettit, 1967; Virk et al., 1967, 1970b; Virk, 1971b].
Castro and Squire [1967] proposed that for polyethylene oxide solutions, there is a maximum drag reduction asymptote expressed as:

\[ f' = \left( \frac{Re}{1500} \right)^{1/3} \]  

(2.4)

where \( f' \equiv \frac{f}{16 / Re} \). From this the asymptote can be written as: \( f = 1.398 Re^{-2/3} \).

At almost the same time, Giles and Pettit [1967] found in their drag reduction measurements on the same polymer that the minimum limit for the friction factor is described by:

\[ \frac{l}{\lambda} = 870 \log Re \lambda^{\frac{1}{2}} - 16.1 \quad \text{or} \quad \frac{l}{f} = 348 \log Re f^{\frac{1}{2}} - 53.9 \]  

(2.5)

or simply in the form:

\[ \lambda = \frac{l}{\sqrt{Re}} \quad \text{or} \quad f = 0.25 Re^{-0.5} \]  

(2.6)

where \( \lambda = 4f \). It should be noted that in the literature, authors often used different definitions of the friction factor.

Virk [Virk et al., 1967, 1970b; Virk, 1971b] proposed an asymptote for maximum polymer drag reduction:

\[ f^{-\frac{1}{2}} = 19.0 \log Re f^{\frac{1}{2}} - 32.4 \]  

(2.7)

Virk suggested that this asymptote is independent of the nature of the polymer solution, concentration, solvent and pipe diameter. In other words, this equation is universally
valid. However, some exceptions were observed. For example, drag reduction greater than that predicted by Virk’s asymptote has been reported by McMillan et al. [1970, 1971] and Hershey et al. [1975] in their aluminum disoap systems, by Lee et al. [1974] in their polymer/fiber mixed system, and by Sylvester and Smith [1979] in the Dowell-APE (an aluminum salt of an alkyl phosphate ester) in kerosene system. More recently, Bewersdorff and Thiel [1993] measured higher drag reduction than that predicted by Virk’s asymptote in their experiments on the TTAB/NaSal system in a 49 mm pipe. Chara et al. [1993] also measured smaller friction factors than predicted by Virk’s asymptote for the Habon-G system. Because the equation was derived from polymer drag reduction data, it is not surprising that for systems other than polymer solutions, drag reduction has been reported to exceed this asymptote. However, Berman [1978] suggested there is no well-defined maximum drag reduction asymptote. This is apparently not true since based on data for cationic surfactants in water and aluminum disoaps in hydrocarbons, Zakin et al. [1996] have proposed a new asymptote for non-polymeric drag reducers:

\[ f = 0.32 R e^{-0.55} \]  

(2.8)

This asymptote expressed friction factor as an explicit function of Reynolds number and is easy to plot. It can be seen that the new asymptote predicts friction factors which are significantly lower than those predicted by Eq. 2.7 (Fig. 2.3).

2.2.6 Mechanism of Drag Reduction

Since the first paper concerning drag reduction was presented [Toms, 1949], numerous researchers have been working on the mechanism of drag reduction.
Figure 2.3  Newtonian friction factors and drag reduction asymptotes.
Three theories have been proposed to predict the onset of polymer drag reduction: length scale [Virk and Merrill, 1969], time scale [Fabula et al., 1966; Hershey, 1965; Hershey and Zakin, 1967a], and strain energy storage models [Walsh, 1967]. In the length scale model [Virk and Merrill, 1969], it was suggested that when the ratio of the polymer length scale ($R_G$, radius of gyration) and the turbulent length scale ($v/u_T$) reaches a certain value, the onset of drag reduction occurs. The time scale model [Fabula et al., 1966; Hershey, 1965; Hershey and Zakin, 1967a] states that drag reduction begins when the relaxation time of the polymer molecule in solution equals a characteristic flow time or some multiple of it. This is equivalent to a constant Deborah number. Berman and George [1974] concluded from their experimental results that the time scale onset prediction is remarkably accurate, while the prediction by the length scale model is precisely opposite to certain experimental results.

The most interesting model among the three is the energy storage model proposed by Walsh [1967]. Based on a mechanism of polymer-turbulence interaction, it suggests that the polymer molecules store excess energy for small scale disturbances near the wall so that these small scale instabilities will not grow. Thus, there exists the possibility to convect energy from the high strained wall region to the unstrained core of the pipe flow. The model states that drag reduction begins when strain energy convection becomes comparable to kinetic energy diffusion. The experimental study of Berner and Scrivener [1980] is consistent with this model. Berner and Scrivener [1980] used laser doppler anemometry (LDA) to measure the velocity fluctuations in polymer drag reduction flow.
They found the buffer layer thickness is increased, and the number of small scale energy dissipative structures is decreased. Their results confirm that polymer drag reduction is due to a change in energy exchanges mainly in the buffer layer. Virk [1975a] acknowledged that the strain energy does seem implicated in drag reduction.

Ryskin [1987] constructed a theory for drag reduction based on the "yo-yo" model he proposed. The yo-yo model says that the polymer chain unravels if the strain rate exceeds a critical value. The elongation of a polymer chain follows the elongation of the fluid element. The central portion of the chain is straightened out first and remains stretched. Then the two coiled portions at the ends simultaneously diminish in size, so the polymer chain is greatly extended in length. If the flow becomes weak, the extended chain will curl back into a coil. The stretched central portion generates large additional stress via a dissipative mechanism [Ryskin, 1987]. His theory predicts a very large viscosity increase for polymers in turbulent flow regions. He then related this viscosity increase to drag reduction. Even though Ryskin [1987] repeatedly referred to extensional flow in his discussion, he used intrinsic viscosity in his model rather than extensional viscosity.

Drag reduction induced by polymers appears to be associated with near wall effects. Wells and Spangler [1967] were the first to study drag reduction by injecting polymer solutions into the centerline and near the wall. They found that drag reduction didn't occur unless the polymer is present at the wall. Their conclusions were confirmed by the recent work of Smith and Tiederman [1991], who injected polymer solution at the centerline of
a flow and measured the concentration distribution and the drag reduction. Unbroken threads of concentrated polymer solution were observed for more than 200 pipe diameters downstream. They found that as long as there is no polymer in the $y^+<50$ region, there is no drag reduction. Even at low concentrations in that region, drag reduction was measured. They concluded that drag reduction is caused by polymer in the wall region and not by modification of the turbulent flow in the center region. Virk [1971a] found in his rough pipe experiments that the onset for polymer solutions is unaffected by roughness, which was confirmed by Bewersdorff and Thiel [1993] for $Re<30,000$. Their results at higher Reynolds number were not in agreement, which may reflect behavior differences of polymers versus surfactants. Virk concluded from his results and some velocity profile measurements that the region of interest to drag reduction is $5<y^+<50$ [Virk, 1975a]. The upper limit is consistent with the results of the injection experiments [Smith and Tiederman, 1991]. Virk [1975a] also suggested that the polymer-turbulence interaction responsible for drag reduction happens in the buffer zone near the position of peak turbulent energy production, $y^+=15$. He then concluded that drag reduction occurs because polymer molecules interfere with the turbulent bursting process.

Ohlendorf et al. [1984, 1986a] hypothesized that in surfactant solutions the presence of rod-like micelles and a shear induced structure are responsible for the drag reduction capability. Ohlendorf et al. [1984] classified surfactant drag reduction flow into three regions based on their experimental results on CTASal (CTAB+NaSal). Region I is an extension of the laminar flow region. At low temperatures, this region persists into the
turbulent flow region giving drag reduction. This is similar to one of the two types of polymer drag reduction. Region II is between Region I and Region III. In Region II, the drag reduction can be approximately represented by Virk's maximum drag reduction asymptote. In Region III drag reduction is lost and the solution returns to normal Newtonian turbulent flow. At some high temperature, onset was observed in Region II. Thus the two types of polymer drag reduction can be seen with one surfactant system by varying the temperature. Ohlendorf et al. [1984; 1986a] suggested that in Region I, a shear induced pseudo-lattice exists with lattice planes sliding past each other and absorbing the turbulence transverse to the direction of flow. In Region II, the lattice is broken into smaller ordered clusters which damp the turbulent eddies in the near-wall region, while in the core region, the SIS damp the large scale turbulence. At the critical shear stress (Region III), the turbulent forces are so large that the SIS is destroyed and the drag reduction vanishes. They believed that the rod-like micelles are not destroyed, however. The rapid complete reversibility of the drag reduction must stem from the undestroyed rod-like micelles because it takes a long time to form rod-like micelles. However, Bewersdorff et al. [1989b] found in their small-angle neutron scattering studies on the TTAB/NaSal system that when drag reduction is lost at the critical wall shear stress, the micelle length distribution is broader and the average rod length decreases, which means the micellar structure is partially broken.

In a later paper, Bewersdorff and Ohlendorf [1988] divided Region II into two regions giving a total of four regions. In the new Region III, they observed nearly constant friction
factors. They believed that at high shear rate (Region IV), the superordered structures are destroyed and the rod-like micelles rotate in the flow. This was shown not to be completely true by their later SANS experimental results [Bewersdorff et al., 1989b].

A more detailed review about microstructure and its rheological properties will be given in later sections. The relationship between rheological properties and drag reduction will be discussed.

### 2.2.7 Applications of Drag Reduction

The first commercial use of polymer drag reduction was to increase the throughput of crude oil in the Trans Alaska Pipeline System (TAPS) by injection of high polymer downstream from one or more of the pipeline pump stations [Burger et al., 1982; Horn et al., 1989]. After screening tests, two potential drag reducing polymers were tested in a 14-inch pipeline. One of them, Conoco Inc.'s CDR™ drag reducer, was selected. While in the screening tests it was found that drag reduction increases with increasing velocity and decreasing diameter, little difference was found between the 14-inch pipeline test and the 48-inch TAPS line. This provided useful information for any future scale-up tests. Drag reduction was maintained at from 6% to 23%. While this appears low, the TAPS throughput was increased by 15%, an amount representing more than 1% of total U.S. crude consumption [Burger et al., 1982]. One important feature in this application is the low concentration (up to 25 ppm) of polymer. Recent reports claim concentrations of improved polymer are now an order of magnitude or more lower. Since the polymer
degraded in the next centrifugal pump downstream from the injection, multiple injections were necessary in bottleneck sections of the pipeline.

Zakin et al. [1971] explored the possibility of using CTAB/1-naphthol solution as a hydraulic transport medium. They found that the surfactant solution can not only reduce the pressure drop in transporting silica sand and plastic particles, but can also decrease the critical velocity (the minimum velocity to keep particles in suspension) of the flow. Despite these potential advantages, however, several problems were noted. The first problem was instability. The CTAB/1-naphthol solution degraded on aging and the interactions between the surface of the solid particles and the soap reduced the effective surfactant concentration. In addition, the high temperature limit for effective drag reduction for this surfactant system was 48°C, which limits its use. These problems obviously make the use of CTAB/1-naphthol in hydraulic transport unlikely. Myska and Vocel [1977] studied another surfactant solution, the mixture of α-naphtol and caraethoxipentadecyl-trimethylammonium bromide, in a suspension flow. They found that the larger the pipe, the greater the drag reduction. A limiting velocity was found, above which, the pressure drop increases sharply because of degradation of the micelles.

A promising application of surfactants as drag reducers is for use in district heating and cooling systems (DHC), in which hot water or cold water is circulated to buildings in a district to provide space heating/cooling. District heating systems can utilize waste heat from power generating or cogenerating stations. By utilizing drag reducers in such
systems, pumping costs can be reduced to make the systems more efficient for existing systems, and capital investment can be saved for new systems. The drag reducers used in such systems must be effective in the temperature ranges in the systems and they must be mechanically stable, due to the fact that the solution is circulated again and again, screening out the use of polymers. Several field tests using surfactants have been carried out in primary and secondary systems in Europe [Kleuker et al., 1991; Hammer, 1991; Pollert et al., 1994], Canada [Young, 1994] and the US [Rose et al., 1984; Gasljevic and Matthys, 1996] with promising results.

Field tests in Völklingen, Germany [Kleuker et al., 1991] and in Herning, Denmark [Hammer, 1991] showed significant drag reduction in primary sections of commercial district heating systems. Pollert et al. [1994] reported a field test of a surfactant drag reducer, Habon G, which was tested in a secondary system of a district heating system in the Czech Republic. They eliminated one of three system pumps after the addition of the surfactant and the system operated without any difficulties for a winter. Maximum pumping energy savings were over 40%. They concluded that surfactant drag reducers in the secondary system may not be as effective as in the primary system due to the greater number of singularities in the former. Surfactant was lost during the test from leakage and from adsorption on the walls of the circulation systems, and re-addition of surfactant was needed. No significant reduction in heat transfer was observed. This was attributed to the high resistance of scale built up on the walls of heat exchanger tubes so that the increased
resistance of the surfactant solution heat transfer coefficient had only a small effect on the overall heat transfer.

Young [1994] tested a surfactant drag reducer, 9-octadecen-bis(2-hydroxyethyl)-methyl-ammonium-3-methyl salicylate, over a 50-foot long, 6-inch diameter pipe section in a 200-ton chillier water-based air conditioning system. Drag reduction over 70% was observed over a temperature range of 5-10°C. No drag reduction was observed over the circulating pumps and control valves. Overall pressure drop was reduced by 40%. The discrepancy was due to the fact that the system contained many sharp pipe bends and diameter transitions on which the drag reducing additive had no effect. He concluded that the use of drag reducers is clearly more advantageous in systems involving liquid transport over substantial distances through straight pipes of uniform diameter. Heat transfer rate was reduced by 55% in the air coolers and 35% in the air cooling coils. The surfactant drag reducing system showed no deterioration over six months and no separation following a three week shutdown. It was estimated that the payback period for the cost of the additives is less than two weeks based on the pumping power savings.

Gasljevic and Matthys [1996] reported their field test results in a building-size hydraulic cooling system. A reduction in pumping power of about 30% was achieved at the same flow rate. A reduction in pressure drop of 40% was measured in 6” elbows. The overall heat transfer reductions in the chiller’s evaporator and in an air cooling coil were found to
be 30% and 20%, respectively, whereas the drag reduction in these exchangers was 60% and 35%.

Steiff and Klopper [1996] summarized the benefits of application of cationic surfactants as drag reducers in district heating systems (DHS). With the addition of surfactant drag reducers in existing DHS, pumping costs can be reduced, flow rate can be increased, the heat source can be shifted to waste heat, and the supply temperature can be reduced by increasing the flow rate to obtain the same heat output. In addition, for applications in new systems, smaller pipes and pumps can be used. They also summarized the requirements for surfactant drag reducers. Application problems do exist, however. Heat transfer is a major concern as heat transfer reduction can reach 70% or more in tube-tube exchangers. In plate heat exchangers, however, the reduction in heat transfer coefficients is much smaller [Christensen and Zakin, 1991]. The influence of drag reducing flow on readouts of flow meters was also investigated by Steiff and Klopper [1996]. They found that due to the strong influence of drag reducers on turbulent flows, most common flow meters, such as impeller meters, orifice plates, venturi tubes and Pitot tube flow meters, do not produce correct readings of flow rate. Only the magnetic inductive and ultrasonic (the type whose signal passes through the whole flow profile) meters can reliably be used to measure flow rates in drag reducing flow. They also mentioned that since the toxicity of Dobon G (similar to Habon G) is quite low, no additional treatment is needed in Germany.
2.3 Rheology

In 1920, a chemistry professor at Lehigh University, Eugene Bingham, coined a new word, "rheology," to represent the study of flow and deformation [Macosko, 1994]. This word comes from the Greek verb πείρω, to flow. In practice rheology has usually been restricted to the study of the constitutive relations between force and deformation in materials, primarily liquids [Macosko, 1994].

For some liquids, the stress is proportional to the strain rate:

\[ \tau = \eta \cdot \dot{\gamma} \]  

(2.9)

where \( \eta \) is viscosity. Fluids with constant \( \eta \) are called Newtonian fluids. Water is a typical Newtonian fluid. However, many important liquids, such as blood, polymers, paint, foods and surfactant solutions, don't follow this relationship and they are called non-Newtonian fluids. Rheology deals mainly with these materials.

Decades of research on polymers and other materials have proved that rheology is a very useful tool in interpreting changes with microstructure of materials. Some well known correlations have been established, such as the relationship between the intrinsic viscosity and polymer molecular weight and the relationship between linear viscoelasticity and the entanglements of polymer chains. Through rheological studies, some of the unique behaviors of materials can be interpreted in terms of microstructure change.
As discussed in previous sections, efforts have been made to clarify the mechanism of surfactant drag reduction by several characterization methods, including turbulence measurements, rheology measurements, and small angle light scattering measurements. Research done in surfactant solution rheology will be reviewed in this section. In many rheological studies, surfactant solutions of higher concentration than those used in drag reduction were used for characterization, and thus the results of these studies may not be suitable to characterize drag reduction surfactant solutions rheologically. Therefore, only results on solutions with concentrations in the range suitable for drag reduction applications will be included.

2.3.1 Shear Viscosity

Ekwall et al. [1971] measured the viscosity of 0.036% (CMC) up to 26% CTAB solutions without additives. They found that the reduced viscosity increased with concentration. At concentrations between 9% and 11%, the curve had a change in slope. They believed this occurred where the spherical micelles changed to rod-like micelles. At a concentration of 26%, a narrow two phase region appears where the micellar aqueous solution is in equilibrium with the mesomorphic middle soap [Ekwall et al., 1971].

With the presence of salts, the viscosities of the surfactant solutions are quite different from those without salt. It has been shown that the addition of salts to anionic and nonionic surfactants can change surfactant viscosity dramatically. Pilpel [1966] found that when the concentration of KCl increased from 0.6M (4.47%) to 1.2M (8.94%) in a
0.035M (1.12%) potassium oleate solution, the solution viscosity increased from 10 to 70 poises, and then the solution viscosity decreased with further addition of salt. The potassium oleate concentration is about five times the concentration at which Savins [1967] studied drag reduction of this anionic system, however. Chang and Zakin [1985] also found a large effect of salt addition in a nonionic system. On the other hand, for a cationic system, Stainsby and Alexander [1953] reported that there is only a small viscosity change compared with that of water for a 0.44 M cetylpyridinium chloride with 1.0 M NaCl solution. It seems the effect of the added salts depends on the nature of surfactant, the salts and the concentration range.

The effect of organic additives on the viscosity is even more significant. Stainsby and Alexander [1953] found that in the presence of NaCl, the CPyCl solution viscosity increases sharply with increasing concentration of chlorobenzene to a peak and then decreases sharply. The peak viscosity of the solution can be thousands of times greater than that of the solution without chlorobenzene. Rehage and Hoffmann [1991] also observed a similar peak for a CPyCl solution with sodium 4-methyl benzoate as counterion. Wan [1968] studied the effect of salicylate on the viscosity of various cationic surfactants. She found that the viscosity increases with increasing salicylate to a peak and then decreases. Larsen et al. [1973] studied the effect of organic additives on the viscosity of a 0.1 M CTAB/0.1 M NaBr solution. They found that additives such as benzene, n-hexanol, benzoic acid, chloroform and methylene chloride can increase the solution viscosity up to two orders of magnitude. They also noted that while both ethanol and
hexane have little or no effect, n-hexanol causes a great change. However, in the absence of NaBr in the solution, all these organic additives have only small effects on the viscosity.

These dramatic viscosity changes are believed to be caused by changes in the micellar structure. Doi and Edwards [1978a, b] established an equation for the viscosity of a dilute rod-like micellar solution:

$$\eta_0 = \eta_s (1 + \hat{c}L^2) \quad (2.10)$$

where $\eta_0$ is the viscosity of the solution at zero shear rate, $\eta_s$ is the viscosity of the pure solvent, $\hat{c}$ is the number of rods per unit volume and $L$ is the length of rods. The $\hat{c}$ can be calculated by a simple equation:

$$\hat{c} = \frac{c_M M}{\pi \rho r^3 L} \quad (2.11)$$

where $c_M$ is the surfactant concentration, $M$ is the molecular weight of the surfactant monomers, $r$ is the radius of the rod-like micelles and $\rho$ is the density of the solution. Substitution of Eq. 2.11 into Eq. 2.10 leads to:

$$\eta_0 = \eta_s (1 + KL^2) \quad (2.12)$$

where $K = c_M M / \pi \rho r^3$. This equation is only valid for dilute solutions according to Doi and Edwards [1978a, b]. From this equation, it can be seen that the viscosity increases in proportion to the square of the rod-like micelle length. The addition of salts promotes the growth of rod-like micelles and results in the rapid increase in the viscosity.
Interference arises when the rotational volumes of the rods actually touch one another or even more when the rods begin to overlap. The condition for overlapping rods is
\[ \dot{\gamma} \gg 1/L^3 \] (2.13)
For concentrated solution, i.e., when Eq. 2.13 is satisfied, Doi and Edwards [1978a, b] proposed a different equation for the viscosity
\[ \eta_0 = \eta_s [1 + (\dot{\gamma}L^3)^3] \] (2.14)
By substitution of Eq. 2.11 into Eq. 2.14, one can have:
\[ \eta_0 = \eta_s (1 + K^3 L^6) \] (2.15)
Thus for concentrated solutions or solutions with long rods, viscosity increases very rapidly with the rod length.

2.3.2 Viscoelasticity

Though viscosity changes with shear and additives, shear viscosity at high shear rates (>1000 s⁻¹) of drag reducing surfactant solutions is relatively constant, about two to five times that of water. Obviously, drag reduction is not caused by the slightly higher shear viscosity. On the other hand, many authors who studied drag reducing surfactant systems [Savins, 1967; Gravsholt, 1976; Elson and Garside 1983; Ohlendorf et al., 1984, 1986a, b; Rose et al., 1984, 1989; Rehage et al., 1986; Bewersdorff and Ohlendorf, 1988; Chou, 1991b; Bewersdorff and Thiel, 1993; Stern et al., 1994; Gyr and Bewersdorff, 1995] have stated that viscoelastic rheological properties of the surfactant solutions are responsible for the occurrence of drag reduction. Viscoelasticity is often observed in biological and
macromolecular systems, and it can also be observed in dilute drag reducing polymer and surfactant systems.

Gravsholt [1976] found that dilute aqueous CTA-X systems, where X is a substituted benzoic acid, are viscoelastic. Viscoelasticity in surfactant systems can be induced by the addition of three different types of added molecules: a second, oppositely charged surfactant, organic counterions and some uncharged compounds like esters or aromatic hydrocarbons [Rehage and Hoffmann, 1991]. Hoffmann and Rehage [1987] claimed that most of the viscoelastic surfactant systems are cationic surfactants having a cetylpyridium or a trimethylammonium head group with different anionic counterions. Later investigations showed that hydroxyethyl groups substituted for the methyl groups give similar behavior.

The viscoelasticity can be simply characterized by the swirl decay time (SDT) which was proposed and used by Nash [1956a, b]. He set up a swirling motion in a fixed volume of solution in a flask and noted the time between stopping the vessel rotation and the cessation of the solution movement before recoil, which he defined as SDT. The smaller the SDT is, the greater the viscoelasticity of the solution. Elson and Garside [1983] measured the SDT of CTAB/1-naphthol solutions against the relative amount of 1-naphthol and the temperature. One of their important observations was that the critical wall shear stress at which drag reduction is lost reaches a maximum when the solution has a minimum swirl decay time (SDT) or maximum viscoelasticity. This optimum point
occurs at counterion to surfactant ratio of 1.0 at high surfactant concentration (0.98 mM and above) and at the ratio of 1.75 at low surfactant concentration (0.39 mM). This result relates solution viscoelasticity to drag reduction.

The first normal stress difference, \( N_1 \), is another characteristic of viscoelasticity. Hu and Matthys [1995] reported \( N_1 \) values over 300 Pa for 5 mM Ethoquad T/13-50 (tallow tris-hydroxyethyl ammonium acetate) with 5 mM NaSal solutions. They also found that the relaxation of \( N_1 \) can be fit by a double exponential function. Myska et al. [1996] showed high \( N_1 \) values for C18TASal solutions at temperatures of 30°C and above, but also observed zero \( N_1 \) at 20°C where the solution is drag reducing.

It is generally agreed that strong elastic forces arise from interaction between elongated, rod-like micelles [Elson and Garside, 1983; Rehage and Hoffmann, 1991]. Hoffmann et al. [1984b] observed that the viscosity and the viscoelasticity of surfactant solutions rise abruptly when the length of the rod-like micelles exceeds their mean separation distance. They believed that these rheological properties are caused by a 3-D dynamic network which is formed as soon as the length exceeds the mean separation distance. Ulmius et al. [1979] proposed that a long-range periodic structure is responsible for the viscoelasticity in the solutions.

Shikata et al. [1987a] classified the viscoelasticity of CTASal solutions into three types. Type I and Type II are for low and intermediate ratios of counterion to surfactant,
respectively. Type III is for a high concentration ratio. Type I behaviors are similar to the features observed for unentangled flexible-chain polymer systems. Beginning at Type II, surfactant solutions behave like polymer systems with entanglement, which means the formation of an entanglement network. Type III can be represented by the Maxwell model. They further suggested that the relaxation time is affected by the free salicylate concentration and the free salicylate molecules behave like a catalyst for a disentangling reaction [Shikata et al., 1988a; 1991].

2.3.3 Network and Shear Induced Structure (SIS)

The fact that some surfactants can be effective drag reducing additives and may increase in viscosity under shear suggested to some researchers that some kind of network structure exists or is formed under shear in surfactant solutions, equivalent to entanglements formed in polymer solutions. As early as 1954, based on both hydrophobic and electrostatic energy considerations, Pilpel [1954] developed a model to explain the formation of gels. He concluded that gel formation is caused by the conversion of spherical micelles into long, interlinked cylindrical micelles. He believed that the viscoelastic properties develop as a result of the interlinking and suggested that this network structure is similar to the one that exists in elastic solids such as rubber, gelatin, and plastic materials.

The evidence from dynamic viscoelastic measurements [Hoffmann et al., 1984a, b; Shikata et al., 1987a; Wunderlich et al., 1987; Strivens, 1989; Shikata and Kotaka, 1991]
suggests that a fully entangled network exists. Strivens [1989] studied the CTAB-SA (salicylic acid) system at concentrations of 0.1, 0.01 and 0.001 M. He found that no viscoelasticity was detectable in the 0.001 M solution. The viscosity and stress relaxation data for the 0.1 M solution were found to be well-described by a Maxwell model, but not for the 0.01 M and 0.001 M solutions. The storage modulus ($G'$) and loss modulus ($G''$) curves for the 0.01 M and 0.1 M solutions cross each other, and $G'$ reaches a plateau value for the 0.1 M solution. Similar results were obtained by Shikata et al. [1987a] when they studied the CTAB/NaSal system. They kept the concentration of CTAB at 0.1 M and changed the amount of NaSal to vary the ratio of NaSal to CTAB. They found that above a ratio of 0.275, the $G'$ and $G''$ plots cross each other, and the cross point moves to a higher frequency with increase in ratio. When the ratio reaches 0.5, $G'$ reaches a plateau and the plateau value doesn't change with further addition of NaSal. Since the plateau is a consequence of cross-links between the aggregates [Hoffmann et al., 1984b], they concluded that a fully entangled network is already formed when the molar ratio of NaSal/CTAB reaches 0.5. At high angular frequencies the solution should behave as an elastic body.

Hoffmann et al. [1985a] suggested that the rod-like micelles can be held together in bundle-like structures by adhesion forces which are strong enough to overcome the electrostatic repulsion between the micelles. They suggested that these adhesion forces are due to van der Waals forces or to the interfacial tension between the rods and the aqueous phase.
As mentioned in Section 2.1.4, network structure has been observed in surfactant systems by using cryo-transmission electron microscopy (cryo-TEM) [Bellare et al., 1988; Vinson and Talmon, 1989; Walter et al., 1991; Clausen et al., 1992; Cochin et al., 1992]. In preparing samples for cryo-TEM, significant shear is applied. Thus, the network structure observed may be induced by shear.

Several researchers have suggested that such network structures may be induced by shear. Ohlendorf et al. [1986a] performed rheological studies on 1000 ppm C14TASal and 1000 ppm C16TASal solutions (CTAB or CTAC plus equimolar NaSal). The rod-like micelles in their solution were believed to have an average length of 15 to 40 nm and a diameter of 4 nm. The average separation between them is larger than 50 nm. For their solution, \( c \) is less than \( 1/L^3 \), i.e., the condition for overlapping rods in Eq. 2.13 is not satisfied and therefore, these rod-like micelles should have no interaction with each other. Based on this, the individual micelles should not be able to affect the flow up to a high shear rate. However, they found the viscosity measured in a Couette flow cell is slit width dependent. Furthermore, in measuring the shear viscosities of the solutions, they found that at some shear rate between 10 to 100 s\(^{-1}\), the viscosity of the system increased abruptly. This phenomenon was also reported in several other papers [Ohlendorf et al., 1986b; Rehage et al., 1986; Bewersdorff and Ohlendorf, 1988; Lindner et al., 1990; Bewersdorff, 1989a, 1996]. These researchers observed that the viscosity was usually very low at low shear rates and then at a critical shear rate, viscosity suddenly increased
to high values; in some cases the increase was 2.5 times. In their data, the viscosity before
the jump was never higher than the viscosity immediately after the jump. Their viscosity
jumps depended on concentration, temperature and shear rate. The critical shear rate
where the jump occurred increased with surfactant concentration and with temperature
and the jump was only observed at low temperature. The solutions were always shear
thinning after the jump. The above authors suggested that the increase in viscosity was
induced by an abrupt change in the microstructure of the surfactant solutions.

However, data from other researchers didn't show this viscosity jump. Rose and Foster
[1989] measured the viscosity of 0.2 % CTASal + 0.2% NaSal solution. They found the
viscosity at room temperature decreases with increasing shear rate from 1 s⁻¹ up to 500 s⁻¹,
i.e., the solution exhibits shear thinning behavior. Earlier measurements on CTAB/l-
naphthol solutions by Elson and Garside [1983] gave shear thinning behavior at low shear
rates (below 300 s⁻¹) and constant viscosity at high shear rate. Myska et al. [1996] also
observed only shear thinning for a C18TAC solution at 1.6 and 5 mM concentrations with
2.5 times (molar) of NaSal. These shear thinning observations support the concept of
alignment of the rod-like micelles as shear increases. Lindner et al. [1990] showed that
the viscosity jump observed by Ohlendorf et al. [1986a] held only for fresh solutions.
After subjecting the solution to turbulent flow for several hours (stressed solution), the
viscosity was lower than that of fresh solution, and no viscosity jump was observed. No
explanation was offered for this discrepancy. From their small angle neutron scattering
measurements, they concluded that the rod-like micelles are broken up by the forces in
the turbulent flow field and form smaller micelles which build up loose but lasting superstructures which are stable with shear and have constant (lower) viscosity.

The discrepancy between the two different observations regarding the viscosity jump may be explained by observations made by Shikata et al. [1987a], Hoffmann and Rehage [1987] and Hu and Matthys [1996]. As mentioned above, Shikata et al. [1987a] classified the viscoelasticity of CTAC solutions into three types in terms of different ratios of NaSal to surfactant. Type II and Type III with intermediate and high NaSal concentration behave like entangled polymer solutions while Type I with low NaSal concentration behaves like unentangled flexible-chain polymer systems. Hoffmann and Rehage [1987] classified viscoelastic surfactant solutions into two types. In the first and more general type, the structures causing viscoelastic behavior are present in the stagnant solution, which is the same as Type II and Type III of Shikata et al. [1987a]. In the second type viscoelasticity is observed only after a certain threshold shear rate is exceeded, which is similar to Type I of Shikata et al. [1987a]. Systems of the second type are called shear induced viscoelastic systems. Recently, Hu and Matthys [1996] suggested an identical classification. For surfactant solutions in which networks already exist, no shear is needed to induce a superstructure and no viscosity jump is apparent. This explanation is reasonable if one notes that the systems with viscosity jump have a 1:1 or lower counterion/surfactant ratio and higher ratios give no jump.
Rehage et al. [1986] found that both the first normal stress difference and flow birefringence do not show up in the first ten seconds of shearing, and then they both jump to a steady state level. The first normal stress difference, $N_1$, is another characteristic of viscoelasticity. Hu and Matthys [1995] observed similar shear stress and first normal stress difference behaviors, i.e., low or zero stress values in the first tens of seconds for a 5 mM Ethoquad T/13-50 (tallow tris-hydroxyethyl ammonium acetate) with 5 mM NaSal solution followed by a rapid increase to the plateau value.

According to its proposers, the SIS only exists in certain shear rate ranges [Ohlendorf et al., 1984; Hoffmann et al., 1985a; Ohlendorf et al., 1986a; Rehage et al., 1986]. The SIS is formed after the shear rate exceeds a well defined threshold value which is defined by concentrations and ratios, while at very high shear rates, the SIS is no longer stable. Lindner et al. [1990], however, proposed a loose but long lasting (several months) superstructure for surfactant solutions after experiencing turbulent flow. Wunderlich et al. [1987] found the shear induced structure in laminar flow gave an extinction angle close to zero in their flow birefringence measurements on TTASal solutions. They believed the SIS consists of small clusters of rod-like micelles and can be formed only when the shear rate exceeds a certain threshold value, as shown by their kinetic model. They claimed that the product of the relaxation time of the SIS and the critical shear rate, at which the SIS forms, is a constant of the order of 100, but did not show how they measured the relaxation time of the SIS. The decay of the SIS is believed to be a multistep process as also shown by Shikata et al. [1988a, b], Hu and Matthys [1995] and data in this work.
Two spatial arrangements of the rod-like micelles in the SIS have been proposed by Ohlendorf et al. [1986a]: a) Build-up of a pseudo-lattice from the rods with lattice planes sliding past each other and in which the rod-like micelles are preferentially aligned in the flow direction. b) A pearl-string model in which aligned rods are held together by attractive forces like pearls on a string and with the strings oriented in the direction of the flow parallel to one another. Bewersdorff and Ohlendorf [1988] proposed two different models for the structure of SIS: coalescence of the rod-like micelles to form very long flexible rods that act like high molecular weight polymers, or the build-up of ordered structures of individual rods by cooperative electrostatic interaction. However, there are still no direct experimental observations to support these models of shear induced structure.

In conclusion, an entanglement network in surfactant solutions under certain conditions appears to exist. While it seems likely that this network is formed by shear, this can only be shown deductively. Furthermore, what forces exist at the entanglement points is still unknown and thus no spatial structure of the network can be certain.

2.3.4 Extensional Viscosity

Research on polymer drag reduction led to a proposal by many researchers that high extensional viscosity is responsible for drag reduction by polymer additives [Landahl, 1977; Durst et al., 1982; Hoyt, 1986; Barnes et al., 1989; Bewersdorff and Thiel, 1993].
These researchers stated that the extensional viscosity of dilute polymer solutions can be large compared to that of the Newtonian solvent. This results in an additional resistance against vortex stretching and turbulent eddy growth, and leads to reduction of energy dissipation or drag reduction.

Nearly a century ago, Trouton [1906] established that the fluid viscosity in uniaxial extensional flow is three times the shear viscosity for Newtonian fluids. Research on extensional rheometry did not make significant progress until the 1970s because of the difficulty in measuring it [Macosko, 1994].

For high viscosity polymer solutions and melts, there are a number of effective ways to measure extensional viscosity, such as homogeneous stretching, fiber spinning, lubricated flow, contraction flow, open-syphon method [Barnes et al., 1989]. However, these methods require that the sample have sufficiently high viscosity and thus they are not suitable for dilute surfactant solutions.

Fuller et al. [1987] first introduced the opposing nozzle geometry for measuring extensional viscosity of low viscosity solutions. They gave data on several Newtonian fluids and for solutions of xanthan gum and polyacrylamide (PAM). Tests with the Newtonian fluids gave Trouton ratios around 3, while for xanthan gum solutions, Tr is a constant larger than 3, and for PAM solutions, the extensional viscosity increased with extensional rate and reached a plateau.
Schunk et al. [1990] did a numerical analysis on the flow of Newtonian fluids between opposed nozzles. Their results showed that pure extension is achieved only in areas near the stagnation point and near the symmetry axis (see Fig. 3.9 for a schematic of the opposing nozzle geometry). Flow in other regions is a mixture of shear and extensional flows. Similar results were obtained by Schunk and Scriven [1990] for polymer solutions.

Ng et al. [1996] reported the Trouton ratios from an RFX for three Newtonian fluids: glycerol / water, wheat syrup / water and N-decane / polybutene. The Tr values scatter from 2.2 to about 4.0. Most of the solutions have shear viscosity 1 poise and up. Trouton ratios of several polymer solutions with different characteristics were also presented. They proposed that the ratio of Trouton ratio of polymer to Trouton ratio of solvent represents the extensional character of the solutions.

Hermansky and Boger [1995] used the RFX to measure the Trouton ratio of Newtonian fluids with shear viscosities ranging from 1 cp to 77 cp. They found that the departure of Tr from 3 increases with decreasing shear viscosity of the fluids and with increasing strain rate. Especially for the 1 cp fluid (carbon tetrachloride at 18°C), Tr increases from about 30 at 5000 s⁻¹ to about 150 at 20000s⁻¹, and for the 3.6 cp, the range of Tr is from 15 to 50. According to this observation, they proposed an inertial correction for the extensional viscosity measurements. However, Dontula et al. [1997] pointed out this correction is incorrect. They further pointed out that even though Anklam et al. [1994]
made a correct statement: “this (inertial) contribution opposes the force due to the fluid extension,” Anklam et al. [1994] subtracted their inertial correction term from measured apparent extensional viscosity instead of adding. However, Dontula et al. [1997] proposed that in light of theoretical considerations and experimental observations, the use of systematic corrections to extensional viscosity measurements on non-Newtonian liquids is not recommended.

Pasquali and Scriven [1996], Dontula et al. [1997] and Jain et al. [1997] reported that the quantity measured in opposed nozzles devices is not the “true” extensional viscosity of the liquids. It includes contributions from dynamic pressure, shear on the nozzles and liquid inertia. Even though an equation taking account of these effects has been proposed by Pasquali and Scriven [1996], no quantitative correction can be made [Dontula et al., 1997]. Jain et al. [1997] gave a chart counting relative contributions from different effects based on numerical simulation. Dontula et al. [1997] further suggested that the extensional viscosities of liquids whose shear viscosities are lower than 50 mPa s cannot be reliably measured with RFX. However, both Dontula et al. [1997] and Jain et al. [1997] suggested that the RFX can be used as an indexer rather than using the measured apparent extensional viscosities quantitatively.

There are only a limited number of reports in the literature on extensional rheology for surfactant systems. Prud’homme and Warr [1994] reported very high extensional viscosities for the tetradecyltrimethylammonium salicylate (TTASal) aqueous solution at
concentrations of 15.3 mM and higher. Wang et al. [1994] discussed the effect of elongational flow on micelles. They suggested that elongational flow is more effective than shear in causing coagulation between micelles. Lin et al. [1994] showed extensional viscosity up to 400 poise for 20 mM cetyltrimethylammoniumbromide (CTAB) with 14 mM 5-methylsalicylic acid as counterion. Walker et al. [1996] used RFX to measure extensional viscosity of CPyCl (cetylpyridinium chloride) / NaSal (in brine) systems at 1.4% and 4% concentrations. The latter authors observed an increase-peak-decrease behavior. They suggested that the onset of the increase in extensional viscosity coincides with the onset of nonlinear viscoelasticity, as evidenced by the onset of shear thinning.

It should be noted that the surfactant concentrations studied using the RFX are much higher than those used in drag reduction studies, however. Little can be found in the literature regarding extensional viscosity measurements on drag reducing surfactant systems. It would be expected that with lower concentrations, the data from RFX may be more troublesome. Nevertheless, they can still be used for qualitative comparisons. Data presented in Chapter 5 of this work show that while surfactant drag reducers usually have shear viscosities no more than ten times that of water at high shear rates, most of them show unusually high extensional viscosity.

2.4 Flow Birefringence

Flow birefringence has long been acknowledged to be a valuable method to investigate the flow properties and dynamic behavior of macromolecular and colloidal liquids. The
fluid can be studied under actual flow conditions without disturbing the flow if the experiment is properly designed. However, there are two major drawbacks to flow birefringence measurements [Janeschitz-Kriegl, 1983]. First, only clear solutions can be investigated. Second, the method is not direct. A lot of theoretical deductions are needed before useful information can be obtained from the measurements. If the stress-optical rule (see Section 3.3.4) relating rheological properties and the optical measurements can be invoked, valuable rheological information can be obtained.

Flow birefringence measurements involve determination of the polarization state of light transmitted through a flowing sample. Since the polarization state of the transmitted beam is measured, these methods are referred to as polarimetry methods. In such methods, the polarization state of the emerging light is determined from the measurements of light intensity, the actual experimental observable. Early flow birefringence measurement techniques were limited to steady-state studies because of the incapability of treating simultaneous changes in the birefringence and the extinction angle [Frattini and Fuller, 1984a].

There are three classes of polarimetry methods, namely, fringe methods, pointwise compensation methods and polarization modulation methods. In the fringe methods, the flowing samples are placed between two mechanically coupled polarizers whose transmitting axes are crossed. The whole flow field is illuminated and the fringe patterns are observed to determine the birefringence and extinction angle. The advantage of this method is that it is simple. However, it can not handle time-dependent flows since the
flow birefringence and the extinction angle can not be determined simultaneously at a given spatial position. The second disadvantage is that it can not handle materials with weak birefringence, such as dilute solutions, because they produce very few fringes.

The pointwise compensation methods place the flowing sample between two polarizers, as in the fringe methods. In this method only one point is illuminated instead of the whole field. Another difference is that a compensator with known retardation is placed between the flow sample and the analyzer. The retardant angle is then determined by rotating the two polarizers and the compensator. While this class of methods provides pointwise measurements, they still can not measure unsteady-state flows. A disadvantage is the limited spatial resolution.

The polarization modulation methods modify the light beam in a time-harmonic manner. The only difference between this method and conventional flow birefringence is the addition of a modulator between the incident polarizer and the flow cell. This method can measure transient flows.

Osaki et al. [1979] described a modified flow birefringence system which was able to measure fast response times. They placed a Couette flow cell between two crossed polarizers and measured the intensity of the transmitted light as a function of time. However, determination of the flow birefringence and the extinction angle requires two experiments with different orientation of the polarizers with respect to the flow direction.
There is always a question as to whether the two experiments have the same conditions except for the orientation angle of the polarizers.

Steady state flow birefringence measurements on surfactants were performed by Hoffmann et al. [1985a] using the compensation and modulation methods. They tested different mixtures of TPySal and TTASal with a total concentration of 25 mM, which is much higher than the concentrations usually used in drag reduction. In general, the extinction angle decreased with the shear rate, but the rates of decrease were quite different as the composition of the mixtures changed. For most of the solutions, the extinction angle decreased to below 5° at a shear rate of 100 s⁻¹. If their data are compared with data from polymer solutions, there are a lot of differences. The extinction angle of an 1.2% cellulose nitrate in cyclohexanone solution stays at 27° up to a shear rate of 15,000 s⁻¹ [Janeschitz-Kriegl, 1960]. This difference may be attributed to stronger entanglements between polymer molecules that resist alignment compared to surfactant micelles due to the greater flexibility of the polymer molecules.

Wunderlich et al. [1987] reported that the saturation value of flow birefringence increased linearly with the concentration and decreased with temperature for surfactant solutions. They observed no flow birefringence when the concentration of TTAS was below 1.5 mM although drag reduction is observed in this concentration range. It is possible that the absence of observable flow birefringence in this concentration range is due to compensation of form and intrinsic birefringence [Schorr and Hoffmann, 1985]. The
addition of NaBr to the TTAS solutions decreases the saturation value of flow birefringence [Wunderlich et al., 1987]. The stress-optical rule was also checked by Wunderlich et al. [1987]. They found that in the relaxation mode of the flow birefringence, the first normal stress difference is proportional to the flow birefringence. However, because the extinction angle becomes zero, they ignored another component of the rule, i.e., the proportionality between the shear stress and the flow birefringence. Therefore, no definite conclusion concerning the validity of the stress-optical rule for these surfactant solutions can be drawn.

Rehage and Hoffmann [1988] studied the 100 mM CPyCl / 60 mM NaSal system at 20 °C. They calculated the stress-optical coefficient for the system to be $C = -2.2E-7 \text{ (1/Pa)}$, which is only valid for $\dot{\gamma} < 1 \text{ s}^{-1}$. Rehage et al. [1986] reported a stress-optical coefficient of $C = -2E-7 \text{ (1/Pa)}$ for a 5 mM TTAS solution. They measured the extinction angle, $\chi = 0$, so they ignored the shear stress equation (see Eq. 3.30) and only used the normal stress equation (see Eq. 3.31). The coefficient is not valid for high shear rates. From this $C$ and shear stress, $\chi$ was calculated back to be 0.6° which was said to be within their experimental error. So they concluded the law holds for surfactant solutions.

Oh and Park [1992] studied transient flow birefringence of calf skin collagen solutions. They used a PMFB (photoelastic modular flow birefringence) system, which is capable of measuring simultaneously the flow birefringence and the extinction angle. They found that the relaxation of birefringence shows two distinct relaxation times. The initial rapid
drop corresponds to the relaxation of a short chain (monomer) as well as long chains, but slow decay follows due to relaxation of long chains only.

Hu et al. [1993] performed unsteady state flow birefringence measurements on a 1 mM CTAB / NaSal system. They found the flow birefringence jumped to a plateau after 10 seconds at a shear rate of 100 s⁻¹ and the induction time was inversely proportional to the shear rate. They proposed that shear-induced coagulation results in self-assembling of surfactant molecules to form exceedingly large micelles.

Shikata and Pearson [1994] used a PMFB system to measure the flow birefringence of CTAB/NaSal solutions. The CTAB concentration varied from 10 mM to 100 mM and the NaSal concentration from 150 mM to 400 mM. Their concentrations are much higher than those used in drag reduction studies. They found that for these concentrated systems the extinction angle stays at 10° for very low shear rates so that the stress-optical rule can hold for such systems with a stress-optical coefficient of -3.1×10⁻⁷ (1/Pa). However, when the shear rate reached 6.3 s⁻¹, they observed instability in the flow birefringence and extinction angle measurements. In this case, the extinction angle reached a value about of 0.5° in the beginning of the experiment and then the value oscillated over a wide range. They claimed that this instability always happened when the extinction angle approached zero under so-called strong flow conditions (shear rate > 6 s⁻¹). They concluded that the stress-optical rule holds for wormlike micellar systems but apparently only at high concentration and very low shear rate.
3.1 Chemicals and Solution Preparation

The surfactants and counterions used in this research are listed in Tables 3.1 and 3.2, respectively. Most of surfactants were donated by Akzo Chemical (now Akzo Nobel), a few are from different sources. Most of surfactants are industrial versions of corresponding pure chemicals and thus the alkyl groups of these surfactants are actually mixtures of different hydrocarbon chains. Table 3.3 lists the distributions of hydrocarbon chains for these surfactants. It should be specifically pointed out that Ethoquad O/12 contains an oleyl group, Arquad S-50 contains a soya group and Ethoquad T/13-50 contains a tallow group. Inorganic chemicals used in this work, such as EDTA, FeCl₃, CuCl₂ and NaOH, were purchased from Fisher Chemical. All chemicals were used as received.

Surfactant solutions are prepared following the procedures described below. According to the concentration to be tested, the proper amount of surfactant is weighed into a beaker. The beaker is filled with the proper amount of distilled water and is then mixed by a
<table>
<thead>
<tr>
<th>Trade Name</th>
<th>Chemical Structure</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>TTAB</td>
<td>C_{14}H_{20}-N(CH₃)₃Br</td>
<td>Sigma Chem. Co.</td>
</tr>
<tr>
<td>Arquad 16-50</td>
<td>C_{16}H_{14}-N(CH₃)₂Cl</td>
<td>Akzo Nobel</td>
</tr>
<tr>
<td>Arquad 18-50</td>
<td>C_{18}H_{17}-N(CH₃)₂Cl</td>
<td>Akzo Nobel</td>
</tr>
<tr>
<td>Arquad S-50</td>
<td>Soya-N(CH₂)₃Cl</td>
<td>Akzo Nobel</td>
</tr>
<tr>
<td>Arquad T-50</td>
<td>Tallow-N(CH₃)₂Cl</td>
<td>Akzo Nobel</td>
</tr>
<tr>
<td>CTAB</td>
<td>C_{16}H_{31}-N(CH₃)₃Br</td>
<td>Aldrich Chem. Co., Inc.</td>
</tr>
<tr>
<td>CTAC</td>
<td>C_{16}H_{31}-N(CH₃)₃Cl</td>
<td>Aldrich Chem. Co., Inc.</td>
</tr>
<tr>
<td>Ethoquad O/12</td>
<td>Oleyl-N(CH₃)(C₂H₄OH)₃Cl</td>
<td>Akzo Nobel</td>
</tr>
<tr>
<td>Ethoquad O/13-50</td>
<td>Oleyl-N(C₂H₄OH)₃Ac</td>
<td>Akzo Nobel</td>
</tr>
<tr>
<td>Ethoquad T/13-50</td>
<td>Tallow-N(C₂H₄OH)₃Ac</td>
<td>Akzo Nobel</td>
</tr>
<tr>
<td>Habon G</td>
<td>C_{16}H_{33}-N(CH₃)₂(C₂H₄OH)(3-OH-2-naphthoate)</td>
<td>Hoechst</td>
</tr>
<tr>
<td>Brij 30</td>
<td>polyoxyethylene (4) lauryl ether</td>
<td>ICI Americas Inc.</td>
</tr>
<tr>
<td>Brij 97</td>
<td>polyoxyethylene (10) oleyl ether</td>
<td>ICI Americas Inc.</td>
</tr>
<tr>
<td>OMA 3/4</td>
<td>C_{18}H_{35}CONHC₆H₄(OH)(OC₂H₄)₃ or 4OH</td>
<td>Akzo Nobel</td>
</tr>
<tr>
<td>C16 betaine</td>
<td>C_{16}H_{33}-N''(CH₃)₂CH₂COO⁻</td>
<td>Akzo Nobel</td>
</tr>
<tr>
<td>Na-LAS</td>
<td>CH₃(CH₂)mCH(CH₂)(9-m)CH₃</td>
<td>Akzo Nobel</td>
</tr>
</tbody>
</table>

Table 3.1 Surfactants tested.
<table>
<thead>
<tr>
<th>Trade Name</th>
<th>Chemical Structure</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium Salicylate</td>
<td>2-OH-C₆H₄-COONa</td>
<td>MCB Manufacturing Chemicals, Inc.</td>
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<tr>
<td>2-Cl-benzoic acid</td>
<td>2-Cl-C₆H₄-COOH</td>
<td>Aldrich Chem. Co., Inc.</td>
</tr>
<tr>
<td>3-Cl-benzoic acid</td>
<td>3-Cl-C₆H₄-COOH</td>
<td>Aldrich Chem. Co., Inc.</td>
</tr>
<tr>
<td>4-Cl-benzoic acid</td>
<td>4-Cl-C₆H₄-COOH</td>
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</tr>
<tr>
<td>2-OH-1-naphthoate</td>
<td>2-OH-1-COOH-C₁₀H₆</td>
<td>Aldrich Chem. Co., Inc.</td>
</tr>
</tbody>
</table>

Table 3.2 Counterions tested.

<table>
<thead>
<tr>
<th>Percentage</th>
<th>Arquad 12-50</th>
<th>Arquad 16-50</th>
<th>Arquad 18-50</th>
<th>Oleyl</th>
<th>Soya</th>
<th>Tallow</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₁₀H₂₁</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₁₂H₂₅</td>
<td></td>
<td>97</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₁₄H₂₉</td>
<td>2</td>
<td>12</td>
<td>1</td>
<td>2</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td>C₁₆H₃₁</td>
<td></td>
<td></td>
<td>75</td>
<td>5</td>
<td>4</td>
<td>16</td>
</tr>
<tr>
<td>C₁₈H₃₇</td>
<td></td>
<td></td>
<td>4</td>
<td>1</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td>C₁₈H₃₅</td>
<td></td>
<td></td>
<td>11</td>
<td>90</td>
<td>14</td>
<td>12</td>
</tr>
<tr>
<td>C₁₈H₃₃</td>
<td></td>
<td></td>
<td></td>
<td>37.5</td>
<td>55</td>
<td>42</td>
</tr>
<tr>
<td>C₂₀H₄₁</td>
<td></td>
<td></td>
<td></td>
<td>37.5</td>
<td>14</td>
<td>4</td>
</tr>
</tbody>
</table>

Table 3.3 Hydrocarbon chain distribution of some surfactants (%).
magnetic stirrer. For some surfactants with poor solubility in water at room temperature, heating is needed to dissolve the surfactants. The well-mixed surfactant solution is then slowly poured into a big container whose volume depends on the purpose for which the solution is being prepared, i.e., a small one for birefringence and rheology studies and a large one for drag reduction studies. The counterion is prepared in a separate beaker with a procedure similar to that for the surfactant. For counterions in acid form, an equimolar amount of NaOH is added to neutralize them and to form sodium salts which are soluble in water. The counterion solution is added to the container and distilled water is then added to give the desired volume. The prepared solution is mixed for enough time to make it homogeneous. Then the solution is left at least over night before the tests.

3.2 Drag Reduction Measurements

By a force balance, the wall shear stress in a fully developed pipe flow is related to the pressure drop by the following equation:

$$\tau_w = \frac{\Delta PD}{4L}$$ \hspace{1cm} (3.1)

where $\Delta P$ is the pressure drop, $D$ the pipe diameter and $L$ the pipe length. The Fanning friction factor is defined by:

$$f = \frac{\tau_w}{\frac{1}{2}\rho V^2}$$ \hspace{1cm} (3.2)

where $V$ is the mean flow velocity and $\rho$ is the density. Substitution of Eq. 3.1 into Eq. 3.2 leads to:
\[ f = \frac{\Delta PD}{2\rho V^2 L} = \frac{\pi^2 D^4 \Delta P}{32\rho L Q^2} \quad (3.3) \]

where \( Q \) is the volume flow rate. In Eq. 3.3, \( \Delta P \) and \( Q \) need to be measured and then \( f \) can be calculated. The percent drag reduction, \( \% DR \), is defined in terms of \( f \) and \( f_s \) as:

\[ \% DR = \frac{f_s - f}{f_s} \times 100 \quad (3.4) \]

where \( f \) and \( f_s \) represent the friction factors of the solution and the solvent respectively at the same flow rate. Values of \( \% DR \) lie between 0 and 100. A fluid is drag reducing if the \( \% DR \) is positive, and the greater the value, the more effective it is. The \( f_s \) can be either measured or calculated by the well known von Karman equation:

\[ f_s^{-\frac{1}{4}} = 4.0 \log(Re f_s^{\frac{1}{2}}) - 0.4 \quad (3.5) \]

The Reynolds number for pipe flow is defined by:

\[ Re = \frac{\rho V D}{\mu} = \frac{4\rho Q}{\pi \mu D} \quad (3.6) \]

where \( \mu \) is the viscosity. For ease of comparison, the solvent physical properties are used to calculate \( Re \) and \( f \) in the above equations.

Except those in the stability studies (Section 6.2), drag reduction experiments were performed in a circulation system whose schematic is shown in Fig. 3.1. The test section of the system is a 48-inch long stainless steel tube with inside diameter of 0.243 inch \( (L/D=197.5) \). The pump is an Oberdorfer bronze rotary gear pump (Model 11500), driven by a 2 hp Vickers variable speed drive. The pumping rate is controlled by a Dayton SCR motor controller (Model 4Z377B) connected to the drive. A wire mesh strainer is
Figure 3.1  Schematic of drag reduction measurement system.
installed on the pump suction line to prevent large particles from entering the pump. Two four gallon accumulators in the system, whose top is filled with pressurized air when running, served to dampen pressure fluctuations in the loop.

To control temperature, the system is insulated with fiber glass insulation to prevent heat loss to the environment. The system is equipped with a PolyScience chilling unit (Model KR-60A) which includes a 1/2-hp compressor and a constant temperature circulator. A 50% ethylene glycol and 50% water mixture is used as the coolant. Heat is removed from the test system by the coolant passing through a stainless steel shell and tube heat exchanger. The refrigeration load is about 4200 Btu/hr at 50°F. The lowest temperature attainable in the test system is 2°C. To prevent freezing of the solution, no lower temperature was attempted. High temperature runs were carried out using a 2 kW heater, which is connected to a temperature controller which controlled temperature to ±1.0°C. Since the maximum sheath temperature for the heaters used is 350°F (177°C), the operating temperature in the system is confined to below 150°C. Fluid temperatures at the inlet and outlet of the test section were both measured by J-type thermocouples.

Pressure drops were measured by a Validyne differential pressure transducer (Model DP 15-52; range = 0-200 psi). The pressure transducer was calibrated by using a high accuracy pressure gauge. Flow rates were measured with a Rosemount Series 8700 magnetic flow meter. To calibrate the flow meter, the lower end of the flow meter was first disconnected from the loop. With water filling the whole system, the pump was run.
at a desired speed and the water coming out from the opened end collected for a given period of time. The water was then weighed and the flow rate calculated. Changing the pumping speed and following the same procedure described above, a relationship between the measured flow rate and the reading of the flow meter was determined.

When the system was filled with solution, the whole system was closed off from the atmosphere at room temperature (20-28 °C). With increasing temperature, the system pressure is well above one atmosphere so that the solution will not boil at temperatures above 100°C. The solution was heated to the test temperature under circulating conditions and allowed to stabilize for 1 hour before data were taken. Then the flow rate was altered by adjusting the pump speed. After at least five minutes of running at each flow rate, the pressure drop and the flow rate were simultaneously recorded. After tests on one solution were finished, the system was flushed with water. The washing process was repeated until there was no visible surfactant solution in the draining water.

A correction factor is applied to the friction factor to account for entrance and exit effects [Chou, 1991b]. Water is often run to calibrate the system and the correction factor is used to bring the water data to follow the von Karman equation. While an accurate error analysis is difficult to perform, it can be estimated from drag reduction data on water (Fig. 3.2) which shows that the absolute error in drag reduction is about ±5%.
Figure 3.2 Drag reduction of water.
For the stability studies, which were done at University of California at Santa Barbara, drag reduction tests were performed in a different recirculation system (Fig. 3.3). The system was set up with new half-inch carbon steel pipes (D=16.2 mm). These pipes had no contact with surfactant until the test began and they were naturally rusty from standing. PVC pipes were used in a small portion of the system to make necessary connections. The test section has an L/D of over 750 to minimize the entrance and end effects. Due to the limitation of the centrifugal pump used, the system can only accommodate a flow rate of 6.0 to 7.8 GPM, corresponding to Reynolds number of 30,000 to 40,000. A cooling unit using room temperature air as cooling media was installed on line such that the system was run at room temperature, in the range of 21 to 24°C.

3.3 Flow Birefringence

3.3.1 Theoretical Background

When light passes from a vacuum into a material body, the speed of light is reduced by a factor which is the reciprocal of the refractive index [Kliger et al., 1990]. A body that retards all polarizations to the same degree, independent of propagation direction is said to be isotropic. In other words, the refractive indexes of an isotropic body are independent of the direction, while for anisotropic materials, the refractive index is direction dependent.
Figure 3.3 Schematic of drag reduction measurement system for stability studies set up in UCSB.
Birefringence results from the anisotropy of the system. When polarized light passes through an isotropic material, no birefringence can be observed, while if the material is anisotropic, birefringence is observed. For a fluid system, no matter what shape the particles have, when the solution is static, particles will have random orientations such that statistically, the solution is isotropic. However, under external forces, any anisotropic particles will align with the flow field and the solution will show anisotropy. The alignment of the particles under electrical fields gives electric birefringence [Schorr and Hoffmann, 1985], while flow birefringence results from alignment of the particles in a shear or extensional flow field.

Flow birefringence is a valuable method for the study of micellar shape and size. For a system with spherical micelles, no flow birefringence should be observed because of the isotropy of the solution, while for rod-like micellar solutions under shear, flow birefringence is measurable. Thus flow birefringence can distinguish between spherical and rod-like micellar shapes. A simple shear flow field is shown in Fig. 3.4. Direction 1 is the flow direction and direction 2 is perpendicular to the flow direction and points to the direction of increasing velocity. Direction 3, sometimes called the neutral direction, is normal to the 1-2 plane.

Birefringent materials have one or more characteristic directions referred to as optical axes, and light propagating along these axes experiences a single refractive index regardless of its polarization state. Here, we only discuss uniaxial birefringent materials,
Figure 3.4 Simple shear schematic.
i.e., with only a single optical axis. The optical axis lies in the 1-2 plane as shown in Fig. 3.4. If the polarized light goes along direction 3, i.e., the light is perpendicular to the 1-2 plane, and if it is polarized parallel to the optical axis, the light experiences a so-called extraordinary refractive index, \( n_e \) or \( n_1 \). This principle refractive index is in the direction nearest the direction of flow and has an angle, \( \chi \), with the flow. The light polarized normal to the optical axis experiences an ordinary refractive index, \( n_o \) or \( n_2 \). The real portion of the complex refractive index determines the phase lag/advance of the wave.

The birefringence, \( \Delta n \), is defined as the difference, \( n_1 - n_2 \), along the optical axes.

### 3.3.2 Evaluation of Birefringence

The polarization state of an incident light beam can be represented by a 4×1 Stokes vector, while the polarization state of the emerging light beam from a polarization optical device is represented by a new Stokes vector which is the product of the Mueller matrix of the optical device and the Stokes vector of the incident light. The first component of the Stokes vector is the intensity of the light. To calculate the emerging light intensity, one can simply pick the first component of the Stokes vector. For different optical elements, there are different Mueller Matrices to represent their polarization effects (see Table 3.4).

A photoelastic modular flow birefringence (PMFB) system (Fig. 3.5) was used in this research. Monochromatic, partially polarized red light from a Helium-Neon laser goes through an incident polarizer, which is oriented at \( \pi/2 \), and then a photoelastic modulator
Ideal Polarizer, transmitting axis oriented at $\alpha$:

$$
\begin{bmatrix}
1 & \cos(2\alpha) & \sin(2\alpha) & 0 \\
\cos(2\alpha) & \cos^2(2\alpha) & \cos(2\alpha)\sin(2\alpha) & 0 \\
\sin(2\alpha) & \cos(2\alpha)\sin(2\alpha) & \sin^2(2\alpha) & 0 \\
0 & 0 & 0 & 0
\end{bmatrix}
$$

Ideal Circular Polarizer, right (+) or left (-) circular polarization:

$$
\begin{bmatrix}
1 & 0 & 0 & \pm1 \\
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 \\
\pm1 & 0 & 0 & 1
\end{bmatrix}
$$

Retarding Element of Retardation, $\delta$, oriented at $\alpha$:

$$
\begin{bmatrix}
1 & 0 & 0 & 0 \\
0 & \cos^2(2\alpha) + \sin^2(2\alpha)\cos(\delta) & \cos(2\alpha)\sin(2\alpha)[1 - \cos(\delta)] & -\sin(2\alpha)\sin(\delta) \\
0 & \cos(2\alpha)\sin(2\alpha)[1 - \cos(\delta)] & \sin^2(2\alpha) + \cos^2(2\alpha)\cos(\delta) & \cos(2\alpha)\sin(\delta) \\
0 & \sin(2\alpha)\sin(\delta) & -\cos(2\alpha)\sin(\delta) & \cos(\delta)
\end{bmatrix}
$$

Table 3.4 Mueller Matrices for Some Typical Polarizing Optical Elements [Galante, 1991].
Figure 3.5  Schematic of flow birefringence measurement system.
(PEM), which is oriented at $\pi/4$. The PEM consists of a rectangular, calcium fluoride optical element which is sinusoidally strained along its longitudinal axis by a piezo-active crystal cemented to one edge of the element and oscillating at the resonant frequency of the element. Light incident on the PEM experiences a time dependent phase retardance:

$$\delta_{PEM} = A \cdot \sin(\omega t) \quad (3.7)$$

where $A$ is the amplitude of the retardance and $\omega$ is the frequency of the PEM (43 kHz).

The emerging light from the PEM goes through the Couette flow cell in which the light experiences a retardation, $\delta$. The birefringence is defined by [Frattini and Fuller, 1984a]:

$$\Delta n = -\frac{\lambda \delta}{2 \pi L} \quad (3.8)$$

where $\Delta n$ is the birefringence, $L$ is the optical path length (42.86 mm for the Couette flow cell used in the experiment) and $\lambda$ is the wavelength of the light (632.8 nm for the He-Ne laser used).

After the flow cell, the light goes through an analyzer oriented at $-\pi/4$ and finally a PIN photodiode detector. The polarization state of the emerging beam from the analyzer to the detector can be represented by the ordered multiplication $[A][F][PEM][P][S_0]$, where $A$ is the analyzer, $P$ is the incident polarizer, $F$ is the Couette flow cell, PEM is the photoelastic modulator and $S_0$ is the Stokes vector of the incident light beam. The intensity of light at the detector is the first component of the resulting vector of the multiplication:
\[
I = (I_0 / 2)[1 + \cos(2\chi_0) \sin(2\chi_0)(1 - \cos \delta) \cos \delta_{PEM} + \cos(2\chi_0) \sin \delta \sin \delta_{PEM}] \quad (3.9)
\]

Fourier series expansion of \( \cos \delta_{PEM} \) and \( \sin \delta_{PEM} \) gives:

\[
\cos \delta_{PEM} = J_0(A) + 2 \sum_{m=1}^{\infty} J_{2m}(A) \cos(2mA) \quad (3.10)
\]

\[
\sin \delta_{PEM} = 2 \sum_{m=0}^{\infty} J_{2m+1}(A) \sin[(2m+1)\alpha] \quad (3.11)
\]

where \( J_m(A) \) is the Bessel function of the first kind of order \( m \). If the amplitude of the voltage supplied to the PEM is adjusted so that \( J_0(A) = 0 \) for the He-Ne laser light source, substitution of Eqs. 3.10 and 3.11 into Eq. 3.9 gives:

\[
I(t) = I_{dc} + I_{\omega} \sin(\alpha t) + I_{2\omega} \sin(2\alpha t) + \ldots \quad (3.12)
\]

and:

\[
I_{dc} = I_0 / 2 \quad (3.13)
\]

\[
I_{\omega} = 2J_1(A) \sin(\delta) \cos(2\chi_0) I_{dc} \quad (3.14)
\]

\[
I_{2\omega} = 2J_2(A)[1 - \cos(\delta)] \sin(2\chi_0) \cos(2\chi_0) I_{dc} \quad (3.15)
\]

where \( I_0 \) is the intensity of the incident beam and \( A \) is the setpoint amplitude of the PEM. The theoretical values of the Bessel functions \( J_1(A) \) and \( J_2(A) \) are 0.51907 and 0.43170, respectively. However, these equations are strictly valid only in the limit of perfect optical alignment and exact determination of the PEM setting for which \( J_0(A) = 0 \) [Frattini and Fuller, 1984a]. Thus to improve the experimental accuracy, \( J_1(A) \) and \( J_2(A) \) are determined by a calibration process which is described elsewhere [Galante, 1991].
Having these three intensities, $I_0$, $I_u$ and $I_{2\omega}$, we can obtain:

$$
\cos(\delta) = \frac{-R_{2\omega}^2 \pm R_{\omega}^2 \sqrt{1 - R_{\omega}^2 - R_{2\omega}^2}}{R_{\omega}^2 + R_{2\omega}^2} \quad (3.16)
$$

$$
\cos(2\chi_0) = \frac{R_{\omega}}{\sin(\delta)} \quad (3.17)
$$

where $R_{\omega}$ and $R_{2\omega}$ are defined as:

$$
R_{\omega} = \frac{I_{\omega}}{[2I_{dc}J_1(A)]} \quad (3.18)
$$

$$
R_{2\omega} = \frac{I_{2\omega}}{[2I_{dc}J_2(A)]} \quad (3.19)
$$

Now, the flow birefringence can be calculated from Eq. 3.8, and $\chi_0$ from Eq. 3.17.

However, in determining the value of $\delta$, there are two problems. One is that there are two solutions from Eq. 3.16. Another is that $\delta$ may be larger than 180° or $\pi$. The solution of Eq. 3.16 only returns $\delta$ values in the range of [0, $\pi$]. However, both problems can be solved. Note from Eq. 3.17 that $R_{\omega}$ has the same sign as $\sin(\delta)$ because $\chi_0$ is always less than 45° such that $\cos(2\chi)$ is positive. Thus the interval $\delta$ is in can be determined by observing the change of $R_{\omega}$ versus time. This is very critical to establish transient birefringence measurements and will be discussed in detail in the next section.

In the preceding analysis, the value of $\chi_0$ is measured with respect to the direction normal to the orientation of the initial polarizer. In practice, by orienting the incident polarizer perpendicular to the flow direction, $\chi_0$ is equal to $\chi$, the extinction angle with respect to the flow direction, which is what we want to measure.
However, we can still determine $\chi$ even if the incident polarizer is not perpendicular to the flow direction. If the optical coordinate is displaced by an angle $-\beta$ (The orientation angle of a particular element is designated positive when the element is rotated counterclockwise when looking against the direction the light beam travels.), $|\beta| < \pi/4$, then:

$$X_0 = X^P + \beta$$  \hfill (3.20)

If the flow is reversed, then:

$$X_0 = -X^P + \beta$$  \hfill (3.21)

Let $R_{i0}^+, R_{i0}^-$ and $R_{-i0}^-, R_{-i0}^+$ represent $R_{i0}$ and $R_{-i0}$ for forward and backward direction measurements, respectively. By using Eqs. 3.17, 3.20 and 3.21 and the fact that $\delta$ is independent of the flow direction, we have:

$$R_{i0}^+ + R_{i0}^- = 2 \sin(\delta) \cos(2\chi \cos(2\beta)$$  \hfill (3.22)

The sign of $\delta$ can be determined by this equation for points where $|\delta| < \pi/2$ because $\cos(2\chi) \cos(2\beta)$ is positive as $\chi$ and $\beta$ are less than $\pi/4$. We also have:

$$\cos(2\chi^0_0) = \cos[2(\beta \pm \chi)] = \frac{R_{i0}^\pm}{\sin(\delta)}$$  \hfill (3.23)

$$\sin(2\chi^0_0) = \sin[2(\beta \pm \chi)] = \frac{R_{i0}^\pm \sin(\delta)}{R_{i0}^\pm [1 - \cos(\delta)]}$$  \hfill (3.24)

Then the correct value and sign of $\chi$ and $\beta$ can be determined by the following trigonometric identities using the above two equations:

$$\cos(4\chi) = \cos[2(\beta + \chi)] \cos[2(\beta - \chi)] + \sin[2(\beta + \chi)] \sin[2(\beta - \chi)]$$  \hfill (3.25)
\[
\begin{align*}
\cos(4\beta) &= \cos(2(\beta + \chi))\cos(2(\beta - \chi)) - \sin(2(\beta + \chi))\sin(2(\beta - \chi)) \\
\sin(4\chi) &= \sin(2(\beta + \chi))\cos(2(\beta - \chi)) - \cos(2(\beta + \chi))\sin(2(\beta - \chi)) \\
\sin(4\beta) &= \sin(2(\beta + \chi))\cos(2(\beta - \chi)) + \cos(2(\beta + \chi))\sin(2(\beta - \chi))
\end{align*}
\] (3.26) (3.27) (3.28)

Once the difference is calculated, it can be utilized in future experiments as long as the system isn't altered in any way.

The Couette flow cell, whose outer cylinder is rotating, has an outside diameter of the inner cylinder of 37 mm and the inside diameter of the outer cylinder of 38 mm, which makes a gap of 0.5 mm. The shear rate can be varied from 0 to 1400 s\(^{-1}\). The temperature of the flow cell is controlled by an outer jacket in which a 50% ethylene glycol solution is circulated by a pump and heated or cooled by a temperature controlling unit. The flow cell can be sealed from the atmosphere and it can be pressurized up to 20 psig, which enables measurements to be made above 100°C. Also the flow cell can be placed under vacuum so that the bubble problem, which is a major difficulty in these measurements [Smith, 1992], can be partially solved in the flow cell. However, in the temperature range from 20°C to 90°C, no positive or negative pressure is applied so that pressure is not a factor we need to consider in interpreting the data. The whole flow system stands on a separate base from that of the optical system so that vibrations from the motor won't interfere with the stability of the light beam.

One voltage meter and two lock-in amplifiers are connected with the PIN photodiode detector such that appropriate signals can be picked up. A data acquisition card connects
the meters and a 486 computer which records the data. The computer can also control the mechanical system.

A set of calibration procedures is carried out once a month to ensure that all optical elements are normal to the light. Two Bessel functions $J_1(A_C)$ and $J_2(A_C)$ are measured in the calibration process. This calibration process is well described in the literature [Galante, 1991].

3.3.3 Establishment of Transient Flow Birefringence Measurements

The flow birefringence system has a time resolution of 1 ms. However, the controlling program was only designed to run the instrument in a steady state mode [Smith, 1992]. The original setting was to start the motor and run over a time period which the user can specify. Data were not taken until the end of that time period. Then one thousand data points were taken and recorded by computer. The average birefringence and extinction angle were then calculated. To modify the system to be able to measure transient flow birefringence, it was necessary to re-program the controlling system so that the instrument can run transient measurements.

First, the controlling program, written in Basic computer language, had to be modified. The main modification was in the data acquisition part of the program. Before the motor is commanded to start, 500 points are taken and recorded by the computer. At time zero, the motor starts and data are taken according to intervals shown in Table 3.5:
<table>
<thead>
<tr>
<th>No.</th>
<th>Points</th>
<th>Sequence Time (s)</th>
<th>Time Interval (s)</th>
<th>Motor State</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>500</td>
<td>-40</td>
<td>~0.08</td>
<td>no moving</td>
</tr>
<tr>
<td>1</td>
<td>200</td>
<td>10</td>
<td>0.05</td>
<td>starting</td>
</tr>
<tr>
<td>2</td>
<td>100</td>
<td>10</td>
<td>0.1</td>
<td>running</td>
</tr>
<tr>
<td>3</td>
<td>200</td>
<td>40</td>
<td>0.2</td>
<td>running</td>
</tr>
<tr>
<td>4</td>
<td>240</td>
<td>120</td>
<td>0.5</td>
<td>running</td>
</tr>
<tr>
<td>5</td>
<td>Run Time / 1 (s)</td>
<td>Run Time</td>
<td>1.0</td>
<td>running</td>
</tr>
<tr>
<td>6</td>
<td>100</td>
<td>5</td>
<td>0.05</td>
<td>stops at the end</td>
</tr>
<tr>
<td>7</td>
<td>200</td>
<td>10</td>
<td>0.05</td>
<td>no moving</td>
</tr>
<tr>
<td>8</td>
<td>250</td>
<td>50</td>
<td>0.2</td>
<td>no moving</td>
</tr>
<tr>
<td>9</td>
<td>240</td>
<td>120</td>
<td>0.5</td>
<td>no moving</td>
</tr>
<tr>
<td>10</td>
<td>Rex Time /1 (s)</td>
<td>Rex Time</td>
<td>1.0</td>
<td>no moving</td>
</tr>
<tr>
<td>11</td>
<td>500</td>
<td>-40</td>
<td>~0.08</td>
<td>no moving</td>
</tr>
</tbody>
</table>

Table 3.5  Running Sequence in Transient Flow Birefringence Measurements.
The time intervals are set in a way that during the start-up and cessation of the flow, small intervals, 0.05 s for each point, are used. Then during the first three minutes after the motor starts or stops, the intervals gradually increase to 1 s / point, which is used in the following measurements. The shear time and the relaxation time are inputted through user interaction when the program is executed but both of them are at least 180 s. The last 500 points are combined with the first 500 points taken to evaluate the zero point to take account of possible zero point shifting. However, for those systems which need extremely long times to relax, such as Habon G solutions, the readings are nowhere near zero even after a long relaxation time such as 180 minutes. In those cases, the final 500 points are discarded and only the first 500 points are used to get the base line. The data processing program, which is run on a VAX workstation, is designed to automatically identify cases like these.

To evaluate transient flow birefringence, the data processing program needed major revision. As stated in the last section, the retardation angle, $\delta$, may be much larger than $\pi/2$ depending on the isotropy of the system. When the flow starts, $\delta$ is in the $[0, \pi/2]$ interval, and then $\delta$ may go to a higher level by getting into a different interval, such as $[\pi/2, \pi], [\pi, 3\pi/2], [3\pi/2, 2\pi]$ and so on. $\delta$ is the largest in the steady state section and it decreases when the shear stops and finally goes back to zero. Though there is a simpler method -- by observing the readings of $I_\omega$ [Smith, 1992] -- it should be pointed out that it is only suitable for steady state measurements, not for transient measurements. An accurate measure of time when $\delta$ goes over to a new interval can not be obtained by
observation. Two parameters were used to notify the data processing program in which interval the $\delta$ should be in at any particular point of time. These two parameters were obtained by user interaction on displaying the $R_n$ vs. Time curve, which should look like a sine curve as explained in the last section. The computer reads these two parameters and the time they correspond to. During the calculation of flow birefringence and angle, the $\delta$ values are adjusted accordingly so correct results can be obtained.

The retardation angle, $\delta$, is largest in the steady state region and it should start to go back to zero value after the shear stops. Thus, in the relaxation process, it has to go from its steady state high value through each of several smaller intervals, for example, from $[\pi, 3\pi/2]$ to $[\pi/2, \pi]$ to $[0, \pi/2]$. When $\delta$ crosses the border of each interval, the two parameters need to be changed accordingly. The calculation results in the extinction angle going from a steady state value, which is usually close to $0^\circ$, back to $45^\circ$, the equilibrium value.

### 3.3.4 Stress Optical Rule

One important aspect of flow birefringence measurements is the stress-optical rule. This rule states that the refractive index tensor is proportional to the stress tensor:

$$ n = C \cdot \tau $$

(3.29)

where $C$ is the stress-optical coefficient. This rule can also be expressed in component form for simple shear flow:
\[ \Delta n \cdot \sin(2\chi) = 2C \tau_{12} \]  
\[ \Delta n \cdot \cos(2\chi) = C(\tau_{11} - \tau_{22}) \]

where \( \tau_{12} \) is the shear stress and \( (\tau_{11} - \tau_{22}) \) is the first normal stress difference.

The basis of the stress-optical rule is that the stresses and birefringence are caused by the same physical process: the chain orientation of macromolecules [Janeschitz-Kriegl, 1983]. The stress-optical rule has been shown to be valid for polymer melts and solutions with flexible chains [Galante, 1991], while it is not valid for systems of stiff polymers. For larger deformations, higher stresses or reduced chain flexibility, it will fail.

If it holds, the stress-optical rule can be used to measure the stresses in a 2D flow field. The advantage over traditional rheological methods is that the optical technique doesn't disturb the flow.

3.4 Rheological Measurements

Some basic rheological properties and relationships are introduced in this section. However, for more complete information on rheology, readers are referred to some excellent rheology books such as those by Macosko [1994] and by Bird et al. [1987].

3.4.1 Solution Viscosity

For Newtonian fluids, the ratio of shear stress to shear rate is constant, which is defined as viscosity. However, for non-Newtonian fluids, this ratio is not constant. For
convenience, people still called this ratio apparent viscosity. But readers do need to keep in mind that this viscosity is not constant for non-Newtonian fluids.

The ratio of the solution viscosity, \( \eta \), to the solvent viscosity, \( \eta_s \), is defined as the relative viscosity, \( \eta_r \):

\[
\eta_r = \frac{\eta}{\eta_s}
\]  

(3.32)

3.4.2 Steady State Shear Measurements

Rheological properties are measured in simple shear flow or extensional flow, called rheometric flow. The flow is usually two dimensional and has one or two velocity components. The simplification makes rheological calculations simple so that quick measurements are possible. There are many ways to generate rheometric flow fields. However, here only the two most common types are introduced: cone and plate and Couette cell geometries.

A schematic of a cone and plate is shown in Fig. 3.6. To have a uniform shear flow field in the gap between cone and plate, the following condition must exist [Macosko, 1994]:

- Steady, laminar, isothermal flow;
- \( v_r = v_\theta = 0 \);
- \( \beta < 0.10 \) rad ( \( \sim 6^\circ \));
- Negligible body forces;
- Spherical liquid boundary.
If we assume that these conditions are met:

\[ \tau_{12} = \frac{3M}{2\pi R^3} \]  
(3.33)

\[ \dot{\gamma} = \frac{\Omega}{\beta} \]  
(3.34)

\[ \eta = \frac{\tau_{12}}{\dot{\gamma}} \]  
(3.35)

\[ \gamma = \frac{\phi}{\beta} \]  
(3.36)

\[ N_1 = \tau_{11} - \tau_{22} = \frac{2F_z}{\pi R^2} + 0.15\rho\Omega^2 R^2 \]  
(3.37)

where \( M \) is torque, \( \Omega \) is angular velocity of the rotating plate, \( \gamma \) is strain, \( \phi \) is the angular displacement, \( F_z \) is normal force measured on the fixed cone and \( R \) is the radius of the cone. In the measurements, shear rate can be changed by changing the angular velocity of the plate and then the torque and the normal force can be measured by a transducer on the cone. Then the viscosity and the first normal stress difference can be calculated by Eqs. 3.35 and 3.37, respectively. It should be noted that in Eq. 3.37, an inertial correction term has been included.

The second type of commonly used rheometer is a Couette cell. A schematic of a Couette cell is shown in Fig. 3.7. To have a uniform shear flow field in the gap between cone and plate, again, requires [Macosko, 1994]:

- Steady, laminar, isothermal flow;
Figure 3.6  Schematic of cone and plate rheometer.

Figure 3.7  Schematic of a Couette rheometer.
• \( \nu_0 = r \Omega \) only and \( \nu_r = v_r = 0 \);
• Negligible gravity and end effects;
• Symmetry in \( \theta \), \( \partial / \partial \theta = 0 \).

If the conditions are met:

\[
\tau_{ij} = \frac{M_i}{2\pi R_i^2 L} \tag{3.38}
\]

\[
\dot{\gamma} = \frac{2\Omega}{R_o - R_i} \tag{3.39}
\]

\[
\gamma = \frac{\theta \tilde{R}}{R_o - R_i} \tag{3.40}
\]

where the subscript \( o \) denotes the outer cylinder and \( i \) denotes the inner cylinder, \( L \) is the depth of the Couette cell, \( \tilde{R} = (R_o + R_i) / 2 \) is the mean radius, and \( \theta \) is the angular displacement. It should be noted that with a Couette cell it is difficult to measure the normal stress and thus it is not normal practice to measure \( N_1 \) with a Couette cell.

First normal stress differences, \( N_1 \), were measured using a Rheometrics RMS 800 rheometer. A cone and plate fixture, as described above, 50 mm in diameter and 0.04 radians in cone angle, was used. There is a collar wall surrounding the plate such that the dilute solutions can be effectively contained in the fixture. Due to the limited sensitivity of the transducers, the lowest shear rate tested was 25 s\(^{-1}\). Also no measurements could be made at shear rates above 800 s\(^{-1}\), because of foaming of the surfactant solutions. One big disadvantage of the RMS 800 rheometer available is that the temperature is controlled by an oven instead of a bath. Heated air is blown from a heat gun to raise the temperature to
the specified value. Even when the desired temperature is reached, the air continues to be blown. The water-based dilute surfactant sample between the cone and plate is quickly evaporated by the flowing air. Thus, no test can be run above room temperature. Also there is no liquid nitrogen hooked up to the rheometer so tests below room temperature can not be run. Thus, the only choice left is to run at room temperature and most results for $N_1$ shown in this work were done at $22 \pm 2^\circ C$. With careful control, $30^\circ C$ can sometimes be reached without serious evaporation problems.

The step rate method was used, i.e., a fixed steady shear rate was applied to the sample at zero time and held long enough to reach steady state. Then the motor was turned off to allow the sample to relax to the point where zero level was reached for both $N_1$ and shear stress measurements. The sample was allowed to rest for at least 300 seconds to eliminate any possible “memory effect” of the viscoelastic solution. This effect may affect the results if the rate sweep test method is used. In this method the shear rate is ramped up so the sample has no time to relax. In that procedure, the data at each shear rate depends on both current and historical shear. Shorter rest times may give memory effects as noted by Hu and Matthys [1997]. For their surfactant system, a 300 second rest time was adequate to eliminate memory effects.

Inertia effects are very significant for $N_1$ values less than 1000 Pa in the range of shear rates of interest. Macosko [1994] gave a correction term: $-0.15\rho\Omega^2 R^2$. However, the equation given in Macosko [1994] is not correct. In measuring $N_1$ for water, the RMS output gave negative numbers, which are in good agreement with the values calculated by
this term (Fig. 3.8). \( N_1 \) for water should be zero. Thus, the correction term, \(-0.15\rho\Omega^2 R^2\), should be subtracted from the rheometer output, giving an increase in \( N_{1,\text{corrected}} \). \( N_1 \) Data presented in this work have all been corrected by:

\[
N_{1,\text{corrected}} = N_{1,\text{reading}} - (-0.15\rho\Omega^2 R^2)
\]  

(3.41)

where \( \rho \) is solution density, \( \Omega \) is angular velocity and \( R \) is cone radius. Since the correction term does not depend on solution viscosity and the water density is virtually unchanged by the addition of surfactant, this correction is also applicable to drag reducing surfactant solutions.

Shear viscosity was either measured concurrently with \( N_1 \) on the RMS 800 or on a different rheometer, RFSII, which is equipped with a much more sensitive transducer. A Couette cell was used with a cup diameter of 34 mm and bob diameter of 32 mm, giving a gap of 1 mm. The bob length was 32 mm. Temperature was controlled by a fluid bath to \( \pm 0.5^\circ\text{C} \) of the desired temperature. However, the RFSII is not equipped to measure normal stress.

3.4.3 Linear Viscoelasticity and Dynamic Measurements

When a viscoelastic material is subjected to a step increase in strain, the stress relaxes following an exponential function. The stress relaxation modulus can converted to a relaxation modulus by being divided by strain:

\[
G(t) = \frac{\tau(t)}{\gamma}
\]  

(3.42)


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Figure 3.8  Measured first normal stress difference data and correction for water.
For polymeric liquids, typically when $\gamma < \gamma_c = 0.5$, all $G(t)$ vs. $t$ data fall on the same curve. This linear dependence of stress relaxation on strain is called linear viscoelasticity. There are several small strain experiments which characterize linear viscoelasticity. In a sinusoidal oscillation experiment (commonly called a dynamic experiment) the material is subject to a sinusoidal strain. The stress also oscillates sinusoidally but is shifted by a phase angle, $\delta$:

$$\gamma = \gamma_o \sin(\omega t)$$

$$\tau = \tau_o \sin(\omega t + \delta) = \tau_o' \sin \omega t + \tau_o'' \cos \omega t$$

The stress can be decomposed into two waves of the same frequency (Eq. 3.44) giving rise to two dynamic moduli:

$$G' = \frac{\tau_o'}{\gamma_o}$$

$$G'' = \frac{\tau_o''}{\gamma_o}$$

where $G'$ is the elastic or storage modulus and $G''$ is the viscous or loss modulus.

Because of its greater sensitivity to low torque measurements, dynamic measurements were carried out with a Rheometrics RFSII rheometer. The Couette cell described above was used. Two types of experiments were carried out. One is the so-called frequency sweep, in which the dynamic moduli are measured against different frequencies under a constant strain. Another is the so-called strain sweep, in which the dynamic moduli are measured against different strains under constant frequency. Before the frequency sweep experiment can be carried out, a strain sweep test has to be done to determine what strain
should be used so that the material stays in the linear viscoelasticity range, otherwise results are meaningless. Fig. 3.9 shows results from a typical strain sweep experiment for surfactant solutions.

Fig. 3.9 shows that with small strain, data points are scattered. When the strain exceeds a certain value, here 0.05 rad, the moduli become constant until strain reaches a value of 1 rad, at which $G'$ starts to decrease. Thus, for any strain between 0.05 rad and 1 rad, the moduli remain constant and the results thus are independent of strain. This region is the linear viscoelasticity region. For surfactant systems, strains of 0.5 rad were generally chosen in frequency sweep tests.

3.4.4 Extensional Viscosity Measurements

Extensional flow is different from shear flow. The velocity gradient in the extensional flow is in the flow or axial direction, rather than perpendicular to the flow direction as in shear flow. Shear flow is exactly half rotation and half extension and is a "marginally weak" flow [Rheometrics, 1991]. Extensional flow is much stronger in terms of deforming macromolecular chains.

There are many different ways to measure extensional viscosity for high viscosity polymer solutions and melts, such as homogeneous stretching, fiber spinning, lubricated flow, contraction flow, open-syphon method [Barnes et al., 1989]. However, these methods require that the sample have a high viscosity and thus they are not suitable for
Figure 3.9  Typical strain sweep data for the Ethoquad O/12 (5 mM) / NaSal (12.5 mM) system. Frequency is 20 rad/s.
dilute surfactant solutions. Opposing nozzle geometry, first proposed by Fuller et al. [1987], is the only method suitable for dilute low viscosity solutions.

Fig. 3.10 shows a schematic of the opposing nozzle geometry. Solution is drawn into (for uniaxial extensional flow) or expelled from (for biaxial extensional flow) the nozzles. Between the two nozzles, a flow field is generated as shown in Fig. 3.10 (for uniaxial extensional flow). Numerical analysis has shown that the flow field is pure extensional flow along the center line connecting the centers of the two nozzles and is a mixture of extensional flow and shear flow elsewhere [Schunk and Scriven, 1990; Schunk et al., 1990]. By measuring the torque acting on the fixed arm (left arm in Fig. 3.10), an apparent extensional viscosity can be calculated (Eqs. 3.47-3.49).

\[
\sigma = \frac{4F_0}{\pi D^2} \tag{3.47}
\]

\[
\dot{\varepsilon} = \frac{8Q}{\pi GD^2} \tag{3.48}
\]

\[
\eta = \frac{\sigma}{\dot{\varepsilon}} = \frac{F_0 G}{2Q} \tag{3.49}
\]

Nozzles with jet diameters of 0.5 mm, 1 mm and 2 mm were used to cover apparent extension rates from 5 s\(^{-1}\) to \(10^4\) s\(^{-1}\). The separation gap between the two jets was set to be equal to the nozzle diameter. Samples were kept in a 250 ml jacketed beaker to allow temperature control of ±0.5°C by circulation of a temperature controlled ethylene glycol solution. Solutions were sucked into the nozzle by a syringe pump to generate extensional
flow between the two nozzles. Experiments were repeated three times, and the average was reported.

However, as reviewed in Chapter 2, the quantity measured in the RFX is not the "true" extensional viscosity of the liquids. It includes contributions from dynamic pressure, shear on the nozzles and liquid inertia [Pasquali and Scriven, 1996; Dontula et al., 1997; Jain et al., 1997]. However, currently no quantitative correction can be made [Dontula et al., 1997]. Also, even though Dontula et al. [1997] suggested that the extensional viscosities of liquids whose shear viscosities are lower than 50 mPa s, which include almost all drag reducing surfactant solutions, cannot be reliably measured with the RFX, since the opposing nozzle geometry is the only technique available for low viscosity fluids, we will refer to the output of the RFX as extensional viscosity. The apparent
extensional viscosities measured by the RFX are used as an indexer to make comparisons among drag reducing surfactant solutions, as suggested by Dontula et al. [1997] and Jain et al. [1997].

To estimate how much the RFX output differs from "true" extensional viscosity for low viscosity solutions, extensional viscosity measurements were performed on water at different temperatures and the Trouton ratio, Tr, was calculated (Fig. 3.11). It can be seen that at low temperatures, 20°C and 30°C, the Tr is around 20 to 30. The maximum Tr value is about 40. The results agree with Hermansky and Boger's [1995] data. They reported that for a 1 cp fluid (carbon tetrachloride at 18°C), Tr increases from about 30 at 5000 s⁻¹ to about 150 at 20000s⁻¹, and for a 3.6 cp fluid, the range of Tr is from 15 to 50, as reviewed in Chapter 2. However, it should be recognized that with high extensional viscosity surfactant solutions, the error associated with extensional viscosity measurements is lower than that for water, which has very low extensional viscosity. Therefore, we take the ratio of extensional viscosity to shear viscosity of 20 as a clear dividing line between Newtonian and non-Newtonian extensional behavior, i.e., only if the ratio is higher than 20 will the fluid be considered as high in extensional viscosity.

Another trend that should be noted is that at high temperature, the measured extensional viscosity values increase from negative at low extensional rates to positive at high rates. Also with increasing temperature, the curves shift to the right (Fig. 3.11). Very large negative extensional viscosities may be obtained particularly at high temperatures. This is
Figure 3.11 Ratio of extensional viscosity to shear viscosity of water measured on the RFX.
probably a combination of effects: the transducer reading being near or below its lower limit, inertial effects and cavitation. The transducer used has a full scale reading of 1.3 g. While its accuracy is not specified in the user's manual, it is reasonable to estimate that the transducer has an absolute error of 1/1000 of its full scale. Thus the transducer has an absolute error of 1.3 mg. At low extensional rates and high temperatures, where extensional viscosities are small, the force measured is of the order of a milligram or less. Thus the uncertainty in the force readings may be larger than the readings and anomalous effects are not surprising.

The inertial effect will cause readings from rheometers to be negative as in the first normal stress difference case (see Section 3.4.2). Dontula et al. [1997] pointed out that the statement: "this (inertial) contribution opposes the force due to the fluid extension" by Anklam et al. [1994] is correct, i.e., the inertial correction term should be added to the measured apparent extensional viscosity. Thus, the readings obtained without an inertial correction should be less than the actual extensional viscosity. The third effect, cavitation, though it was not observed in the measurements, might occur at high temperature.

The difference between the apparent measured extensional viscosity and the actual extensional viscosity is also dependent on the residence time of fluid elements in the extensional flow field. This effect will be further discussed in Chapter 5.
3.5 Separation

Attempts have been made to try to use adsorption, ultrafiltration and reverse osmosis methods to separate surfactants and counterions from aqueous solutions. Experimental details are discussed in the following sections.

3.5.1 Methods of Analyses

To measure the effectiveness of separation processes, methods to analyze the concentration of surfactants and counterions are needed. The following analysis methods were adapted from methods provided by Akzo Chemicals [Akzo, 1977].

3.5.1.1 Spectrophotometric Method

Spectrophotometric analysis makes use of selected wavelengths of electromagnetic radiation for the qualitative or quantitative determination of samples [Manahan, 1986]. A block diagram of a spectrophotometer is shown in Fig. 3.12. Light from the source is focused into a beam of light that passes through a monochromator and a band of radiation with a narrow wavelength span is selected. Then the beam passes through the sample and a reagent blank. The light traversing the blank is assigned a radiant power of $P_0$. The light passing through the sample has a radiant power, $P$. The path length of the light beam path through both the blank and the sample is designated $b$. The values of $P$ and $P_0$ are measured by a light detector.
Figure 3.12 Block diagram of apparatus for spectrophotometric measurements

The transmittance, $T$, is defined by:

$$T = \frac{P}{P_0}$$  \hspace{1cm} (3.50)

and absorbance, $A$, is defined by:

$$A = \log \frac{P_0}{P} = \log \frac{1}{T}$$  \hspace{1cm} (3.51)

The key relationship in absorption spectrophotometry is:

$$A = abC$$  \hspace{1cm} (3.52)

This is the Lambert-Beer Rule, known commonly as Beer's Law, where $a$ is the absorptivity, $b$ is the light path length through the sample and $C$ is the concentration. As absorptivity, $a$, is characteristic of an absorbing species at a specified wavelength, and $b$ is a constant, usually 1 cm, absorbance is directly proportional to concentration.

If several different materials in the sample show absorption peaks at the same or a close by wavelength, then the reagent blank should include all materials at the same
concentrations as in the sample except the material under investigation such that the measured absorbance is only contributed by the target material.

3.5.1.2 Spectrophotometric Method for Cation (Adapted from Akzo [1977]):
Quaternaries form yellow-colored complexes with sulfonphthalein dyes buffered at pH 5.6. These complexes can be extracted into chloroform. Using a spectrophotometer set at 425 nm, the absorbance is measured against a reagent blank, all except the quaternary. By comparing this to a standard curve, the weight of the quaternary in the sample can be determined. The detection limit is 1 ppm.

The buffered indicator is prepared from a mixture of the following chemicals containing dyes (#3 and #4):

1) 420 ml 0.1M aqueous citric acid;
2) 580 ml 0.2M aqueous disodium phosphate;
3) 50 ml 0.2% bromocresol green in methanol;
4) 50 ml 0.2% bromophenol blue in methanol.

The indicator should appear blue and is stable over two months.

For all analyses or to establish the standard curve, the following procedures should be followed (pipets should be used for all volume measurements to minimize the error):

1) Pipet 20.0 ml of the buffered indicator to a clean 250 ml separatory funnel.
2) Pipet 1.0 ml of the sample solution at a concentration which will maintain the mass of the surfactant in the range of 60 μg to 100 μg (perform dilution if necessary).
3) Pipet 10.0 ml of chloroform into the funnel and 5 ml of saturated NaCl solution. Shake funnel to mix contents well. Vent the funnel.

4) Add 50 ml of deionized water to the funnel and shake. Allow the chloroform layer to separate out. Discard the first 2-3 ml of the chloroform layer that comes out of the funnel. Then collect approximately 5 ml to detect its absorbance.

5) Set the wavelength of the spectrophotometer to 397 nm, at which the chloroform layer has its peak absorbance as found by scanning the resulting chloroform solution in the range of 200 nm to 800 nm. Make sure to remove all finger prints and traces of liquid from the outer wall of the quartz cuvette before it is put into machine. Always use a reagent blank as reference. Wait 3 minutes (or longer) until the absorbance does not change. Read and record the absorbance.

Unknowns are compared with the calibration curve obtained from a series of solutions of known concentration.

3.5.1.3 Spectrophotometric Method for NaSal (Developed at UCSB)

For NaSal, a spectrophotometric method without using an indicator was used [Lu, 1994a]. An aqueous solution containing only counterions is scanned on the spectrophotometer to determine at which wavelength the absorbance is a maximum (363 nm for naphthoate ion and 322 nm for salicylate ion). Thus, these two wavelengths are used for the two counterions, respectively. A standard curve is obtained by the calibration process using solutions of known concentration. When the absorbance is measured on a
sample of unknown concentration, the concentration of counterion can be obtained from the appropriate standard curve.

However, for surfactant solutions which have been in contact with iron compounds, especially the samples from drag reduction tests and reverse osmosis tests, solutions are red-like and thus the method failed. For these samples, a new method had to be developed.

NaSal reacts with Fe$^{3+}$ to form a yellow complex. The difference between the absorbance readings of the FeCl$_3$ solution before and after the addition of NaSal solution is proportional to the concentration of NaSal.

The following procedure should be followed in the analysis of NaSal which has been in contact with Fe$^{3+}$:

1) Add 10 ml of 0.1M FeCl$_3$ solution in a clean 100 ml beaker,
2) Add 1 ml of the NaSal sample,
3) Add 50 ml deionized water and mix the solution well,
4) Run the resulting solution at wavelength of 528 nm (found by scanning) in the spectrophotometer against the reagent blank, which includes everything except NaSal, and read the absorbance.
A calibration curve should be established by measuring the absorbance of samples of known concentration. The presence of the surfactant has no effect on the absorbance of NaSal [Lu, 1994b].

3.5.2 Adsorption

A 4000 ml beaker is filled with the surfactant solution. The solid adsorbent is added, the time is noted, and a mixer is used to ensure complete mixing of the two phases. The mixer is turned off after 30 minutes. The adsorbent is allowed to settle for a few moments, and then a 100 ml sample is drawn off the top of the solution into a clean, dry beaker. Using a clean, dry Erlenmeyer flask, any solid in this supernatant liquid is separated from the sample using vacuum filtration and general filter paper. If the filtered liquid is not totally clear, it is re-filtered two or three times. This is especially true if a high adsorbent to surfactant ratio is tested. Once the sample is filtered, the concentrations of quaternary ammonium surfactant and the salicylate in the filtrate are measured by the methods described above. The adsorbents used in the adsorption tests are listed in Table 3.6.

3.5.3 Ultrafiltration

Since surfactants form large micelles which are large enough to be retained by ultrafiltration membranes, ultrafiltration is a candidate method to separate surfactants from solutions.
Table 3.6 Adsorbents Used in the Separation Experiments.

To determine which ultrafiltration Molecular Weight Cut Off (MWCO) membrane would be most suitable for the solutions, a "dead-end" method was used initially. MWCO is the molecular weight below which molecules pass through the membrane. The solution is forced through the membrane by compressed air. The filtrate is collected, and the concentration of cationic surfactant in the filtrate is analyzed.

Two ultrafiltration cartridges manufactured by A/G Tech. Co. were employed in the ultrafiltration experiments, 10 K MWCO and 100 K MWCO hollow fiber membrane. The membrane areas of both cartridges were 0.007 m².

To minimize gel layer formation, "Cross-Flow-Modules" were used (Fig. 3.13). Surfactant solution is pumped from a reservoir through the ultrafiltration cartridge under a fixed pressure, which is adjusted by the valves on the inlet and outlet of the cartridge.
The transmembrane pressure is determined from two pressure gauges installed at the inlet and the outlet of the cartridge.

\[
\text{Transmembrane Pressure} = \frac{P_{\text{inlet}} + P_{\text{outlet}}}{2} - P_{\text{permeate}}
\]  
(3.53)

Figure 3.13 Schematic of ultrafiltration system.

The maximum pressure the ultrafiltration cartridge can bear is 20 psi, so the pressure in the cartridge should not exceed 20 psig.

The permeate is collected, and the volume of the permeate is recorded vs. time. The retentate is returned to the reservoir. Because the volume throughput rate of the permeate is small, the concentration of the surfactant in the reservoir increased slowly with time.
3.5.4 Reverse Osmosis

Ultrafiltration can separate particles from solution in the size range of 0.005 μm to 1 μm, whereas reverse osmosis can separate particles in the size range of 0.0005 μm to 0.01 μm. So ultrafiltration can separate surfactant micelles while reverse osmosis may be effective to separate excess NaSal.

The process for reverse osmosis is similar to that for ultrafiltration, except that the cartridge used here is a hollow fiber reverse osmosis cartridge. Also the operating pressure can be as high as 200 psi so the pump used here is a high pressure pump.

Only sodium salicylate solution was tested in the reverse osmosis system to check its ability to separate this counterion.

3.6 Cryo-TEM

Cryo-TEM (cryogenic temperature transmission electron microscopy) images shown in this work were obtained through collaboration with Dr. Y. Talmon of the Department of Chemical Engineering, Technion-Israel Institute of Technology and with Drs. L.E. Scriven and H.T. Davis of Department of Chemical Engineering and Materials Science, University of Minnesota, and two of their students, Dr. X. Li and Y. Zheng. Procedures to obtain cryo-TEM images are outlined below.
Surfactant solution specimens were prepared for cryo-TEM in a controlled temperature and humidity chamber, by applying a small drop of the studied solution onto a perforated holly carbon film supported on an electron microscope grid, blotting it to form a thin (~0.2 μm) liquid film, and rapidly plunging the grid into liquid ethane at its freezing point, thus vitrifying the liquid [Talmon, 1996]. By avoiding crystallizing the water the microstructure is not disturbed and the images obtained reflect the true microstructures in the original solutions. Images of the vitrified samples were recorded with either a Philips CM12 or a JEOL 2000FX transmission electron microscope operated at 100 kV, using Gotam cooling holders at about -170°C. Low-dose images were taken at 4 μm nominal underfocus. The blotting to form the thin film subjects the solution to very high rates of flow deformation.
CHAPTER 4

RESULTS AND DISCUSSION - FLOW BIREFRINGENCE

4.1 Steady State Flow Birefringence

An extensive steady state flow birefringence study was carried out on drag reducing surfactant solutions previously [Smith, 1992]. In this section, only new data are reported.

Figs. 4.1 and 4.2 show flow birefringence and extinction angle for Arquad S-50 (5 mM) / NaSal (12.5 mM) solution in a Couette cell. Flow birefringence increases with shear rate and decreases with increasing temperature. The S-50 solution showed strong birefringence at 20, 40 and 60 °C. The system showed weak birefringence at 70 °C. As temperature is raised, birefringence of S-50 in the shear rate range up to 1400 s\(^{-1}\) is lost before drag reduction is lost. This discrepancy was noted earlier for the Ethoquad T/13-50 / NaSal surfactant system [Stern et al., 1994]. The extinction angle, \(\chi\), is 45° at very low shear rates and decreases with increasing shear rate. At high shear rates, the extinction angle is very small which means the micellar structure is well aligned with the flow. With increasing temperature, the extinction angle is larger at the same shear rate or the onset
Figure 4.1 Flow birefringence results for the Arquad S-50 (5 mM) / NaSal (12.5 mM) system.
Figure 4.2  Extinction angle results for the Arquad S-50 (5 mM) / NaSal (12.5 mM) system.
shear rate at which the extinction angle begins to decrease increases. These results are consistent with what Smith [1992] observed.

Figs. 4.3 and 4.4 show birefringence and extinction angle for the Ethoquad O/12 (5 mM) / NaSal system at two different counterion to surfactant ratios, $\xi = 0.6$ and 1.0. The $\xi = 1.0$ system has much higher birefringence and much lower extinction angle values than the $\xi = 0.6$ system. This means that the $\xi = 1.0$ system has longer thread-like micelles than the $\xi = 0.6$ system such that the anisotropy of the solution is larger. Since larger micelles are more easily aligned, they have smaller extinction angles as well. In both cases, the extinction angles at high shear rates are less than 5°.

Fig. 4.5 shows birefringence data for Habon G solutions at four different concentrations: 1, 2, 3 and 5 mM. Birefringence increases with concentration at low concentrations. The 3 mM solution has the same birefringence as the 5 mM solution. The Habon G (5 mM) solution has higher birefringence than other systems studied at the same concentration. This may be because the counterion in Habon G is reacted with the cation and thus a chemical bond is formed between counterion and cation. Habon G solution, though classified as a cationic surfactant, is actually neutral. Also, no other negative ions, such as Cl⁻, Br⁻ or Ac⁻, are competing with the naphthoate. A possible cross section structure of rod-like micelles is proposed as shown in Fig. 4.6. In other surfactant systems with addition of equimolar counterions, some of the counterions may stay in the electron double layer rather than directly bind with the cation. Thus, the positive charges on...
Figure 4.3 Flow birefringence results for the Ethoquad O/12 (5 mM) / NaSal system at different counterion to surfactant ratios, $\xi$. 

$\Delta n \times 10^6$

Shear Rate (s$^{-1}$)

$T = 20 \, ^{\circ}C$
Figure 4.4  Extinction angle results for the Ethoquad O/12 (5 mM) / NaSal system at different counterion to surfactant ratios, $\xi$. 
Figure 4.5 Flow birefringence results for Habon G solutions at four different concentrations.
headgroups of Habon G molecules may be more completely neutralized than for other surfactants, resulting in more stable and longer thread-like micelles. In fact, the Habon G (5 mM) solution is so viscous that air bubbles trapped in the solution stay there for tens of hours. When the Couette cell of the birefringence system is filled with this solution, experiments can not start for at least twelve hours because of the air bubbles and the long lasting birefringence induced by the stresses caused by the solution addition process. This usually doesn’t happen for other surfactant systems.

4.2 Relaxation Process of Flow Birefringence

4.2.1 General Relaxation Behavior and Effect of Shear Rate

Figs. 4.7 to 4.9 show the flow birefringence relaxation process for Ethoquad O/12 (5 mM) / NaSal (3 mM) solution at different shear rates. At a low shear rate, 5 s⁻¹, the steady state flow birefringence is at a very low level (Fig. 4.7). The relaxation process can be fit
Figure 4.7 Relaxation of flow birefringence for the Ethoquad O/12 (5 mM) / NaSal (3 mM) solution at 20°C. Shear rate is 5 s⁻¹ and shear stops at time = 0.0. The one step time constant is 215 s.
Figure 4.8  Relaxation of flow birefringence for the Ethoquad O/12 (5 mM) / NaSal (3 mM) solution at 20°C. Shear rate is 100 s⁻¹ and shear stops at time = 0.0. The two step time constants are 11.2 and 113 s, and the one step time constant is 90 s.
Figure 4.9 Relaxation of flow birefringence for the Ethoquad O/12 (5 mM) / NaSal (3 mM) solution at 20°C. Shear rate is 500 s\(^{-1}\) and shear stops at time = 0.0. The two step time constants are 7.2 and 73 s, and the one step time constant is 56 s.
well by a single exponential function (Eq. 4.1) and it is a slow process with a time constant of 215 s.

$$\Delta n = \Delta n_0 e^{\frac{t-t_0}{\tau}}$$

(4.1)

where $\Delta n$ and $\Delta n_0$ are birefringence, $t_0$ is the time when shear stopped, $\tau$ is the relaxation time constant.

At a high shear rate, 100 $s^{-1}$, however, the steady state flow birefringence is over one order of magnitude larger and the relaxation process is more complex (Fig. 4.8). After shear was stopped, the birefringence had a quick and large decrease and then a slow decay process followed. It can be seen that a single exponential function can no longer fit the data well. To improve fitting, a double exponential function is used [Lu and Zakin, 1995]:

$$\Delta n = \Delta n_1 e^{\frac{t-t_0}{\tau_1}} + \Delta n_2 e^{\frac{t-t_0}{\tau_2}}$$

(4.2)

where $\Delta n_1$ and $\Delta n_2$ are birefringence, $\tau_1$ and $\tau_2$ are time constants for the first (fast) and second (slow) step, respectively. Details of the technique for fitting can be found in Matsuoka [1968]. This function was also used to fit rheological data for surfactant solutions [Shikata et al., 1988b; Hu and Matthys, 1995; Lu et al., 1997a] and it will be used in the next chapter.

From Fig. 4.8, it can be seen that the 2-Step Fitting by the double exponential function matches data points much better than the 1-Step Fitting. The 2-step can represent the first fast drop while the 1-step fails to do that. However, fitting by the 2-step is not perfect,
which means that the relaxation process of flow birefringence is a multiple step process. Each step of a multiple step relaxation process has contributions from particles of different sizes. This indicates that there is a wide distribution in particle size in the surfactant solution, i.e., the sheared cationic systems are polydisperse. However, to simplify the data reduction process, only a double exponential function is used.

The relaxation process at 500 s$^{-1}$ (Fig. 4.9) is not significantly different from that at 100 s$^{-1}$. However, the double exponential function fits the data better than at 100 s$^{-1}$.

The two step birefringence relaxation process is also observed in other drag reducing surfactant systems. Also, as reviewed in Chapter 2, Oh and Park [1992] observed the two step relaxation of flow birefringence on calf skin collagen solutions. They explained the quick first step drop as due to relaxation of structure of small molecules as well as large molecules, while the second step is only due to the large molecules. For these drag reducing surfactant systems, we suggest that the first step is due in part to relaxation of individual micelles. When the shear stops, individual micelles rapidly lose their orientation due to thermal motions so that there is a big drop in the flow birefringence. However, the entanglement structure of the micelles takes much longer to relax and is the source of the long lasting birefringence. The entangled micellar network contributes less to birefringence since the cross-links reduce the difference in refractive index in two directions. When flow is stopped, the highly stretched network is released by the flow and the initial quick deformation in the network further reduces the difference in refractive index in the optical axes directions. Thus, the first quick drop in birefringence is mainly
due to relaxation of individual thread-like micelles and small fragments of the network, but also to the contribution from the initial deformation of the network structure. The remaining network, however, needs a much longer time to return to the isotropic state. Thus, a long relaxation tail is observed following the quick drop.

Shear rate not only affects how birefringence relaxes, it also affects the relaxation time constants. Figs. 4.10 and 4.11 show birefringence relaxation time constants by 1-step and 2-step fittings for Arquad 16-50 (5 mM) / NaSal (5 mM) and Ethoquad O/12 (5 mM) / NaSal (5 mM) systems as a function of shear rate. In both cases the relaxation time constants decrease with increasing shear rates. In the 2-step fittings, the time constants of the second step are significantly longer than the first step. The difference may be up to one order of magnitude. The single step fitting time constant lies between the two times obtained by 2-step fitting as expected.

At low shear rates, the relaxation is a one-step process, which is a long relaxation process, however, and it can not be due to the relaxation of single rod-like micelles. It has to be due to the existence and relaxation of a network. As for individual micelles, the orientation is rapid. This indicates that for surfactant systems a network is formed even at low shear rates. At low shear rates, this network is loose but it holds most of the rod-like micelles. It is weakly aligned along the flow direction and the solution shows only moderate birefringence. When the shear stops, the relaxation of this network is slow which keeps the solution birefringent for a long time. As we stated above, the two-step
Figure 4.10 Flow birefringence relaxation time constants for Arquad 16-50 (5 mM) / NaSal (5 mM) solution at 20°C. Time constants were obtained by single step exponential function fitting (Eq. 4.1) and by two step fitting (Eq. 4.2).
Figure 4.11 Flow birefringence relaxation time constants for Ethoquad O/12 (5 mM) / NaSal (5 mM) solution at 20°C. Time constants were obtained by single step exponential function fitting (Eq. 4.1) and by two step fitting (Eq. 4.2).
relaxation of flow birefringence at high shear rate is due to the relaxation of individual micelles and the initial deformation of the network at first and then to the relaxation of the network. At low shear rate, the relaxation is a single step suggesting that there are few free rod-like micelles and the relaxation is caused by relaxation of the network. At high shear rate, a larger fraction of individual rod-like micelles are present in the solution because they were broken off from the network because of the high shear. Their relaxation is fast and the subsequent relaxation of the network gives rise to the two-step process.

4.2.2 Effect of Counterion to Surfactant Ratio

Fig. 4.12 shows the relaxation time constants by 1-step fitting for Arquad 16-50 (5 mM) / NaSal at different counterion to surfactant ratios, $\xi$. In addition to the decreasing relaxation time with shear rate feature discussed in the last section, the relaxation time constants vary with $\xi$. The $\xi = 1.0$ system has the largest relaxation time constants. This is also true for time constants obtained by 2-step fitting for the same systems (Fig. 4.13). It should be noted that the Arquad 16-50 (5 mM) / NaSal (3 mM) system ($\xi = 0.6$) at 10 and 100 s$^{-1}$ (Fig. 4.13) and the Ethoquad 0/12 (5 mM) / NaSal (3 mM) system ($\xi = 0.6$) at 5s$^{-1}$ (Fig. 4.14) can be well fit by a 1-step fitting and thus only 1-step fitting time constants are shown.

For the Arquad 16-50 (5 mM) / NaSal systems, relaxation time increases when $\xi$ increases from 0.6 to 1.0. At $\xi = 0.6$, the micellar network structure is incomplete due to insufficient neutralization of the positive charges of headgroups by counterions. This is

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Figure 4.12 Flow birefringence relaxation time constants by the single exponential function (Eq. 4.1) fitting for Arquad 16-50 (5 mM) / NaSal systems at various counterion to surfactant ratios, $\xi$. 
Figure 4.13  Flow birefringence relaxation time constants by the double exponential function (Eq. 4.2) fitting for Arquad 16-50 (5 mM) / NaSal systems at various counterion to surfactant ratios, $\xi$. 

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Figure 4.14 Flow birefringence relaxation time constants by the double exponential function (Eq. 4.2) fitting for the Ethoquad O/12 (5 mM) / NaSal systems at various counterion to surfactant ratios, $\xi$. 
seen in the cryo-TEM pictures for the Arquad 16-50 (5 mM) / NaSal (3 mM) ($\xi = 0.6$) system [Lu et al., 1997c]. Only several long thread-like micelles were observed and there was no micellar network.

When $\xi$ reaches 2.5, relaxation times significantly decrease, which agrees with rheological data to be discussed in the next chapter. Also, cryo-TEM pictures show the thread-like micellar network at $\xi = 2.5$ is denser than that for $\xi = 1.0$ [Lu et al., 1997c]. It is not clear what mechanism causes the decrease in relaxation time when $\xi$ increases over 1.0. Shikata et al. [1988a] suggested that the free salicylate molecules accelerate the disentangling process of the micellar network. No mechanism was provided, however.

For the Ethoquad O/12 systems (Fig. 4.14), the difference in relaxation time constants for $\xi = 0.6$ and $\xi = 1.0$ systems is not significant. Both systems have similar relaxation time constants. The cryo-TEM pictures of these two systems show little difference in terms of network density [Lu et al., 1996b, 1997c].

4.2.3 Effect of Counterion Structure

Section 4.2.2 showed birefringence relaxation data for different surfactant systems with different ratios of counterion to surfactant. The relaxation time constants of those systems are usually less than 5 min. In this section, birefringence relaxation of a series of unusual systems will be discussed.
Figs. 4.15-4.17 show birefringence relaxation data for Habon G (1 mM) solution. As discussed previously, the Habon G solutions have higher birefringence than other surfactant systems at the same concentrations. The relaxation also takes an unusually long time compared with other surfactant systems.

At 5 s⁻¹ (Fig. 4.15), the 1-step exponential function can fit data slightly better than the 2-step. The time constants, in the order of 1000 s, are much larger than those shown above for systems with NaSal as the counterion. When shear rates are increased to 100 (Fig. 4.16) and 500 s⁻¹ (Fig. 4.17), however, the 2-step fit the data much better than the 1-step. The latter can not represent the first quick drop in birefringence. The 2-step doesn’t fit the data very well at the corner of the drop, however. This suggests that the relaxation probably takes more than two steps, as mentioned in the previous section.

The Habon G (2 mM) solution has similar, but slower, birefringence relaxation behaviors compared to the Habon G (1 mM). Table 4.1 summarizes relaxation time constants for these two solutions. The time constants, instead of decreasing with shear rate, show a maximum at a shear rate of 100 s⁻¹ with the exception of the Step 1 time constant of Habon G (1 mM). Except for 1 s⁻¹, the Habon G (2 mM) solution has time constants of about 1 hour in the long step or the single step. Noting that the time constants are not equal to the whole relaxation time, the complete relaxation of flow birefringence takes an even longer time. In fact, the Habon G (5 mM) solution has such a long relaxation time.
Figure 4.15 Relaxation of flow birefringence for the Habon G (1 mM) solution at 20°C. Shear rate is 5 s\(^{-1}\) and shear stops at time = 0.0. The two step time constants are 122 and 1027 s, and the one step time constant is 700 s.
Figure 4.16 Relaxation of flow birefringence for the Habon G (1 mM) solution at 20°C. Shear rate is 100 s\(^{-1}\) and shear stops at time = 0.0. The two step time constants are 17 s and 1145 s, and the one step time constant is 855 s.
Figure 4.17 Relaxation of flow birefringence for the Habon G (1 mM) solution at 20°C. Shear rate is 500 s\(^{-1}\) and shear stops at time = 0.0. The two step time constants are 17 s and 1177 s, and the one step time constant is 807 s.
Table 4.1  Birefringence relaxation time constants (seconds) for the Habon G solutions at 1 mM and 2 mM concentrations.

<table>
<thead>
<tr>
<th>System</th>
<th>Shear Rate (s⁻¹)</th>
<th>1</th>
<th>5</th>
<th>100</th>
<th>500</th>
</tr>
</thead>
<tbody>
<tr>
<td>Habon G (1 mM)</td>
<td>Single Step</td>
<td>-</td>
<td>700</td>
<td>855</td>
<td>807</td>
</tr>
<tr>
<td></td>
<td>Step 1</td>
<td>-</td>
<td>122</td>
<td>17</td>
<td>17</td>
</tr>
<tr>
<td></td>
<td>Step 2</td>
<td>-</td>
<td>1027</td>
<td>1145</td>
<td>1177</td>
</tr>
<tr>
<td>Habon G (2 mM)</td>
<td>Single Step</td>
<td>543</td>
<td>3125</td>
<td>3550</td>
<td>3046</td>
</tr>
<tr>
<td></td>
<td>Step 1</td>
<td>90</td>
<td>81</td>
<td>130</td>
<td>95</td>
</tr>
<tr>
<td></td>
<td>Step 2</td>
<td>1062</td>
<td>4651</td>
<td>5128</td>
<td>4348</td>
</tr>
</tbody>
</table>

that the whole system has to be run for more than 10 hours to collect enough data to give a reliable fit, which was not done for this reason. The relaxation time constants for the Habon G (5 mM) solution are estimated to be of the order of 10 hours.

Similar behavior was observed in the Arquad 16-50 (5mM) / 2-OH-1-Naphthoate (5mM) system (Fig. 4.18), which also shows a 2-step long relaxation process.

The differences between the 2-hydroxy-1-naphthoate systems and the salicylate systems must be in the counterions. Recall that Arquad 16-50 has the same alkyl group as Habon-G. Also the differences in head groups do not induce large differences in relaxation times for flow birefringence as we observed similar birefringence relaxation behaviors for both Arquad 16-50 and Ethoquad O/12. The latter has two hydroxyethyl groups in its headgroup and the former has three methyls. Thus the effect must be due to the differences between the hydroxy-naphthoates and salicylate counterions.
Figure 4.18 Flow birefringence data for the Arquad 16-50 (5 mM) / 2-OH-1-naphthoate (5 mM) system.
Thus, the difference in the relaxation behaviors must be caused by the effects of the different counterions on the microstructures of the micelles. In the previous section we noted that the naphthoate counterions in Habon G are reacted with the cationic surfactant and thus they are much more effective in neutralizing the positive charges of headgroups. For the Arquad 16-50 and Ethoquad O/12 surfactants with 2-hydroxy-1-naphthoate systems, the hydroxy naphthoate binds more strongly with the headgroup than salicylate and thus it more effectively neutralizes the positive charges. NMR studies [Smith, 1992; Smith et al., 1994a] showed that hydroxy-naphthoates penetrate deeper into the cationic surfactant micelles than salicylate (Fig. 4.19). This deeper penetration causes the rod-like micelles in solution containing naphthoate counterions to be more rigid than those with salicylate which does not penetrate as deeply. Under shear, the more rigid micelles can be completely aligned allowing numerous hydrogen bonds to be formed between micelles. H-bondings between micelles can also be formed between the more flexible micelles, but the density of the H-bondings would be lower than those between the highly aligned rigid micelles. These intermicellar H-bondings act as bridges between micelles and form a dense network. The rate of breakdown of the strongly hydrogen-bonded network is slower for surfactant systems with naphthoates as counterions than for the more flexible salicylate systems. Thus the rigid micelles formed with hydroxy-naphthoate counterions promote formation of a persistent network structure.
4.3 Relaxation Process of Extinction Angle

Due to the modification of the birefringence measurement technique done in this research, as described in Chapter 3 (see section 3.3.3), the transient extinction angle can also be measured. Fig. 4.20 shows the extinction angle, $\chi$, data for Ethoquad O/12 (5 mM) / NaSal (3 mM) solution at 500 s$^{-1}$. The $\chi$ quickly drops from 45° to the steady state value around 5° upon the start of shear (at -5 min.). After the shear stops, the extinction angle goes back to its equilibrium value, 45°, contrary to some other data showing that the extinction angle decreases to or stays at a value near 0° [Osaki et al., 1979; Frattini and Fuller, 1986; Hu et al., 1993]. The extinction angle also takes a long time to get back to 45°, but no initial rapid increase in the extinction angle is observed. This can be explained by recognizing that the extinction angle is the average over all the particles, while the birefringence is greatly dependent on the anisotropy of the solution, i.e., a little
Figure 4.20 Extinction Angle for the Ethoquad O/12 (5 mM) / NaSal (3 mM) solution at 20°C. Shear rate is 500 s⁻¹ and shear is applied at t = -5 min. and stops at time = 0.0.
drop in anisotropy will cause a big drop in birefringence. Due to large amount of noise usually accompanying the extinction angle data, no fitting can be done.

Frattini and Fuller [1986] explained their observations of decrease of the extinction angle from dichroism measurements as due to polydispersity of the system. They suggested that in a polydisperse suspension under shear, the small particles reach a steady extinction angle which exceeds that of the average particle. Following cessation of flow, the small particles relax more quickly than the average particle and as time progresses they no longer contribute to the dichroism signal. Thus the observed extinction angle after cessation of shear is lower than the steady state value.

This explanation does not answer the following question, however. At the beginning of the shear flow, the extinction angle for anisotropic particles decreases from 45°. Unoriented anisotropic particles should give this reading. Thus, it is not apparent why the extinction angle does not go back to its original value of 45° after the anisotropic solution is fully relaxed.

This anomalous result of the relaxation of the extinction angle may be caused by incorrect determination of the decrease in the magnitude of the retardation angle (see section 3.3.3), as it is not clear how the relaxation of the extinction angle was evaluated in the above three reports. As stated in Section 3.3.3, the retardation angle (see Section 3.3.2) decreases from its maximum steady state value to zero upon cessation of shear. If the
retardation angle in steady state was used to calculate the extinction angle (see Eq. 3.17), the correct result will not be obtained. Thus, it is possible that the extinction angle reported after the cessation of the shear was incorrectly evaluated.

Hu et al. [1993] stated that the retention of the extinction angle at its small plateau value over the same time period in which birefringence drops to zero indicates that the long-term alignment of the micellar structure in the flow direction persists. This obviously is self-contradicting since when birefringence drops to zero level, the orientation of the micellar structure must no longer exist. Their report of the persistence of the zero extinction angle suggests that there is an error in their interpretation of their reading.

4.4 Stress-Optical Rule

The flow birefringence, $\Delta n$, and the extinction angle, $\chi$, can be linearly related to the shear stress and the first normal stress difference through the Stress-Optic Law [Coleman, et al., 1970, Janeschitz-Kriegl, 1983]. This law states that there is a simple proportionality between the refractive index tensor, $\mathbf{n}$, and the stress tensor, $\tau$:

$$\mathbf{n} = C \cdot \tau$$

(3.29)

where $C$ is the stress-optical coefficient. For simple shear flow, the law simply states:

$$\Delta n \cdot \sin(2\chi) = 2C \tau_{12}$$

(3.30)

$$\Delta n \cdot \cos(2\chi) = C(\tau_{11} - \tau_{22})$$

(3.31)

where $\tau_{12}$ is the shear stress and $\tau_{11} - \tau_{22} = N_1$ is the first normal stress difference.
It was noted by Stem et al. [1994] that for these dilute drag reducing surfactant systems, Eq. 3.30 can not be followed, because as shear rate increases, the extinction angle, \( \chi \), approaches zero so that the left hand side of Eq. 3.30 is zero while the shear stress doesn’t vanish with increasing shear rate and in fact increases [Stem et al., 1994]. However, it may be more appropriate to state that since for dilute drag reducing surfactant systems, the extinction angle usually approaches a very small value and thus the stress optical coefficient calculated by Eq. 3.30 may be subject to large error. This, however, does not necessarily mean that the stress-optical rule is invalid for these surfactant systems. There is a way to work around this problem, though. The sum of the squares of Eqs. 3.30 and 3.31 gives:

\[
\Delta n^2 = 4C^2 \tau_{12}^2 + C^2(\tau_{11} - \tau_{22})^2 \tag{4.3}
\]

and thus:

\[
C = \frac{\Delta n}{\sqrt{4\tau_{12}^2 + (\tau_{11} - \tau_{22})^2}} = \frac{\Delta n}{\sqrt{4\tau_{12}^2 + N_i^2}} \tag{4.4}
\]

Note in Eq. 4.4 that the stress-optical coefficient, \( C \), should have the same sign as the birefringence, \( \Delta n \), and thus a positive sign is selected for the square root of \( \Delta n^2 \).

With Eq. 4.4, no extinction angle data are needed to calculate the stress-optical coefficient and thus any error associated with the extinction angle measurement has no effect on the calculation of the coefficient. Fig. 4.21 shows \( C \) calculated separately by Eqs. 3.30, 3.31 and 4.4. It can be seen that the \( C \) values obtained by Eq. 3.31 coincide with those by Eq. 4.4. This is because the shear stress is only about 10% of the first
normal stress difference and the extinction angle is close to zero such that \( \cos(2\chi) \) is close to 1.0. In the extreme case of ignoring \( \tau_{12} \) in Eq. 4.4 and assigning 1.0 to \( \cos(2\chi) \) in Eq. 3.31, the two equations are identical. On the other hand, the coefficient calculated by Eq. 3.30, using shear stress data and the sine function of the small extinction angle, does scatter more than the other two methods. This suggests that Eq. 4.4 should be used to calculate the stress-optical coefficient.

The stress-optical coefficient, however, decreases with shear rate instead of being constant (Fig. 4.21). The coefficient decreases nearly 80% over the shear rate range of 25 to 100 s\(^{-1}\). At shear rates over 200 s\(^{-1}\), the decrease is much slower. An average of these slowly decreasing points gives: \( C = -3.1 \times 10^9 \) (Pa\(^{-1}\)).

The stress-optical coefficients are also calculated for Arquad 16-50 (5 mM) / NaSal systems at two other counterion to surfactant ratios (Figs. 4.22 and 4.23). For the \( \xi = 0.6 \) and 1.0 systems, \( C \) values calculated by Eq. 3.30 are higher than those by Eqs. 3.31 and 4.4 (see Figs. 4.22 and 4.23). As stated above, this discrepancy may be caused by error in the extinction angle. The coefficients for all three systems decrease with shear rate at low shear rates. This "shear decreasing" behavior is caused by different trends of birefringence and stresses at low shear rates, i.e., stresses increase with shear rate quicker than the birefringence. For all three systems (\( \xi = 0.6, 1.0 \) and 2.5), \( C \) values are more or less constant. If values obtained by Eq. 4.4 are used for comparison, they vary by less than \( \pm100\% \) from mean values above 100s\(^{-1}\) for \( \xi = 2.5 \) and \( \pm50\% \) from mean values.
Figure 4.21 Stress-optical coefficient calculated by three different methods for the Arquad 16-50 (5 mM) / NaSal (12.5 mM) system.
Figure 4.22 Stress-optical coefficient calculated by three different methods for the Arquad 16-50 (5 mM) / NaSal (5 mM) system.
Figure 4.23 Stress-optical coefficient calculated by three different methods for the Arquad 16-50 (5 mM) / NaSal (3 mM) system.
above 25s⁻¹ for ζ = 0.6 and 1.0. The coefficients increase as ζ increases to 1.0 and show little change at ζ = 2.5.

The same increase in stress-optical coefficient with increasing ζ was also observed with the Ethoquad O/12 (5 mM) / NaSal systems (Fig. 4.24). For these two O/12 systems, the coefficients tend to be more constant than the Arquad 16-50 systems, especially for the ζ = 1.0 system. However, Habon G systems at four different surfactant concentrations behave somewhat differently (Fig. 4.25). The coefficients for the 1 mM Habon G system vary considerably. The 3 and 5 mM systems vary less than ±100% about their means. In general the constant increases with Habon G concentrations, but the data are scattered and there are crossovers.

The stress-optical coefficients calculated from steady state data vary from system to system. In most cases, the coefficients are not constant, which may imply that the stress-optical rule is not applicable to these drag reducing surfactant systems, at least at the shear rate ranges studied. However, it may be necessary to look at transient data before any conclusion is drawn. Fig. 4.26 shows normalized flow birefringence and stress combination: \( \sqrt{4r_{12}^2 + N_r^2} \) for the Ethoquad O/12 (5 mM) / NaSal (5 mM) system after cessation of a steady state shear of 100s⁻¹. The reason for looking into this system at this shear rate is because the data of Fig. 4.24 suggest that it follows the stress-optical rule. According to Eq. 4.4, the two quantities plotted in Fig. 4.26 should superpose if the stress-optical rule is valid since both are normalized. However, this is obviously not the
Figure 4.24 Stress-Optical Coefficient calculated by Eq. 4.4 for the Ethoquad O/12 (5 mM) / NaSal systems at various counterion to surfactant ratios, $\xi$. 
Figure 4.25 Stress-Optical Coefficient calculated by Eq. 4.4 for the Habon G system at different concentrations.
Figure 4.26 Normalized transient flow birefringence and stress combination: 
\[ \sqrt{4\tau_{iz}^2 + N_i^2} \] (see Eq. 4.4) upon cessation of steady state shear for the Ethoquad O/12 (5 mM) / NaSal (5 mM) system at 100 s\(^{-1}\).
case. Thus, the stress-optical rule is not valid for this surfactant system in this range of shear rates. This is consistent with the observation that the birefringence relaxes more slowly than normal stress and shear stress for these surfactant systems.
CHAPTER 5

RESULTS AND DISCUSSION - DRAG REDUCTION AND RHEOLOGY

5.1 Drag Reduction Results

Since in this chapter, rheological results will be discussed to correlate with drag reduction, some relevant drag reduction results are presented in this section first.

5.1.1 Effect of Counterion Structure for Cationic Surfactant Systems

Drag reduction measurements were carried out on 5 mM Arquad 16-50 aqueous solution, with 12.5 mM 2-, 3- or 4-Cl benzoate as counterions. The effective drag reduction temperature ranges for these three surfactant systems have been reported in Smith et al. [1994b]. Arquad 16-50 / 2-Cl-benzoate showed no drag reduction at any temperature, while the 3-Cl system was drag-reducing from 30°C to 50°C, providing up to 70% drag reduction, but showed no drag reduction at temperatures beyond that range (Fig. 5.1).

Drag reducing surfactant solutions have two upper critical limits. At some upper critical temperature, they lose their effectiveness and return to water-like behavior. Similarly, at some upper critical wall stress, whose value depends on temperature, they also lose their effectiveness. In both cases the loss of effectiveness is reversible and drag reduction
capability is regained if the temperature is lowered or the flow rate is reduced. In the case of temperature, this is caused by a transformation of thread-like to spherical micelles, and in the case of shear it is probably caused by break up of the network of thread-like micelles. As will be discussed later, both of these processes are reversible.

The Arquad 16-50 / 4-Cl-benzoate system had a broader drag-reducing temperature range, from 20°C up to 70°C (Fig. 5.2). The maximum drag reduction was about the same as that for the 3-Cl-benzoate system. The results for this surfactant with chlorobenzoates are similar to Chou's [1991b] data on Kemamine Q-2983C (C_{22}H_{43}-N(CH_3)3Cl) with the same counterions. At 50°C he found less than 50% drag reduction for the 2-Cl system and none at higher or lower temperatures, and wide drag reduction effective temperature ranges, 30 to 110°C, for the 3-Cl and 4-Cl systems. The long unsaturated hydrocarbon chain in Q-2983C (C22) apparently expanded the temperature ranges of thread-like micelle existence for both the 3-Cl and the 4-Cl systems to higher upper temperatures.

5.1.2 Effect of Counterion to Cationic Surfactant Ratio

Chou [1991b] demonstrated that the ratio of counterion to surfactant, $\xi$, has great effect on drag reduction. Similar drag reduction tests were performed on Arquad 16-50 (5 mM)/NaSal and Ethoquad O/12 (5 mM) / NaSal systems at different $\xi$ (Figs. 5.3 and 5.4). Results show that both systems have at best modest drag reducing ability when $\xi = 0.6$. For the Arquad 16-50 (5 mM) / NaSal (Fig. 5.3) systems, when $\xi = 0.6$, there is close-to-zero drag reduction. When $\xi$ increases to 1, there is a large increase in drag reduction.
Figure 5.1 Drag reduction results for the Arquad 16-50 (5 mM) / 3-Cl-benzoate (12.5 mM) solution.
Figure 5.2 Drag reduction results for the Arquad 16-50 (5 mM) / 4-Cl-benzoate (12.5 mM) solution.
Figure 5.3 Drag reduction results for the Arquad 16-50 (5 mM) / NaSal system at different counterion/surfactant ratios, $\xi$. ($\xi = 2.5$ data from Chou [1991b]).
Figure 5.4 Drag reduction results for the Ethoquad O/12 (5 mM) / NaSal system at different counterion/surfactant ratios, $\xi$. ($\xi = 1.9$ and one $\xi = 1.0$ data from Chou [1991b], marked with *).
With further increase in $\xi$, the drag reduction curve shifts to the right, i.e., drag reduction extends to higher Reynolds numbers. For the Ethoquad O/12 / NaSal system (Fig. 5.4), there is also a large increase in drag reduction when $\xi$ increases from 0.6 to 1.0. With further increase in $\xi$, drag reduction extends to a higher Reynolds number but the differences among the $\xi = 1.0, 1.9$ and 2.5 solutions are small. It should be noted that Chou [1991b] reported nearly the same drag reduction performance for the $\xi = 1.0$ system as the $\xi = 0.6$ system. New data show this is incorrect.

5.1.3 An Unusual Cationic Surfactant Drag Reducer

The Arquad S-50 (5 mM) / NaSal (12.5 mM) system is an excellent drag reduction system [Chou, 1991b]. A solution was prepared using surfactant stock (50% surfactant in water and isopropyl alcohol) which is at least five years old to test drag reduction. The results (Fig. 5.5) are in good agreement with Chou's [1991b] data. The system can provide up to 70% drag reduction from 20 °C (lowest temperature measured) up to 80 °C. Note a different presentation of drag reduction results is used in Fig. 5.5. The smaller the friction factor compared with that of water, the greater is the drag reduction. These data are presented because of the unusual rheological character of this system (see Section 5.4.3). If the shear viscosity at the highest shear rate measured in the rheometers is used to estimate the wall shear rate in turbulent flow, effective drag reduction occurs in a range of wall shear rates of 2,000 to 700,000 s$^{-1}$.
Figure 5.5 Drag reduction results for the Arquad S-50 (5 mM) / NaSal (12.5 mM) system.
5.1.4 An Excellent Drag Reducing Cationic Surfactant System

In this section, drag reduction data on an exceptionally good drag reducing surfactant system, Habon G, are presented [Lu et al., 1996d]. Figs. 5.6 to 5.9 show drag reduction results for the Habon G system at 1, 2, 3 and 5 mM. All four systems are able to reach at least 60% drag reduction over a temperature range from 10 to 90°C and the 2 mM system is effective up to 100°C. The peak drag reduction is as high as 75%. Other cationic surfactant systems also give such good drag reduction performance but only at higher concentration, 5 mM.

The Habon G system is unique not only in drag reduction performance, but also in flow birefringence. As we discussed in Section 4.1, the counterions in Habon G are reacted with the cations and thus provide more efficient neutralization. Under ideal conditions, i.e., 100% reacted, the surfactant should have no charge. This difference is probably responsible for the extremely long birefringence relaxation process (see Section 4.2.3) and excellent drag reducing capability. Because of its effectiveness, Habon G was used in several field tests in district heating systems.

5.1.5 Drag Reduction of Nonionic and Zwitterionic Surfactant Systems

Drag reducing cationic surfactants are more toxic and slower in biodegradation compared to nonionic surfactants. Because of these environmental concerns, Akzo Nobel has began to develop low toxicity and fast biodegradable nonionic and zwitterionic surfactant drag reducers as reviewed in Chapter 2. Several potential systems have been investigated.
Figure 5.6 Drag reduction results for the Habon G (1 mM or 500 ppm) system.
Figure 5.7 Drag reduction results for the Habon G (2 mM or 1000 ppm) system.
Figure 5.8 Drag reduction results for the Habon G (3 mM or 1500 ppm) system.
Figure 5.9 Drag reduction results for the Habon G (5 mM or 2500 ppm) system.
Figs. 5.10 to 5.12 show drag reduction results for OMA-3/4 at three concentrations: 2000, 3500 and 5000 ppm. The 2000 ppm solution can only provide up to 35% drag reduction at 2°C. The 3500 ppm solution, however, gives drag reduction up to 70% from 2 to 12°C. Further increase in concentration extends the effective temperature range to 15°C and also the effective Reynolds number range. As will be discussed in Section 5.2.4, nonionic surfactants have a unique temperature, called the cloud point. Drag reduction is only effective around this point according to Zakin and Chiang [1972], Zakin and Lui [1983], Chang and Zakin [1985] and DeRoussel [1993]. This system has a cloud point of 6°C, confirming their conclusion.

Fig. 5.13 shows drag reduction data obtained by DeRoussel [1993] for the Brij 97 (0.85%) / Brij 30 (0.15%) system. This system has a cloud point of 48°C, while drag reduction reaches a maximum at 40°C, illustrating that drag reduction of nonionic surfactants is only effective around the cloud point. It has been found that the cloud point of nonionic surfactants can be changed by adding certain chemicals [Zakin and Chiang, 1972; Zakin and Lui, 1983; Chang and Zakin, 1985]. The data of DeRoussel [1993] are shown here to provide a comparison to a modified system. Fig. 5.14 shows drag reduction in the cloud point temperature region for the Brij 97 (0.85%) / Brij 30 (0.15%) system with 0.45 M Na₂SO₄. As will be shown in Section 5.2.4, this addition changes the cloud point from 48°C to 20.5°C. The maximum in drag reduction was also changed from about 40°C to 18°C confirming again that drag reduction indeed changes with cloud point. The results in Fig. 5.14 show that, for this system, the maximum drag reduction temperature

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Figure 5.10  Drag reduction results for the OMA-3/4 (2000 ppm) system.
Figure 5.11 Drag reduction results for the OMA-3/4 (3500 ppm) system.
Figure 5.12 Drag reduction results for the OMA-3/4 (5000 ppm) system.
Figure 5.13 Drag reduction results for the Brij 97 (0.85%) / Brij 30 (0.15%) system [DeRoussel, 1993].
Figure 5.14 Drag reduction results for the Brij 97 (0.85%) / Brij 30 (0.15%) / Na$_2$SO$_4$ (0.45 M) system.
shifts upward with time. Some precipitation was noticed in the flow system which is believed to be Na₂SO₄. Due to the high concentration of Na₂SO₄ in the system, part of Na₂SO₄ precipitates and the effective Na₂SO₄ concentration in the solution is reduced causing the cloud point as well as the maximum drag reduction temperature to shift to higher temperature.

Fig. 5.15 shows drag reduction data for the C16-betaine (2.5 mM) / Na-LAS (0.5 mM) system. This is a zwitterionic surfactant system. The drag reduction performance was encouraging with the fresh solution. Up to 60% drag reduction was measured and the system was effective to 50°C. However, after the solution remained in the flow system for one day, drag reduction was lost. This loss is attributed to the sensitivity of zwitterionic surfactants to ions in the flow system. A new zwitterionic system is going to be investigated.

5.2 Shear Viscosity

Surfactant solution viscosity is closely related to microstructure. As reviewed in Chapter 2, increases in shear viscosity are considered by some researchers as an indication of shear induced structure. Thus, shear viscosity is addressed first among the rheological properties of surfactant solutions.

5.2.1 Effect of Anion of Cationic Surfactant Salt

Fig. 5.16 shows viscosity data for Arquad 16-50 (5 mM) / NaSal (12.5 mM), CTAC (5 mM) / NaSal (12.5 mM) and CTAB (5 mM) / NaSal (12.5 mM) solutions. These three solutions have the same cation. Arquad 16-50 is the industrial version of CTAC. The
Figure 5.15 Drag reduction results for the C16-betaine (2.5 mM) + Na-Las (0.5 mM) system.
Figure 5.16 Shear viscosity vs. shear rate for the Arquad 16-50, CTAC and CTAB solutions. All surfactants are at 5 mM with 12.5 mM NaSal as counterion. Data were taken in a cone and plate rheometer (RMS 800).
difference between them is that Arquad 16-50 as received contains about 50% isopropyl alcohol and water as solvent and has some C14 and C18 alkyl groups present (see Table 3.3), CTAC contains 75% water as received and CTAB is 100% solid as received.

Even though their chemical structures are very similar, the three surfactant solutions show differences in viscosity at shear rates below 150 s⁻¹. CTAB has a higher viscosity than the other two systems at low shear rates (<150 s⁻¹). CTAC has a viscosity increase at 75-100 s⁻¹ and Arquad 16-50 has one at 100-150 s⁻¹. After the increases, the data for all three coincide.

As reviewed in Chapter 2, Bartet et al. [1980] found that Br⁻ has stronger binding ability on cetyltrimethylammonium (CTA) micelles than Cl⁻. This was due to the smaller hydration radius of bromide ions which enables them to penetrate into the electric double layer more easily and neutralize the surfactant headgroup charges more effectively. Chou [1991b] also found that the critical shear stresses of drag reduction for CTAB/NaSal are higher than those of Arquad 16-50 / NaSal. Even though the salicylate ion has much stronger binding ability than the Cl⁻ or Br⁻ and is also present in large excess, the Br⁻ and the Cl⁻ ions may still interact with the surfactant headgroups. Thus differences in the binding ability of Br⁻ and Cl⁻ apparently affect the strength or length of micelles formed in their respective solutions, and at low shear rates, a different microstructure is apparently formed in the CTAB solution than in the other two. At higher shear rates, shear-induced-
structure (SIS) is apparently formed in the latter two solutions and there is no difference in viscosity at high shear rates.

The isopropyl alcohol in Arquad 16-50 has little effect on the solution properties as shown by the almost identical viscosities of Arquad 16-50 and CTAC.

5.2.2 Effect of Counterion to Cationic Surfactant Ratio

Figs. 5.17 and 5.18 show the effect of shear rate on the shear viscosities of the Arquad 16-50 (5 mM)/NaSal and the Ethoquad O/12 (5 mM)/NaSal systems, respectively, at various counterion to surfactant ratios, $\xi$. Above 25 s$^{-1}$, all systems are shear thinning with some exceptions. One exception is the Arquad 16-50 (5 mM) / NaSal (5 mM) system. Viscosity increases abruptly above a shear rate of 35 s$^{-1}$, reaching a maximum at about 75 s$^{-1}$. The Arquad 16-50 (5 mM) / NaSal (12.5 mM) system has a similar increase in viscosity at shear rates above 100 s$^{-1}$, reaching a maximum at about 150 s$^{-1}$. For the Ethoquad O/12 / NaSal system, an increase in viscosity is observed for the $\xi = 2.5$ system above 150 s$^{-1}$ with a peak at about 200 s$^{-1}$. At high shear rates these three systems are shear thinning after the sudden viscosity increase.

Abrupt increases in viscosity for surfactant systems were taken as evidence of the existence of shear-induced-structures (SIS) by some researchers [Ohlendorf et al., 1986a, b; Rehage et al., 1986; Bewersdorff and Ohlendorf, 1988; Bewersdorff, 1989, 1996]. These researchers observed that the viscosity was usually very low at low shear rates and
Figure 5.17 Viscosity vs. shear rate for the Arquad 16-50 (5 mM) / NaSal system at different counterion/surfactant ratios, $\xi$. 
Figure 5.18 Viscosity vs. shear rate for the Ethoquad O/12 (5 mM) / NaSal system at different counterion/surfactant ratios, $\xi$. 

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then at a critical shear rate, viscosity suddenly increased to high values; in some cases the increase was 2.5 times. The term “jump” was used to describe this sudden increase. In their data, the viscosity before the jump was never higher than the viscosity immediately after the jump. Their viscosity jumps depended on concentration, temperature and shear rate. The critical shear rate where the jump occurred increased with surfactant concentration and with temperature and the jump was only observed at low temperatures. The solutions were always shear thinning after the jump. The above authors suggested that the increase in viscosity was induced by an abrupt change in the microstructure of the surfactant solutions.

Hoffmann and Rehage [1987] classified viscoelastic surfactant systems into two types. In the first and more general type, the structures causing viscoelastic behavior are present in the stagnant solution. In the second type viscoelasticity is observed only after a certain threshold shear rate is exceeded. Systems of the second type were called shear-induced viscoelastic systems [Hoffmann and Rehage, 1987]. This implies that for low surfactant concentrations and with low counterion to surfactant ratios (solutions of the second type), the network structure is weak or incomplete. Shear is needed to induce the formation of a network and viscoelasticity. For surfactant systems with high surfactant concentrations and high counterion to surfactant ratio, a network exists in the solutions and no shear should be needed to promote viscoelasticity.
Some of the data in Figs. 5.17 and 5.18 appear to contradict their hypothesis since sudden viscosity increases happen at high counterion-surfactant ratio, where shear should not be needed to induce the network formation. It should be pointed out, however, that the abrupt viscosity increases observed here differ from the viscosity "jumps" above the initial plateau viscosities observed for SIS by those authors. In our case, the increase in viscosity never doubles and the initial viscosities at low shear rates are greater than the peak after the increase. Thus, these sudden increases in viscosity are apparently caused by network structure rearrangement under shear. It is possible that the absence of jumps in viscosity for the solutions with lower $\xi$ in Figs. 5.17 and 5.18 is because measurements at shear rates below 25 s$^{-1}$ were not possible. Viscosity jump for these solutions may occur at lower shear rates.

It is not obvious if the abrupt viscosity increase around 200 s$^{-1}$ for the Ethoquad O/12 (5 mM) / NaSal (12.5 mM) system is a shear effect or a time effect. If it is shear effect, then right after the application of shear at a critical shear rate, the solution should assume the higher viscosity. If it is a time effect, the new high viscosity is attained after a certain length of time of shear. Thus, we examined the stress development over a longer time period for both shear stress and normal stress at shear rates around 200 s$^{-1}$. Figs. 5.19 to 5.21 show these data at 150, 200 and 250 s$^{-1}$ shear rates, respectively. Overshoot for both shear stress and $N_1$ is observed at the far left. At 150 s$^{-1}$, steady average levels were reached in less than 5 seconds after overshoot for both shear stress and normal stress but with some oscillations in $N_1$. When the shear rate was increased to 200 s$^{-1}$ or 250 s$^{-1}$, the
Figure 5.19 First normal stress difference and shear stress vs. time for the Ethoquad O/12 (5 mM) / NaSal (12.5 mM) solution at 150 s\(^{-1}\). Shear stopped at 100 s.
Figure 5.20 First normal stress difference and shear stress vs. time for the Ethoquad O/12 (5 mM) / NaSal (12.5 mM) solution at 200 s\(^{-1}\). Shear stopped at 100 s.
Figure 5.21 First normal stress difference and shear stress vs. time for the Ethoquad O/12 (5 mM) / NaSal (12.5 mM) solution at 250 s\(^{-1}\). Shear stopped at 100 s.
shear stress quickly reached an initial steady level after overshoot. However, after about 30 seconds for the 200 s⁻¹ shear rate (Fig. 5.20) and 15 seconds for the 250 s⁻¹ (Fig. 5.21), shear stress increased again to a higher steady level. This latter steady level was reported in Fig. 5.18 as the viscosity at that shear rate. Fig. 5.21 shows that the abrupt viscosity increase observed for this system around 200 s⁻¹ in Fig. 5.18 was actually built-up during the shearing process. Thus, if this increase is called shear-thickening, then it is really a time-dependent thickening process. Accompanying the step increase in shear stress, $N_t$ values showed a small decrease (Fig. 5.20). Thus, surprisingly, whatever change in the microstructure caused the viscosity increase had a smaller, negative effect on $N_t$.

5.2.3 Effect of Cationic Surfactant Chemical Structure

With increasing hydrocarbon chain length, the diameter of worm-like micelles increases. With this effect, one may expect that the solution viscosity increases with increasing hydrocarbon chain length. Fig. 5.22 shows shear viscosity of C14TAB, C16TAB and C18TAC (Arquad 18-50) solutions. All surfactants are at 5 mM and with 12.5 mM NaSal. It can be seen that the C14 system has nearly constant viscosity, while the C16 and C18 systems have higher viscosity and are significantly shear thinning.

As reviewed in Chapter 2, Israelachvili et al. [1976] developed a theory of micellar structure which shows that the value $VH/a$ determines the shape of the micelles (see Table 2.1). Israelachvili [1985] suggested that the cross sectional area, $a$, for CTAB solution with high salt concentration is 45 Å². This value should also be valid for C14TAB and
Figure 5.22 Shear viscosities of C14TAB (TTAB), C16TAB (CTAB) and C18TAC (Arquad 18-50) at 20 °C. All three surfactants are at 5 mM and with 12.5 mM NaSal.
C18TAC since both have the same headgroup as CTAB. Thus, using equations developed by Tanford [1972] (see Eqs. 2-2 and 2-3), for the three surfactant systems, C14TAB (TTAB), C16TAB (CTAB) and C18TAC (Arquad 18-50), V/la can be calculated (Table 5.1). According to Israelachvili et al. [1976], with increasing V/la value, micelles change in shape from spherical to rod and then to lamellar. Table 5.1 shows that the V/la values for the above surfactants fall into the rod-like micelle region (see Table 2.1), which confirms the existence of rod-like micelles in these solutions. The V/la values in Table 5.1 increase slightly with alkyl chain length, but the increase is not significant.

<table>
<thead>
<tr>
<th>N</th>
<th>V (Å³)</th>
<th>l (Å)</th>
<th>a (Å²)</th>
<th>V/la</th>
</tr>
</thead>
<tbody>
<tr>
<td>14</td>
<td>404</td>
<td>19.21</td>
<td>45</td>
<td>0.4673</td>
</tr>
<tr>
<td>16</td>
<td>457.8</td>
<td>21.74</td>
<td>45</td>
<td>0.4680</td>
</tr>
<tr>
<td>18</td>
<td>511.6</td>
<td>24.27</td>
<td>45</td>
<td>0.4684</td>
</tr>
</tbody>
</table>

Table 5.1  V/la for C14, C16 and C18-trimethyl ammonium chloride (bromide) surfactants.

As reviewed in Chapter 2, the micelle length or the micelle aggregation number does increase with increasing hydrocarbon chain length [Wennerstrom and Lindman, 1979; Rosen, 1989]. Thus, the longer alkyl chain surfactants tend to form longer rod-like micelles, explaining the higher viscosity of the C16 and C18 solutions compared with C14 solution.
On the other hand, with increasing alkyl chain length, the radius of the rod-like micelles formed increases. More surfactant headgroups can be packed in the cross section because the larger radius provides a larger perimeter. As discussed above, surfactants with longer alkyl chains tend to form longer micelles. Thus at a fixed molar concentration fewer micelles will be formed in these surfactant solutions. The smaller number of long micelles are more easily aligned under shear and so the solutions of C16 and C18 are highly shear thinning. Nevertheless, it is surprising that the C14TAB solution shows no shear thinning.

5.2.4 Viscosity of Nonionic Surfactant Systems

Nonionic surfactant solutions are clear until the temperature rises to the cloud point. It is generally believed that nonionic surfactant molecules are dehydrated at temperatures near the cloud point. The shear viscosity of nonionic surfactants has the unusual property of increasing around the cloud point, in contrast to cationic surfactants, whose shear viscosity decreases with increasing temperature.

Fig. 5.23 shows the relative viscosity of OMA-3/4 (5000 ppm) solution. The cloud point, determined by visual observation, is 6°C. It can be seen that the solution has its highest relative viscosity at 5°C at high shear rates while at low shear rates the relative viscosities at 10°C and at 15°C are higher than that at 5°C.
Figure 5.23 Relative shear viscosity of the OMA-3/4 (5000 ppm) system.
The change of relative viscosity around the cloud point can be seen more clearly in the Brij 97 (0.85%) / Brij 30 (0.15%) system (Fig. 5.24). The cloud point of this solution is 48°C, determined by visual observation. The relative viscosity reaches a peak value at 45°C. The relative viscosity decreases when the temperature approaches or moves away from 45°C. It is suggested that when temperature approaches the cloud point, a large microstructure is formed causing the viscosity to increase. When the temperature exceeds the cloud point, separation into two phases occurs and the viscosity decreases.

The cloud point of nonionic surfactants can be adjusted by adding certain chemicals. Fig. 5.25 shows the cloud point change with the addition of phenol or sodium sulfate. With addition of both chemicals, the cloud point of the surfactant decreases linearly. Phenol is much more effective than sodium sulfate in terms of amount needed. However, due to the toxicity of phenol, especially for open systems such as drag reduction and rheology measurements, sodium sulfate was used to alter the cloud point of this surfactant system.

Fig. 5.26 shows the relative viscosity of the Brij system with addition of 0.45 M sodium sulfate. The visually observed cloud point of this new system is 20.5°C. Relative viscosity reaches a maximum at 17°C and 18°C. Compared with results shown in Fig. 5.24, the peak relative viscosity at low shear rates is increased over one order of magnitude. Also without sodium sulfate, the system is shear thickening, while with sodium sulfate, the system is shear thinning. Obviously, sodium sulfate causes
Figure 5.24 Relative shear viscosity of the Brij 97 (0.85%) / Brij 30 (0.15%) system.
Figure 5.25 Cloud point of the Brij 97 (0.85%) / Brij 30 (0.15%) system with addition of phenol or sodium sulfate.
Figure 5.26 Relative viscosity of the Brij 97 (0.85%) / Brij 30 (0.15%) / Na₂SO₄ (0.45 M) system.
microstructure formation. The shear thickening seen in Fig. 5.24 suggests that high shear also promotes microstructure formation.

5.3 Swirl Decay Time (SDT)

There is no clear definition of what rheological property best represents viscoelasticity. However, as implied by the name, "viscoelasticity," a viscoelastic solution should have some elastic character. Thus, if a viscoelastic solution is forced to rotate, it should move in the opposite direction of the rotation after the outer force is removed, i.e., it should be able to recoil. This provides a simple method to identify viscoelastic solutions. Nash [1956a, b] proposed that the swirl decay time (SDT) can be used to characterize viscoelasticity. He set up a swirling motion in a fixed volume of solution in a flask and noted the time between the stopping of the vessel rotation and the cessation of the solution movement before recoil, which he defined as SDT. The shorter the SDT is, the greater the viscoelasticity of the solution.

Table 5.2 shows SDT results for two surfactant systems. A 100 ml beaker was filled with 60 ml of surfactant solution, and then the solution was placed on a magnetic mixer with a one-inch stirring bar. The speed of the mixer was set to a fixed value. SDT was measured as the difference between the time at which the mixer was stopped and the time when the solution started to recoil.
Table 5.2  Swirl Decay Time (s).

All solutions showed recoil when the motion was stopped, which means that all solutions were viscoelastic. The data in Table 5.2 show that when the counterion/surfactant ratio, $\xi$, is 0.6, SDT was significantly longer than those for other ratios. Thus, the solutions at $\xi = 0.6$ are less viscoelastic than the others. There were no significant differences in SDT among the solutions with $\xi \geq 1$.

However, it should be pointed out that the SDT can only be used to qualitatively compare the viscoelasticity of solutions being set up in rotational motion under the same conditions. The SDT should not be used to compare results obtained under different set-ups.

5.4 First Normal Stress Difference

Even though recoil observations can give qualitative results of viscoelasticity, it can not be used as comparison of viscoelasticity universally. First normal stress difference, $N_1$, is often reported as a measure of viscoelastic behavior [Macosko, 1994]. In this section,
some $N_1$ results are presented and the limitation of the representation of viscoelasticity by $N_1$ is discussed.

5.4.1 Effect of Counterion Structure for Cationic Surfactant Systems

Fig. 5.27 shows $N_1$ data for Arquad 16-50, CTAC and CTAB solutions. All surfactants are 5 mM with 12.5 mM NaSal. It can be seen that CTAB has the highest $N_1$ values among the three systems at shear rates below 400 s$^{-1}$. Arquad 16-50 has a little higher $N_1$ values than CTAC at low shear rates and has the same $N_1$ values as CTAC at high shear rates.

As discussed in section 5.2.1, the stronger binding ability of bromide ions compared to chloride ions may be responsible for the high shear viscosity of the CTAB system. Fig. 5.27 shows that this strong binding ability also gives higher viscoelasticity for the CTAB solution. However, it is not clear what causes the difference in $N_1$ between Arquad 16-50 and CTAC.

Another surfactant series studied is Arquad 16-50 (5 mM) with three isomeric counterions, 2-Cl-benzoate, 3-Cl-benzoate and 4-Cl-benzoate. All counterions are at 12.5 mM. $N_1$ was measured at 20 °C for the three solutions. The 3-Cl system was measured at 30°C as well (Fig. 5.28).
Figure 5.27 First Normal Stress Difference for Arquad 16-50, CTAC and CTAB solutions. All surfactants are at 5 mM and with 12.5 mM NaSal as counterion.
Figure 5.28 First normal stress difference results for the Arquad 16-50 (5 mM) / 2-, 3- or 4-Cl-benzoate (12.5 mM) systems.
At 20°C, the Arquad 16-50/4-Cl-benzoate system showed significant first normal stress differences, while the other solutions gave essentially zero values up to shear rates of about 200 s\(^{-1}\). \(N_1\) values were negative for 2-Cl and 3-Cl systems at shear rates above 200 s\(^{-1}\). The negative \(N_1\) values at high shear rates are believed to be at least partially due to uncertainty in the large inertial correction term which dominates at high shear rates for low viscosity systems. Recall that at 20°C, no drag reduction for the 2-Cl and 3-Cl systems was recorded, but high drag reduction for 4-Cl. Thus it seems that the \(N_1\) results correlate with drag reduction results for all three surfactant systems at 20°C.

However, at 30°C the Arquad 16-50 / 3-Cl-benzoate (5/12.5 mM) system still showed no \(N_1\), while it was drag-reducing. Thus, the correlation between drag reduction and \(N_1\) does not hold in this case. It is not surprising, though, since we have found that another good drag-reducing surfactant system had no significant \(N_1\) as well [Lu et al., 1997a]. This will be discussed later in this section.

Another example of viscoelastic behavior is solution recoil as discussed in the last section. Recoil was observed in the 4-Cl solution at 20 and 30°C, and in the 3-Cl solution at 30°C and also at 20°C if the solution was clear. No recoil was observed for 2-Cl at any temperature. Precipitation occurred in the 3-Cl solution at 20°C after the solution was subjected to high shear, after which no recoil was observed. This will be addressed later in this chapter.
From both \( N_1 \) and recoil results, we conclude that the 4-Cl system is viscoelastic and drag reducing, while the 2-Cl system is non-viscoelastic and non-drag-reducing. Even though the 3-Cl system shows no \( N_1 \) values, the recoil results indicate that it is viscoelastic for clear solutions at 20°C or at 30°C and above and it is drag-reducing at 30°C and above. Thus, recoil is well correlated with drag reduction for the 2-Cl and 4-Cl systems. The correlation of recoil with drag reduction for the 3-Cl system gives apparently anomalous results which will be discussed later.

As proposed by Chou [1991b] and confirmed by Smith et al. [1992, 1994a], the differences in drag reduction performance of their Kemamine Q-2983C / 2-, 3- or 4-Cl-benzoate systems are due to the different substituent group positions on the benzoate ring. Through NMR studies, Smith et al. [1994a] found that these three counterions take the orientations at the micelle-water interface shown in Fig. 5.29. Chlorine is a hydrophobic substituent and thus it prefers to stay in the hydrocarbon portion of the micelle. As seen in Fig. 5.29, the 3-Cl and 4-Cl benzoates position their chlorine atom favorably in the hydrocarbon region, while the chlorine in the 2-Cl is unfavorably positioned in the water phase. The 2-Cl-benzoate, therefore, forms only spherical micelles.

The difference in the orientation of the counterions certainly affects the rheological behaviors of these surfactant systems. At certain temperatures, the 4-Cl and 3-Cl systems show viscoelasticity, while the 2-Cl system is not viscoelastic. However, caution must be exercised when correlating viscoelasticity with drag reduction, because of the observation
of an apparently non-viscoelastic surfactant that is highly drag-reducing, which will be discussed in Section 5.4.3.

5.4.2 Effect of Counterion to Cationic Surfactant Ratio

Figs. 5.30 and 5.31 show first normal stress difference results for 5 mM Arquad 16-50 / NaSal and the 5 mM Ethoquad O/12 / NaSal solutions at various counterion-surfactant ratios. At \( \xi = 0.6 \), \( N_1 \) values for both systems increase at low shear rates to a low level and then decrease with increase in shear rate, and for the Arquad 16-50 / NaSal system (Fig. 5.30), \( N_1 \) vanishes at high shear rates. When \( \xi \) increases to 1, \( N_1 \) values of both systems increase with shear rate at low shear rates (< 100 s\(^{-1}\)) and reach a plateau at high shear rates. The plateau \( N_1 \) values are much higher than those for \( \xi = 0.6 \). This is consistent with the SDT results presented above. The Ethoquad O/12 / NaSal system has
Figure 5.30 First normal stress difference ($N_1$) for the Arquad 16-50 (5 mM) / NaSal systems at different counterion/surfactant ratios, $\xi$. 

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Figure 5.31 First normal stress difference ($N_1$) for the Ethoquad O/12 (5 mM) / NaSal systems at different counterion/surfactant ratios, $\xi$. 
a little higher plateau level for $N_1$ than the Arquad 16-50 / NaSal system. For both surfactant systems, if $\xi$ further increases to 2.5, $N_1$ increases with shear rate up to the highest shear rate tested (800 s$^{-1}$) and there is no plateau. It is interesting to note that at low shear rates, $N_1$ values at $\xi = 2.5$ are smaller than those at $\xi = 1$, while at high shear rates, the former are larger than the latter. That is, the $N_1$-shear rate curve actually shifts to the right (lower $N_1$ at low shear rates) when the ratio increases. This trend was confirmed by an additional test on the Ethoquad O/12 / NaSal system at $\xi = 1.9$. The $\xi = 1.9$ curve lies between the $\xi = 1$ and the $\xi = 2.5$ curves (Fig. 5.31).

These first normal stress difference data show that the Arquad 16-50 and the Ethoquad O/12 systems are both viscoelastic, though the magnitudes of the $N_1$ values vary with counterion / surfactant ratio. The viscoelasticity is associated with micellar networks, as shown in the cryo-TEM pictures which we will discuss in Section 5.8.2

5.4.3 Effect of Cationic Surfactant Chemical Structure

Fig. 5.32 shows first normal stress difference results for three surfactant systems: Ethoquad O/12 (5 mM) / NaSal (12.5 mM), Ethoquad O/13-50 (5 mM) / NaSal (12.5 mM) and Ethoquad T/13-50 (5 mM) / NaSal (12.5 mM). These three systems have similar good drag reduction performance at 20°C to 30°C [Chou, 1991b]. However, $N_1$ values at the same temperature, about 22°C (room temperature, see Section 3.4.2), are much different for them. The O/12 solution had the largest $N_1$ values at all shear rates (25-800 s$^{-1}$). The O/13 and T/13 systems had similar values of $N_1$, although T/13 is a
Figure 5.32 First normal stress difference results for the Ethoquad O/12, the Ethoquad O/13-50 and the Ethoquad T/13-50 systems. All surfactants are at 5 mM with 12.5 mM NaSal.
little higher at shear rates above 250 s\(^{-1}\). Despite the differences among the \(N_1\) values for the O/12, O/13-50 and T/13-50 systems, all of them showed recoil and positive \(N_1\), and thus they are all viscoelastic. One surfactant system, Arquad S-50 (5 mM) / NaSal (12.5 mM), has been found which behaves very differently in this regard. Let us examine \(N_1\) results for the Arquad S-50 system (Fig. 5.33, Sample 1 curve).

Surprisingly, \(N_1\) is close to zero up to a shear rate of about 500 s\(^{-1}\). According to Chou [1991b], the S-50 solution is an excellent drag reducer. To verify that the sample of S-50 was not significantly changed by aging, a fresh solution of S-50 / NaSal was prepared to recheck Chou's [1991b] drag reduction results. The drag reduction results were in good agreement with those of Chou [1991b] (see Section 5.1.3). \(N_1\) measurements were also made on this fresh solution before it was introduced into the drag reduction system (see Fig. 5.33, Sample 2 curve). The two curves in Fig. 5.33 are in excellent agreement with each other, neither showing significant \(N_1\) values. The negative \(N_1\) values at high shear rates are believed to be due to uncertainty in the large inertial correction term which dominates at high shear rates for low viscosity systems such as the S-50/NaSal system.

From the drag reduction (see Section 5.1.3) and flow birefringence results (see Section 4.1) one would expect the S-50 system to be viscoelastic with significant \(N_1\) values and to demonstrate recoil. Other good drag reducing surfactants, such as Arquad 16-50 / NaSal and Ethoquad O/12 / NaSal, have \(N_1\) values of hundreds of Pascals in this shear rate range (see Figs. 5.30 and 5.31) and, when rotation of a solution in a beaker is stopped,
Figure 5.33 First normal stress difference results for the Arquad S-50 (5 mM) / NaSal (12.5 mM) system.
they show recoil. As noted, the surprising $N_1$ results with S-50 were double-checked to make sure that there was no experimental error. $N_1$ measurements at higher temperatures could not be made due to the lack of a proper temperature control system on the RMS 800 rheometer but $N_1$ values generally decrease with temperature for these types of cationic surfactant systems [Stern et al., 1994; Myska et al., 1996].

Even though the first normal stress difference, $N_1$, is an indication of viscoelasticity, viscoelastic systems may not have non-zero $N_1$. This will be discussed in Section 5.9.2.

To further clarify if the system is viscoelastic, simple recoil measurements were performed. No recoil was observed for this system and the swirl decay time is over twenty seconds, much longer than for other surfactant systems (see Table 5.2) and close to that of water. Thus, along with no overshoot at the start-up of shear flow discussed in the next section, the Arquad S-50 (5 mM) / NaSal (12.5 mM) system appears not to be viscoelastic. It should be noted, however, Arquad T-50 (5 mM) / NaSal (12.5 mM), which has very similar surfactant chemical structure to the S-50, does have large $N_1$ and shows strong recoil and thus is viscoelastic. The only difference between T-50 and S-50 is that the S-50 has more multiple double bonds and more trans double bonds [Shapiro, 1997].

However, whether a solution is viscoelastic is dependent on the time scale. Theoretically, Newtonian fluids, like water, can be viscoelastic at extremely high shear rates, i.e., at very
small experimental time scales. Thus, rather than saying that the S-50 solution is non-viscoelastic, it is more accurate to say that the solution is non-viscoelastic in the range of time scales of the rheological measurements performed. Turbulent energy spectra of surfactant drag reducing solutions are shifted to lower frequencies compared with water and the high frequency components are attenuated [Myska et al., 1995]. Their data on Habon G solutions showed that most of the energy is below 1000 Hz frequency in a 40 mm tube, which is higher than the highest shear rate we could reach (< 800 s\(^{-1}\)) in normal stress measurements and the frequency in dynamic measurements (< 100 rad/s or 16 Hz). Thus, the \(N_1\) values obtained are for lower frequencies than the highest frequencies in turbulent flow. It is possible, however, that at higher shear rates (smaller time scale), the S-50 solution may show viscoelastic behavior.

5.5 Start-Up Stress Development

Both shear stress and normal stress develop in different ways at the start-up of steady state shear. In this section, different behaviors are examined in correlation with the viscoelasticity of the surfactant systems.

5.5.1 Effect of Counterion to Cationic Surfactant Ratio

Figs. 5.34 and 5.35 show the transient responses of shear and normal stress in the start-up of steady state shear flows at 100 s\(^{-1}\) and 500 s\(^{-1}\) for the Arquad 16-50 (5 mM) / NaSal (3 mM) \((\xi = 0.6)\) system in a 50 mm cone and plate fixture (see Section 3.4.2). At 100 s\(^{-1}\) (Fig. 5.34), both shear stress and normal stress assume constant small values for over 10
Figure 5.34 Stress development in the start-up of steady state shear flow at shear rate of 100 s⁻¹ for the Arquad 16-50 (5 mM) / NaSal (3 mM) system.
Figure 5.35 Stress development in the start-up of steady state shear flow at shear rate of 500 s\(^{-1}\) for the Arquad 16-50 (5 mM) / NaSal (3 mM) system.
seconds after the shear starts and then increase to higher plateau values. At 500 s\(^{-1}\) (Fig. 5.35), however, this initial period didn’t appear, both stresses increase gradually to the plateau at low shear rates. The normal stress showed some negative values, which are believed to be due to errors in the transducer readings at low values.

For the Arquad 16-50 (5 mM) / NaSal (5 mM) (ξ = 1.0) system at 100 s\(^{-1}\) (Fig. 5.36), the stresses increased to an initial plateau without going through an induction period as in the ξ = 0.6 case. After initial plateauing for over 20 seconds, both stresses increase further to their final plateaus. At higher shear rate, 500 s\(^{-1}\) (Fig. 5.37), however, both the induction period and the initial plateau are eliminated. The normal stress rises rapidly to the final plateau, while the shear stress showed a large overshoot, then a drop and then increased to the plateau.

The Arquad 16-50 (5 mM) / NaSal (12.5 mM) (ξ = 2.5) system (Figs. 5.38 and 5.39), on the other hand, differs from the two systems with lower ratios. At both shear rates, 100 s\(^{-1}\) and 500 s\(^{-1}\), both shear stress and normal stress showed a large overshoot and then rapid decrease to the final plateau. The peak value of shear stress overshoot is two to three times the plateau value, while normal stress overshoot is smaller but still nearly twice the plateau value.

Data in Figs. 5.34-5.39 show that the stress development is strongly counterion ratio dependent. For ξ = 0.6, there is insufficient counterion to neutralize all the positive
Figure 5.36 Stress development in the start-up of steady state shear flow at shear rate of 100 s⁻¹ for the Arquad 16-50 (5 mM) / NaSal (5 mM) system.
Figure 5.37 Stress development in the start-up of steady state shear flow at shear rate of 500 s\(^{-1}\) for the Arquad 16-50 (5 mM) / NaSal (5 mM) system.
Figure 5.38 Stress development in the start-up of steady state shear flow at shear rate of 100 s$^{-1}$ for the Arquad 16-50 (5 mM) / NaSal (12.5 mM) system.
Figure 5.39 Stress development in the start-up of steady state shear flow at shear rate of 500 s$^{-1}$ for the Arquad 16-50 (5 mM) / NaSal (12.5 mM) system.
charges on the surfactant headgroups and thus either a very weak or no micellar network exists in the solution. Thus, it is not surprising that no overshoot is observed when shear is applied since overshoot is due to the over-reaction of the network structure to the applied shear. On the contrary, when $\xi = 2.5$, a strong surfactant network is formed in the solution and, as expected, significant overshoot is observed. $\xi = 1.0$, however, is a critical ratio. Both shear and normal stresses show overshoot at high shear rate but not at low shear rate, though the normal stress overshoot at high shear rate is small. At low ratio ($\xi = 0.6$ and $1.0$) and low shear rates, the stresses develop in two steps, i.e., stresses go through either an induction period or an initial plateau. At high shear rates, however, all stresses, even ones at low ratio, reach a plateau in a single step (if overshoot is not considered as a step). Thus, increase in the shear rate has a similar effect on micellar network formation as increase in the amount of counterion. The trend in stress start-up observed here agrees with that reported by Hu and Matthys [1996] for similar concentrations of surfactants. Smaller overshoot of normal stress compared to shear stress was also observed by Rehage and Hoffmann [1988] in a 100 mM CPyCl / 60 mM NaSal system at a shear rate of 1s$^{-1}$. They observed no overshoot at a very low shear rate, 0.05s$^{-1}$.

Since overshoot is shear rate dependent, let us closely examine overshoot at different shear rates in more detail. Fig. 5.40 shows overshoot of shear stress at the start-up of steady state shear for the Ethoquad O/12 (5 mM) / NaSal (12.5 mM) system at five different shear rates. For this surfactant system, shear stress overshoots are observed at all five shear rates and reach similar peak values at shear rates of 150, 200, 250 and 500 s$^{-1}$. 

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while the peak for overshoot at 100 s\(^{-1}\) is significantly lower than those at the other four shear rates (Fig. 5.40). The time required for the shear stress to reach its overshoot peak decreases with increasing shear rate. The peaking times for the 150 and 200 s\(^{-1}\) results are the same as those for the 250 and 500 s\(^{-1}\) results. However, if the shear stresses are normalized by their respective peak values and plotted against reduced time: \( (t \cdot \dot{\gamma}) \) (Fig. 5.41), it can be seen that all peaks come close to each other except the 250 s\(^{-1}\) peak shifts to smaller reduced time. The average reduced time for the other four peaks is: 64. If smaller time steps had been used in these experiments so that the exact times and the peak values had been measured, the coincidence of reduced times for peak values might be improved.

The first normal stress difference behavior (Fig. 5.42) is similar to that of the shear stress. The peak for overshoot at 100 s\(^{-1}\) is significantly lower than those at the four other shear rates and the time for normal stress to reach its overshoot peak decreases with increasing shear rate. Again, the peaking times for the 150 and 200 s\(^{-1}\) results are the same, as are the 250 and 500 s\(^{-1}\) results. However, normal stress behavior differs from shear stress behavior in that the overshoots at 100, 250 and 500 s\(^{-1}\) are small while large overshoots are observed at 150 and 200 s\(^{-1}\).

The lower peak values of both shear and normal stresses at 100 s\(^{-1}\) and their trend, i.e., small or no overshoot at lower shear rate, is consistent with the results of Rehage and Hoffmann [1988] as mentioned above. Apparently, this shear rate is insufficient to fully
Figure 5.40 Stress development in the start-up of steady state shear flow of the Ethoquad O/12 (5 mM) / NaSal (12.5 mM) system at five different shear rates.
Figure 5.41 Shear stress normalized by overshoot peak values versus reduced time, $(t \cdot \gamma)$, in the start-up of steady state shear flow of the Ethoquad O/12 (5 mM) / NaSal (12.5 mM) system at five different shear rates.
Figure 5.42 Development of the first normal stress difference in the start-up of steady state shear flow for the Ethoquad O/12 (5 mM) / NaSal (12.5 mM) system at five different shear rates.
extend the micellar network and release energy stored in the network. The large
overshoots at 150 s⁻¹ and above indicate that the shear forces above 150 s⁻¹ are large
enough to fully extend the micellar structure causing some form of rearrangement of the
structure. N₁ and shear stress data at longer times will be described in the next section.

It should be pointed out that using the stresses normalized by steady state values to judge
the effect of shear rate on overshoot may be misleading. The ratio of peak value of
overshoot to the ultimate plateau value for 100 s⁻¹ is higher than that for other shear rates,
while the 100 s⁻¹ has the smallest overshoot peak value. Overshoot is caused by release of
the energy stored in the network when it reorganizes itself under shear. Only the absolute
value of the overshoot peak represents the available energy the network can release. The
fact that the shear stress data in Fig. 5.40 showing that the peak values at higher shear
rates (150 to 500 s⁻¹) are nearly the same supports this point.

5.5.2 Effect of Cationic Surfactant Chemical Structure
Normal stress start-up data are shown in Fig. 5.43 for the Arquad S-50 (5 mM) / NaSal
(12.5 mM) system at 100 s⁻¹ and 500 s⁻¹ shear rates. Note that the ordinate scale has been
magnified compared to Fig. 5.33. Shear stress start-up data are shown in Fig. 5.44 for 500
s⁻¹, 1000 s⁻¹ and 1500 s⁻¹. There is no overshoot for any of them. The observation that
there is no overshoot could be caused by slow response of the rheometers. To rule this
possibility out, stress relaxation data are examined in the next section which shows that
Figure 5.43 Transient normal stress development during start-up of steady state shear measurements for the Arquad S-50 (5 mM) / NaSal (12.5 mM) system at 20 °C. Shear rates are 100 s⁻¹ and 500 s⁻¹.
Figure 5.44 Transient shear stress development during start-up of steady state shear measurements for the Arquad S-50 (5 mM) / NaSal (12.5 mM) system at 20 °C. Shear rates are 500, 1000 and 1500 s$^{-1}$. 

T = 20 °C

Shear Rate (s$^{-1}$)
- - - - 500
- - - - 1000
- - - - 1500
relaxation time constants are longer than the rheometer response time. Thus, the S-50 system indeed has no overshoot.

As discussed in the last section, the Arquad S-50 (5 mM) / NaSal (12.5 mM) system has zero $N_1$ values and has no recoil. Here we have also shown that the system does not have overshoot. Since overshoot is another characteristic of viscoelastic solutions [Brodkey, 1996], it can be concluded that the S-50 system is not viscoelastic while it is drag reducing and has a micellar network [Lu et al., 1997a]. This is the first drag reducing system observed experimentally for which no normal viscoelastic behavior was observed.

5.6 Stress Relaxation

5.6.1 Effect of Counterion to Surfactant Ratio for Cationic Surfactant Systems

Shear and normal stress data for all systems were examined for relaxation behavior. As found earlier in flow birefringence measurements [Lu and Zakin, 1995a; see also Section 4.2], the relaxation process for both $N_1$ and shear stress is two-step, i.e., a quick drop followed by a slow decay. This was also reported by Shikata et al. [1988b] for 100 mM CTAB / NaSal solutions at various NaSal concentrations for shear rates higher than a critical value, and by Hu and Matthys [1995] for an Ethoquad T/13-50 (5 mM) / NaSal (5 mM) ($\xi = 1.0$) solution. However, Hu and Matthys [1996] claimed that the stress relaxation is a one step process at high counterion to surfactant ratio. Our data show that even at a counterion to surfactant ratio, $\xi$, of 2.5, for all systems studied, the stress always showed a rapid drop and then a slow relaxation process after the shear stopped. Thus, the
relaxation appears to be a two-step process which can be fit with a double exponential function as used for birefringence relaxation (see Section 4.2) and for rheological data by several researchers [Shikata et al., 1988b; Hu and Matthys, 1995; Lu et al., 1997a]:

\[
T = T_0 e^{-\frac{t-t_0}{\tau_1}} + T_2 e^{-\frac{t-t_0}{\tau_2}}
\]

(5.1)

where \( T, T_1 \) and \( T_2 \) are shear stress or normal stress, \( t_0 \) is the time when shear stopped, \( \tau_1 \) and \( \tau_2 \) are time constants for the first (fast) and second (slow) step, respectively. Details of the technique for fitting can be found in Matsuoka [1968].

Fig. 5.45 shows stress relaxation for the Arquad 16-50 (5 mM) / NaSal (12.5 mM) system. The two-step fitting clearly fits the data much better than the one-step fitting. One-step fitting obviously can not represent the initial quick drop after the shear stopped (see Fig. 5.45). Shikata et al. [1988b] reported that the qualitative features of the relaxation were about the same for all the systems in their study over a range of \( \xi \) of 0.7 to 4.0. In their experiments, the relaxation was a one-step process at low shear rates and a two-step process at shear rates higher than a critical value. Whether it was one-step or two-step was not ratio dependent.

Figs. 5.46 and 5.47 show the two time constants for Arquad 16-50 (5 mM) / NaSal at three \( \xi \)’s and for Ethoquad O/12 (5 mM) / NaSal at four \( \xi \)’s. In addition to one obvious feature, i.e., \( \tau_1 < \tau_2 \), all time constants, except one, decrease with increasing shear rate. The one exception is the Arquad 16-50 (5 mM) / NaSal (3 mM) system, whose second-
Figure 5.45 Relaxation of shear stress for the Arquad 16-50 (5 mM) / NaSal (12.5 mM) system. Shear rate is 200 s\(^{-1}\) and shear stopped at 200 s. The data are fit by a double exponential function (Eq. 5.1) and by a single exponential function.
Figure 5.46 Shear stress relaxation time constants for the Arquad 16-50 (5 mM) / NaSal systems at different counterion / surfactant ratios, \( \xi \). The fitting was done by using Eq. 5.1.
Figure 5.47 Shear stress relaxation time constants for the Ethoquad O/12 (5 mM) / NaSal systems at different counterion / surfactant ratios, $\zeta$. The fitting was done by using Eq. 5.1.
step relaxation time increases with shear rate. This increase was also observed by Shikata et al. [1988b] for the 100 mM CTAB / NaSal system at low NaSal concentration. When $\xi$ increases from 0.6 to 1.0, relaxation times don't change much except for Arquad 16-50 (5 mM) / NaSal (3 mM) Step 2. However, when $\xi$ increases above 1.0, relaxation times for both steps significantly decrease. It is not clear why the $\xi = 2.5$ system has shorter relaxation times than the $\xi = 1.0$ system. Shikata et al. [1988a] suggested that the relaxation time is affected by the free salicylate concentration because the free salicylate molecules behave like a catalyst for a disentangling reaction and thus with increasing NaSal concentrations, relaxation times decrease. However, this is a speculation rather than a persuasive explanation. Nevertheless, data show that increase in the ratio, $\xi$, over unity, has the same effect on relaxation time as increase in the shear rate. The trends in changes of relaxation times with shear rate agree with those reported by Shikata et al. [1988a, b] and by Hu and Matthys [1995].

Fig 5.48 shows the relaxation processes for shear stress and for normal stress for Ethoquad O/12 (5 mM) / NaSal (5 mM). The first normal stress difference, $N_1$, has longer time constants for both steps. This may be related to the rapid recoil of this highly viscoelastic surfactant solution. Upon removal of shear, this surfactant solution began to recoil in 1.7 s as indicated by the SDT results (see Table 5.2). The recoil motion is in the opposite direction to the shear flow, so the shear stress is reduced to zero quickly. The SDT lies between the first step and the second step relaxation time constants. This may be related to different shear rates used. There is no control of shear rate in SDT measurements.
Figure 5.48 Normalized Shear Stress and First Normal Stress Difference vs. Time for the Ethoquad O/12 (5 mM) / NaSal (5 mM) system. Shear stopped at 200 s. Both stresses are normalized by their respective plateau values. The two-step relaxation time constants are shown for both stresses. $N_1$ takes longer to relax than shear stress.
5.6.2 Effect of Cationic Surfactant Chemical Structure

In Section 5.5.2, it was shown that the Arquad S-50 (5 mM) / NaSal (12.5 mM) system does not have overshoot. It should be pointed out that no overshoot would be observed if the relaxation time of the surfactant solution is shorter than the rheometer response time. Thus, it is necessary to check the relaxation time of the Arquad S-50 system. Fig. 5.49 shows the relaxation of shear stress following a shear for 30 s at a constant shear rate of 500 s\(^{-1}\). By fitting the relaxation data with an exponential function (see Fig. 5.49, 1-Step Fitting), we have:

\[
\tau = 1.150e^{\frac{t-30}{0.152}} \text{ (Pa)}
\]  

(5.2)

with an \(R^2\) of 0.87. Thus, we have a relaxation time constant, \(\tau\), of 0.152 s at 500 s\(^{-1}\). However, the relaxation of surfactant solutions often involves multiple steps as we discussed in last section. Thus, to improve fitting, the double exponential function (Eq. 5.1) is used giving:

\[
\tau = 0.361e^{\frac{t-30}{0.240}} + 6.945e^{\frac{t-30}{0.033}} \text{ (Pa)}
\]  

(5.3)

From Fig. 5.49 (2-Step Fitting), we can see that Eq. 5.3 fits the data much better than Eq. 5.2. From Eq. 5.3, the time constants are 0.240 s for the long relaxation tail and 0.033 s for the initial quick relaxation. On the other hand, the RMS 800 and RFS II rheometers can reach shear rates in 0.010 s in steady state measurements and the transducer’s response time is 0.005 s [Werzen, 1996]. Therefore, the rheometers can respond in much shorter times than the relaxation time of the surfactant solution and the absence of overshoot is not due to slow rheometer response time.
Figure 5.49 Relaxation of shear stress following a shear at constant shear rate of 500 s\(^{-1}\) for the Arquad S-50 (5 mM) / NaSal (12.5 mM) system at 20 °C.
The relaxation time of S-50 gives $\lambda \cdot \dot{\gamma} > 1$ for the shear rates we studied rheometrically and thus the viscoelastic properties should be evident if the solution is viscoelastic. Thus, the Arquad S-50 / NaSal (5 mM / 12.5 mM) shows unusual flow behavior. It lacks the normal characteristics of viscoelastic solutions (near zero $N_1$, no recoil and no stress overshoot), yet it is a good drag reducer (Section 5.1.3) and shows strong flow birefringence (Section 4.1).

5.7 Dynamic Shear

5.7.1 Effect of Counterion Structure for Cationic Surfactant Systems

It has been shown in previous sections that the Arquad 16-50 (5 mM) / n-Cl-benzoate (12.5 mM) ($n = 2, 3$ or 4) systems behave differently from each other due to the different positions of the chlorine group. Figs. 5.50-5.51 show dynamic shear measurement results for the 3-Cl and 4-Cl systems.

The reason why the data for the 2-Cl system are not presented is that the $G'$ and $G''$ values are near zero. However, both the 3-Cl and 4-Cl systems have increasing $G'$ and $G''$ with frequency (Figs. 5.50 and 5.51). For the latter two systems, $G''$ values are larger than $G'$ at low frequency and viscous properties dominate. Above about 10 rad/s for both systems, the storage modulus, $G'$, curve crosses the loss modulus, $G''$, curve and $G'$ values become larger than $G''$. Thus, elastic properties dominate at high frequency. At around 25 rad/s, $G''$ starts to drop to zero meaning that the solutions become more elastic. The trend continues to about 40 rad/s where $G'$ reaches a maximum while $G''$ reaches zero and the
Figure 5.50 Storage modulus, $G'$, and loss modulus, $G''$, of the Arquad 16-50 (5 mM) / 3-Cl-benzoate (12.5 mM) system at 20 °C.
Figure 5.51 Storage modulus, $G'$, and loss modulus, $G''$, of the Arquad 16-50 (5 mM) / 4-Cl-benzoate (12.5 mM) system at 20 °C.
solutions are fully elastic. The results up to 40 rad/s are consistent with other dynamic measurement results [Lin et al., 1994; Shikata et al., 1987a]. However, with further increase in frequency, $G'$ approaches zero while $G''$ increases. At a frequency of about 80 rad/s, both $G'$ and $G''$ reach zero as do the Ethoquad O/12 systems, which will be discussed in next section. Lin et al. [1994] observed similar results in their 20 mM CTAB/14 mM 5-methylsalicylic system using another RFSII rheometer. They attributed zero values of $G'$ and $G''$ to limitations of the transducer. Our data showed that the torque was within the transducer useable range. It is unlikely that the zero value points are just bad data points, as the same behavior was observed in different surfactant systems [Lin et al., 1994], and they were repeatable. Polymer samples with higher viscosity and elasticity tested on the same machine do not show zero values for $G'$ and $G''$ in this frequency range. It may be due to inertial effects. Even though the inertial effect is only dependent on system density and should be independent of system viscosity, the inertial effect doesn’t contribute significantly to results for systems with high dynamic viscosities. It does, however, affect low viscosity systems, such as the ones described here, especially at high frequency.

5.7.2 Effect of Counterion to Cationic Surfactant Ratio

Figs. 5.52-5.54 show dynamic shear measurement results on Ethoquad O/12 (5 mM) / NaSal solutions at various counterion to surfactant ratios, $\xi$. 

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Figure 5.52 Dynamic viscoelasticity measurement results for the Ethoquad O/12 (5 mM) / NaSal (3 mM) system.
Figure 5.53 Dynamic viscoelasticity measurement results for the Ethoquad O/12 (5 mM) / NaSal (5 mM) system.
Figure 5.54 Dynamic viscoelasticity measurement results for the Ethoquad O/12 (5 mM) / NaSal (12.5 mM) system. T = 20 °C.
When $\xi = 0.6$, both $G'$ and $G''$ are so small that the rheometer fails to measure them correctly as indicated by highly scattered points (Fig. 5.52, please note ordinate scale). For $\xi = 2.5$, both $G'$ and $G''$ increased with frequency to a peak and then dropped down to zero. The $G'$ curve crosses the $G''$ curve at 10 rad/s and $G'$ values become larger than $G''$ values. This means the solution is viscoelastic as shown also by the large $N_1$ values. The $\xi = 1.0$ system had the same trends in $G'$ and $G''$ but with lower $G'$ and $G''$ values than the $\xi = 2.5$ system. A plateau for $G'$ was not observed for either system. Other researchers have observed that $G'$ reached a plateau at high frequency with surfactant concentrations two orders of magnitude higher than ours [Shikata et al., 1987a; Clausen et al., 1992]. They concluded that this plateau indicated that at high angular frequencies the surfactant solutions behaved as elastic bodies and fully entangled networks existed. The lower concentration surfactant solutions studied here behaved differently with both $G'$ and $G''$ reaching peaks and then dropping to zero. To check if the zero values of $G'$ and $G''$ were caused by too high an imposed strain (0.5 rad) on the system for it to stay in the linear viscoelasticity range at high frequency, a dynamic measurement at a fixed frequency of 100 rad/s with varying strain (strain sweep) was performed. Fig. 5.55 shows the two moduli plotted against strain. The results showed that no linear viscoelasticity range existed at this frequency for this surfactant system, and both $G'$ and $G''$ were zero for strains from lower than 0.001 rad to over 1 rad except two positive points for $G''$, which are believed to be random error. As discussed in the last section, the inertial effect may cause this.

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Figure 5.55 Strain sweep dynamic viscoelasticity measurement for the Ethoquad O/12 (5 mM) / NaSal (12.5 mM) system at frequency of 100 rad/s. $T = 20 ^\circ C$. 

$\omega = 100 \ \text{rad/s}$

$G'$

$G''$
5.7.3 Prediction of $N_1$ from Dynamic Data

Laun [1986] proposed an empirical equation to relate the normal stress coefficient, $\psi_1$, to the dynamic moduli:

$$\psi_1 = \frac{N_1}{\dot{\gamma}^2} = 2 \frac{G'}{\omega^2} \left[ 1 + \left( \frac{G'}{G''} \right)^2 \right]^{0.7} \tag{5.4}$$

This equation sets the frequency (in units of rad/s) equal to the shear rate (in units of 1/s) even though the two quantities have different units. Using this equation, $N_1$ can be calculated from $G'$ and $G''$ moduli data.

Fig. 5.56 shows first normal stress difference calculated by Laun's rule from dynamic shear measurements and the comparison with steady state $N_1$ data for Ethoquad O/12. Since the moduli dropped to zero at frequencies above 25 rad/s, no calculations can be made for frequencies above this value. On the other hand, steady state shear measurements were not able to be made for shear rates below 25 s$^{-1}$, thus, there is only one point where they overlap. Nevertheless, the two measurements are in reasonable agreement with each other where they overlap.

Laun's Rule was also applied to the Arquad S-50 (5 mM) / NaSal (12.5 mM) system and the result is shown in Fig. 5.33 (Laun’s Rule curve). Up to the maximum useful frequency about 65 rad/s, after which zero values of $G'$ or $G''$ appear, $N_1$ values calculated by Laun’s rule are in fairly good agreement with steady state results. Both of them show very small $N_1$ values.
Figure 5.56 Comparison of first normal stress difference data from steady shear measurements with prediction of Laun's rule from dynamic shear measurements for the Ethoquad O/12 (5 mM) / NaSal (12.5 mM) system.
It should be mentioned that this rule is not very useful for our dilute drag reducing surfactant solutions with the rheological equipment available. The dynamic shear measurements can only be made up to a frequency of about 60 rad/s. The steady state $N_1$ shear measurements, on the other hand, can not be performed for shear rates under 25 s$^{-1}$. Thus the two measurements have only a small range of overlap and no general conclusion regarding the validity of Laun's rule on dilute drag reducing surfactant systems can be drawn.

5.8 Extensional Viscosity

Extensional viscosity has been suggested to be a key variable associated with drag reduction by polymer additives [for example, Landahl, 1977; Durst et al., 1982; Hoyt, 1986; Bewersdorff and Thiel, 1993]. These researchers stated that the extensional viscosity of dilute polymer solutions can be large compared to that of the Newtonian solvent. This results in an additional resistance against vortex stretching and turbulent eddy growth, and leads to reduction of energy dissipation or drag reduction.

In this section, apparent extensional viscosity results on dilute drag reducing surfactant systems are presented and discussed along with drag reduction data and microstructure. Also the ratio of apparent extensional viscosity to shear viscosity is calculated. This ratio may be different from the so called Trouton ratio, which is the ratio of apparent extensional viscosity to zero shear viscosity. Since in our drag reducing surfactant systems, zero shear viscosity usually can not be measured with the rheometers available.
(see Section 5.2), we use shear viscosity at the same shear rate as the apparent extensional viscosity to calculate this ratio.

5.8.1 Effect of Anion of Cationic Surfactant Salt

Figs. 5.57 and 5.58 show apparent extensional viscosity and the ratio of apparent extensional viscosity to shear viscosity, respectively, for the CTAB (5 mM) / NaSal (12.5 mM), CTAC (5 mM) / NaSal (12.5 mM) and Arquad 16-50 (5 mM) / NaSal (12.5 mM) systems.

All three surfactant systems show very high apparent extensional viscosity and show extensional thinning behavior. The ratio of apparent extensional viscosity to shear viscosity is a constant over 100 at an extensional rate range of 25 to 750 s⁻¹. The constant values of this ratio, however, show that both shear viscosity and apparent extensional viscosity decrease with increasing rates and they decrease at about the same rate.

As noted in previous section, the CTAB / NaSal solution has the highest viscosity (Section 5.2) and viscoelasticity (Section 5.4) at low shear rates. It also has the highest apparent extensional viscosity at low extensional rates. All three systems have similar values at high extensional rates. It is not clear why the Arquad 16-50/NaSal has higher apparent extensional viscosity than CTAC. It may be because the molecular weight distribution of the alkyl group in Arquad 16-50 is broader and it contains some C18.
Figure 5.57 Apparent extensional viscosity for Arquad 16-50, CTAC and CTAB solutions. All surfactants are at 5 mM and with 12.5 mM NaSal as counterion.
Figure 5.58 Ratio of apparent extensional viscosity to shear viscosity for Arquad 16-50, CTAC and CTAB solutions. All surfactants are at 5 mM and with 12.5 mM NaSal as counterion.
Because of its high apparent extensional viscosity and low shear viscosity, the Arquad 16-50 system has the highest extensional to shear viscosity ratio.

5.8.2 Effect of Counterion Structure for Cationic Surfactant Systems

It was shown in previous sections of this chapter that the position of the chlorine group on the benzoate counterion has a great effect on drag reduction and rheological properties. It has a large effect on apparent extensional viscosity as well. Figs. 5.59 and 5.60 show apparent extensional viscosities for Arquad 16-50 with three isomeric counterions: 2-Cl, 3-Cl or 4-Cl benzoate at 30 and 20°C, respectively. The 4-Cl system shows apparent extensional viscosity as high as 30 poise at both 20 and 30 °C, while the 2-Cl system showed low apparent extensional viscosity at both temperatures. The results correspond well with both drag reduction and viscoelasticity for both solutions, i.e., the highly drag reducing system has high apparent extensional viscosity, high first normal stress difference and strong recoil, while the non-drag reducing 2-Cl system showed none of these properties. Special attention is called to the 3-Cl data shown in Fig. 5.60. The 3-Cl system showed only moderately high apparent extensional viscosity at 20°C. Due to a phase change in the 3-Cl solution, which will be discussed in Section 5.10, there was a large drop in the apparent extensional viscosity of the 3-Cl solution at an extensional rate of about 900 s⁻¹. The low apparent extensional viscosity was maintained even after the extensional rate was lowered. At 30°C, however, the 3-Cl solution showed high apparent extensional viscosity, comparable with the 4-Cl system, and no sudden change was observed (Fig. 5.59). Thus, the correlation between drag reduction (see Section 5.1.1) and
Figure 5.59 Apparent extensional viscosity for Arquad 16-50 (5 mM) / 2-, 3- or 4-Cl-benzoate (12.5 mM) solutions at 30°C.
Figure 5.60 Apparent extensional viscosity for Arquad 16-50 (5 mM) / 2-, 3- or 4-Cl-benzoate (12.5 mM) solutions at 20°C. Note that for the 3-Cl system, apparent extensional viscosity started at about the 3 P level with a clear solution. At an extensional rate of about 900 s\(^{-1}\), the solution became cloudy and the apparent extensional viscosity dropped to a very low level. Even when the extensional rate was lowered as denoted by the arrow, the solution remained cloudy with the lower apparent extensional viscosity.
high apparent extensional viscosity at high extensional rate also appears to hold for the 3-
Cl system.

The hydrophobic chlorine group in 4-Cl-benzoate resides in the micellar phase (Fig.
5.29), its favorable position. Thus, this system has high apparent extensional viscosity.
The chlorine in 2-Cl-benzoate, however, resides in the water phase, which is unfavorable
and thread-like micelles are either not formed or are unstable after formation (see Figs.
5.104 and 5.105 in Section 5.10 for cryo-TEM microstructure images). Even though the
chlorine group in the 3-Cl is also in the hydrophobic phase, it may be rotated into the
water phase under flow conditions, especially in turbulent flow where stresses on the
micelles may be high, and at high temperature, when Brownian motion of molecules is
strong. This can explain why the Arquad 16-50 (5 mM) / 3-Cl-benzoate (12.5 mM)
solution has a lower upper temperature limit for drag reduction, 50°C, compared to 70°C
for the 4-Cl system (see Section 5.1.1). The low temperature limit for drag reduction of
the 3-Cl system (20°C) is caused by precipitation under shear at 20°C, which will be
discussed in more detail in Section 5.10. The surfactant solution is subject to very strong
shear and extensional forces in turbulent flow and it is believed that a precipitate is
formed at 20°C so that no drag reduction is observed.

Both 4-Cl-benzoate and 2-OH-benzoate are counterions which can promote formation of
thread-like micelles and thus surfactant systems with these two counterions are drag
reducing and have high apparent extensional viscosity. Comparing them side by side,
however, there are some differences. Fig. 5.61 shows apparent extensional viscosity data for these two counterions with the same surfactant, Arquad 16-50. While the apparent extensional viscosity is the same at high extensional rate, the 2-OH-benzoate has much higher apparent extensional viscosity at low rates than 4-Cl-benzoate. It has also been observed that in drag reduction, these two surfactant systems behave slightly different [Chou, 1991b]. The critical wall shear stresses, above which drag reduction falls below 50% as defined by Chou [1991b], for the 2-OH-benzoate system (Table 5.3) are greater than those for the 4-Cl-benzoate with the same surfactant, Arquad 16-50, at low temperatures (< 50°C). However, at 60 and 70 °C, the critical wall shear stresses of the 4-Cl-benzoate system are equal to or greater than those for the 2-OH-benzoate system. This may be due to hydrogen bonding formed between micelles caused by hydroxy groups. H-bonding would enhance the network structure at low extensional rates thus giving higher apparent extensional viscosity. However, at high extensional rates, the H-bonds may be broken by the higher stresses and provide no enhancement in apparent extensional viscosity.

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>10</th>
<th>15</th>
<th>20</th>
<th>30</th>
<th>40</th>
<th>50</th>
<th>60</th>
<th>70</th>
<th>80</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-OH-benzoate</td>
<td>M</td>
<td>190</td>
<td>220</td>
<td>300</td>
<td>-</td>
<td>190</td>
<td>130</td>
<td>45</td>
<td>N</td>
</tr>
<tr>
<td>4-Cl-benzoate</td>
<td>N</td>
<td>-</td>
<td>156</td>
<td>145</td>
<td>149</td>
<td>-</td>
<td>130</td>
<td>92</td>
<td>N</td>
</tr>
</tbody>
</table>

Table 5.3 Critical Wall Shear Stress (Pa) of the Arquad 16-50 with NaSal or 4-Cl-benzoate Counterions. M represents 20% to 50% drag reduction measured, and N represents less than 20% drag reduction measured [Chou, 1991b].

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Figure S.61 Apparent extensional viscosity for Arquad 16-50 (5 mM) / 4-Cl-benzoate (12.5 mM) and Arquad 16-50 (5 mM) / NaSal (12.5 mM) solutions at 20°C.
5.8.3 Effect of Counterion to Cationic Surfactant Ratio

Data in previous sections have shown that the counterion to surfactant ratio has large effects on drag reduction (see Section 5.1.2) and viscoelasticity (see Section 5.4.2). In this section, the effect on apparent extensional viscosity is shown. Figs. 5.62 and 5.63 show apparent extensional viscosities and apparent extensional viscosity ratios for the Arquad 16-50 (5 mM) / NaSal system at different counterion to surfactant ratios, $\xi$. There is a significant increase in the apparent extensional viscosity when the ratio, $\xi$, increases from 0.6 to 1.0. The same increase is also observed for the Ethoquad O/12 (5 mM) / NaSal system (Fig. 5.64). For the Arquad 16-50 system, the apparent extensional viscosity at $\xi = 2.5$ is slightly higher at low extensional rates and about the same at high rates as the $\xi = 1.0$ solution. However, this is not the case for the Ethoquad O/12 system, whose $\xi = 2.5$ apparent extensional viscosities are surprisingly lower than the $\xi = 1.0$ values (Fig. 5.64). This corresponds with what we observed in cryo-TEM pictures, which show the micellar network density has little or no change when NaSal concentration increases from 5 mM to 12.5 mM for Arquad 16-50 systems, but show that the network density actually decreases slightly for the Ethoquad O/12 system [Lu et al., 1997c].

The apparent extensional viscosities of Arquad 16-50 solutions decrease with increasing extensional rate above about 50 s$^{-1}$ (Fig. 5.62). The rate of decrease is approximately the same as that of shear viscosity as shown by the nearly rate independent extensional to shear viscosity ratios (Fig. 5.63). Similar behavior is seen for the Ethoquad O/12 system (Figs. 5.64 and 5.65). For $\xi = 2.5$, at low extensional rates, both surfactant systems show
Figure 5.62 Apparent extensional viscosity of the Arquad 16-50 (5 mM) / NaSal system at different counterion/surfactant ratios, $\xi$. 

$T = 20 \, ^\circ\text{C}$

Extensional Viscosity (P)

Extensional Rate (s$^{-1}$)

- $\xi = 0.6$
- $\xi = 1.0$
- $\xi = 2.5$
Figure 5.63 Ratio of apparent extensional viscosity to shear viscosity of the Arquad 16-50 (5 mM) / NaSal system at different counterion/surfactant ratios, $\xi$. 

$T = 20 ^\circ C$
Figure 5.64 Apparent extensional viscosity of the Ethoquad O/12 (5 mM) / NaSal system at different counterion/surfactant ratios, $\xi$. 

T = 20 °C
Figure 5.65 Ratio of apparent extensional viscosity to shear viscosity of the Ethoquad O/12 (5 mM) / NaSal system at different counterion / surfactant ratios, $\xi$. 
an apparent extensional viscosity peak before extensional thinning at higher extensional rates. Walker et al. [1996] observed similar increase-peak-decrease behavior on CPyCl (cetylpyridinium chloride) / NaSal systems at 1.4% and 4% concentrations. They suggested that the onset of the increase in apparent extensional viscosity coincides with the onset of nonlinear viscoelasticity, as evidenced by the onset of shear thinning. Because of the low concentrations of our surfactant solutions and the limitations of the rheometers, we could not identify the onset point of shear thinning in most cases.

When $\xi \geq 1.0$, the ratios of apparent extensional viscosity to shear viscosity shown in Figs. 5.63 and 5.65 are around 100-300, well above 3 which is the value for Newtonian fluids. For $\xi = 0.6$, this ratio is less than 20. This significant difference may explain the performances of these surfactant systems in drag reduction as shown in Section 5.1.2.

5.8.4 Effect of Cationic Surfactant Chemical Structure

5.8.4.1 Cationic Surfactants

TTAB, CTAB and Arquad 18-50 were chosen to compare the effect of hydrocarbon chain length on rheological behavior. All three have three methyl groups in their head group. TTAB and CTAB contain bromide ion and Arquad 18-50 has chloride.

Fig. 5.66 shows apparent extensional viscosities of TTAB solutions at 20, 30 and 40°C. Apparent extensional viscosity increases with extensional rate to a peak and then decreases. With increasing temperature, the apparent extensional viscosities decrease
Figure 5.66 Apparent extensional and shear viscosity of TTAB (5 mM) / NaSal (12.5 mM) solutions at 20, 30 and 40 °C.
significantly and the peak shifts to higher rates of extension. Extensional thickening means the surfactant micelles are being extended, while extensional thinning means the micelles and the micellar network are being deformed. With increasing temperature, micelles become shorter [Missel et al., 1980, 1983; Elson and Garside, 1983; Hoffmann et al., 1985b; Myska et al., 1996]. In shear flow longer micelles are more easily aligned. Similarly, in extensional flow longer micelles are more easily extended because the longer the micelles are, the higher the extensional gradient they experience since the extensional gradient is in the direction of extensional flow. Thus, for the longer micelles, the peak extensional rate at which the micelles are fully extended is smaller at lower temperature.

Fig. 5.67 shows the apparent extensional viscosities of three surfactant solutions at 20°C. The apparent extensional viscosities at low extensional rates increase with chain length, while at high extensional rates, apparent extensional viscosities of all three are close to each other. On the other hand, at low shear rates, the shear viscosities of C16 and C18 are significantly higher than those of C14. This causes the ratio of apparent extensional viscosity to shear viscosity to increase in the reverse order of that of apparent extensional viscosity (Fig. 5.68).

Apparent extensional viscosity data at different temperatures for the C18TAC system are shown in Fig. 5.69. The C18TAC system has much higher apparent extensional viscosities than the TTAB system (Fig. 5.66), not only at 20°C, but also at 30 and 40°C. At temperatures above 40°C, the TTAB system shows negative apparent extensional
Figure 5.67  Apparent extensional viscosities of C14TAB (TTAB), C16TAB (CTAB) and C18TAC (Arquad 18-50) at 20 °C. All three surfactants are at 5 mM and with 12.5 mM NaSal.
Figure 5.68 Ratio of apparent extensional viscosity to shear viscosity of C14TAB (TTAB), C16TAB (CTAB) and C18TAC (Arquad 18-50) at 20 °C. All three surfactants are at 5 mM and with 12.5 mM NaSal.
Figure 5.69 Apparent extensional viscosities of the Arquad 18-50 (5 mM) / NaSal (12.5 mM) system.
viscosity with the RFX. The C18TAC system, on the other hand, shows positive apparent extensional viscosity up to 60°C before its values become negative.

Another surfactant system of interest is Habon G. Figs. 5.70-5.73 show apparent extensional viscosities for Habon G at four different concentrations: 1 mM, 2 mM, 3 mM and 5 mM. For 1 mM and 2 mM solutions, 40°C is the highest temperature at which positive apparent extensional viscosities can be measured. For 3 mM and 5 mM, however, the apparent extensional viscosities are positive up to 60°C. In contrast to the TTAB system (Fig. 5.66), apparent extensional viscosities of the Habon G system, especially at 3 and 5 mM, show only small temperature dependence. For the 5 mM Habon G system, apparent extensional viscosities in the range of 20 to 60°C collapse onto one curve. One general feature of apparent extensional viscosities for Habon G solutions at different concentrations is that the solutions are all extensional thinning, i.e., apparent extensional viscosity decreases with increasing extensional rate.

We shall next compare four surfactant systems which have different cationic surfactant chemical structures: Ethoquad O/12, Ethoquad O/13-50, Ethoquad T/13-50 and Arquad S-50 at 5 mM concentrations with 12.5 mM NaSal. Fig. 5.74 shows apparent extensional viscosity data for these four surfactant systems at 20°C. All four systems have very high apparent extensional viscosities compared with the shear viscosity. At low extensional rates O/13 is the highest and the other three are close to each other. The apparent extensional viscosities for all four solutions are close to each other at high rates.
Figure 5.70 Apparent extensional viscosities of the Habon G (1 mM) system.
Figure 5.71 Apparent extensional viscosities of the Habon G (2 mM) system.
Figure 5.72 Apparent extensional viscosities of the Habon G (3 mM) system.
Figure 5.73  Apparent extensional viscosities of the Habon G (5 mM) system.
Figure 5.74  Apparent extensional viscosity for Ethoquad O/12 (5 mM), Ethoquad O/13-50 (5 mM), Ethoquad T/13-50 (5 mM) and Arquad S-50 (5 mM); all surfactants with NaSal (12.5 mM).
Recognizing that shear viscosities might affect values of apparent extensional viscosity, ratios of apparent extensional viscosity to shear viscosity at corresponding rates were plotted (Fig. 5.75). The ratios at high rates were in the order: S-50 > O/13 ≥ T/13 > O/12, which is the reverse of the order for N₁ (see Section 5.4.3). This is probably because solutions with high N₁ usually have high shear viscosity as well.

Since the Arquad S-50 system is not viscoelastic as discussed in Sections 5.4.3 and 5.5.2, additional data for this system at different temperatures are shown in Figs. 5.76 and 5.77.

S-50 has very high apparent extensional viscosities at 20-50 °C, and lower apparent extensional viscosities at 70-80 °C. The apparent extensional viscosities increase with extension rate at 20, 30 and 50 °C and, after reaching a maximum, decrease with further increase in rate. The readings at 70 and 80°C are much lower and are more difficult to measure accurately and hence have more uncertainty. The apparent extensional viscosity to shear viscosity ratio was also calculated and is shown in Fig. 5.77. At 20-50 °C, the ratio exceeds one hundred. For 70 and 80 °C, the ratio is still of the order of ten. Recall that S-50 is an effective drag reducer up to 80 °C (see Fig. 5.5). Thus, it appears that the high ratios of apparent extensional viscosity to shear viscosity correlate well with drag reduction effectiveness. High extensional ratio, as shown previously for other drag reducing systems, again shows correlation with drag reduction performance. There is, however, uncertainty in the reduced apparent extensional viscosity values found at high temperatures.
Figure 5.75 Ratios of apparent extensional viscosity to shear viscosity for Ethoquad O/12 (5 mM), Ethoquad O/13-50 (5 mM), Ethoquad T/13-50 (5 mM) and Arquad S-50 (5 mM); all surfactants with NaSal (12.5 mM).
Figure 5.76 Apparent extensional viscosity for the Arquad S-50 (5 mM) / NaSal (12.5 mM) system.
Figure 5.77 Apparent extensional viscosity to shear viscosity ratio for the Arquad S-50 (5 mM) / NaSal (12.5 mM) system.
Jones et al. [1987] proposed that any departure from the value 3 of Trouton ratio can be associated unambiguously with viscoelasticity. However, it is obviously not true for the non-viscoelastic S-50 system, which has high apparent extensional viscosity.

5.8.4.2 Nonionic Surfactants

In section 5.2.4, shear viscosity was shown to reach a peak value at temperatures just below the cloud points of nonionic surfactant solutions. Apparent extensional viscosity of these systems is examined here.

Figs. 5.78 and 5.79 show apparent extensional viscosity and extensional to shear viscosity ratio for the Brij 97 (0.85%) / Brij 30 (0.15%) / Na$_2$SO$_4$ (0.45 M) system. Shear viscosity reaches a maximum at 17 and 18°C (see Fig. 5.26). Apparent extensional viscosity also peaks at 17°C (Fig. 5.78). The ratio peaks at 17°C as well, which means that the apparent extensional viscosity increase with temperature is at least proportionate to the increase in shear viscosity. Thus, the apparent extensional viscosity data support our explanation of the microstructure effects on the shear viscosity-temperature variations of nonionic surfactant systems.

5.8.5 Summary of Extensional Viscosity Results

Data in this section show that there is a generally good correlation between drag reduction and high apparent extensional viscosity. The mechanism of surfactant drag reduction is probably due to suppression of small scale turbulent eddies [Landahl, 1977; Durst et al.,
Figure 5.78  Apparent extensional viscosity of the Brij 97 (0.85%) / Brij 30 (0.15%) / Na₂SO₄ (0.45 M) system.
Figure 5.79 Ratio of apparent extensional viscosity to shear viscosity of the Brij 97 (0.85%) / Brij 30 (0.15%) / Na$_2$SO$_4$ (0.45 M) system.
In the bursting and growth of these eddies, extensional motions dominate. With the addition of surfactant drag reducers, apparent extensional viscosity is greatly increased thus increasing the resistance of the fluid in the eddies to extensional flow and suppressing formation and growth of small scale eddies. Since dissipation of the high frequency energy in the bursting eddies is a major cause of energy loss in turbulent flow, the correlation of drag reduction and high apparent extensional viscosity is not surprising. These data provide the first experimental demonstration that drag reduction and apparent extensional viscosity coincide.

5.9 Constitutive Equations for Surfactant Systems

The fundamental problem in surfactant drag reduction is that the mechanism is still unknown. The way to solve this problem may not be limited to experimental investigations. Theoretical studies with numerical or molecular simulation may help to solve this problem. However, in the equation of motion and the energy equation, an expression is needed for the stress tensor in terms of various kinematic tensors. That is, a "constitutive equation" for the stress is required. Due to the limited current understanding of the microstructures of surfactant systems, it is difficult to develop surfactant constitutive equations from molecular theories as was done for polymers. However, with rheological data available for drag reducing surfactant solutions, it is not difficult to test constitutive equations which are well-established for polymer solutions. In this section, several empirical and theoretical models are tested against rheological data presented in this chapter and qualitative conclusions regarding the suitability of the models will be given.
5.9.1 Maxwell Model

According to the Maxwell model [Bird et al., 1987], $G'$ and $G''$ follow a relaxation process with a single time constant:

$$\tau + \lambda \tau(t) = -\lambda G_0 \gamma(t) = -\pi \gamma(t) \quad (5.5)$$

where $\tau(t) = \left( \frac{\partial \tau}{\partial t} + [v \cdot \nabla \tau] \right) = [\nabla v^T \cdot \tau + \tau \cdot \nabla v] = \frac{D \tau}{Dt} - [\nabla v^T \cdot \tau + \tau \cdot \nabla v], \quad$ convected time derivative of $\tau$, and $\gamma(t) = \dot{\gamma}$ [Bird et al., 1987]. For small amplitude oscillation flow, the Maxwell model gives:

$$G' = \frac{G_0 \omega^2 \tau^2}{1 + \omega^2 \tau^2} \quad (5.6)$$

$$G'' = \frac{G_0 \omega \tau}{1 + \omega^2 \tau^2} \quad (5.7)$$

With proper transformation, we have:

$$\left( \frac{G' - \frac{1}{2} G_0}{2} \right)^2 + G''^2 = \frac{1}{4} G_0^2 \quad (5.8)$$

which is an equation for a circle. This implies that if a system can be described by a Maxwell model, then $G'$ and $G''$ data for such a system should form a semicircle on a $G'$ vs. $G''$ plot. This plot is the so-called Cole-Cole plot.

A Cole-Cole plot was made for the $G'$-$G''$ data of the Ethoquad 0/12 (5 mM) / NaSal (12.5 mM) system (Fig. 5.80). The data points do not fit on a semicircle curve above
Figure 5.80 Cole-Cole plot for the Ethoquad O/12 (5 mM) / NaSal (12.5 mM) system. T = 20 °C.
about 90 degrees, which means that these data are not well fit by a simple Maxwell model. This is expected, however, since the Maxwell model only predicts linear viscoelasticity while drag reducing surfactant solutions show highly non-linear viscoelasticity, such as non-zero first normal stress difference.

Although the Cole-Cole plot can be used to judge if the system can be described by the Maxwell model, the technique may be difficult to use since the only way to determine the best fit circle is by visual fitting. An improper circle may either lead to incorrect qualitative judgment regarding the fitting of the model or give incorrect parameters of the model if the model actually fits. Also in the presentation of results, the relative scale of the two axes has to be carefully adjusted otherwise the circle will not look like a circle. For these reasons, a different simple transformation of Eq. 5.8 has been developed [Sun, 1995]:

\[ G'^2 + G''^2 = G_0 \cdot G' \]  

(5.9)

This equation states that if \( G'^2 + G''^2 \) is plotted versus \( G' \), then a straight line will be obtained if the model fits the data. The slope of the line is \( G_0 \). In this fitting, the least square method with specification of zero intercept should be used. It gives an unambiguous indication of the suitability of the model and provides the physical constant, \( G_0 \), if the model fits the data. Fig. 5.81 shows fitting of the same data in Fig. 5.80 by this new method. Though a straight line can be obtained for all data points (Fig. 5.81, “All Points” line), the line does not go through most points with low \( G' \) values. A better fit can be obtained for the points of low \( G' \) values (Fig. 5.81, “Partial Points” line), however. If the
Figure 5.81 A new fitting technique for the Maxwell model. Data shown are dynamic shear data of the Ethoquad 0/12 (5 mM) / NaSal (12.5 mM) system.
Maxwell model fits data, the straight line should go through all points. Thus the fitting again shows the Maxwell model doesn’t fit this surfactant system.

5.9.2 Oldroyd’s Fluid B Model

Oldroyd’s Fluid B model (Eq. 5.10) is a quasi-linear model [Bird et al., 1987]. The model now has one more constant and also the partial derivatives are replaced by convected time derivatives [Bird et al., 1987; Brodkey, 1995].

\[
\tau + \lambda_1 \tau^{(1)} = -\eta_0 \gamma^{(1)} + \lambda_2 \gamma^{(2)}
\]

(5.10)

where \(\eta_0\) is zero shear viscosity, \(\lambda_1\) is a relaxation time, i.e., if motion is stopped, \(\tau\) will decay as \(\exp(-t/\lambda_1)\), \(\lambda_2\) is a retardation time, i.e., if stresses are removed, \(\dot{\gamma}\) will decay as \(\exp(-t/\lambda_2)\), and \(\gamma^{(2)} = \frac{D\gamma^{(1)}}{Dt} - (\nabla v^T \cdot \gamma^{(1)} + \gamma^{(1)} \cdot (\nabla v))\), 2nd rate of strain tensor [Bird et al., 1987]. If \(\lambda_2 = 0\), then Oldroyd’s Fluid B model reduces to the Maxwell model. After solving for the steady state shear, we have:

\[
\eta = \eta_0
\]

(5.11)

\[
\Psi_I = 2\eta_0 (\lambda_1 - \lambda_2)
\]

(5.12)

Thus, this model predicts that the system has constant shear viscosity and constant first normal stress difference coefficient. From shear viscosity data shown in previous sections, it can be concluded immediately that Oldroyd’s Fluid B model can not fit drag reducing surfactant solutions. The decreasing first normal stress coefficient with increasing shear rate, to be shown in the next section, also supports the inappropriateness of this model.
However, as a simple model, this model may be good at clarifying the relationship between viscoelasticity and the first normal stress difference. The model shows that the first normal stress difference is actually dependent on the difference of two time constants, \( \lambda_1 \) and \( \lambda_2 \). Highly viscoelastic systems have long relaxation and long retardation times. However, these two time constants may be of any magnitude and may even be equal, and thus give zero \( N_1 \). So we can conclude that while a system with non-zero values of \( N_1 \) is viscoelastic, a viscoelastic system may have zero \( N_1 \) values. This is one of the important conclusions reached in Lu et al. [1997a].

5.9.3 Giesekus Model

Obviously, drag reducing surfactant systems are very complex systems in terms of rheological properties. We may have to use a more complicated model to deal with these surfactant systems. Giesekus [1982] derived a constitutive equation with nonlinear stress terms:

\[
\tau = \tau_s + \tau_p = \tau_p - \eta_s \dot{\gamma} 
\]

\[
\tau_p + \lambda_1 \tau_{p(t)} - \alpha \frac{\lambda_1}{\eta_p} \{ \tau_p \cdot \tau_p \} = -\eta_p \dot{\gamma} 
\]

Giesekus separates the contribution of the solvent from that from the polymer (denoted by subscript p). The solvent is Newtonian while the polymer shows non-linear viscoelastic behavior. When this equation is used for drag reducing surfactant solutions, the solvent is water which is a Newtonian fluid, of course, and terms with subscript p represent
surfactants. By combining these two equations, the Giesekus model can be rewritten as a single equation:

$$
\tau + \lambda_1 \tau_{(1)} - \frac{\lambda_1}{\eta_0} \{ \tau \cdot \tau \} - a \lambda_2 \{ \gamma_{(1)} \cdot \tau + \tau \cdot \gamma_{(1)} \} = -\eta_0 [\gamma_{(1)} + \lambda_2 \gamma_{(2)} - a \frac{\lambda_2}{\lambda_1} \gamma_{(1)}] \tag{5.15}
$$

There are four constants in this model: \( \lambda_1, \lambda_2, \eta_0 \) and \( a \), where \( \lambda_1 \) is the relaxation time constant, \( \lambda_2 \) is the retardation time constant which includes the contribution of the solvent, \( \lambda_2 = \lambda_1 \eta_s/\eta_0 \), \( \eta_0 \) is the zero shear viscosity of solution, \( \eta_0 = \eta_s + \eta_p \), and \( a \) is a modified mobility parameter, \( a = \alpha / [1-(\lambda_2/\lambda_1)] \), which is associated with anisotropic Brownian motion and/or anisotropic hydrodynamic drag on the constituent polymer molecules [Bird and Wiest, 1985; Bird et al., 1987]. If the mobility factor, \( \alpha \), is zero, then the Giesekus model reduces to the Oldroyd's Fluid B model (Eq. 5.10). The material functions for this model are tabulated by Bird et al. [1987] (Table 5.4).

### 5.9.3.1 Steady State Data Fitting

The fitting of this model starts with small amplitude oscillatory shear flow since Eqs. 5.19 and 5.20 give the simplest form. From these two equations, we have:

$$
\frac{\eta' \omega}{\eta''} = \frac{l}{\lambda_1 - \lambda_2} + \frac{\lambda_1 \lambda_2}{\lambda_1 - \lambda_2} \omega^2 \tag{5.22}
$$

Thus the plot of \( \eta' \omega/\eta'' \) vs. \( \omega^2 \) is a straight line if the model fits the data. The slope of that line is \( \lambda_1 \lambda_2/\lambda_1 - \lambda_2 \) and the intercept is \( l/(\lambda_1 - \lambda_2) \), from which \( \lambda_1 \) and \( \lambda_2 \) can be calculated. Then the zero shear viscosity, \( \eta_0 \), which can not be obtained from steady state
For Steady Shear Flow:

\[
\eta = \frac{\lambda_2 + (1 - \frac{\lambda_2}{\lambda_1}) (1-f)^2}{\eta_0} \frac{1}{1+(1-2\alpha)f}
\]

(5.16)

\[
\frac{\Psi}{2\eta_0(\lambda_1 - \lambda_2)} = \frac{f(1-\alpha f)}{(\lambda_1 \dot{\gamma})^2 \alpha (1-f)}
\]

(5.17)

\[
\frac{\Psi}{\eta_0(\lambda_1 - \lambda_2)} = \frac{-f}{(\lambda_1 \dot{\gamma})^2}
\]

(5.18)

where \( f = \frac{1-\chi}{1+(1-2\alpha)\chi} \); \( \chi^2 = \frac{\sqrt{1+16\alpha(1-\alpha)(\lambda_1 \dot{\gamma})^2}-1}{8\alpha(1-\alpha)(\lambda_1 \dot{\gamma})^2} \).

For Small-Amplitude Oscillatory Shear Flow:

\[
\frac{\eta'}{\eta_0} = \frac{l + \lambda_1 \lambda_2 \omega^2}{l + \lambda_2^2 \omega^2}
\]

(5.19)

\[
\frac{\eta''}{\eta_0 \omega} = \frac{\lambda_1 - \lambda_2}{l + \lambda_2^2 \omega^2}
\]

(5.20)

For Steady Elongational Flow:

\[
\frac{\eta_e}{3\eta_0} = \frac{\lambda_2 + (1 - \frac{\lambda_2}{\lambda_1})}{\lambda_1} \frac{1}{6\alpha} \left[ 3 + \frac{1}{\lambda_1 \dot{\varepsilon}} \left( \sqrt{l - 4(l - 2\alpha)\lambda_1 \dot{\varepsilon} + 4\lambda_2^2 \dot{\varepsilon}^2} \right) \right. \\
\left. - \sqrt{l + 2(l - 2\alpha)\lambda_1 \dot{\varepsilon} + \lambda_2^2 \dot{\varepsilon}^2} \right]
\]

(5.21)

Table 5.4 Material Functions for the Giesekus model [Bird et al., 1987].
measurements, is obtained from Eqs. 5.19 and 5.20 by either visual fitting or by using an optimization software. SOLVER function of Microsoft EXCEL (version 7.0) was used in this work.

The material function expressions for steady state shear flow are so complicated that no straightforward mathematical way can be used to fit the data with the model. Thus the SOLVER function of EXCEL is used again to obtain the mobility factor, $\alpha$, from steady state data. With all four constants known, the apparent extensional viscosity can be calculated from Eq. 5.21. Through fitting, it was observed that the apparent extensional viscosity predicted by the model is very sensitive to the value of $\alpha$. This suggests that $\alpha$ should be obtained by fitting apparent extensional viscosity data with the model. But since the RFX apparent extensional viscosity data are not obtained from steady elongational flow, which will be discussed later, $\alpha$ obtained in this way would be incorrect.

Several highly viscoelastic drag reducing surfactant systems were chosen for fitting by the Giesekus model. Figs. 5.82-5.85 show fitting results for the Ethoquad O/12 (5 mM) / NaSal (12.5 mM) system at 20°C.

For the Ethoquad O/12 (5 mM) / NaSal (12.5 mM) system, the Giesekus model can fit the dynamic data well except for $\eta''$ data at high frequency (Fig. 5.82). Figs. 5.83 and 5.84 show that with a proper $\alpha$ value, the model can fit the shear viscosity and first normal
Figure 5.82 Dynamic viscosities of the Ethoquad O/12 (5 mM) / NaSal (12.5 mM) system and fitting results by the Giesekus model with constants: $\lambda_1 = 0.166 \text{ s}$, $\lambda_2 = 0.0211 \text{ s}$, $\eta_0 = 0.0192 \text{ Pa s}$ and $\alpha = 0.00022$. 
Figure 5.83 Steady shear viscosity of the Ethoquad O/12 (5 mM) / NaSal (12.5 mM) system and fitting results by the Giesekus model with constants: \( \lambda_1 = 0.166 \) s, \( \lambda_2 = 0.0211 \) s, \( \eta_0 = 0.0192 \) Pa s and \( \alpha = 0.00022 \).
Figure 5.84 Prediction of first and second normal stress differences of the Ethoquad O/12 (5 mM) / NaSal (12.5 mM) system by the Giesekus model with constants: $\lambda_1 = 0.166$ s, $\lambda_2 = 0.0211$ s, $\eta_0 = 0.0192$ Pa s and $\alpha = 0.00022$. 
Figure 5.85 Apparent extensional viscosity of the Ethoquad O/12 (5 mM) / NaSal (12.5 mM) system and fitting results by the Giesekus model with constants: $\lambda_1 = 0.166$ s, $\lambda_2 = 0.0211$ s, $\eta_0 = 0.0192$ Pa s and $\alpha = 0.00022$. 
stress difference data reasonably well. The second normal stress difference can be calculated by the Giesekus model from Eq. 5.18 (Fig. 5.84). It is surprising to see that $-N_2$ values are up to four orders of magnitudes less than $N_1$. For polymers, the value of $-N_2$ is usually of the order of one tenth of $N_1$ [Macosko, 1994]. This can be explained by the nature of the Giesekus model. From Eqs. 5.17 and 5.18:

$$\frac{-N_2}{N_1} = \alpha(\frac{l-f}{2(l-\alpha f)}) = \frac{l-f}{2(l-\alpha f)}$$

(5.23)

For small $\alpha$, $-N_2/N_1$ tends to be very small.

Fig. 5.85 shows the model’s prediction of apparent extensional viscosity for the O/12 system. The model predicts that there is a critical extensional rate range, 2 to 5 s$^{-1}$ in this case, in which apparent extensional viscosity increases from a low plateau to a high plateau. The increase can be as much as three orders of magnitude. At the high plateau region, it is surprising to see that the model predicts apparent extensional viscosities two orders of magnitude higher than the experimental data. This does not prove that the model does not fit data, however. It may be that the experimental data are not correct since they are not steady state data. In the opposing nozzle configuration used in the RFX to measure apparent extensional viscosity, the flow field is a mixture of shear and extensional flow. Fluid elements experience pure extensional flow only at the center line of the flow field. The residence time in this flow field for each element is very short. It is different from steady state shear measurements, where the whole body of the fluid, or all fluid elements, experience the same flow field for the experimental time, which is always...
long enough to ensure that steady state is reached. The average residence time can be calculated by [Rheometrics, 1991]:

\[ t = \frac{1}{\dot{\varepsilon}} + \frac{2}{\dot{\varepsilon}} \ln \left( \frac{D}{d} \right) \]  

(5.24)

where \( d \) is nozzle diameter and \( D \) is the gap between two nozzles. In experiments, the gap is always set to be equal to the nozzle diameter, thus, the residence time is the reciprocal of the extensional rate. For the extensional rates studied, 5 to 10,000 \( \text{s}^{-1} \), the residence time is always less than 0.2 s. As discussed in Section 5.5, most surfactant solutions studied need a much longer time to reach steady state. Thus this residence time is simply not long enough to let the fluid elements fully experience the extensional flow and reach steady state. Thus, our measured values are designated as apparent extensional viscosities. They are an indicator of extensional viscosity and are expected to be lower than the actual extensional viscosity.

Figs. 5.86-5.89 show fitting results for the Arquad 16-50 (5 mM) / 4-Cl-benzoate (12.5 mM) system. The model fitting for \( \eta'' \) is much worse than that for the O/12 system. The model fit the \( \eta'' \) data only in the middle frequency range and was off at both low and high frequencies (Fig. 5.86). However, for shear viscosity and first normal stress difference, the fitting is reasonably good (Figs. 5.87 and 5.88). Again, the model predicts very small second normal stress differences (Fig. 5.88).

Fig. 5.89 shows the fitting results for the apparent extensional viscosity. Now the difference between the model prediction and data is only about one order of magnitude.
Figure 5.86 Dynamic viscosities of the Arquad 16-50 (5 mM) / 4-Cl-benzoate (12.5 mM) system and fitting results by the Giesekus model with constants: $\lambda_1 = 0.191$ s, $\lambda_2 = 0.0131$ s, $\eta_0 = 0.0220$ Pa s and $\alpha = 0.00084$. 

---

0.03

▲ Eta

0.025

Eta Model

— Eta" Model

0.02

0.015

0.01

0.005

0

0.03

0.02

0.015

0.01

0.005

0

Dynamic Viscosity (Pa s)

Frequency (rad/s)

1

10

100

325
Figure 5.87 Shear viscosity of the Arquad 16-50 (5 mM) / 4-Cl-benzoate (12.5 mM) system and fitting results by the Giesekus model with constants: $\lambda_1 = 0.191$ s, $\lambda_2 = 0.0131$ s, $\eta_0 = 0.0220$ Pa s and $\alpha = 0.00084$. 
Figure 5.88 First normal stress difference coefficient of the Arquad 16-50 (5 mM) / 4-Cl-benzoate (12.5 mM) system and prediction of first and second normal stress differences by the Giesekus model with constants: $\lambda_1 = 0.191 \text{ s}$, $\lambda_2 = 0.0131 \text{ s}$, $\eta_0 = 0.0220 \text{ Pa s}$ and $\alpha = 0.00084$. 
Figure 5.89 Apparent extensional viscosity of the Arquad 16-50 (5 mM) / 4-Cl-benzoate (12.5 mM) system and fitting by the Giesekus model with constants: $\lambda_1 = 0.191$ s, $\lambda_2 = 0.0131$ s, $\eta_0 = 0.0220$ Pa s and $\alpha = 0.00084$. 
Significant extensional thinning is observed in the experimental data. As analyzed before, the residence time of fluid elements in the flow field is the reciprocal of extensional rate, thus with increasing extensional rate, fluid elements reside in the flow field for a shorter time and they have less time to reach steady state. This may explain why with increasing extensional rate, apparent extensional viscosity decreases while the model predicts slight extensional thickening.

Figs. 5.90-5.93 summarizes fitting results for the Arquad S-50 (5 mM) / NaSal (12.5 mM) system, a unique non-viscoelastic drag reducing system. The fitting for the dynamic data is reasonably good. But due to the scatter of data points, the model curves do not represent all the data. However, the relaxation time constant, $\lambda_1 = 0.105$ s, is fairly close to the exponential data fitting result, 0.152 s, of the relaxation data (see Section 5.6.2). It should be noted that the retardation time constant, $\lambda_2$, should not be confused with the either of the two step relaxation time constants.

The difficulty in fitting this system came from the $N_1$ data. As discussed earlier, this system has close to zero $N_1$ values at low shear rates and has small negative $N_1$ values at high shear rates. The model, however, does not predict negative $N_1$ values in any case. If all positive $N_1$ values are followed, then the steady state shear data can not be fit. After trial and error, it was decided to fit the viscosity data and the three lowest shear rate $N_1$ points. The results in Fig. 5.91 show that the fits for both $\psi_1$ and viscosity are good. However, for $N_1$, only values at very low shear rates can be fit. The model predicts small
Figure 5.90 Dynamic viscosities of the Arquad S-50 (5 mM) / NaSal (12.5 mM) system and fitting by the Giesekus model with constants: $\lambda_1 = 0.105$ s, $\lambda_2 = 0.00696$ s, $\eta_0 = 0.0137$ Pa s and $\alpha = 0.009$. 
Figure 5.91 Shear viscosity and first normal stress difference coefficient of the Arquad S-50 (5 mM) / NaSal (12.5 mM) system and fitting by the Giesekus model with constants: $\lambda_1 = 0.105$ s, $\lambda_2 = 0.00696$ s, $\eta_0 = 0.0137$ Pa s and $\alpha = 0.009$. 
Figure 5.92 First normal stress difference of the Arquad S-50 (5 mM) / NaSal (12.5 mM) system and prediction of first and second normal stress differences by the Giesekus model with constants: $\lambda_1 = 0.105$ s, $\lambda_2 = 0.00696$ s, $\eta_0 = 0.0137$ Pa s and $\alpha = 0.009$. 
Figure 5.93 Apparent extensional viscosity of the Arquad S-50 (5 mM) / NaSal (12.5 mM) system and fitting by the Giesekus model with constants: $\lambda_1 = 0.105 \text{ s}$, $\lambda_2 = 0.00696 \text{ s}$, $\eta_0 = 0.0137 \text{ Pa s}$ and $\alpha = 0.009$. 
positive $N_1$ values at high shear rates. At 1000 s$^{-1}$, the model predicts about 50 Pa of $N_1$, which is small compared to 200 to 400 Pa observed for most other systems. To examine how $N_1$ values increase with further increase in shear rate, the model prediction of $N_1$ up to 10000 s$^{-1}$ is presented in Fig. 5.92. The model prediction of $N_1$ is only about 180 Pa at 10000 s$^{-1}$. It should be noted that this prediction does not imply the system will be viscoelastic. As mentioned above, if all positive $N_1$ data points are closely followed in fitting, the prediction of $N_1$ at high shear rates will be much lower. Thus, with these close to zero $N_1$ values, it is uncertain whether this model can fit the data.

With the $\alpha$ value obtained for the S-50 system, the ratio -$N_2/N_1$ is higher than for the other two systems and the apparent extensional viscosity predicted by the model is much closer to the experimental data. Again, for the same reason we discussed above, the extensional data points obtained by the RFX can never match the model prediction.

**5.9.3.2 Transient Data Fitting**

Since the Giesekus model can fit the steady state data reasonably well, the question arises as to whether the model can fit transient data as well. Model constants obtained in steady state fitting will be used in transient fitting since these constants, while they may not fit a particular point well, fit the whole range of data the best.

The governing equations for steady state shear flow for the Giesekus model are obtained by proper simplification from the set of equations provided by Bird et al. [1987]:

334
\[
[1 + \lambda_1 \frac{d}{dt}] \tau_{xx} - (2\lambda_1 + 2a\lambda_2) \tau_{xx} \dot{\gamma}_{xx} - \frac{\lambda_1}{\eta_0} (\tau_{xx}^2 + \tau_{yy}^2) = \eta_0 (2\lambda_2 + a\frac{\lambda_2^2}{\lambda_1}) \dot{\gamma}_{xx}^2
\]  
(5.25)

\[
[1 + \lambda_1 \frac{d}{dt}] \tau_{yy} - 2a\lambda_2 \tau_{xx} \dot{\gamma}_{xx} - \frac{\lambda_1}{\eta_0} (\tau_{xx}^2 + \tau_{yy}^2) = \eta_0 a \frac{\lambda_2^2}{\lambda_1} \dot{\gamma}_{xx}^2
\]  
(5.26)

\[
[1 + \lambda_1 \frac{d}{dt}] \tau_{xz} - a\frac{\lambda_1}{\eta_0} \tau_{xx}^2 = 0
\]  
(5.27)

\[
[1 + \lambda_1 \frac{d}{dt}] \tau_{xx} - \lambda_2 \tau_{xx} \dot{\gamma}_{xx} - (\lambda_1 + \lambda_2) \tau_{yy} \dot{\gamma}_{xx} - a\frac{\lambda_1}{\eta_0} (\tau_{xx}^2 + \tau_{yy}^2) \tau_{xx} = -\eta_0 [1 + \lambda_2 \frac{d}{dt}] \dot{\gamma}_{xx}
\]  
(5.28)

\[
\tau_{xx} = \tau_{yy} = 0
\]  
(5.29)

These equations are coupled and thus no analytical solution is possible. A numerical method has to be used. To simplify the solution, the contribution from the solvent is separated and thus \( \lambda_2 \) in these equations can be set to be zero [Shackleford, 1996]. The zero shear viscosity, \( \eta_0 \), is replaced by the zero shear viscosity of the surfactant only, i.e., the solvent contribution is subtracted. Then, in the output of the start-up shear stress, a constant stress contributed by the solvent is added back. However, it should not be added back to the relaxation shear stress since the Newtonian solvent should relax immediately after cessation of shear. The Runge-Kutta fourth order method was used to solve the simplified differential equations. A macro in Microsoft EXCEL (version 7.0) written by Shackleford [1996] was used.

Figs. 5.94 to 5.99 show simulation results for Ethoquad O/12 (5 mM) / NaSal (12.5 mM) at 50, 100 and 500 s\(^{-1}\) shear rates. It should be noted again that since the model constants
Shear Rate $= 50 \text{ (s}^{-1}\text{)}$

**Figure 5.94** Giesekus model prediction of stress development in the start up of steady state shear flow for the Ethoquad O/12 (5 mM) / NaSal (12.5 mM) system. Shear rate is 50 s$^{-1}$ and model constants are: $\lambda_1 = 0.166 \text{ s}$, $\lambda_2 = 0.0211 \text{ s}$, $\eta_0 = 0.0192 \text{ Pa s}$ and $\alpha = 0.00022$. 
Figure 5.95 Giesekus model prediction of stress relaxation upon the cessation of steady state shear flow for the Ethoquad O/12 (5 mM) / NaSal (12.5 mM) system. Shear rate is 50 s\(^{-1}\) and model constants are: \(\lambda_1 = 0.166\) s, \(\lambda_2 = 0.0211\) s, \(\eta_0 = 0.0192\) Pa s and \(\alpha = 0.00022\).
Figure 5.96 Giesekus model prediction of stress development in the start up of steady state shear flow for the Ethoquad O/12 (5 mM) / NaSal (12.5 mM) system. Shear rate is 100 s⁻¹ and model constants are: \( \lambda_1 = 0.166 \) s, \( \lambda_2 = 0.0211 \) s, \( \eta_0 = 0.0192 \) Pa s and \( \alpha = 0.00022 \).
Figure 5.97 Giesekus model prediction of stress relaxation upon cessation of steady state shear flow for the Ethoquad O/12 (5 mM) / NaSal (12.5 mM) system. Shear rate is 100 s\(^{-1}\) and model constants are: \(\lambda_1 = 0.166\) s, \(\lambda_2 = 0.0211\) s, \(\eta_0 = 0.0192\) Pa s and \(\alpha = 0.00022\).
Figure 5.98 Giesekus model prediction of stress development in the start up of steady state shear flow for the Ethoquad O/12 (5 mM) / NaSal (12.5 mM) system. Shear rate is 500 s\(^{-1}\) and model constants are: \(\lambda_1 = 0.166\) s, \(\lambda_2 = 0.0211\) s, \(\eta_0 = 0.0192\) Pa s and \(\alpha = 0.00022\).
Figure 5.99 Giesekus model prediction of stress relaxation upon cessation of steady state shear flow for the Ethoquad O/12 (5 mM) / NaSal (12.5 mM) system. Shear rate is 500 s\(^{-1}\) and model constants are: \(\lambda_1 = 0.166\) s, \(\lambda_2 = 0.0211\) s, \(\eta_0 = 0.0192\) Pa s and \(\alpha = 0.00022\).
used were obtained by optimizing the whole set of data instead of data at a particular shear rate, the steady state model values do not fit all of the experimental points as shown in Figs. 5.83 and 5.84. Thus, in these simulation results, one should look at trends rather than at matching of model values to data points.

Figs. 5.94 and 5.95 show that at 50 s\(^{-1}\), both start up and relaxation processes are well predicted by the model. However, the large overshoots of both stresses at 100 s\(^{-1}\) are not predicted by the model (Fig. 5.96). However, the existence of overshoots at 500 s\(^{-1}\) (Fig. 5.98) are predicted by the model though the magnitude is not as large. The relaxation processes at 100 and 500 s\(^{-1}\) are reasonably well-predicted by the model (Figs. 5.97 and 5.99). One important feature of this model should be noted. The model, with only one relaxation time constant, predicts both the initial quick drop and the following long relaxation process, the so called “two-step” relaxation process which we attempted to fit in Section 5.6 by a double exponential function.

The Giesekus model predicts start-up and relaxation stress development relatively well for the O/12 system. The fitting for the Arquad 16-50 (5 mM) / 4-Cl-benzoate (12.5 mM) system is shown in Figs. 5.100 and 5.101 at 600 s\(^{-1}\). The reason why this high shear rate was chosen is because the steady state values of the model agree well with data at this shear rate (see Figs. 5.87 and 5.88). For the start up stress development, the model gives good predictions. Overshoots in both stresses are predicted by the model though with a smaller magnitude as in the Ethoquad O/12 case. The model prediction of the relaxation
Figure 5.100 Giesekus model prediction of stress development in the start up of steady state shear flow for the Arquad 16-50 (5 mM) / 4-Cl-benzoate (12.5 mM) system. Shear rate is 600 s\(^{-1}\) and model constants are: \(\lambda_1 = 0.191\) s, \(\lambda_2 = 0.0131\) s, \(\eta_0 = 0.0220\) Pa s and \(\alpha = 0.00084\).
Figure 5.101 Giesekus model prediction of stress relaxation upon cessation of steady state shear flow for the Arquad 16-50 (5 mM) / 4-Cl-benzoate (12.5 mM) system. Shear rate is 600 s$^{-1}$ and model constants are $\lambda_1 = 0.191$ s, $\lambda_2 = 0.0131$ s, $\eta_0 = 0.0220$ Pa s and $\alpha = 0.00084$. 
of shear stress agrees very well with the data (Fig. 5.100). However, the model predicts the normal stress should relax more quickly than the data show (Fig. 5.101). This is not the case for the O/12 system discussed above. In steady state fitting, the model doesn't fit the 4-Cl system as well as the O/12 system. This may suggest that the Giesekus model, while it can be applied to drag reducing surfactant systems, may not be suitable for all systems. This should be expected, however, since each surfactant system has its unique microstructure and thus their rheological properties are quite different even though they behave very similarly in drag reduction.

5.9.4 Summary on Modeling of Drag Reducing Surfactant Systems

Drag reducing surfactant systems are very complex systems. Simple models can not describe these systems well enough. A model with nonlinear stress terms, the Giesekus model, can fit rheological data reasonably well for these systems. Table 5.5 lists Giesekus model constants obtained by fitting.

<table>
<thead>
<tr>
<th>Surfactant Systems</th>
<th>$\lambda_1$ (s)</th>
<th>$\lambda_2$ (s)</th>
<th>$\eta_0$ (Pa s)</th>
<th>$\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethoquad O/12 (5 mM) / NaSal (12.5 mM)</td>
<td>0.166</td>
<td>0.0211</td>
<td>0.0192</td>
<td>0.00022</td>
</tr>
<tr>
<td>Arquad 16-50 (5 mM) / 4-Cl-benzoate (12.5 mM)</td>
<td>0.191</td>
<td>0.0131</td>
<td>0.0220</td>
<td>0.00084</td>
</tr>
<tr>
<td>Arquad S-50 (5 mM) / NaSal (12.5 mM)</td>
<td>0.105</td>
<td>0.00696</td>
<td>0.0137</td>
<td>0.009</td>
</tr>
</tbody>
</table>

Table 5.5 Summary of constants for the Giesekus model for three surfactant systems.
Table 5.5 indicates that the Giesekus model predicts a relaxation time constant of 0.1 to 0.2 s for these surfactant systems. The mobility factor, \( \alpha \), is very small for all three systems. It seems that the smaller \( \alpha \) is, the larger the \( N_i \) and the extensional viscosity are.

For the O/12 and 16-50 / 4-Cl systems, the Trouton ratio (extensional viscosity to the zero shear viscosity) at high strain rates is over 2000. For the S-50 system, though the system has close to zero \( N_i \) values in the shear rate range studied, the model still predicts high extensional viscosity, which leads to a Trouton ratio of the order of 200. This may indicate that extensional viscosity is truly responsible for drag reduction, though true extensional viscosity data are lacking due to the problems in measuring apparent extensional viscosity for these surfactant systems.

5.10 Stress Induced Precipitation and Micelle Transformation

It was observed that the Arquad 16-50 (5 mM) / 3-Cl-benzoate (12.5 mM) solution could be clear or cloudy when prepared or kept at 20°C. When the solution was cloudy after prepared, it became clear when heated to 30°C. If the solution then was cooled down to 20°C with no disturbance, the solution remained clear. Thus, precipitation caused by lowering the temperature is reversible with some hysteresis.

However, it was also observed that the clear 3-Cl solution could become cloudy during shear or extensional experiments at 20°C. To examine this phenomenon, a clear 3-Cl solution kept at 20°C was put into the Couette cell of the RFSII and a constant shear rate of 1000 s\(^{-1}\) was applied. After about 230 s, shear viscosity dropped to only about 1.5 times
that of water and precipitation was observed at the same time (Fig. 5.102). The experiment was repeated with a higher shear rate, 1500 s$^{-1}$, and a similar drop was observed after a shorter shear time, 190 s.

The initial apparent viscosities of clear solutions at both shear rates were about the same indicating that they were in the upper Newtonian region. Similar clouding phenomena were also observed in apparent extensional viscosity measurements (see Fig. 5.60) and in a different Couette cell, in which flow birefringence measurements were made. In that case the signal was lost following clouding of the solution at a shear rate of 900 s$^{-1}$. A similar phenomenon was observed at 20 °C for Arquad 18-50 (5 mM) / NaSal (12.5 mM) solution (Fig. 5.103). The solution had been under constant shear of 1500 s$^{-1}$ for over 2000 s before the viscosity dropped and at the same time the solution became cloudy.

In contrast to the reversible change with temperature when precipitation was caused by cooling, the cloudy solutions caused by shear could not be clarified when the stresses were removed. A cloudy sample caused by shear was kept for more than twenty days and the solution remained cloudy. Thus, the precipitation process caused by stress is apparently irreversible. We call this process stress-induced precipitation. However, if the cloudy solution caused by shear was heated up, it became clear.

Cryo-TEM images were taken for the Arquad 16-50 (5 mM) / 3-Cl-benzoate (12.5 mM) system in our collaborating lab at the Department of Chemical Engineering and Materials
Figure 5.102 Viscosity change of the Arquad 16-50 (5 mM) / 3-Cl-benzoate (12.5 mM) solution under constant shear.
Figure 5.103 Viscosity change of the Arquad 18-50 (5 mM) / NaSal (12.5 mM) solution under constant shear of 1500 s\(^{-1}\).
Science, University of Minnesota (Figs. 5.104 and 5.105). The two pictures taken gave different structures. A thread-like micellar network is seen in Fig. 5.105. This is consistent with a clear solution of moderate apparent extensional viscosity observed at low extensional rates. However, the structure in Fig. 5.104 is quite different with vesicles of various sizes. We postulate that these different images are the result of different shear levels that the surfactant solutions were subjected to in the blotting process in preparing the samples. The surfactant solution in Fig. 5.105 was probably subjected to higher shear, and the micelles underwent a phase transformation and vesicles formed.

These results show that there is a structure change at 20°C in the 3-Cl solution when a shear or extensional stress is applied. Moderately high apparent extensional viscosities for the clear solution at this temperature suggest that thread-like micelles and a micellar network or vesicles exist in the clear solution. At high shear, the solution became cloudy; a suspension of crystal-like materials, silvery in color, was formed in the solution, and the thread-like micellar network or vesicle structure was destroyed leading to the very low extensional and shear viscosities observed. The stress levels in turbulent flow are sufficiently high that precipitation probably occurs at 20 °C explaining the absence of drag reduction at that temperature.

Based on the observations of stress-induced precipitation, the cryo-TEM images and drag reduction, and temperature and shear effects, we propose a fixed concentration micelle schematic diagram under different temperature and shear conditions (Fig. 5.106).
Figure 5.104 Cryo-TEM image of a vitrified specimen of the Arquad 16-50 (5 mM) / 3-Cl-benzoate (12.5 mM) solution. Many large vesicles, denoted by V, are seen, some encapsulated in a larger one. Bar = 100 nm.

Figure 5.105 Cryo-TEM image of a vitrified specimen similar to that of Figure 5.104, but in this case the structures seen are thread-like micelles (denoted by small arrows) aligned along the edge of a hole (H) in the specimen. Bar = 100 nm.
Figure 5.106 Proposed phase diagram of the Arquad 16-50 (5 mM) / 3-Cl-benzoate (12.5 mM) system under external forces. Shaded area denotes metastable state. Two way arrow denotes reversible phase change and one way arrow represents process which only proceeds in the arrow direction.
With increasing shear at constant temperature at a certain temperature, such as 20°C for the 3-Cl system, individual thread-like micelles present in the solution form a micellar network and then reform into vesicles. This may be a reversible process. However, with further increase of external forces, the surfactant precipitates in a process which is not reversible by lowering shear. Since all processes across boundaries of a phase diagram should be reversible, the existence of this irreversible process indicates that the region surrounding this process is metastable, as denoted by the shaded area in Fig. 5.106. A dashed line is used to mark the left boundary of the metastable region since it is not a "real" phase boundary. The solutions in the shaded area should be cloudy but they are clear because of the existence of the metastable state. The 3-Cl solution was cooled down without disturbance from a clear solution and it became cloudy after about 2 hours at 15 °C. At temperatures higher than 15 °C, such as 17 °C and 20 °C, the solution was still clear after over 24 hours. Thus, 15 °C is the apparent Krafft point, at which precipitate forms in the solution from metastable state without any external force. The true Krafft point for the solution may be higher (above 20 °C). It should be noted that all processes which cross solid lines in Fig. 5.106 are reversible.

The less highly sheared solution in Fig. 5.105 corresponds to the metastable thread-like micellar network region, while the more highly sheared solution in Fig. 5.104 corresponds to the metastable vesicle region in Fig. 5.106. The blotting step in the preparation of cryo-TEM samples subjects them to very high rates of flow deformation. The subsequent chilling step takes place only a few seconds later. For drag reducing
surfactant solutions at these concentrations, the relaxation time constants are of the order of seconds but changes in the micellar structure may take considerable longer. Thus, micellar structure will depend on the level of shear the sample is subjected to in the blotting and on the time interval between blotting and sample chilling.

The stress levels in turbulent flow are sufficiently high that precipitation probably occurs at 20°C explaining the absence of drag reduction at that temperature. At a higher temperature, such as 30°C, the 3-Cl system is drag reducing, shows recoil and has high extensional viscosity, indicating that there is a micellar network structure existing in the solution. The 30°C for the 3-Cl system corresponds to the region in Fig. 5.106 where with increasing shear, individual thread-like micelles form a micellar network and then are broken into fragments without reforming into vesicles.

A number of authors have measured micellar sizes of cationic surfactant-counterion solutions similar to those studied here and known to be drag reducing [Ohlendorf et al., 1986a; Bewersdorff and Ohlendorf, 1988; Nemoto and Kuwahara, 1994; Hofmann et al., 1994; Myska et al., 1997]. For solutions which were not subjected to shear they measured large but finite micellar lengths ranging from 18 to nearly 2000 nm. Since with a network, the micelle size measured by the diffusion coefficient in light scattering should be infinite, individual thread-like micelles must exist in these static measuring systems instead of a network. This corresponds to the region at the bottom of the Fig. 5.106 schematic. With shear, individual thread-like micelles form a network, which may
correspond to the Shear Induced Structure (SIS) described by some researchers. With further increase in shear, that network may be broken into fragments. That stress corresponds to the critical shear stress at which drag reduction is lost. However, this process is reversible if shear is lowered.

Lowering temperature can also cause precipitation, of course, but subsequent heating reverses that. The highest temperature at which precipitation can occur with shear corresponds to the lower temperature limit of drag reduction as drag reduction is measured under conditions in which the solution is subjected to very high wall shear and turbulent eddy extensional stresses. For the 3-chloro system it is just below 30 °C. At high temperatures (above 50 °C), the 3-chloro thread-like micellar network reforms into spherical micelles as shown in Fig. 5.106. The temperature at which this occurs defines the upper temperature limit of drag reduction. However, this process is reversible and drag reduction is regained when the temperature is lowered.
CHAPTER 6

RESULTS AND DISCUSSION - APPLICATION STUDIES

In previous chapters, characterization of drag reducing surfactant systems has been presented. On the application side, even though surfactant drag reducers are potentially effective, some questions remain to be answered before large scale industrial applications are feasible. These questions include how to separate surfactants and counterions from the solutions if this becomes necessary, what is the long term stability, and what are the corrosion effects and the toxicity. In this chapter, results from small scale laboratory investigations on separation and on stability will be presented.

6.1 Separation of Cationic Surfactant and Counterion

Even though the surfactant counterion concentrations used in drag reduction are less than 5000 ppm, they may be high enough to kill fish if directly discharged into a river or lake due to their ability to reduce surface tension and affect fish gills' ability to obtain oxygen. On the other hand, large amount of surfactants may foul waste water processing systems. For practical applications, such as district heating or cooling systems, the total volume of the systems is usually very large. In the case of system cleaning, system breakdown and other emergency situations, the surfactant and counterion have to be separated from the
solution before the solution can be discharged into the sewer system. In the following sections, different separation methods are tested to separate surfactants from the solution.

6.1.1 Adsorption

The remaining surfactant and counterion concentrations after adsorption of Ethoquad T/13-50 (1700 ppm) / NaSal (1500 ppm) (ξ = 2.5) on various adsorbents are summarized in Tables 6.1 and 6.2. The concentrations were determined by methods described in Section 3.5.1.

<table>
<thead>
<tr>
<th>Ratio of Adsorbent to Surfactant (wt.)</th>
<th>Sigma Bentonite</th>
<th>Sigma Activated Carbon</th>
<th>Mineral Colloid B.P.</th>
<th>Darco G-60 Activated Carbon</th>
<th>Barnebey &amp; Sutcliffe Activated Carbon</th>
<th>Nucon International Activated Carbon</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5/1.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>&gt;600</td>
<td></td>
</tr>
<tr>
<td>3.0/1.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>&gt;700</td>
<td>&gt;600</td>
</tr>
<tr>
<td>3.9/1.0</td>
<td>0</td>
<td>410</td>
<td>0</td>
<td>280</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.9/1.0</td>
<td>0</td>
<td>360</td>
<td>0</td>
<td>260</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.9/1.0</td>
<td>0</td>
<td>270</td>
<td>0</td>
<td>125</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.0/1.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>&gt;600</td>
<td>&gt;600</td>
</tr>
<tr>
<td>7.0/1.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>&gt;600</td>
</tr>
<tr>
<td>7.8/1.0</td>
<td>0</td>
<td>21</td>
<td>0</td>
<td>1.3</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 6.1 Remaining cationic surfactant concentration (ppm) in solution after the adsorption of Ethoquad T/13-50 + NaSal (1700 ppm/1500 ppm).

For the cationic surfactant, both Sigma Bentonite and Mineral Colloid B.P. do an excellent job (Table 6.1). The remaining surfactant concentration for both adsorbents is very close to zero. The lowest ratio of adsorbent to surfactant tested was 3.9:1 (wt).

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Lower ratios may also do the job. For Sigma Activated Carbon and Darco G-60 Activated Carbon, the non-adsorbed surfactant concentration decreases with increasing ratio of adsorbent to surfactant. When the ratio reaches 7.8 to 1, the concentration of non-adsorbed surfactant is 21 ppm and 1.3 ppm for the two activated carbons, respectively.

We also tested two other activated carbon samples, Barnebey & Sutcliffe Activated Carbon and Nucon International Activated Carbon. Neither of them was suitable for adsorbing Ethoquad T/13-50 from solution. The remaining concentration of surfactant in both cases is higher than 600 ppm at any ratio of adsorbent to surfactant from 1.5:1.0 to 7.0:1.0. The activated carbon from Nucon International Inc. did not mix with the solution even with rigorous mixing. The poor results for the Barnebey & Sutcliffe sample may be because of its large particle size.

<table>
<thead>
<tr>
<th>Ratio of Adsorbent to Surfactant (wt.)</th>
<th>Sigma Bentonite</th>
<th>Sigma Activated Carbon</th>
<th>Mineral Colloid B.P.</th>
<th>Darco G-60 Activated Carbon</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.9/1.0</td>
<td>925</td>
<td>745</td>
<td>875</td>
<td>510</td>
</tr>
<tr>
<td>4.9/1.0</td>
<td>920</td>
<td>625</td>
<td>1040</td>
<td>355</td>
</tr>
<tr>
<td>5.9/1.0</td>
<td>930</td>
<td>450</td>
<td>1045</td>
<td>375</td>
</tr>
<tr>
<td>7.8/1.0</td>
<td>955</td>
<td>295</td>
<td>1100</td>
<td>290</td>
</tr>
</tbody>
</table>

Table 6.2 Remaining NaSal concentration (ppm) after the adsorption of Ethoquad T/13-50 + NaSal (1700 ppm/1500 ppm).

The concentration of NaSal remaining in the solution after adsorption was higher than 250 ppm in all cases (Table 6.2). This is because the excess NaSal in the solution ($\xi = 2.5$) is not associated with the surfactant molecules which form micelles. Therefore it
does not separate with the surfactant but is free in the solution. Sigma Bentonite and
Mineral Colloid B.P. which adsorb the surfactant very well, do not adsorb NaSal well.
The remaining concentration of NaSal is around 900-1100 ppm in both cases. The two
activated carbons in Table 6.2 at a high ratio of adsorbent to surfactant (7.8/1.0) both do a
good job of removing surfactant and a fairly good job of recovering NaSal. In both cases,
the concentration of remaining NaSal is around 290 ppm. We chose the 1500 ppm NaSal
solution for our separation studies as it represents the most difficult separation. In our low
temperature drag reduction tests, however, good results were also obtained at 900 ppm
NaSal. Separation for the 900 ppm NaSal solution should be easier to accomplish.

In conclusion, adsorption is a feasible method to separate the cationic surfactant from the
solution. The contact time is short, the required devices are just a mixer and a simple
filtration system to separate the adsorbent at the end of the adsorption, and the operation
is quite simple. It is also able to treat large quantities of solution, such as 3000 gallon
solutions, if a suitable tank with a mixer is available. With activated carbon the
quaternary surfactant and NaSal can be adsorbed simultaneously but the NaSal adsorption
is incomplete. Since removal of NaSal by adsorption on activated carbon is not complete,
other separation techniques for the counterion following adsorption of the cationic
surfactant were studied, namely ultrafiltration and reverse osmosis. A drawback to
adsorption is that the surfactant may not be recoverable from the adsorbent. The
separation of isopropyl alcohol present in some quaternary surfactants was not studied. It
would probably be captured by the activated carbon.

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6.1.2 Ultrafiltration

Before selection of a membrane for ultrafiltration, a simple experiment called a "dead end" test was carried out. In the "dead end" test, the solution is pushed by high pressure through a membrane and it is the only way the solution can go. Large molecules are retained by the membrane and small molecules go through. The results for "dead end" tests are given in Table 6.3, where UF nK represents ultrafiltration membrane with MWCO (Molecular Weight Cut Off) of nK, i.e., molecules with molecular weight of n*1000 and higher will not be able to go through the membrane.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>UF 10K</th>
<th>UF 30K</th>
<th>UF 100K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Filtrate Concentration (ppm)</td>
<td>11</td>
<td>22</td>
<td>67</td>
</tr>
<tr>
<td>Filtrate Flow Rate (ml/min)</td>
<td>0.04</td>
<td>0.23</td>
<td>0.16</td>
</tr>
</tbody>
</table>

Table 6.3  Cationic surfactant concentration in the filtrate for "dead end" ultrafiltration of Ethoquad T/13-50 + NaSal (1700 ppm/1500 ppm) (ΔP = 40 psi).

The multiple values in Table 6.3 represent changes of the values with time. Times ranged from 6 minutes to 30 minutes. In the "dead end" tests, the concentration and the flow rate of the filtrate changed with process time except in the UF 10K case. As the process continued, a gel layer was formed above the membrane. The surfactant concentration in the gel layer was much higher than the original feed concentration. This layer of gel resisted the flow of filtrate through the membrane so that the flow rate of the filtrate
decreased with time. The gel layer was also responsible for the increase of concentration in the filtrate.

Based on these results, ultrafiltration membranes with MWCO of 10K and 100K were tested in Cross-Flow-Modules ultrafiltration (see Section 3.5.3).

The results of the ultrafiltration tests are summarized in Figs. 6.1 to 6.3. The pressure difference between the two sides of the membrane was kept at 20 psi. The feed flow rate was kept at 40 L/hr.

Fig. 6.1 shows that for both the 10 K and the 100 K membrane, the flow rate of the permeate was constant. A linear fitting can be run on all three curve and an excellent linear fitting is found for each of them (Table 6.4). These constant flow rates were maintained for the following reasons. First, the high flow rate of feed (40 liters/hr) and the "Cross-Flow-Modules" used both minimize and even eliminate the formation of a gel layer, which usually decreases the flow rate greatly. Second, the running time was relatively short, only a maximum of 17% of the feed passed through the membrane in this time frame. That means the concentration of the feed didn't increase very much. The concentration of the feed is an important factor affecting the permeate flow rate. Comparing the slopes of the three lines of Fig. 6.1, the flow rate of the permeate for the 100 K membrane is over 2.5 times that of the 10 K membrane (see also Table 6.4). And for the 100 K membrane, the flow rate for a solution with 750 ppm NaSal ($\xi = 1.25$) was
Figure 6.1 Volume of permeate versus time for ultrafiltration of Ethoquad T/13-50 (1702 ppm) / NaSal with different membranes and NaSal concentrations.
Figure 6.2  Cationic surfactant concentration in permeate in ultrafiltration of Ethoquad T/13-50 (1702 ppm) / NaSal with different membranes and NaSal concentrations.
Figure 6.3 NaSal concentration in permeate in ultrafiltration of Ethoquad T/13-50 (1702 ppm) / NaSal with different membranes and NaSal concentrations.
Table 6.4  Ultrafiltration flow rate of Ethoquad T/13-50 (1702 ppm) / NaSal with different membranes and NaSal concentrations.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>10K</th>
<th>100K</th>
<th>100K</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaSal Concentration (ppm)</td>
<td>1500</td>
<td>1500</td>
<td>750</td>
</tr>
<tr>
<td>Flow Rate (L/hr)</td>
<td>0.097</td>
<td>0.25</td>
<td>0.40</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.9999</td>
<td>0.9998</td>
<td>0.9954</td>
</tr>
</tbody>
</table>

higher than that of a solution with 1500 ppm ($\xi = 2.5$), which may be due to the higher viscosity for the 1500 ppm NaSal solution. However, the flow rates are very low for all cases. For example, for the 100 K membrane, the flow rate is 0.25 liters/hr for the 1500 ppm NaSal solution, or the flux is 35 liters/hr m$^2$. To treat 3000 gallons of solution with a cartridge having a membrane area of 6 m$^2$, if we assume that the feed concentration doesn't affect the effluent rate, it would take about 53 hours. Actually a much longer time will be needed as the speed will decrease very significantly as the solution becomes more and more concentrated. Other factors, such as possible failure of the membrane during the operation, also have to be taken into consideration.

Fig. 6.2 shows that for the 10 K membrane, the concentration of Ethoquad T/13-50 in the permeate is as low as 10 ppm but, as noted, the flow rate of the permeate is too low to be put to practical use. The 100 K membrane separates the cationic surfactant very well at the beginning of the operation. Its operation is not stable, however. In some cases, the concentration of the surfactant in the permeate was as high as 200 ppm, which means that only 88% of the cationic surfactant in the feed was separated.
The amount of salicylate in the permeate depends on the excess salicylate present. We can see from Fig. 6.3, that the concentration of NaSal in the permeate didn’t depend on the membrane used, it only depended on the concentration of the feed. When a feed of 1500 ppm NaSal was used, 700-800 ppm NaSal came out in the permeate. For the 750 ppm NaSal feed, only 300 ppm NaSal was present in the permeate. This reflects the large excess concentration of NaSal unbound to the micelle. In contrast to the separation of the quaternary surfactant the concentration of the NaSal in the permeate didn’t change with operation time for both membranes.

In conclusion, the UF membrane can effectively separate the cationic surfactant with the smaller size membrane. But even for the large pore size membrane, the flow rate of the permeate is too low to treat large amounts of the solution and this membrane does not separate excess NaSal effectively. The general advantages of using ultrafiltration are that the operation can be continuous, and the surfactant can be recovered.

6.1.3 Reverse Osmosis

Permeates from reverse osmosis for the 900 ppm sodium salicylate solutions without surfactant were analyzed (see Section 3.5.1). It was found that the NaSal concentration in the permeate ranged from 20 ppm to over 200 ppm of NaSal. However, there were some problems with the analyses. As mentioned earlier, a spectrophotometer is used to analyze the concentration of the surfactant and counterions. In the reverse osmosis experiments, the resulting solution was red in color. Because the analysis method was calibrated using
clear solution, the analysis results may not be valid for solutions which are different in color from the calibration solution. Checking the Merck index, it was found that the NaSal reacts with even a trace of iron ion to form some red material.

It was generally concluded that reverse osmosis may be able to separate the sodium salicylate but further study is needed. Also a new analysis method independent of sample color needs to be developed.

6.2 Drag Reduction Stability of Cationic Surfactant Systems

6.2.1 Loss of Drag Reduction

A continuous long term drag reduction test was performed in the iron pipe loop described in Section 3.2. The solution used in the test was 2300 ppm Ethoquad T/13-50 with 2000 ppm NaSal. Drag reduction was above 80% for about 27 days and then it dropped to near zero in one day (Fig. 6.4).

In other different flow systems without iron pipes, it had also been observed that drag reduction of the same solution was lost after three days to forty days depending on the set-up of the system [Gasljevic, 1995]. In a small volume flow system using a turbine pump, which had not been in service for a year prior to the test, drag reduction was lost in three days. In a 40 gallon flow system using a centrifugal pump, drag reduction lasted as long as 40 days [Gasljevic, 1995]. The loss of drag reduction was also observed for
Figure 6.4 Drag reduction test for Ethoquad T/13-50 (2300 ppm) / NaSal (2000 ppm). Drag reduction was lost on day 27.
Habon G (500 ppm) solution and for a zwitterionic surfactant system (see Section 5.1.5) in the flow system described in Fig. 3.1.

To clarify if this loss of drag reduction is due to mechanical effects or chemical effects, further experiments were designed and performed. Gasljevic [1995] showed that this loss is neither caused by mechanical shear nor by exposure to air. However, he showed that intensive mixing of air into the solution did cause loss of drag reduction in 10 days of circulation. However, this effect is significant only when there is considerable air mixed in the solution. Mere contact of the solution with air has no effect on drag reduction.

**6.2.2 Effect of Adsorption**

Thus there must be some chemical interaction between the fluid and the flow system hardware which affects the formation of rod-like micelles and the micellar network structures needed for drag reduction. These interactions may either remove surfactant molecules and so decrease the surfactant concentration below the second critical micellar concentration (CMC₂), or increase the CMC. In either case, micelles will fail to form or formed micelles will be destroyed leading to loss of drag reduction. First, the effects of possible adsorption of surfactant molecules on the walls was investigated.

A drag reduction test was performed in the drag reduction system described in Fig. 3.3 (Section 3.2). The system had no contact with surfactant prior to the test. The test started with low surfactant and NaSal concentrations. Then the concentrations were increased step-wise. Concentrations and drag reduction were measured.
It was observed that the color of the solution changed from clear to yellow immediately after the filling the system with the surfactant solution. It should be noted that with water running in the system, there was no visible color. The system is built with new iron pipes, which were rusty in nature, and water could wash little rust from the wall. The surfactant solution, however, appeared to be able to wash the rust away from the wall. A simple test was performed in the lab. A piece of rusty carbon steel was immersed in a static surfactant / NaSal solution. After a while, all rust was removed from the part surface and clean metal surface was exposed. The solution became discolored by rust. No more rust was deposited on the part while more and more rust became suspended in the solution. Thus it can be concluded that surfactant molecules are able to attach to the rust particles and keep them suspended in the solution.

After rust was removed from the carbon steel walls of the flow system, the wall was still able to adsorb surfactant molecules. This was confirmed by concentration measurements (see Section 3.5.1). Samples were taken when the system was running and concentration measurements were performed on samples with sufficient mixing such that the measured concentrations represent those of the flowing solutions in the system. With continuous monitoring of the concentrations, the difference between the amount added into the system and the bulk concentration, i.e., the amount adsorbed by the wall plus any loss, could be plotted against the total amount added (Fig. 6.5). It can be seen that the amount of surfactant adsorbed to the wall has a saturation level. Adsorption increased rapidly as
Figure 6.5  Cumulative amount of surfactant and NaSal lost in flow system for the Ethoquad T/13-50 / NaSal system with step-wise increased total concentrations.
surfactant was added but the total adsorbed amount increased only slightly with further addition of the surfactant and reached a plateau. This is a typical adsorption isotherm. The loss of the NaSal was less than 10% of the total amount added. This much NaSal may be held by surfactant molecules adsorbed on the wall. The molar ratio of the adsorbed NaSal to the surfactant adsorbed on the wall is 0.5:1 to 0.7:1.

The surface area of the wall in the system can also be calculated. Then the adsorption densities of surfactant and NaSal on the wall, if all materials lost are assumed to be adsorbed by the wall, can be plotted against the total concentration (Fig. 6.6). Again, there is a plateau for the cationic surfactant adsorption. However, if these adsorption densities are compared with the results of other researchers on the adsorption of surfactant on metal oxides [e.g. Colic, 1995], it can be found that the densities here are three orders of magnitude higher. The discrepancy must come from the surface area, i.e., in addition to the internal wall surface, there are other surfaces adsorbing surfactant molecules as well. One must conclude that there is certain amount of surfactant adsorbed by rust particles and they are not moving with the fluid and have settled down somewhere in the system.

During the field test carried out in the Czech Republic, Pollert et al. [1994] increased the surfactant concentration from 100 ppm to 1000 ppm in ten incremental steps. They found that there was a big difference between the concentration based on the amount added and the measured concentration in the system. The difference was about 600 ppm for most
Figure 6.6 Adsorption density based on total amount lost in the system and the wall area of the flow system for the Ethoquad T/13-50 / NaSal system. Total concentrations were increased step-wise.
parts of the whole test, similar to what we found in this test. The loss was attributed to adsorption on the wall. Drag reduction was observed soon after the first dosing though that was short-lived due to low effective concentration. At higher concentrations, drag reduction was stable despite the loss. Thus, it can be concluded that the adsorption of surfactants on the wall should have no effect on drag reduction if the total concentration of surfactant is high enough to saturate the wall and rust in the system.

6.2.3 Effects of Fe(OH)₃

As the wall of the flow system can only remove a limited amount of the surfactant from solution, but drag reduction is lost after some time period, then there must be some materials in the flow which interact chemically or physically with the surfactant.

In the flow system (Fig. 3.3), most of the material is iron pipe and fittings. Also, copper tubing, PVC pipes and some rubber o-rings are present in the system. PVC is generally inert to this dilute surfactant solution. Rubber o-rings have very little surface area and they should not have a large negative impact on drag reduction. The remaining two materials are iron and copper.

Obviously, the large quantity of rust from iron pipes plays an important role. Rust is not likely to affect the solubility of the solution. Therefore it must be removing or destroying surfactant and/or NaSal molecules. There are probably two different mechanisms for the
effects of rust on surfactants and NaSal. First, it adsorbs surfactant molecules and second, free ferric ions in solution may react with them.

The surfactant molecules can be easily adsorbed by rust particles. According to a lab test, when the molar ratio of rust to surfactant reaches 3:1, 79% of surfactant in a 5 mM (about 2300 ppm) solution is adsorbed on the rust particles (Fig. 6.7). However, the amount of surfactant adsorbed to the rust can hardly be quantitatively determined as it depends on the total surface area of the particles rather than on the amount of the material. For rust under turbulent flow, the particles can be very fine due to the strong dispersing power of the flow, but they may also aggregate into larger particles and settle down somewhere in the system. As found in a study by Colic [1995], the stability and the particle size of metal oxides are greatly dependent on the surfactant concentration in the suspension. For the same reason, the particle size of metal hydroxides in the drag reducing surfactant solution also varies with the relative amount of surfactant. Thus, the interaction between the surfactant molecules and the rust particles is a complex one.

To better understand the adsorption behavior of rust particles toward the surfactant in drag reduction systems, the concentration of surfactant was monitored for the drag reduction test shown in Fig. 6.4. Samples were taken under flow condition and precautions were taken to exclude any solution from the dead volume. Then concentration measurements were performed in two different ways. The first measurements were performed on the samples with good mixing and the results from these measurements
Figure 6.7  Adsorption of Ethoquad T/13-50 (5 mM or 2300 ppm) / NaSal (12.5 mM or 2000 ppm) by Fe(OH)$_3$. 

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represent the total amount of surfactant in the bulk solution since the rust particles are all suspended in the flow and any surfactant adsorbed by them is included in the measured concentrations (Fig. 6.8, "With Suspended Rust" curve). Before the second measurements were taken, the samples were allowed to sit for some time to let rust particles settle to the bottom of the sample bottle as much as possible and then concentration measurements were performed on the top layer of the sample. The results from the second measurements represent surfactant concentrations in solution excluding the portion of surfactant adsorbed by settled rust particles (Fig. 6.8, "Rust Partially Settled" curve). The reason that no separation force stronger than gravity was applied to settle rust particles was to avoid removal of adsorbed surfactant from the rust particles. Initially, complete settling of the rust particles was possible since a clear top solution was obtained. However, at a later point in the drag reduction experiment (see Fig. 6.4), a stable suspension containing some of the rust particles in the surfactant solution was formed and the top layer was no longer clear. The rust particles in suspension didn't settle down after two months of storage. For these samples surfactant concentration included that part of the surfactant adsorbed to the suspended rust particles.

The surfactant concentration in the bulk solution is relatively high at all times (Fig. 6.8, "With Suspended Rust" curve), even after drag reduction was lost (refer to Fig. 6.4). The surfactant concentration excluding the surfactant adsorbed by the settled rust particles first quickly dropped to near zero. Later when a stable suspension was formed, the surfactant concentration was higher since part of the surfactant was adsorbed by the
Figure 6.8 Sulfactant concentration change in the drag reduction test shown in Fig. 6.4. Drag reduction was at a high level before it dropped to near zero in day 27. Concentrations were measured with and without separating rust.
suspended rust particles (Fig. 6.8, "Rust Partially Settled" curve). The increase is due to the increase in the amount of the rust particles. The more stable rust suspension was the result of the size change of the particles (smaller particles are more easily suspended) caused by the interaction with the surfactant. As mentioned above, this interaction was also reported by Colic [1995] on surfactant/metal oxide systems. At the point just before the stable suspension was formed, the surfactant concentration after rust particles were settled was close to zero. Surfactant concentration with complete removal of rust particles can not be measured for the suspended rust because any forceful removal would affect the adsorption of surfactant by the rust particles. However, surfactant molecules are probably all held by the rust particles, as denoted by the dash line in Fig. 6.8. This means that the total surface area of the rust particles in the system at and after that point of time is large enough to adsorb all the surfactant molecules. However, drag reduction remained at a high level over 27 days (see Fig. 6.4). Thus, there must have been sufficient surfactant molecules in the bulk solution to form micelles. This result suggests that there is a dynamic competition between the micelle formation process and the adsorption process. Even when the adsorption capacity is large enough to hold all surfactant molecules, enough surfactant molecules can still desorb from the rust particles to form a significant number of micelles under turbulent flow conditions. Thus, the concentration of surfactant available for micelle formation is between the "With Suspended Rust" curve and the "Rust Completely Settled" curve (Fig. 6.8).
There may be a chemical reaction between the rust and the surfactant or salicylate. Rust under wet conditions in the presence of oxygen is usually in the form of Fe(OH)$_3$ [Fontana, 1986]. Iron oxides may also coexist, but they are usually more stable than hydroxides. Thus, only the hydroxide is of interest here. The ferric hydroxide can be dissolved to a very limited extent in water based on its very small solubility product constant, $10^{-40}$ [Manahan, 1986]. The Fe$^{3+}$ ions can strongly react with NaSal with an equilibrium constant, $10^{28}$ [Perrin, 1958; Martell and Smith, 1977]. However, from a chemical equilibrium calculation, at the conditions in the system, reaction between the free ferric ion and salicylate is insufficient to move the equilibrium between the ferric hydroxide and the ferric ions to any significant extent, i.e., the rust is not being dissolved by salicylate. Thus, the rust should have no effect on salicylate.

Uncertainty remains, however, regarding interactions between ferric ions and the surfactant. This surfactant has three hydroxyethyl groups on its head group and an acetate ion as anion. A series of qualitative experiments were designed and performed to check if reactions occur and, if so, of what type. The first experiment was to mix equal volumes of 50% Ethoquad T/13-50 and 0.1 M FeCl$_3$. The color of the mixture changed to dark yellow and some precipitate was formed. Keeping in mind that each surfactant molecule contains an acetate ion, a 6.5% acetic acid solution was prepared (the concentration corresponds to the acetate ion concentration in the 50% surfactant). Again, this solution was mixed in equal volume with 0.1 M FeCl$_3$. As expected, the color only lightened due to the dilution. Thus, the acetate ion is not responsible for any reaction. To further check
if the hydrogen-carbon chain or other groups react with metal ions, a similar experiment was performed with a CTAB ($C_{16}H_{33}-N(CH_{3})_{3}Br$) solution. There was no color change except the dilution effect. Thus, there is a possibility that there is a chelating reaction between the ferric ions and the three hydroxyethyl groups in the head group of the surfactant.

The chemical equilibrium constant for the reaction between Fe$^{3+}$ ions and surfactant remains unknown. However, again, due to the very small solubility product constant of Fe(OH)$_3$, this reaction is not likely to remove a significant amount of surfactant from the micelles.

In summary, the negative effect of rust on drag reduction is from its adsorption of surfactant, not from chemical reactions by free Fe$^{3+}$ ions.

6.2.4 Effects of Cu(OH)$_2$

In addition to the observation of the loss of drag reduction in the iron pipe flow system as shown in Fig. 6.4, it has also been repeatedly observed that drag reduction was lost in flow systems without any iron parts [Gasljevic, 1995]. In fact, in a separate test, when drag reduction was lost quickly in a flow system with a high pressure pump, the loss of drag reduction was attributed to mechanical shear [Gasljevic, 1995]. However, it has been shown that mechanical shear doesn’t cause permanent loss of drag reduction. All these high pressure pumps are made of brass (alloy of copper and zinc). The solution after
losing drag reduction in these systems is usually greenish, which is the characteristic
color of copper compounds. Thus copper compounds may play an important role in the
loss of drag reduction of surfactant solutions.

The product of copper corrosion under wet condition is mostly copper hydroxide
[Fontana, 1986], even though other copper compounds may coexist. In the drag reduction
experiment shown in Fig. 6.4, Cu(OH)$_2$ was not observed as the light green/blue color of
Cu(OH)$_2$ could be masked by the brown color of the rust. To study the effect of Cu(OH)$_2$
on drag reduction, a separate drag reduction test was carried with fresh 2300 ppm
Ethoquad T/13-50 and 2000 ppm NaSal solution (Fig. 6.9). Drag reduction was stabilized
at above the 80% level after one day. Then 5 mM Cu(OH)$_2$, prepared by mixing CuCl$_2$
with a stoichiometric amount of NaOH, was added to the system. As NaCl has little effect
on the rheological properties of this surfactant system, it should be expected that it has no
effect on drag reduction as well. This test should check the effect of Cu(OH)$_2$ on drag
reduction. Drag reduction dropped to a lower level immediately upon the addition but it
soon recovered to about the 70% level. Then over a period of 12 hours, drag reduction
dropped to near zero. This experiment showed that the presence of Cu(OH)$_2$ is fatal to
drag reduction. The recovery of drag reduction by adding EDTA shown in Fig. 6.9 will be
discussed in Section 6.2.5.2.

To better understand the effects of copper hydroxide on this surfactant system, Cu(OH)$_2$
was prepared as described above and different amounts were added to the Ethoquad T/13-
Figure 6.9 Drag reduction change of Ethoquad T/13-50 (2300 ppm) / NaSal (2000 ppm) solution with addition of Cu(OH)$_2$ and then by EDTA.
50 (5 mM) / NaSal (12.5 mM) system. Concentrations of both surfactant and NaSal were measured after the solid copper hydroxide was separated (Fig. 6.10). It is interesting to note that both concentrations were decreased significantly. These decreases in concentration are due to two different effects, i.e., adsorption and possible chemical reactions.

When preparing Cu(OH)$_2$ in the lab, it was observed that the solid particles are very fine such that the solution looks cloudy. The settlement of the solid particles took a much longer time than the ferric hydroxide. Thus, copper hydroxide may have a much larger adsorption capacity than ferric hydroxide in the same amount. Then, the loss of surfactant may be mostly due to the adsorption while there may be other reasons for the loss of NaSal.

In addition to the adsorption effect, copper hydroxide may also react with the surfactant and/or NaSal. In analyzing the chemical reactivity of Cu(OH)$_2$, one should keep in mind that this hydroxide has a much larger solubility product constant, $10^{-18}$, compared with Fe(OH)$_3$ [Manahan, 1986].

It has been found that there is a reaction between Cu$^{2+}$ and NaSal with an equilibrium constant $10^{-2.8}$ [Perrin, 1958; Martell and Smith, 1977]. Combining the solubility product constant of Cu(OH)$_2$, $10^{-18}$, it seems that the copper hydroxide can not react with salicylate to any significant extent. However, it has been reported that there is a
Figure 6.10 Concentration change of surfactant and counterion with addition of different amounts of Cu(OH)$_2$ for the Ethoquad T/13-50 (5 mM) / NaSal (12.5 mM) solution.
dehydration reaction between copper hydroxide and sodium salicylate [Jacobson, 1949; Wolff, 1901]:

\[
\text{Cu(OH)}_2 + 2 \text{HO-C}_6\text{H}_4\text{-COONa} \rightarrow \text{CuO}_2(\text{C}_6\text{H}_4\text{-COONa})_2 \downarrow + 2 \text{H}_2\text{O}
\]

The product of this reaction is in crystal form, and it will settle down. It is also noted that one mole of copper hydroxide can react with two moles of sodium salicylate. However, according to our measurements, with the addition of 15 mM of Cu(OH)_2 to a solution with 12.5 mM NaSal, there was still about 3.7 mM of NaSal left. This means this reaction is not complete under the conditions we studied.

To clarify the interaction of copper ions with this particular surfactant. A series of lab tests were performed with copper ions and the surfactant, similar to those described in the last section with ferric ions. When 0.1 M CuCl_2 solution was added to the Ethoquad T/13-50 solution (without NaSal), the blue color of the CuCl_2 solution was changed to dark green and some precipitation was observed. There was no color change if CuCl_2 was added to CTAB (C_{16}H_{33}-N(CH_3)_3Br) solution or to acetic acid solution. Thus, as in the case of iron, the results show that the three hydroxyethyl groups in this surfactant may react with positively charged copper ions. The extent of this reaction is determined by the relative value of the equilibrium constant of this reaction and the solubility product constant of Cu(OH)_2. No quantitative analysis can be done before the equilibrium constant of this reaction is determined. However, qualitatively, one would expect this reaction can, to a larger extent, take surfactant molecules away from micelles.
In conclusion, because of the presence of copper hydroxide in this surfactant solution, concentrations of both surfactant and salicylate are reduced. The reaction between copper hydroxide and salicylate forms insoluble crystals and reduces the effective concentration available to form micelles. In turn, this solid sludge-like material, along with copper hydroxide particles, may adsorb surfactant molecules to a great extent. In addition, reaction between surfactant and copper hydroxide can not be excluded at this point.

6.2.5 Recovery of Drag Reduction

As the reasons for the loss of drag reduction have been clarified, some methods to recover drag reduction can be worked out and tested. In this section, several methods, including replenishment, chelating of metal ions and removing of metal hydroxides, are discussed.

6.2.5.1 Effect of Replenishment on the Drag Reduction

For a surfactant solution which had lost its drag reducing ability in the flow system, drag reduction tests were continued by adding either surfactant or NaSal. Drag reduction was measured. Typical drag reduction results are presented in Fig. 6.11. During the test, either surfactant concentration or salicylate concentration was increased by 1000 ppm, as described by the step-like lines.

It should be noted that at the beginning of this test, there was already a large quantity of rust in the solution. Drag reduction became unstable, i.e., it lasted only several days. It can be seen from Fig. 6.11, that drag reduction could always be regained with the addition
Figure 6.11 Drag reduction recovery of Ethoquad T/13-50 / NaSal solution with the addition of surfactant or NaSal. Concentrations of either surfactant or salicylate were increased 1000 ppm step-wise in the test. In the last step, no drag reduction was recovered after addition of 1000 ppm NaSal. Then 1000 ppm surfactant was added.
of surfactant. The addition of NaSal could recover drag reduction when rust was present in relatively small amounts. The drag reduction recovery lasted a shorter time than by surfactant addition. The addition of NaSal didn't have any effect when the amount of rust was high. Drag reduction regained by replenishment is always somewhat lower than the level in previous steps, which agrees with what Gasljevic [1995] observed.

With the addition of surfactant, micelle formation is again possible as the surfactant concentration exceeds the critical micellar concentration. Thus drag reduction was regained. However, with more and more rust formed in the system and also possible changes in the rust particle size due to the increase in free surfactant concentration, the adsorption become dominant again and the available surfactant concentration was reduced to below the critical value for formation of rod-like micelles.

The addition of NaSal actually reversed the adsorption process which was taking surfactant molecules away from the micelles. As confirmed in the experiments, there was always a very high portion (90%) of the total added NaSal available in the solution. However, when the adsorption of surfactant reached a certain level, the addition of NaSal could no longer remove surfactant molecules from the rust. Only the addition of more surfactant to the system could form micelles to give drag reduction.

The general conclusion is that the replenishment of surfactant can always recover drag reduction but to a lower level.
6.2.5.2 Chelating Process to Remove Metal Ions

Since free metal ions are fatal to drag reduction due to their reactivity with the surfactant and the counterion, a method was sought to remove these metal ions and to recover drag reduction.

EDTA (ethylenediaminetetraacetic acid) is well known for its strong chelating ability with free metal ions. Even though a large amount of metal hydroxides, not free metal ions, exists in the solution, the addition of EDTA was tried to see if it could remove these hydroxides by shifting the chemical equilibrium between the hydroxides and the free ions.

In the surfactant solutions to which Fe(OH)$_3$ and Cu(OH)$_2$ had been added, certain amounts of disodium EDTA were added. It was observed that for solutions with Fe(OH)$_3$, with up to a 2:1 molar ratio of EDTA to Fe(OH)$_3$, Fe(OH)$_3$ was still present in the solution. However, for solutions with Cu(OH)$_2$, when the ratio of EDTA to Cu(OH)$_2$ reached 1:1, the solution was clear, i.e., all Cu(OH)$_2$ was decomposed. Furthermore, viscoelasticity was also recovered.

This can be easily explained by chemical equilibrium considerations. Even though the equilibrium constant of the reaction between EDTA and ferric ion is as high as $10^{25}$, as mentioned above, the solubility product constant of ferric hydroxide is only $10^{-40}$. Therefore, EDTA can not shift the equilibrium between the ferric hydroxide and the ferric ions to decompose any significant amount of ferric hydroxide. Thus, even though any free
Fe$^{3+}$ present in trace amounts chelates with EDTA, Fe(OH)$_3$ can not be removed by EDTA. For Cu(OH)$_2$, the situation is much different as it has a much larger solubility product constant, $10^{-18}$, and the equilibrium constant of the reaction between EDTA and Cu$^{2+}$ is $10^{17.5}$ [Manahan, 1986]. Thus Cu(OH)$_2$ can be removed up to the available amount of EDTA, i.e., for a 1:1 and up ratio of EDTA to Cu(OH)$_2$, all of the Cu(OH)$_2$ can be removed.

For the drag reduction test shown in Fig. 6.4, EDTA was added after drag reduction was first lost. There was no drag reduction regained. This shows that the loss of drag reduction in this iron pipe system was caused by the iron rust, not by copper hydroxide.

Another drag reduction test was performed with fresh 2300 ppm Ethoquad T/13-50 / 2000 ppm NaSal solution (see Fig. 6.9). Drag reduction up to 80% was measured as expected. After the addition of 5 mM Cu(OH)$_2$, drag reduction was lost. Then, 5 mM EDTA was added to the system and drag reduction to 80% was immediately recovered and was stable at that level over seven days (the test was stopped while it was still drag reducing). This proves that the addition of EDTA causes recovery of drag reduction lost because of the presence of Cu(OH)$_2$.

6.2.5.3 Removal of Rust

While Cu(OH)$_2$ can be removed by addition of EDTA, the problem remains as to how to remove iron rust on line, i.e., without taking the solution out of the system.
One idea to remove the rust is to reduce it to ferrous hydroxide, and then, due to the larger solubility product constant of ferrous hydroxide, EDTA can be used to decompose it.

For the drag reduction test shown in Fig. 6.4, when drag reduction was first lost, EDTA was added and no drag reduction was regained, as mentioned in the last section. Then sodium hydrosulfite was added to the system. The color of the solution immediately changed to gray, which is the characteristic color of iron(II) compounds. Drag reduction was regained and reached a peak of 75% (first peak in Fig. 6.12). However, drag reduction was lost again after about eight hours as the color of the solution changed back to brown, which is the characteristic color of ferric compounds. This is due to the oxidation effect of oxygen. The color change of the solution to brown started from the interface of the solution and air. A repeat test was performed for the solution without drag reduction by adding EDTA and sodium hydrosulfite. Drag reduction was regained (second peak in Fig. 6.12) and lost in about same time period as in the first test. A lot of black/gray solid suspension was formed in the solution after the second test. Thus, this technique to remove rust could not provide long-term drag reduction recovery.

There are other methods to remove rust such as by filtration. However, as discussed earlier, surfactant molecules are adsorbed by rust particles. Thus, when the rust particles
Figure 6.12 Drag reduction recovery of the Ethoquad T/13-50 / NaSal solution with the addition of EDTA and sodium hydrosulfite. Drag reduction was lost in the iron pipe system (see Fig. 6.4). Time scale follows that in Fig. 6.4.
are separated by filtration, surfactant molecules attached to them are also removed and drag reduction can not be recovered.

Another method is to pre-treat the flow system with certain on-line cleaners, which are designed to remove rust before adding the surfactant and counterion. In fact, the surfactant solution itself may be a good cleaner to remove the rust.

Removal of rust from iron pipe systems is not a simple problem. Further investigation is needed.

6.2.6 Other Chemical Effects

It was observed that natural rubber and vinyl (garden hose) caused permanent degradation of the Ethoquad T/13-50 / NaSal solution [Gasljevic, 1995]. When even short sections of rubber hose or garden hose were present in the circulation loops, degradation of the solution was very fast. Synthetic rubber like butyl (the most common material for O rings) did not show degrading effects, at least in the case of the O rings which were abundant in the circulation systems. These effects also need further investigation.

6.2.7 Summary

Loss of drag reduction in an iron pipe flow system was investigated in this section. A series of drag reduction and chemical tests show that drag reduction by cationic surfactant systems may be lost after a certain length of time. This loss is mainly caused by the
adsorption of surfactant molecules on rust particles. For flow systems where copper hydroxide is present, drag reduction is lost quickly due to the chemical reaction between the surfactant and copper compounds.

Recovery of drag reduction was also investigated. Drag reduction can be recovered by adding surfactant or NaSal. However, addition of NaSal can only recover drag reduction for a short time (5 hours) when the amount of rust is not large and it fails to recover drag reduction if rust is present in large quantities. Addition of EDTA can recover drag reduction loss caused by copper hydroxide but it can not recover that caused by ferric hydroxide. If ferric hydroxide is reduced to ferrous hydroxide by addition of a reducing agent, addition of EDTA can recover drag reduction for a short time period (8 hours). These phenomena can be explained by chemical equilibrium considerations.

Even though the removal of ferric hydroxide is not simple, in any practical flow system, the rust problem should not be very serious. The formation of rust is proportional to the surface area of the flow system. Thus, the concentration of rust in the system is proportional to the surface area per unit volume. For circular pipes, surface area per unit volume is inversely proportional to the diameter. Thus, the rust concentration in large pipes would be much lower than that in small pipes. If drag reduction can last 27 days in the half-inch iron pipe system, as shown in Fig. 6.4, since the amount of the rust is proportional to the surface area / volume ratio of the flow system, then drag reduction should persist for about 110 days in a 2" iron pipe system and longer in a larger pipe.
system. In addition, in any practical flow system, some measures are always taken to reduce the corrosion rate, such as using corrosion inhibitors, cleaning the whole system periodically, deaerating the water, etc. Thus, in conclusion, the application of drag reducing cationic surfactant systems to practical flow systems is very promising in spite of their finite effective life time in rusting systems.
CHAPTER 7

CONCLUSIONS

Cationic surfactants with proper counterions are effective in drag reduction and show unique rheological and rheo-optical characteristics. The effectiveness of drag reduction and rheological properties are dependent on surfactant and counterion chemical structure and their concentrations.

Counterion structure is an important factor. Three isomeric counterions, 2-, 3- or 4-Cl-benzoate, have different effects on the rheological and drag reduction behaviors and on the microstructures of dilute solutions of a cationic surfactant, Arquad 16-50. The 2-Cl system has no drag reduction, low apparent extensional viscosity, no viscoelasticity and spherical micelles. This is because the hydrophobic chlorine resides in a hydrophilic environment. The chlorine in 4-Cl-benzoate counterion resides in the hydrocarbon phase of the Arquad 16-50 thread-like micelles. Thus, the system has a thread-like micellar network structure, is drag reducing over the temperature range of 20-70°C and has high apparent extensional viscosity at both 20°C and 30°C. The 4-Cl system is also viscoelastic.
The 3-Cl system, however, is unique. Since the chlorine group in 3-Cl-benzoate resides in the hydrophobic phase, the system is drag reducing over a temperature range, 30-50°C, narrower than the 4-Cl system. The 3-Cl system has high apparent extensional viscosity at 30°C. At 20°C, 3-Cl particles precipitate from solution at high shear or extensional rates, leading to loss of drag reduction and low apparent extensional viscosity. At 20°C, the 3-Cl system may have one of three different microstructures: thread-like micelles, vesicles or precipitation, depending on external forces. A stress induced precipitation phenomenon is observed. It is summarized in a schematic diagram proposed to describe microstructure transformations of a 3-Cl surfactant solution under different temperature and shear conditions.

The anion in the cationic surfactant also induces differences in rheological properties. The CTAB (5 mM) / NaSal (12.5 mM) system has higher shear viscosity and apparent extensional viscosity at low strain rates than the CTAC (5 mM) / NaSal (12.5 mM) system. This difference is probably due to the stronger binding ability of the Br⁻ ions to the positive cation compared to the Cl⁻. The industrial version of CTAC, Arquad 16-50 (with IPA), behaves similarly to the CTAC.

Both 4-Cl-benzoate and 2-OH-benzoate are counterions which can promote formation of thread-like micelles for cationic surfactants and thus surfactant systems with these two counterions are drag reducing and have high apparent extensional viscosity. However,
while the apparent extensional viscosities are the same at high extensional rate, the 2-OH-benzoate has much higher apparent extensional viscosities at low rates than 4-Cl-benzoate. It has also been observed that in drag reduction, the critical wall shear stresses for the 2-OH-benzoate system are greater than those for the 4-Cl-benzoate at low temperatures [Chou, 1991b]. This may be due to hydrogen bonding between micelles by hydroxy groups.

Viscoelasticity and apparent extensional viscosity increase with increasing alkyl chain length in the range of C14 to C18. However, the shear viscosities of C16 and C18 are significantly higher than those of C14 causing the ratio of apparent extensional viscosity to shear viscosity to decrease in the reverse order of that of the apparent extensional viscosity. This is due to the longer thread-like micelles formed in surfactant solutions with longer alkyl groups.

The rheology of drag reducing cationic surfactants also depends on counterion to surfactant ratio. Arquad 16-50 (5 mM) / NaSal and Ethoquad O/12 (5 mM) / NaSal were investigated at various counterion to surfactant ratios. The systems with ratios of 0.6 up to 2.5 are drag reducing, birefringent, viscoelastic and have high apparent extensional viscosity. At $\xi = 0.6$, the systems have at best modest drag reducing ability, low apparent extensional viscosity and small $N_1$ values which tend to vanish with increasing shear rates. When $\xi$ increases to 1, there is a large increase in drag reduction, apparent extensional viscosity and $N_1$, all of which reach a plateau. Flow birefringence data also
indicate that the $\xi = 1.0$ system has much higher birefringence and much lower extinction angle values than the $\xi = 0.6$ system. This means that the $\xi = 1.0$ system has longer thread-like micelles than the $\xi = 0.6$ system such that the anisotropy of the solution is larger. With further increase in $\xi$, the increase in drag reduction and $N_1$ is not as significant. For Arquad 16-50 systems, the apparent extensional viscosities at $\xi = 2.5$ are close to those at $\xi = 1.0$. However, for the Ethoquad O/12 systems, apparent extensional viscosities at $\xi = 2.5$ are surprisingly lower. This corresponds with cryo-TEM pictures, which show the micellar network density has little or no change when $\xi$ increases from 1.0 to 2.5 for Arquad 16-50 systems, but show the network density actually decreasing slightly for the Ethoquad O/12 systems.

Stress development is strongly counterion ratio dependent. There is no overshoot observed for $\xi = 0.6$ systems since either a very weak or no micellar network exists in the solution. Significant overshoot is observed for the $\xi = 2.5$ systems. For the $\xi = 1.0$ systems, overshoot is observed at high shear rate but not at low shear rate. At low counterion ratio ($\xi = 0.6$ and 1.0) and low shear rates, the stresses develop in two steps, i.e., stresses go through either an induction period or an initial plateau. At high shear rates, however, all stresses, even at low counterion ratio, reach a plateau in a single step. Thus, increase in the shear rate has a similar effect on micellar network formation as increase in the amount of counterion. For solutions at low counterion ratio ($\xi = 0.6$ and 1.0) and low shear rates, shear is needed to induce micellar network formation and
viscoelasticity as shown by the two-step stress development. High shear promotes
micellar network formation and thus has the same function as using a high ratio of
counterion. The solutions with higher than unity ratio are inherently viscoelastic in nature,
i.e., no shear is needed to induce network structure. These systems show high $N_1$ and
significant overshoot.

Overshoot is also shear rate dependent. Overshoots reach similar peak values when shear
rates exceed a critical values and show lower levels at lower shear rates. However,
overshoot peaks are observed at roughly equal reduced times, $(t \cdot \dot{\gamma})$.

Shear stress, first normal stress difference and flow birefringence of these surfactant
systems relaxes in two or more steps. A double exponential function can fit these data
well. The first step takes less than 10% of the time for the second step. The relaxation
time constants generally decrease with increasing shear rate and increase with counterion
to surfactant ratio up to $\xi = 1.0$. Excess counterion causes the relaxation time to decrease.
The reason for this is not clear although it has been suggested that the free salicylate ions
behave like a catalyst for a disentangling reaction. Thus, increase in the ratio, $\xi$, over
unity, has the same effect on relaxation time as increase in the shear rate.

Comparing three relaxation times of the surfactant systems, flow birefringence takes a
longer time to relax than the first normal stress difference, while both take longer times
than the shear stress. Birefringence, which is related to the anisotropy of the solution, is

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the most sensitive measurement. Both stress measurements are limited by the sensitivity of the transducers. The shear stress relaxes the fastest because of the rapid recoil of these highly viscoelastic surfactant solutions which generate stresses in the opposing direction. Extremely long flow birefringence relaxation processes were observed for Habon G solutions and for surfactants with hydroxynaphthoates as counterions.

Even though cryo-TEM pictures show crosslinked micellar networks for the surfactant systems, small amplitude measurements show no plateau for \( G' \), which is usually taken as indication of the existence of fully entangled networks. At high frequency, both \( G' \) and \( G'' \) surprisingly drop to zero. This may be due to inertial effects, which contribute significantly to results for low viscosity systems. Thus, small amplitude measurements for these drag reducing surfactant solutions are limited to frequencies below 30 to 60 rad/s depending on the surfactant system.

Two rheological properties have been suggested as responsible for drag reduction: first normal stress difference and extensional viscosity. \( N_1 \) doesn't correlate with drag reduction. Ethoquad O/12 (5 mM) / NaSal (12.5 mM), Ethoquad O/13-50 (5 mM) / NaSal (12.5 mM), Ethoquad T/13-50 (5 mM) / NaSal (12.5 mM) and Arquad S-50 (5 mM) / NaSal (12.5 mM) systems have similar drag reducing ability, but \( N_1 \) values vary over a wide range. Further, Arquad S-50 (5 mM) / NaSal (12.5 mM) has no \( N_1 \), while it is birefringent, drag reducing and has a thread-like micellar network. The system also shows no recoil and no stress overshoot with shear start-up, and thus does not appear to be
viscoelastic. However, the system has high apparent extensional viscosity, with apparent extensional viscosity-to-shear viscosity ratios above 100 at low temperatures. This study presents the first experimental evidence of correlation of high apparent extensional viscosity and thread-like micellar network microstructure with drag reduction for surfactant systems. Also this is the first example of a non-viscoelastic surfactant solution which is drag reducing. It is proposed that the special character of the highly unsaturated alkyl chain in S-50 is responsible for its unique rheological properties.

Even though apparent extensional viscosities measured are not steady state values, a correlation between drag reduction and high apparent extensional viscosity has been established. For all good drag reducing systems (DR% > 50%), at 20°C the ratios of apparent extensional viscosity to shear viscosity are all around 100-300, well above 3 which is the value for Newtonian fluids. For high temperatures, however, the apparent extensional viscosity measured by the RFX may appear negative, which may be caused by cavitation and inertial effects, and thus no clear correlation can be made. It is generally observed that apparent extensional viscosity decreases with increasing temperature, except for Habon G solutions, whose apparent extensional viscosity has little temperature dependence before it turns to be negative.

For some systems, apparent extensional viscosity increases with extensional rate to a peak and then decreases. Extensional thickening means the surfactant micelles are being extended, while extensional thinning means the micelles and the micellar network are
being deformed. Most of systems, however, show extensional thinning. This is partially caused by the fact that residence time of fluid elements in the extensional flow field decreases with increasing extensional rate and thus they have less time to reach steady state.

Three different types of constitutive equations have been tested to fit the rheological data of drag reducing surfactant systems. Both the linear Maxwell model and the quasi-linear Oldroyd Fluid B model can not describe drag reducing surfactant systems. The nonlinear Giesekus model, however, can fit data reasonably well for surfactant systems with a very small mobility factor. The model predicts very high apparent extensional viscosity at high shear rates, even for the Arquad S-50 (5 mM) / NaSal (12.5 mM) system, which is non-viscoelastic. This is strong evidence that extensional viscosity is responsible for drag reduction. Extensional viscosity causes drag reduction by suppression of formation and growth of turbulent eddies.

Drag reduction is the most sensitive indicator of a certain intrinsic property of these surfactant systems. When the magnitude of that property reaches a certain level, surfactant systems are drag reducing. While this property may be extensional viscosity, due to the limitations in extensional viscosity measurement techniques, a complete correlation can not be established.
A technique for transient flow birefringence measurements has been established. Relaxation of the extinction angle can be correctly measured. A new form of the stress-optical rule for simple shear flow has been proposed, which eliminates the extinction angle from equations such that the large error usually associated with the very small extinction angles of surfactant solutions is not introduced into the stress-optical coefficient calculation. However, the stress-optical coefficients are constant only for certain surfactant systems and are not constant for most surfactant systems. The general conclusion is that this rule is not applicable for dilute drag reducing surfactant systems.

Due to their rapid biodegradation and lower toxicity for marine organisms, nonionic and zwitterionic surfactants are potentially more useful in drag reduction applications than quaternary ammonium cationic surfactants, which have excellent drag reducing properties, but are less environmentally friendly. Nonionic surfactants are drag reducing at temperatures near their cloud points, which can be adjusted by addition of chemicals. Both shear and apparent extensional viscosities of nonionic surfactant solutions reach peak values at temperatures just below the cloud points. These data indicate that large structures are formed in nonionic surfactant solutions at temperatures around the cloud point. The zwitterionic surfactant tested is drag reducing but is not stable.

Two application problems were studied in this work. The first was separation of surfactant and counterion from aqueous solutions. Various separation methods, including adsorption, ultrafiltration and reverse osmosis, were tested. No single method will be able
to effectively and efficiently separate both surfactant and counterion. A two-step system will probably be needed. The system should include an adsorption step which removes surfactant. The recommended adsorbents are Bentonite (available from Sigma Chemical Co.) or Mineral Colloid BP (available from Southern Clay Products, Inc.). To separate NaSal, the reverse osmosis method appears to be the most promising.

The second problem is the long-term stability of drag reducing surfactant systems. It has been shown that drag reduction by cationic surfactant systems may be lost after a certain length of time. This phenomenon results from two primary effects: adsorption of the cationic surfactant on the wall and on corrosion byproduct particles both of which remove the surfactant from solution and lead to loss of drag reduction. In addition, the presence of copper compounds also leads to significant decreases in drag reduction. For the loss of drag reduction caused by copper compounds, the original level of drag reduction can, however, be fully recovered by the addition of chelating agents. The concentration of rust in any system is proportional to the surface area per unit volume. Thus, the rust concentration in large pipes, which are normally used in practical flow systems, should be much lower than that in small pipes. In addition, measures are always taken to reduce the corrosion rate (rust formation) in any practical flow system. Thus, in conclusion, the application of drag reducing cationic surfactant systems to practical flow systems is very promising in spite of their finite effective lifetime in small scale rusting systems.
CHAPTER 8

RECOMMENDATIONS

1. The position of counterions at the micelle-water interface and distribution of counterions in the solutions are not totally clear. It is recommended that NMR and zeta potential measurements be performed on surfactant systems with small step increases, such as 0.1, in counterion to surfactant ratio. The NMR measurements can determine counterion positions at the interface and the zeta potential measurements can determine at which ratio the micelles change their charge sign. The possibilities of peaks in rheological, drag reduction and microstructure density at this ratio should be explored.

2. Since the Giesekus model can fit rheological data reasonably well for drag reducing surfactant solutions, it is recommended that research be carried out to use this model to numerically simulate turbulent pipe flow by solving the equations of motion and the energy equation. The results should be examined against drag reduction data to see whether the model predicts drag reduction.
3. It is recommended that $N_2$ measurements be designed and performed on drag reducing surfactant solutions. The Giesekus model predicts very small $N_2$ values. If the model's prediction is correct, then it would be extremely difficult, if not impossible, to measure $N_2$ by mechanical means. If this is the case, an optical method is recommended. There are some reports in the literature describing flow birefringence systems which can incorporate $N_2$ into the stress-optical rule and thus evaluation of $N_2$ from birefringence measurements may be possible.

4. It is suggested that cryo-TEM pictures be taken under more controlled stress conditions. For Ethoquad T/13-50 and Ethoquad O/13-50 systems, vesicles were observed in some pictures but not in others. Similar repeatability problems existed for other systems also. Thus it is important to control the shear conditions before pictures are taken.

5. It is suggested other viscoelastic properties, including jet swelling and rod climbing, be examined for all drag reducing surfactant solutions. The jet swelling experiments can reach very high shear rates which may approach the shear rate range in drag reduction.

6. It is recommended that the current RFX rheometer be modified such that the measurement part of the system can be sealed and thus pressurized to avoid the cavitation problem. The apparent extensional viscosity measurements using the RFX should also be carried out with proper numerical analysis using the Giesekus model to
correct different effects on the output so that the correct or nearly correct apparent extensional viscosity can be obtained with the available instrument.

7. It is suggested that research be carried out in developing new extensional viscosity measurement methods for dilute surfactant solutions. A possible solution is to suspend the surfactant solution in an immiscible solvent and then use a fiber spinning test to measure extensional viscosity. Great creativity will be needed to develop a method that will work for dilute surfactant solutions.

8. The RMS 800 rheometer should be equipped with a more sensitive transducer such that steady shear and dynamic measurements on dilute surfactant solutions can be carried out at low shear rates. The RMS 800 should also be equipped with a water bath to control temperature such that $N_1$ data at different temperatures can be obtained.

9. With proper modifications of the RFX and RMS 800, rheological measurements on the so-called “gap phenomenon” of the Habon/NaSal system should be carried out. Similar counterion combinations with other surfactant systems should also examined for the “gap phenomenon.”

10. It has been observed in some rheological measurements using a cone and plate fixture that an instability occurs at high shear rates. A block of gel-like solution moves around the periphery of the fixture periodically. It is suggested that visualization
experiments using transparent cone and plate fixtures be carried out to study this effect. A periodic change in shear viscosity was also occasionally observed with the Couette cell. This should also be investigated.

11. It is recommended that small amplitude dynamic measurements be carried out to see if the moduli will drop to zero with a high viscosity solution. Correction for the inertial effects in dynamic measurements should be developed.

12. More extensive application studies should be carried out such that surfactant drag reduction can be extended to practical applications. A long term field test should be carried out to study various problems which may be incurred in practical applications, possible in an Ohio State District cooling system.

13. Efforts should be made to develop an effective one-component surfactant drag reducer, such as Habon G, which is no longer in production. The one-component surfactant may be more effective and will be more easily separated from the solution.

14. Lower toxicity cationic surfactant drag reducers should be developed without sacrificing drag reducing capability.

15. Extensive drag reduction studies should be carried out on nonionic and zwitterionic surfactant systems. If a nonionic or zwitterionic system which is as effective as
cationic surfactant system can be identified and developed, it will help to accelerate practical use of surfactant drag reducers.

16. It was reported in the literature that decyl ammonium bromide forms larger micelles than decyl trimethyl ammonium bromide. It is suggested that the decyl ammonium bromide / NaSal system be investigated for its rheological properties and drag reduction effectiveness.
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