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Drag reducing cationic surfactant solutions for district heating and cooling systems

Chou, Lu-chien, Ph.D.
The Ohio State University, 1991
DRAG REDUCING CATIONIC SURFACTANT SOLUTIONS
FOR DISTRICT HEATING AND COOLING SYSTEMS

DISSERTATION

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

By

Lu-chien Chou, B.S., M. S.

* * * * *

The Ohio State University
1991

Dissertation Committee:

Dr. Jacques L. Zakin
Dr. Richard N. Christensen
Dr. Harry C. Hershey

Approved by

Adviser
Department of
Chemical Engineering
To My Family
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VITA

July 1, 1958 ................................. Taipei, Taiwan, R.O.C.

1980 ........................................... B.S., National Chengkung University,
Tainan, Taiwan

1982 ........................................... M.S., National Taiwan University,
Taipei, Taiwan

1982-1984 ................................. Second Lieutenant Chemical
Engineer, CSF 203 Arsonal, Taiwan

1984-1985 ................................. Process Design Engineer, Dashu
Chemicals, Kaushung, Taiwan

1985-1986 ................................. Instructor, Kwan wu Junior College,
Taipei, Taiwan

PUBLICATIONS


Chou, L. -C., "A Study on the Reaction Kinetics, Rheology and Crystallization of Polyethylene Terephthalate and Related Copolymers", Master Thesis, National Taiwan University, Taiwan, 1982.

**FIELDS OF STUDY**

Major Field: Chemical Engineering

Studies in drag reduction using cationic surfactants
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<tr>
<td>ΔB</td>
<td>Velocity shift from Newtonian law of the wall (eq. 19)</td>
</tr>
<tr>
<td>C</td>
<td>Concentration</td>
</tr>
<tr>
<td>c_c</td>
<td>Critical concentration for drag reducing polymers to show a laminar-to-turbulent transition</td>
</tr>
<tr>
<td>D</td>
<td>Pipe diameter</td>
</tr>
<tr>
<td>DR</td>
<td>Drag ratio (eq. 3)</td>
</tr>
<tr>
<td>%DR</td>
<td>Percent drag reduction (eq. 4)</td>
</tr>
<tr>
<td>f</td>
<td>Fanning friction factor (eq. 2)</td>
</tr>
<tr>
<td>f_s</td>
<td>Fanning friction factor for solvent flow</td>
</tr>
<tr>
<td>G_{intra}</td>
<td>Free energy from intramicellar contribution</td>
</tr>
<tr>
<td>G_{inter}</td>
<td>Free energy from intermicellar contribution</td>
</tr>
<tr>
<td>G_{total}</td>
<td>Total free energy of the surfactant system</td>
</tr>
<tr>
<td>g</td>
<td>Bulk free energy per surfactant molecule</td>
</tr>
<tr>
<td>K</td>
<td>Empirical correction factor for kinetic energy loss</td>
</tr>
</tbody>
</table>
and entrance effect (eq. 60)

\[ k_1 \]

Empirical correction factor for entrance effect (eq. 57)

\[ k_2 \]

Empirical correction factor for kinetic energy loss (eq. 59)

\[ k' \]

Consistency of power law fluid

\[ L \]

Pipe length

\[ M_w \]

Molecular weight

\[ m' \]

Ratio of the polymer molecular weight to the minimum molecular weight of the polymer for entanglement

\[ N_A \]

Avogadro’s constant

\[ N_g \]

Dimensionless geometric packing parameter, \( v/a_0 l_0 \)

\[ N_{Re} \]

Raynolds number

\[ N_{Res} \]

Solvent Raynolds number (eq. 7)

\[ N_{Re'} \]

Generalized Raynolds number (eq. 25)

\[ N_o \]

Micelle aggregation number

\[ n \]

Number of carbon atoms in a surfactant chain

\[ n' \]

Power law exponent

\[ P \]

Polymer type

\[ -\Delta P \]

Pressure drop for drag reducing solutions in a pipe flow

\[ -\Delta P_s \]

Pressure drop for solvent in a pipe flow

\[ R \]

Pipe radius

\[ R_G \]

Radius of gyration
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \mathbf{R}^+ )</td>
<td>Dimensionless pipe radius (eq. 29)</td>
</tr>
<tr>
<td>( r )</td>
<td>Radius of a spherical or rod-like micelle</td>
</tr>
<tr>
<td>( S_p )</td>
<td>Surface area of a plate-like (disk-like) micelle</td>
</tr>
<tr>
<td>( S_r )</td>
<td>Surface area of a rod-like micelle</td>
</tr>
<tr>
<td>( S_s )</td>
<td>Surface area of a spherical micelle</td>
</tr>
<tr>
<td>( U^+ )</td>
<td>Dimensionless velocity (eq. 15)</td>
</tr>
<tr>
<td>( U_\tau )</td>
<td>Shear velocity or friction velocity (eq. 16)</td>
</tr>
<tr>
<td>( u )</td>
<td>Time average local velocity</td>
</tr>
<tr>
<td>( V )</td>
<td>Mean flow velocity (eq. 27)</td>
</tr>
<tr>
<td>( v )</td>
<td>Volume of a surfactant hydrophobic chain (eq. 50)</td>
</tr>
<tr>
<td>( W_1 )</td>
<td>Length of a plate-like (disk-like) micelle</td>
</tr>
<tr>
<td>( W_2 )</td>
<td>Width of a plate-like (disk-like) micelle</td>
</tr>
<tr>
<td>( y )</td>
<td>Distance from pipe wall</td>
</tr>
<tr>
<td>( y_e^+ )</td>
<td>Dimensionless distance from pipe wall where the elastic sublayer ends (eq. 20)</td>
</tr>
<tr>
<td>( y^+ )</td>
<td>Dimensionless distance (eq. 17)</td>
</tr>
</tbody>
</table>

**Greek Symbols**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \beta )</td>
<td>Cross-sectional area ratio of the test tube to that of the entrance pipe (eq. 7)</td>
</tr>
<tr>
<td>( \gamma )</td>
<td>Interfacial free energy per surfactant molecule</td>
</tr>
<tr>
<td>( \zeta )</td>
<td>Characteristic molecular dimension</td>
</tr>
</tbody>
</table>
\[ \eta \] Polymer intrinsic viscosity

\( \ell \) Length of a rod-like micelle

\( \ell_0 \) Length of a surfactant hydrocarbon chain (eq. 51)

\( \mu \) Solution viscosity

\( \mu^o_N \) Free energy per surfactant molecule in micelles (eq. 46)

\( \mu^o_{N,\text{min}} \) Minimum free energy per surfactant molecule in micelles (eq. 47)

\( \mu_s \) Solvent viscosity

\( \nu \) Kinematic viscosity of solution

\( \nu_s \) Kinematic viscosity of solvent

\( \xi \) Mole ratio of counter-ion to surfactant

\( \rho \) Solution density

\( \rho_s \) Solvent density

\( \tau_w \) Wall shear stress (eq. 1)

\( \tau_{wc} \) Critical wall shear stress taken at 50% drag reduction

\( \tau'_{wc} \) Critical wall shear stress taken at minimum friction factor

\( \Phi \) Dimensionless integration value (eq. 30)
CHAPTER I
INTRODUCTION

1.1 Drag Reduction

Drag reduction is the phenomenon in which turbulent flow skin friction can be reduced by the addition of very small quantities of certain drag reducing additives. Although a great deal of research has been carried out in this field, its mechanism is not yet entirely understood. It is, however, generally agreed that this phenomenon is associated with the viscoelastic character of the solutions. Effective drag reducing additives can be classified into three categories, namely, fibers, polymers, and surfactants.

Fibers in suspension are effective in damping turbulence and reducing the energy dissipated in turbulent flows to below that of the suspending medium alone. Their effectiveness increases as the aspect ratio (length/diameter) increases [Lee and Duffy, 1976; Radin, 1974]. Radin [1974] found that drag reduction can always be obtained in fiber suspensions with the aspect ratio of fiber greater than 25-35 if the concentration is sufficiently high. Fibers in aqueous systems are insensitive to water
chemistry and piping materials [Choi et al., 1988] and are removable from the suspension by mechanical separation [Shenoy, 1984]. Furthermore, they are drag reducing in a wide temperature range and are not very sensitive to degradation [Choi et al., 1988; Shenoy, 1984]. However, fiber concentration as high as a few percent may be needed to obtain appreciable drag reduction [Radin, 1974]. This concentration could cause plugging problems in pipeline applications.

Polymers are known to be the most effective drag reducing additives. Some polymers at concentrations as low as 0.02-0.03 part per million have been reported to show detectable drag reduction [Paterson and Albernathy, 1970; Oliver and Bakhtiyarov, 1983]. Linear-structured polymers such as polyethylene oxide and polyacrylamide, with molecular weights above 100,000, can generally reduce turbulent friction of their solvents by up to 70-80%. The first major commercial use of a high molecular weight polymer as a drag reducer was in the Alyeska 48-inch crude oil pipeline [Burger et al., 1980, 1982], where a flow rate increase of up to 32,000 m$^3$/day (2 x 10$^5$ bbls/day) was reported. Recently, a newly developed polymer drag reducer, FLO$^R$, was found to exhibit remarkable drag reduction in crude oil and other hydrocarbon substrates [Motier and Carrier, 1989]. This extremely high molecular weight copolymer ($M_w = 25-35$ million) of 1-butene and $\alpha$-olefins exhibited 30% drag reduction for crude oil in a 6-inch pipe using a dosage of only 5 parts per million [Motier and Carrier, 1989]. Polymers, however, are
not resistant to high mechanical shear such as that encountered in pumps. Degradation can also be caused by skin friction alone [Kenis, 1971; Ting and Little, 1973], and is very sensitive to temperature variation. Results by Durst et al. [1989] and Choi et al. [1988, 1989b] showed that polymer solutions degraded more rapidly at high temperatures than at room temperature. Therefore, high molecular weight polymers are not suited for use in high temperature circulation systems.

Surfactants as drag reducers have received more and more attention in the last few years for use in district heating and cooling systems. In district heating systems (Figure 1), hot water with temperature ranging from 80 to 130°C is circulated in pipelines to homes and industries utilizing waste heat or cogenerated heat supplied by a central control station. It provides a more efficient, less expensive way to supply energy to a district. Since careful controls on effluents from the central station can be maintained, air pollution can be reduced compared with using relatively inefficient heating systems at each home or industry. District heating systems are widely used in northern Europe and are expanding in their use 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. Similar benefits of greater efficiency are obtained in district cooling systems where cold water ranging from 5 to 15°C is circulated thus reducing the need for industrial chillers and home air conditioners. Major
Figure 1. Schematic of District Heating/Cooling system
costs of district heating and cooling systems are the cost of power for pumping the fluid and the capital expenses for pipes, fittings and pumps. In the existing systems, the operating power costs can be greatly reduced by the use of drag reducing additives. For new systems, the capital costs of pipes, fittings and pumps can be reduced. While surfactants also lose their drag reducing ability in high shear regions, they regain their drag reducing characteristics after the stress is reduced [White, 1967; Savins, 1967]. Although a reduction in flow friction is often accompanied by a greater loss in heat transfer coefficient, heat exchangers which can generate high shear flow such as plate heat exchangers can greatly improve the energy exchanging efficiency [Steiff et al., 1991]. In addition, thermal energy loss during transportation in the pipelines is reduced by the use of drag reducers. For all these reasons surfactant drag reducers are good candidates for district heating and cooling systems.

Three types of surfactants, namely, nonionic, anionic and cationic, are known to impart drag reduction. The anionic surfactants have limited applicability because the presence of calcium and magnesium ions in most tap water can cause precipitation by forming insoluble soaps [Shenoy, 1984]. Nonionic and cationic surfactants are both insensitive to cations. However, the former only exhibit drag reduction in a narrow temperature range around the cloud point of the surfactant which restricts their use in district heating or cooling loops in which temperatures vary over wide ranges.
Cationic surfactants, on the other hand, show much broader effective temperature ranges and thus have potential applications in district heating and cooling systems.

1.2 Surfactant Solutions

Surfactants are characterized by molecular structures consisting of a hydrophobic group together with a hydrophilic group, which together are known as amphiphilic structures. In aqueous solutions, in order to minimize the hydrocarbon-water interface, surfactant molecules gather into assemblies called micelles when the concentration exceeds a critical value called the critical micelle concentration or CMC. Based on the rule "like dissolved in like", surfactant molecules in aqueous medium orient their polar ends outwards into the water, while the non-polar portions concentrate in the center of the micelles. Micelles formed at or slightly above the CMC are spherical or ellipsoidal in shape. As surfactant concentration increases, spherical micelles are forced to move closer and closer toward one another, which increases the system energy due to electronic repulsions. In order to lower the system energy, they assume various nonspherical forms. In some cases, they may form extended sheets, while in others, they may form long cylinders. In the presence of electrolytes such as sodium halides [Ikeda et al., 1980; Mazer et al., 1976; Hoffmann et al., 1982], or cosurfactants such as
alcohols with intermediate chain length [Candau and Hirsch, 1982], or organic counter-ions such as salicylate [Hoffmann et al., 1981a; Bewersdorff and Ohlendorf, 1988], the charges on the surfactant headgroups can be partly neutralized or diluted, and the micelles can be packed more closely into a cylindrical form. The formation of cylindrical or rod-like micelles which behave in some ways like fibers or polymers is the necessary condition for drag reduction to occur [Ohlendorf et al., 1984; 1986a].

1.3 Objectives of This Research

Evaluations of the effectiveness of cationic surfactants and aromatic counter-ions were the major objectives of this research. The first phase of the work was to develop useful surfactant formulae for use in district heating systems. Emphasis was placed on the development of drag reducers which can show good drag reducing capability at temperatures as high as possible. Researchers in Germany [Wellinghoff et al., 1986] have reported that a commercial surfactant, DOBON, was effective from 80°C to a temperature as high as 140°C. It was our goal to develop drag reducers which are effective at even higher temperatures and to determine how the molecular structure of the surfactant and of the counter-ion affect the temperature range. Surfactants with different chemical structures were to be tested for drag reducing capability. The most effective counter-ions known were salicylate
[Ohlendorf et al., 1984, 1986a; Rose et al., 1984] and 3-OH-2-naphthalate [Wellinghoff et al., 1986]. Associated with our first goal was an effort to see whether other aromatic counter-ions could also induce drag reduction and how their chemical structure affected the effectiveness. Little is known about the possible relationship between the drag reducing effectiveness of surfactant solutions and their micellar structure. Variables which might affect the drag reducing behavior of surfactant systems such as concentration, solution pH and corrosion inhibitors were examined in this study. Another goal was to give reasonable physico-chemical explanations for the drag reducing capability of different surfactant systems so that better criteria for choosing surfactant drag reducers appropriate to the needs of different operating systems can be provided.

A second phase involved similar efforts for district cooling applications. Building space cooling, currently provided primarily by electricity-driven equipment, represents a significant and steadily increasing share of total U.S. energy consumption. Attempts were made to find surfactant formulae which are effective drag reducers in district cooling systems. The major challenge was to cope with the phase separation problem due to the poor solubility of surfactants in water at low temperatures. It was our goal to discover drag reducers which are effective at or lower than 5°C.

A third major goal of the research was to deal with the scale-up of drag reduction for surfactant systems. Although a great deal of research has been
carried out on this subject for polymer drag reducers, none of the scale-up criteria has been applied to surfactant solutions. It was therefore attempted to study the drag reducing behavior of various surfactant solutions in different sizes of pipes and to examine the applicability of the existing scale-up criteria. The feasibility of using surfactant drag reducers in large pipe systems with sizes comparable to those of commercial pipelines was also a major concern. Field tests in circulation systems were therefore scheduled.
2.1 The Drag Reduction Phenomenon

The phenomenon was first noted in 1946 by Mysels and his students [1949, 1971] who found that the skin friction for gasoline in pipe flow was significantly reduced by the addition of napalm, an aluminum disoap. However, it was Toms [1948, 1977] who first identified polymers as effective drag reducers, and made the first publication to disclose the phenomenon. Therefore, it is sometimes referred to as the "Toms Effect". The term "Drag Reduction" was first used by Savins [1964].

Since the early work by Toms and Mysels, a tremendous amount of research has been done in this field, most of which has been focused on drag reduction in dilute polymer solutions. In recent years, interest in drag reduction using aqueous surfactant solutions has increased. Although these two categories of drag reducers are morphologically different (micelles against long chain molecules), they are similar in a number of aspects. For example, experimental evidence from rheological measurements [Rehage
and Hoffmann, 1983; Hoffmann et al., 1984b, 1985; Shikata, 1987a, 1989; Thurn et al., 1985] has indicated that entangled networks which are very similar to the ones in semidilute or concentrated polymer solutions [Ferry, 1980] exist in surfactant solutions. These workers found by dynamic experiments that, at high angular frequencies, the storage modulus (G') of certain cationic surfactant solutions approaches a constant value. The plateau is an indication of a cross-linking network, and is generally referred to as the rubber plateau in polymer solutions. This indicates that the solution under high angular frequencies behaves as an elastic body. In addition, Ohlendorf et al. [1984] and Hoffmann et al. [1985a] found that, when a certain constant shear rate was applied to the viscoelastic surfactant solutions, the viscosity first increased rapidly with time then decreased to a steady value. This shear-induced state (SIS) or stress overshoot [Shikata et al., 1988b] was also found to occur in some polymer melts [Elliott, 1969]. In their light scattering studies on cetyltrimethylammonium bromide (CTAB) in KBr solutions, Candau et al. [1985, 1987] found that, with increasing surfactant concentration, the intensity of scattered light increased until a maximum was reached, then a decrease was observed. They suggested that the decrease was caused by a formation of a micellar network. The intensity was found to be proportional to the -0.29th power of concentration, which is very close to the value -0.31 derived from polymer network theory. Recently, electron microscopic studies have further confirmed the existence of an

The present review is presented in four parts. In the first section, a review of some of the most important findings and concepts on polymer drag reduction is given. The second section deals with the physical properties of micelles, such as size, shape, and shape transition. Viscoelastic and drag reducing behavior of surfactant systems are considered in the third and the fourth sections.

2.2 Drag Reduction in Dilute Polymer Solutions

This section is intended to introduce some of the terms and experimental facts associated with polymer drag reduction. A more complete picture can be obtained by reference to a number of reviews [Hoyt, 1972, 1977, 1984; Virk, 1975a; White and Hemmings, 1977; Sellin, 1984; Cleary et al., 1991].

There are different types of drag reduction that have been identified by early researchers. Hershey and Zakin [1967a] noted the existence of two kinds of drag reduction, one being characterized by the presence of an onset shear stress above which drag reduction commences, the other being characterized by an extended laminar flow, followed by a normal turbulent region. Savins [1969] extended the categories into four. Later researchers
[Berman, 1978; Virk, 1989] suggested that, basically there were only two types of drag reduction.

The two types of drag reduction are characterized by whether an onset and a laminar-to-turbulent transition can be observed. For randomly coiled polymer solutions, a transition is usually seen when turning from laminar to turbulent flow. In the turbulent flow region, the flow first behaves as a Newtonian fluid until the wall shear stress exceeds a threshold value, where drag reduction starts to occur. On the other hand, polymers with extended conformations usually do not show a clear transition probably because a threshold shear stress has already been reached in the laminar or transition zone [Hershey and Zakin, 1967a; Berman 1978].

2.2.1 The Onset

For randomly coiled polymer solutions, such as aqueous solutions of polyethylene oxide or polyacrylamide, drag reduction does not occur until a certain wall shear stress is exceeded. This is presumably due to uncoiling of the molecules in the extensional flow field, or the entanglement of many molecules reaching the size of turbulent eddies [Berman, 1978; Virk, 1989]. The threshold stress is a function of polymer parameters such as type and molecular weight distribution, and the goodness of the solvent. It decreases with increasing molecular weight and radius of gyration [Virk, 1975a]. White
[1966], Virk [1975a] and Hershey [1965], found the onset shear stress was independent of pipe diameter which led to the onset Reynolds number being proportional to the \( \frac{8}{7} \)th power of the pipe diameter. Virk [1970a, 1975a] and Gold et al. [1973] suggested that the onset wall shear stress was independent of polymer concentration. However, the results from most other researchers have shown a decrease of the shear stress with increasing concentration [Hershey, 1965; Hansen and Little, 1971; Whitsitt et al., 1969; Paterson and Abernathy, 1970]. In predicting the onset phenomenon, three different theories have been proposed, namely, length scale, time scale, and strain energy storage models. Virk's length scale model [Virk, 1969] suggests that when the ratio of the polymer length scale \( R_G \) (radius of gyration) and the turbulent length scale \( (\nu/\nu_\tau)^2 \) reaches a certain value, drag reduction takes place. In the time scale hypothesis, it was suggested that onset occurs when the time scale ratio (or Deborah number), which is defined as the ratio of polymer relaxation time and the turbulent time scale \( (\nu/\nu_\tau)^2 \), is around unity [Fabula et al., 1966; Hershey, 1965; Hershey and Zakin, 1967b]. Since polymer size is several orders of magnitude smaller than the turbulent eddy size at onset, while the polymer relaxation time is about the same order as the turbulent time scale [Virk, 1969; White and Hemmings, 1977], most researchers support the time scale model [Fabula et al., 1966; Hershey and Zakin, 1967b; Berman and George, 1974; Berman, 1977a; Gustavsson, 1977; Hunston and Zakin, 1980]. Based on Gaussian bead-spring theory, Kohn
[1974] proposed a strain energy storage model, in which he suggested the polymer molecules stored energy when strained by high shear stress near the wall, and released it by relaxation when transported to the low shear region at the core. When strain energy convection is comparable to energy diffusion, drag reduction occurs. Kohn’s model predicted a decrease in onset Deborah number as polymer concentration increases.

2.2.2 Maximum Drag Reduction Asymptote

The existence of a maximum drag reduction asymptote for dilute polymer solutions has been noted by early researchers [Castro and Squire, 1967; Giles and Pettit, 1967; Virk, 1967]. Giles and Pettit [1967] were the first to show their asymptote in a form analogous to the von Karman equation (see eq. 9, Chapter III). Virk et al. [1970b] also obtained an equation [eq. 10, Chapter III] by correlating the flow data for different polymer solutions from a number of sources. This latter maximum drag reduction asymptote has been most commonly cited by drag reduction researchers. Virk et al. suggested that this asymptote is insensitive to the polymer solutions employed, although to reach the asymptote different concentrations might be needed for different polymer species. Since the equation was empirically derived from polymer drag reduction data, and since the scatter was about 10% in the turbulent region [Virk et al., 1970b], it
is not surprising that in some studies, especially for systems other than polymer solutions, drag reduction has been reported to exceed this asymptote. For instance, drag reduction greater than that predicted by Virk's asymptote has been reported by Hershey et al. [1975] in their aluminum disoap systems, and by Lee et al. [1974] in their polymer/fiber mixed system. In the latter case, drag reduction as high as 95% was reported [Lee et al., 1974]. For cationic surfactant solutions, such as the CTAB/1-naphthol systems studied by White [1967], and the tetradecyltrimethylammonium salicylate systems studied by Bewersdorff and Ohlendorf [1988], maximum drag reduction data seem to follow Virk's asymptote quite well.

2.2.3 Concentration Effect

In general, drag reduction at a fixed Reynolds number increases as polymer concentration increases until a certain concentration (often called saturation concentration) is reached. Beyond this concentration, a further increase in concentration leads to a levelling off [Hoyt, 1986], or a decrease [Goren and Norbury, 1967; Kenis, 1971] in drag reduction. The initial increase in drag reduction is presumably due to the increasing number of molecules present which causes the decay of more turbulent eddies, while the decrease is probably caused by increase in solution viscosity.
A slope increment is sometimes used to characterize drag reduction effectiveness of randomly coiled polymer solutions. It has been defined as the slope difference between a drag reducing solution and the solvent in a von Karman plot ($f^{-1/2}$ vs. $N_{Re}^{1/2}$). Virk [1970a] showed the slope increment is proportional to $C^{1/2}$. Berman and Yuen [1977c], on the other hand, suggested a dependence on $C^{2/3}$ at low polymer concentrations (less than 1 ppm), and on $C^{1/2}$ at higher concentrations.

2.2.4 Molecular Weight and Polydispersity Effect

For the same polymer species an increase in molecular weight results in a decrease in onset shear stress and in the amount of polymer required to obtain the same level of drag reduction [Virk 1975a]. Paterson and Abernathy [1970] pointed out that drag reducing effectiveness was mainly controlled by the highest molecular weight species in the distribution. Modern gel permeation chromatography technique allows separation of the high molecular weight portions of the polymer. Using this technique, Berman [1977b], and recently Jacobs et al. [1989], were able to study the molecular weight effect. Their results confirmed the conclusion reached by Paterson and Abernathy [1970]. Hunston and Reischman [1975], in their study of drag reduction of polystyrene in benzene solutions, found that the onset shear stress was primarily determined by the highest molecular weight
fraction of polymer. Hunston and Reischman [1975] also found that, when 2.5 ppm of a high molecular weight polystyrene (7.1 million) was combined with 25 ppm of a low molecular weight one (1.8 million), the drag reduction obtained was almost identical to that of using the high molecular weight sample alone. However, when the amount of low molecular weight polymer was increased to 100 ppm, it made a significant contribution to the drag reducing effectiveness of the mixture. This is in accordance with the results of McCormick et al. [1990a, 1990b], who found the drag reducing efficiency of a given polymer species can be well correlated by its pervaded volume fraction, $C[\eta]$, where $[\eta]$ is the intrinsic viscosity, regardless of the variation in molecular weight. McCormick et al. [1990b] suggested that good drag reduction can be achieved by low molecular weight polymers if their concentrations (volume fractions) are high enough. However, McCormick et al. also pointed out that there might be a low molecular weight limit for the volume fraction correlation [1990b]. Liaw et al. [1971] defined a critical concentration, $C_c'$, as the concentration which separates the dilute drag reducing region and the concentrated drag reducing polymer solutions. When polymer concentration exceeded $C_c'$, a laminar-to-turbulent transition was not observed in their experiments. Liaw et al. found that the critical pervaded volume, $C_c[\eta]$, was related to polymer molecular structure and was insensitive to the goodness of the solvents. Flexible polymers like polyethylene oxide or polydimethyl siloxane had low values of $C_c[\eta]$ for a
given molecular weight. They also proposed that m', defined as the ratio of polymer molecular weight to minimum molecular weight for entanglements to occur [Liaw, 1968; Liaw et al., 1971], is a useful measure of molecular weight for predicting drag reducing efficiency. According to Liaw et al. [1971], good drag reduction was always obtained if the m' value of the polymer was greater than 50. Poor drag reduction was found when m' was lower than 15 even if the polymers were highly flexible.

2.2.5 Molecular Conformation and Solvent Effect

As mentioned earlier, coiled polymer molecules usually show a different type of drag reduction than extended ones. Efforts have been made by a number of workers to study the effect of molecular conformation on drag reduction by changing the interactions between polymer molecules and solvent. Hershey and Zakin [1967a] found the drag reducing ability of polyisobutylene was improved when the solvent was switched from benzene (a poor solvent) to cyclohexane (a good solvent), indicating that the more expanded molecules had a greater effect than the unexpanded ones. 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.
Molecular conformation can also be altered by changing the salinity of the polyelectrolyte solution as was demonstrated by Virk [1975b, 1989] and recently by Rochefort and Middleman [1989]. These authors found polyacrylamide in low salt aqueous medium, where the polymer molecules expanded due to charge repulsions, produced more drag reduction than in high salt solutions in which molecules coiled. The molecular conformation of polyacrylic acid can be varied by changing the pH value of the solution in that at low pH the polymer molecules collapse due to protonation, while at high pH the molecules expand due to charge repulsions. Parker and Hedley [1972], and Banijamali et al. [1974] have reported greater drag reduction in high pH than in low pH solutions. The solvent effect was further demonstrated by Kwack et al. [1981], who studied the drag reduction of polyethylene oxide in tap water from three different cities and found different drag reducing efficiencies. They attributed this to the different ion content and levels of pH in the waters.

2.2.6 Diameter Effect

For Newtonian fluids in the turbulent region, flow behavior is well described by the von Karman equation, each Reynolds number corresponding to a specific friction factor. On the other hand, in the case of viscoelastic fluids, it has long been recognized that for a given Reynolds number, the
same polymer solution in different diameters of pipes gave different values of the friction factor. In general, the percent drag reduction observed in large pipes is smaller than that obtained in small pipe systems [White, 1966; Savins, 1964]. The diameter effect and the scale-up process are of importance since they are directly associated with applications in industry. Scale-up will be discussed in Chapter III.

2.3 Micellar Characteristics

2.3.1 The CMC

The magnitude of the critical micelle concentration (CMC), the concentration above which micelles start to form, is a direct indication of the tendency to form spherical micelles. Factors known to affect the CMC in aqueous medium are the nature of the surfactant and the presence of added salts. The effect of temperature on CMC is less pronounced. In general, an increase in temperature results in a slight increase in CMC [Rosen, 1978]. The CMC usually decreases with increase in the hydrophobic characteristic of the surfactant. For surfactants with a common hydrophilic headgroup, the CMC is approximately halved by each addition of a methylene group to the hydrophobic chain [Rosen, 1978]. The CMC is also affected, to a somewhat lesser extent, by the hydrophilic group species. Stigter [1974] examined the
CMC's of five surfactants each having a different type of headgroup, and proposed that the CMC was higher when the ionic charge on the headgroup was closer to the \( \alpha \)-carbon atom of the alkyl chain.

The effect of adding inorganic salts on surfactant CMC has been extensively studied by Anacker and Ghose [1963, 1968] using light scattering measurements. They found the ability of the anions to depress the CMC of dodecyltrimethylammonium bromide increased in the order:

\[
F^- < \text{CHO}_2^- < IO_3^- < Cl^- < BrO_3^- < Br^- < NO_3^- 
\]

This sequence parallels the so-called lyotropic series (or Hofmeister series) by Bruins [1932]. In their recent study, Underwood and Anacker [1987a] found good correlation of CMC with the hydration enthalpy and hydration size of the added ions. They suggested that the most effective anions in promoting micellization are those which interact the least with water. Organic salts of the aliphatic type can also reduce surfactant CMC. Underwood and Anacker [1985, 1987b] have shown that an increase in hydrophobicity of the organic counter-ion resulted in a decrease in CMC. Counter-ions of the aromatic acid type, such as substituted benzoates and benzenesulfonates, have been reported to reduce surfactant CMC to an order of magnitude lower than inorganic and aliphatic counter-ions [Gravsholt, 1976; Underwood and Anacker, 1985, 1987b].
2.3.2 Micelle Shape and Size

Micelles are believed to be of spherical or roughly spherical shape at surfactant concentrations above the CMC, and remain so until a second critical concentration, CMC_{II}, is reached [Porte, 1984; Hoffmann et al., 1984a]. Above the CMC_{II}, micelles assume a more compact rod-like or disk-like form, depending on the nature of the surfactant species [Hoffmann et al., 1984a].

The radius of the spherical micelles is approximately equal to the fully extended length of the hydrophobic chain [Tartar, 1955]. Upon the addition of low concentrations (e.g. < 0.05M) of inorganic salts, the spherical shape can still be retained [Nicoli et al., 1981, 1984; Nicoli and Dorshow, 1985; Briggs et al., 1982; Dorshow et al., 1982, 1983; Corti and Degiorgio, 1978, 1981]. However, the aggregation number changes with the nature of the foreign salts. Ford et al. [1966] studied the effect of added halides on dodecylpyridinium micelles and concluded that the micellar aggregation number increased with a decrease in hydration, and an increase in the polarizability of the halides (Cl<Br<I). A more complete study of the salt effect has been performed by Anacker and Ghose [1963, 1968], who reported the order of effectiveness in increasing aggregation number in dodecytrimethylammonium micelles was:
and in cetylpyridinium micelles, it was:

\[ IO_3^- < HCO_2^- < BrO_3^- < F^- < Cl^- < NO_3^- < Br^- < ClO_3^- < SCN^- < ClO_4^-, I^- \]

At high salt concentrations, the CMC$_{II}$ of the surfactant is reduced, resulting in a micellar shape transformation from sphere to rod [Debye and Anacker, 1951; Missel et al., 1980, 1983]. For example, the CMC$_{II}$ for cetyltrimethylammonium bromide (CTAB) in aqueous medium is approximately 0.3 M (10% by weight) [Ekwall et al., 1971; Gotz and Heckmann, 1958]. However, rod-like micelles several hundred nanometers long were detected by dynamic light scattering measurements in 0.004 M CTAB solution if 0.2 M sodium bromide was added [Nicoli et al., 1981]. Evidence to show that the micelles in solutions of high ionic strength are rod-like has been provided by a number of investigators using different experimental techniques. Debye and Anacker [1951] studied the CTAB/KBr system using static light scattering and found the data were well-interpreted by assuming a rod model rather than a sphere or a disk model. Young et al. [1978], among others [Flamberg and Pecora, 1981; Van De Sande and Persoons, 1985], combined results from both static and dynamic light scattering techniques, and concluded that the micelles in high concentration salt solutions were rod shaped. Evidence from nuclear magnetic resonance [Staples and Tiddy, 1978] and magnetic birefringence [Porte et al., 1980] also supported the formation of rod-like micelles, rather than "a secondary
aggregation of spherical micelles" proposed by Tanford [1972, 1974]. Based on geometric and energy considerations, Israelachvili et al. [1976] have proposed that the micelle shape was determined by the dimensionless parameter, \( \frac{v}{a_o \ell_o} \), where \( v \) and \( \ell_o \) are the volume and length of the surfactant hydrophobic chain, and \( a_o \) is the optimal surface area occupied by each surfactant headgroup. According to Israelachvili et al., micelles were spherical for \( \frac{v}{a_o \ell_o} < \frac{1}{3} \), rod-like for \( \frac{1}{3} < \frac{v}{a_o \ell_o} < \frac{1}{2} \), and disk-like for \( \frac{1}{2} < \frac{v}{a_o \ell_o} < 1 \). Since the addition of salt partially screens the electrostatic headgroup repulsion which results in a reduction of \( a_o \), a shape transformation from sphere to rod can be induced.

The length of the rod-like micelles has been shown to increase with increasing concentration of surfactant and salt, and with decreasing temperature [Missel et al., 1980; Porte and Appell, 1981; Nicoli et al., 1981]. With an increase in surfactant chain length, micellar length becomes more sensitive to the variations of temperature and salt concentration [Missel et al., 1983; Nicoli et al., 1981]. For surfactants with a common hydrophobic chain, increasing the headgroup size results in a decrease in micelle size. This has been demonstrated by Geer et al. [1971] who studied the effect using a light scattering technique by sequentially replacing the protons on the decylammonium headgroup with methyl or ethyl groups. They proposed that the larger headgroups tended to keep the counter-ions from approaching the charge center and thus disfavored micellar growth. Similar
results were obtained by Venable and Nauman [1964] on tetradecylammonium homologs and by Malliaris et al. [1986] on cetylammonium homologs. They attributed this effect to the increased hindrance in packing the headgroups on the micellar surface.

Micellar growth is strongly affected by the type of foreign salts. In general, the effect of salt on the aggregation number of rod-like micelles increases with increasing lyotropic number of the anion. Therefore, those anions which can more effectively reduce surfactant CMC are usually more efficient in inducing micellar growth. This is not surprising since the formation of both the spherical and the long, rod-like micelles is strongly controlled by the charges on the surfactant headgroups. Salts with greater ability to neutralize these charges will certainly favor both the micellar formation and growth. Using ionic exchange theory in combination with spectrophotometrical measurements, Bartet et al. [1980] were able to show the binding ability of different anions on CTAB micelles increased in the order:

\[ F^- < OH^- < CO_3^{2-} < AcO^- < B_4O_7^{2-} < HPO_4^{2-} < Cl^- < SO_4^{2-} < Br^- < NO_3^- \]

Gamboa et al. [1981], using the same ionic exchange model but with different experimental techniques, also obtained the same order indicated above.

Aromatic acid anions are known to be able to promote micellar growth even more effectively. The presence of salicylate ions on the properties of cetylpyridinium micelles has been extensively studied by Hoffmann et al.
[1981a, 1981b, 1982, 1984a, 1985a] using electric birefringence, static and dynamic light scattering, and small angle neutron scattering. They found that in the presence of a few millimoles per liter of salicylate, micelles grew to be several hundred angstroms long, despite the fact that the surfactant concentration was only a few millimoles per liter. In the presence of these aromatic salts, surfactant solutions showed both high viscosities and viscoelastic characteristics. This will be further reviewed later.

2.3.3 Micellar Size Distribution

There is some uncertainty about the size distribution of micelles. Mukerjee [1972, 1978] theoretically approached the micellar formation on the basis of a stepwise association model in which micelles of different sizes in a solution are in a multiple equilibrium state. According to the model, the size distribution index or polydispersity, defined as the ratio of the micellar weight average molecular weight to the number average molecular weight, was found to be close to unity when the micellar sizes are small. If the micelles are considerably larger, the model predicts a wide size distribution, with a polydispersity value of 2.0 when surfactant concentration is sufficiently high. The model also predicts that the weight average molecular weight is proportional to the square root of concentration, which was found to be consistent with the experimental results [Mukerjee, 1972]. Following
Mukerjee's work, a number of authors have also reached the same conclusion based on thermodynamic analysis that large micelles are polydisperse [Tanford, 1974; Israelachvili et al., 1976; Missel et al., 1980; Benedek, 1985]. In their chemical potential ladder model, Missel et al [1980] also include the effect of foreign salts on micellar size and polydispersity. These workers successfully used the Gouy-Chapman double layer theory, which considers the electric field built up on the micellar surface, to account for the influence of salts. Porte and Appell [1981], on the other hand, modified the model by further considering the effect of salt species on the micellar growth. Experimental evidence supporting a wide micelle size distribution in surfactant solutions was provided by a number of authors. In their dynamic light scattering studies on NaCl solutions of sodium dodecyl sulfate (SDS), Mazer et al. [1976] found the variance, which is related to the second moment of the micelle diffusivity (or size) distribution, was quite large, being about 35% on average. This indicates that micelles of different sizes were present in the solutions. Similar results were also reported by Missel et al. [1980] for the same surfactant systems.

The conclusion on micellar polydispersity is not unequivocal. On the basis of successive associations, Ikeda [1984] proposed a thermodynamic model of micellar growth. Instead of assuming an equal association constant of monomer to the rod-like micelles in each step, he suggested that the constant should be inversely proportional to the aggregation number, which
led to a Poisson distribution of the micellar size. Experimental support of monodisperse rod-like micelles was also provided by Ikeda et al. [1981] from light scattering results of SDS/sodium halide solutions. In their electric birefringence studies of cetylpyridinium salicylate (CPySal) solutions, Hoffmann et al. [1984] also found the rod-like micelles were monodisperse. They suggested that the intermicellar interactions, which were ignored by most of the other researchers in their thermodynamic derivations, are responsible for the narrow distribution in micellar size.

2.3.4 Micellar Flexibility

The flexibility of rod-like micelles has been a disputed subject. Nagarajan [1982] suggested the micelles were rigid based on viscosity calculations. A rigid-rod model had also been assumed by Debye and Anacker [1951] and by Young et al. [1978] in the interpretation of their light scattering results. Ikeda et al. [1980], on the other hand, supported the flexible rod model based on their light scattering results. They suggested the molecular pitch can be used to determine the stiffness of rod-like micelles. The molecular pitch was defined as the ratio between micellar length and aggregation number, where micellar length is obtained by measuring the radius of gyration and the aggregation number is calculated from the molecular weight of the micelles. If the micelles can be considered as rigid,
the pitch should be independent of the aggregation number. Ikeda et al. [1980] found, for dodecyldimethylammonium micelles at high NaCl concentration, the pitch decreased with increasing aggregation number, indicating the micelles were flexible. There is now more evidence in favor of the flexible or semi-flexible model. For example, The results from dynamic and static light scattering measurements have been shown to be well-interpreted by introducing a parameter called persistence length which is a measure of the resistance to curvature of the rod [Appell and Porte, 1981; Appell et al., 1982; Van De Sande and Persoons, 1985]. Studies using three complementary techniques, namely, dynamic light scattering, magnetic birefringence, and NMR, have been performed by Porte et al. [1980] who concluded that the micelles were flexible. Hoffmann et al. [1984b] pointed out that rods might be rigid or flexible depending on a number of factors such as ionic strength, micelle charge density, interfacial tension, and the chain length of the surfactant. The effect of micelle charge density on micellar flexibility was also addressed by Olsson et al. [1986] who suggested that the flexibility of micelles is strongly dependent on the degree of counter-ion binding. Olsson et al. proposed that micelles are most flexible when counter-ion binding to micelles reaches 100% (i.e. when the molar ratio of counter-ion to surfactant in a micelle is 1:1). Micelles become more and more rigid as the degree of counter-ion binding increases.
2.4 Viscosity Properties of Surfactant Solutions

2.4.1 Solution Viscosities

An increase in viscosity and elasticity of the surfactant solution is strongly related to the presence of rod-like micelles and the possible network they form. The viscosities of aqueous solution of CTAB, in the absence of foreign salts, has been studied by Ekwall et al. [1971], who found the solution viscosity increased steadily with increasing surfactant concentration until the concentration reached 11% by weight, where the viscosity increased steeply. Their light scattering results also showed a similar rise in total intensity at about the same surfactant concentration, indicating a structural change occurred in the solution. Ekwall et al. inferred that, at this concentration, the micelles experienced a shape transformation from spherical to rod-like form.

The addition of inorganic salts has a dramatic influence on solution viscosities. Philippoff [1951] has shown that, as concentration is raised above CMC, surfactant solutions can be classified into three different regions: Region 1 - electrolyte absent; Region 2 - moderate content of electrolyte; Region 3 - high concentration surfactant solution without electrolyte, or low concentration solution with high content of electrolyte. These three regions are well-identified by their relative viscosities, and by the temperature
dependence of viscosity. The solution in Region 3 is highly viscous, and the viscosity is a strong function of temperature [Philippoff, 1951]. Based on both hydrophobic and electrostatic energy considerations, Pilpel [1954] developed a model to explain the micellar shape transition and the effect of added salts. He inferred that the viscoelastic properties of the salt-added surfactant solution is caused by the inter-linking of the long, rod-like micelles throughout the solution. According to Pilpel, this network structure is similar to the one that exists in elastic solids such as rubber, gelatin, and plastic materials.

It is interesting to note that the addition of inorganic salts has a greater effect on solution viscosity of anionic surfactants than of cationic surfactants. For example, for a 0.035 M potassium oleate solution, Pilpel [1966] reported that the solution viscosities ranged from 1,000 to 70,000 centipoises when the amount of added KCl increased from 0.6 to 1.2 M. By using a 0.2% (about 0.006 M) sodium oleate solution in combination with KCl (0.47 to 1.34 M), Savins [1969] was able to observe drag reduction. On the other hand, in the presence of 1.0 M NaCl, the viscosity of a 0.44 M cetylpyridinium chloride solution is only four times that of water [Stainsby and Alexander, 1953]. Generally speaking, in order to see significant viscosity increase in cationic surfactant solutions, organic additives alone, or both organic and inorganic additives must be present [Larsen et al., 1973].
Larsen et al. [1973] studied the effect of organic additives on the viscosity of CTAB solution (0.1 M). They found that, for over a dozen additives studied, the effect on CTAB viscosity was small. However, upon addition of 0.1 M of NaBr, some organic additives such as benzene, n-hexanol, benzoic acid, and carbon tetrachloride can increase the viscosity by two orders of magnitude. This cooperative effect was also noted earlier by Stainsby and Alexander [1953] who studied the viscosities of cetylpyridinium chloride (CPyC) solution in the presence of NaCl. They found that in concentrated CPyC solutions (0.4 M) the intrinsic viscosities of the solutions first decreased to a minimum, then increased with increasing NaCl, but the changes were small. With the addition of an appropriate amount of a third component, chlorobenzene, the viscosity of the mixture rose to several hundred times the original value. Marked streaming birefringence was observed in the flow solution. However, excess addition of chlorobenzene can disrupt the viscous structure and bring down the viscosity.

The presence of aromatic alcohol can change the surfactant viscosity as well. Nash [1956] observed the gel-like properties of CTAB solutions with the addition of 1- or 2-naphthol, and proposed a swirl decay time (SDT) method to characterize their viscoelastic behavior. The SDT is measured by swirling a fixed volume of solution and noting the time required for the flow motion to stop and reverse. Hence the smaller the SDT of the solution observed, the greater its viscoelasticity is. The cooperative effect was again
demonstrated by the work of Nash [1956] who found the SDT values of the CTAB/naphthol solutions were always smaller if 0.002 M KNO₃ was present. Nash [1956] suggested the viscoelastic properties were caused by rod-like micelles in the solution. He also proposed the 1-naphthol molecules should adsorb on the micellar surface, with their hydroxyl groups pointing to the micelle.

The addition of aromatic acids or their salts, particularly the derivatives of benzoate and benzenesulfonate, has been shown to have a dramatic effect on cationic surfactant solutions. Wan [1968] studied the viscosity of various cationic surfactants in the presence of salicylic acid and found the viscosity increased with increasing salicylic acid until a maximum was reached. Further addition of the additive tended to reduce the viscosity. Wan also noticed that the solutions she studied exhibited shear thinning behavior. Elson and Garside [1983], in their study of alkyltrimethylammonium halide/1-naphthol systems, also found the solutions exhibited shear thinning behavior under low shear rates (0-300 s⁻¹) especially in the low temperature regime, while under high shear rates (300-2500 s⁻¹) the viscosities approached constant values. Similar findings were also reported by Rose and Foster [1989] in their CTAB/salicylate system. The most extensive study associated with the effects of aromatic acid counter-ions on surfactant viscosity was the work by Totten et al. [1986], who systematically examined
different derivatives of benzoate and benzenesulfonate in tetradecyltrimethylammonium bromide (TTAB) solutions. Totten et al. studied three different benzene functional anions in TTAB solutions and found the solution viscosity increased in the order: carboxylate < sulfinate < sulfonate. They also concluded that an ortho active hydrogen substitution such as OH, SH, or NH$_2$ to the counter-ion containing the acid group causes a significant viscosity increase in the TTAB solution. Other factors which can affect solution viscosity, such as temperature, total concentration, stoichiometric ratio between surfactant and counter-ion, and solution pH, were also considered by these authors.

2.4.2 Viscoelastic Properties

The viscoelastic behavior of surfactant solutions is most easily visualized by the recoil of small air bubbles trapped in the solution when a rotatory motion of the vessel containing the solution is stopped. The time between the stopping of the vessel rotation and the cessation of the bubble movement before recoil, has been proposed by Nash [1956] as a measure of the degree of viscoelasticity. Hoffmann and Rehage [1986] have pointed out that there are two type of viscoelastic surfactant systems. In the first type, the structures which are responsible for the viscoelastic behavior are already present in the solution at rest. The second type is featured by Newtonian
behavior under low shear rates, and viscoelastic behavior when a threshold shear stress is exceeded.

Dynamic viscoelastic experiments have been used by a number of researchers [Rehage and Hoffmann, 1983; Hoffmann et al., 1984b; Thurn et al., 1985; Strivens 1989; Shikata et al., 1987a, 1988b, 1989] to probe the micellar structure in surfactant solutions. Through this technique, it is possible to obtain information without disturbing the micellar structure in the quiescent solution. Hoffmann et al. [1984b] studied a 25 mM solution of cetylpyridinium salicylate (CPySal) solution and found the solution showed mechanical properties similar to those of temporary entangled polymer solutions. Strivens [1989] studied the CTAB/salicylic acid system at concentrations of 1, 10, and 100 mM respectively. He found the viscoelasticity for the 1 mM solution was undetectable. For the 10 mM solution, the storage modulus (G') and loss modulus (G'') curves cross each other, but no plateau value for G' was observed. This corresponds to a polymer solution in the semi-dilute region. As the concentration was increased to 100 mM, both the crossover point and the plateau were observed. In this case, a fully entangled network has been formed. Shikata et al. [1987a] studied the effect of molar ratio on the viscoelastic properties of salicylate/CTAB systems by keeping the concentration of CTAB constant and varying the amount of NaSal in the solutions. They found that the G' plateau reached a constant value at a NaSal/CTAB molar ratio of 0.5 and was
unaffected by further addition of the NaSal. Since the plateau value is an
indication of the entanglement density of the network, they concluded that a
fully entangled network is already formed when the molar ratio of
NaSal/CTAB reaches 0.5. This has been confirmed by Clausen et al. [1991],
who studied a similar system (NaSal/CTAC) by cryo-transmission electron
microscopy and found no difference in network structure upon further
addition of NaSal after the NaSal/CTAC ratio reached 0.25.

When the surfactant solution is at such a concentration that the
average length of the rod-like micelles is smaller than their mean spacing
(for CPySal system, this corresponds to 7.7 mM [Hoffmann et al., 1984b]),
viscoelasticity cannot be detected for the solution at rest. The solution
behaves like a Newtonian fluid under low shear stress. However, at some
higher fixed shear rate, solution viscosity increases with time to several
times higher than the zero shear viscosity until a maximum is reached, then
decreases over a period of time to a steady value. When the shear strain is
removed, the viscosity is reduced to the zero shear value over periods
ranging from several seconds to a few minutes for different conditions.
Hoffmann et al. [1981b, 1984a, 1985a] have extensively studied this shear
induced state (SIS) phenomenon. They suggested that the micelles
experienced some changes during the shear process. A possible explanation
is that under the shearing conditions the micelles were induced to form
larger and probably overlapping rods [1984a]. Similar observations on SIS have also been reported by Shikata et al. [1988b] and by Strivens [1989].

2.5 Drag Reduction in Surfactant Solutions

Drag reduction in surfactant solutions has not been as extensively studied as in polymer solutions. A review with special regard to micellar systems has been given by Shenoy [1984].

2.5.1 Anionic and Nonionic Surfactants

Since the early observations by Mysels et al. [1949] of drag reduction by napalm-thickened gasoline, drag reduction of anionic surfactants in nonaqueous media has been investigated by a number of researchers [Radin et al., 1969; Baker et al., 1970; McMillan et al., 1971; Hershey et al., 1975; Zakin, 1972]. These surfactants are primarily lithium, sodium, or aluminum salts of disoaps, and are presently the only known effective surfactant drag reducers in hydrocarbon-based media. They are generally very sensitive to water content and to aging [Zakin, 1972]. The concentration needed to obtain good drag reduction is usually high, being approximately equal to a few thousand parts per million [Radin et al., 1969; McMillan et al., 1971]. McMillan et al. [1971] found that an aluminum dioctoate was very effective
at a concentration as low as 800 ppm. McMillan et al [1971] proposed that there exists a minimum concentration below which micelles form a metastable structure which can be destroyed by aging or upon high shear stress. Above this concentration, micellar structures were insensitive to aging and, when broken down by high shear, reformed upon standing.

Anionic surfactants in aqueous medium were investigated by Savins [1967, 1969], who studied the effects of various parameters such as surfactant species, ionic strength, temperature, and pipe diameter. Some interesting characteristics were observed by Savins. First, he found that there exists a critical shear stress above which drag reduction is rapidly lost. As the shear stress was reduced to below the critical value, drag reduction was entirely regained without any delay. This is in contrast to polymer drag reducers which experience a slow but permanent degradation under high shear stress. The critical shear stress has frequently been used to characterize the effectiveness of drag reduction in surfactant systems. A second feature is that his solution failed to show an onset usually observed for randomly coiled polymer solutions. These anionic surfactant solutions are sensitive to the presence of calcium and magnesium ions, and therefore have limited applications.

Drag reducing nonionic surfactants, which are primarily of the low molecular weight polyoxyethoxylated type, have been studied by Zakin and his students [Zakin and Lui, 1983; Chang and Zakin, 1985]. These
surfactants have been shown to exhibit drag reduction in the temperature range around the surfactant cloud point. The cloud point can be effectively lowered by the addition of salts.

2.5.2 *Cationic Surfactant Solutions*

2.5.2.1 Naphthols as Additives

Drag reduction studies using cationic surfactant were first made by White [1967, 1969] who investigated the behavior of an equimolar aqueous solution of CTAB and naphthol in pipe flow. White noticed that the critical shear stress above which drag reduction is lost rapidly was independent of pipe diameter. In addition, as previously reported by Savins [1969] in his anionic systems, no onset was observed. White [1972] and Frederick and White [1975] later studied the turbulent velocity profile of the same solution by the pulsed hydrogen bubble technique and found the data points were quite well fitted by Virk's asymptotic velocity equation (see eq. 18, Chapter III). It was found by Poreh et al. [1970] and Zakin et al. [1971] that, for CTAB/1-naphthol systems, the highest critical shear stress occurred at a weight ratio of 2.1 to 1 (approximately 0.8 to 1 on a molar basis). Zakin et al. also found the critical shear stress increased with an increase in total concentration [1971].
Drag reduction studies using various alkyltrimethylammonium homologs (C_{12}, C_{16}, and C_{22}) in association with 1-naphthol have been made by Elson and Garside [1983] in test tubes with diameters ranging from 0.5 to 1 inch. They found that the simple swirl decay time (SDT) method originally proposed by Nash [1956] correlated well with the critical shear stress. The explanation provided by them was that the lower the SDT, the higher the resistance to swirl and hence the most effective turbulence suppression. Interestingly enough, in contrast to the work by Savins [1969] and by White [1967], some results of Elson and Garside showed obvious laminar-to-turbulent transitions. This transition was also seen from the results of Ohlendorf et al. [1984, 1986a, 1986b] in their quaternary ammonium salt/salicylate systems. Concentration effects were also investigated by Elson and Garside [1983], who suggested that the optimal ratio of 1-naphthol/CTAB to show maximum critical shear stress depended on the concentration of CTAB. According to them, at high CTAB concentration, the ratio was about one, while at low CTAB concentration the ratio was greater than unity. The reason an excess amount of 1-naphthol was needed to obtain effective drag reduction was attributed to the partition effect of 1-naphthol between micelles and water. Moonay [1985] compared the drag reducing behavior of CTAB in the presence of 1-naphthol and 2-naphthol respectively at 24°C, and reported no appreciable difference in drag reducing effectiveness between the two systems.
The possibility of using CTAB/1-naphthol solution as a hydraulic transport medium was explored by Zakin et al. [1971]. They found the viscoelastic solution can not only reduce the pressure drop in transporting silica sand and plastic grains, but can also decrease the critical velocity (the minimum velocity required to keep particles in suspension) of the flow. A similar result was obtained by Myska and Vocel [1977] in their studies of suspension flow for polymethylmethacrylate particles in an equimolar mixture of carboxethoxypentadecyltrimethyl ammonium bromide and 1-naphthol.

Although the CTAB/1-naphthol solution is mechanically stable, it is not chemically stable. As reported by Zakin et al. [1971] the solution lost its effectiveness by chemical degradation within a few days. In addition, the drag reducing capability of the solution cannot be retained at temperatures above 48°C, which excludes its use in district heating systems (An upper operation temperature above 80°C is usually necessary for these systems).

2.5.2.2 Aromatic Salts as Additives

Generally speaking, drag reduction of each surfactant system can only be observed in a certain temperature range. This range is strongly affected by the nature of both the surfactant and the counter-ion used.
Among the known aromatic salts, sodium salicylate (NaSal) is probably the most widely studied one. This is probably due to its remarkable ability to promote viscoelasticity when combined with cationic surfactant solutions. Ohlendorf et al. [1984, 1986a, 1986b] were among the first to study the drag reduction of alkyltrimethylammonium and alkylpyridinium surfactants in the presence of salicylate. Their results confirmed some of the findings by early researchers in different surfactant systems [Savins, 1969; White, 1967; Elson and Garside, 1983]. That is, the critical wall shear stress is independent of pipe diameter and is an increasing function of total concentration. While most of the studies by Ohlendorf et al. were made on equimolar mixtures of surfactant and salicylate, Rose et al. [1984] found that the use of excess quantities of salicylate not only enhanced the drag reducing effectiveness (characterized by maximum percent drag reduction and critical wall shear stress), but also extended the upper temperature at which drag reduction can be retained. The effect of adding electrolytes to the cetyltrimethylammonium salicylate system was investigated by Ohlendorf et al. [1986b], who found the critical Reynolds number at which the critical shear stress is reached increased with increasing electrolyte concentration to a maximum, then decreased with further addition of salts due to the salting out effect. They also noticed that the higher the valency of the anion, the lower the concentration needed to increase drag reducing effectiveness.
In addition to salicylate, a few other counter-ions have been reported to be effective in reducing skin friction when mixed with cationic surfactants [Chou et al., 1989a; Ohlendorf et al., 1987; Rose et al., 1988; Teot et al., 1986]. Chou et al. [1989a] proposed that the hydrophilic and hydrophobic groups on aromatic rings of counter-ions should be located as far apart as possible in order to obtain good drag reduction. Murray [1989] and Cleary et al. [1991] found two counter-ions, namely, 2,6-dihydroxybenzoate and 4-methylnsalicylate, when combined with dodecyltrimethylammonium chloride, were effective drag reducers in water/ethylene glycol solutions at temperature as low as -2°C.

Quaternary ammonium salts with longer alkyl chains have been reported to increase the upper temperature at which drag reduction can occur [Chou et al., 1987, 1988; Ohlendorf et al., 1986a; Rose, 1984, 1989]. Ohlendorf et al. [1986a] claimed that the effective drag reduction temperature range for alkyltrimethylammonium salicylate surfactants was essentially invariant, being around 40 to 45°C. It has been shown by Chou et al. [1989a, 1989b] that the incorporation of cis- double bonds into the surfactant chain can greatly enhance the drag reducing effectiveness at low temperatures, but has little effect on the upper temperature limit. They also found that when two or more of the methyl groups on the surfactant headgroup were replaced by groups with greater hydrophilicity such as hydroxyethyl groups, drag reduction can be extended to lower temperatures.
In their drag reduction study on mixed surfactant systems, Chou and Zakin [1991] found that, by properly choosing the mixing ratio of surfactants with different chain lengths, the effective temperature range can be greatly broadened (a temperature range from 115 to below 2°C was obtained). Similar effects were also observed by using more than one kind of counter-ion in the solution [Chou and Zakin, 1991].
CHAPTER III
THEORETICAL BACKGROUND

3.1 Drag Reduction

None of the theories about the mechanism of drag reduction has been confirmed. In fact, it is believed that more than one kind of drag reduction mechanism exists. Vaseleski and Metzner [1974] have shown that the drag reduction caused by fibers in suspensions involved changes in the turbulent core. This was also supported by Lee and Duffy [1976] who used an annular purge impact probe to measure the turbulent velocity profile of aqueous suspensions of paper fibers and found the flow behavior close to the pipe wall was unaffected by the fibers. In contrast, drag reduction induced by polymers appears to be associated with near wall effects. Wells and Spangler [1967] found that, when polymer solutions were injected into the centerline of a water flow, no reduction in local pressure gradient was observed until the polymer solution diffused into the wall region. The mechanistic difference between drag reduction by polymer solutions and by fiber suspensions was demonstrated by Lee et al. [1974], and by Kale and Metzner.
[1974] who tested mixtures of fibers and polymers and obtained greater drag reduction than either individual additive. Recently, the injection of concentrated polymer solution at the centerline of a flow was also investigated by Berman and Sinha [1984], and by Bewersdorff [1984]. These authors found the injected polymer solutions, when in high concentrations, formed an intact thread at the centerline in the flow direction. Although by visualization no polymers apparently diffused to the wall, significant drag reduction was observed. Apparently, the mechanism of this heterogeneous drag reduction is different from that of homogeneous solutions. One proposed explanation for polymeric drag reduction is the formation of long strings and networks by the entanglement of macromolecules which can interact with and suppress turbulent eddies. Although this is possible in concentrated polymer solutions, it is unlikely that the network can be formed in some dilute solutions which, with concentrations of only a few parts per million or less, have been reported to show significant drag reduction [Fisher and Ferdinand, 1971; Oliver and Bakhtiyarov, 1983; McCormick et al., 1990a, 1990b]. Another explanation provided is based on the concept of vortex stretching [Gadd, 1968, 1971]. It was suggested that the elongation of the molecules causes large tensile forces along the streamline which inhibit vortex stretching. The drainage experiment performed by Gadd [1968], in which it was found that the time needed to drain liquids from a tank was longer for polymer solutions than for solvent, seems to give support to this
theory. One other proposed mechanism is based on the increase of elongational viscosity and its effect on turbulent eddy generation and growth. Researchers suggested the existence of a critical stretching velocity (or elongational rate) above which the elongational viscosity becomes very high and it is able to influence the turbulent behavior close to the wall [Hoyt, 1986].

In surfactant solutions, rod-like micelles and the secondary structure they form are believed to be responsible for the drag reduction capability [Ohlendorf et al., 1984a, 1986a]. Ohlendorf et al. [1986a] found that the length of the rod-like micelles in their systems studied was of the order of several hundred angstroms which is one order of magnitude less than the minimum length proposed by Peterlin [1939] for non-interacting rod-like particles to influence the flow. Therefore, Ohlendorf et al. [1986b] suggested that the drag reduction of surfactant solutions is unlikely to be caused by individual rods. Rather, it is probably brought on by the superstructure formed by a network of interacting rods. From the results of their NMR and linear dichroism studies on the CTAB/NaSal surfactant solutions, Ulmius et al. [1979] proposed that a long-range periodic structure is responsible for the viscoelasticity in the solutions. They suggested that the micelles are randomly oriented when the solution is at rest. When a shear stress is applied to the solution, an elastically deformed lattice structure is formed, with each corner of the lattice unit taken up by one rod-like micelle (also see
Hoffmann et al. [1981b]). The changes of micellar structure under high shear stress were explored by Bewersdorff et al. [1986, 1989] and Lindner et al. [1990] using small angle neutron scattering (SANS) technique. They found that the anisotropy of the SANS scattering pattern increases with increasing flow rate, which indicates increasing orientation of rod-like micelles in the flow field. Bewersdorff et al. [1989] found that, even in the turbulent flow region, the alignment of the rod-like micelles in the flow direction increased with increasing flow rate. When the critical wall shear stress, above which drag reduction starts to decrease, was exceeded, a reduction in scattering anisotropy was observed but the scattering curves were nearly the same as that for the solution at rest. Accordingly, they inferred that the breakdown of drag reduction at high shear was not due to scissions of the micelles themselves. Instead, it was the orientation of micelles that was destroyed [Bewersdorff et al., 1986]. Conflicting results were reported on the size changes of rod-like micelles in surfactant solutions after experiencing high shear stress in turbulent flows. Bewersdorff et al. [1989] found by light scattering that the size of the rod-like micelles in a 2.4 mM/2.4 mM TTAB/NaSal solution did not change after a turbulent flow experiment was made. However, they noticed a decrease in the number of rod-like micelles and an increase in the number of spherical ones. In a more recent publication, the same research group [Lindner et al. 1990] reported
that, after a 2.4 mM/2.4 mM TTAB/NaSal solution was continuously sheared in a turbulent flow for several hours, the average micelle size increased.

3.2 Basic Terms

Some fundamental definitions in fluid mechanics are introduced in this section. The wall shear stress in pipe flow is related to the pressure drop by the following equation:

\[ \tau_w = \frac{D}{4L}(-\Delta P) \]  

(1)

where \(-\Delta P\) is the pressure drop, \(D\) the pipe diameter, and \(L\) the pipe length.

The Fanning friction factor is defined by:

\[ f = \frac{\tau_w}{\frac{1}{2} \rho V^2} \]

(2)

where \(V\) is the mean flow velocity and \(\rho\) is the solution density. Since the quantities of drag reducers in the solution are usually small, the solvent density is frequently used to replace the solution density in the above equation.

Savins [1964] defined the drag ratio as:

\[ DR = \frac{-\Delta P}{-\Delta P_s} \]  

(3)
where \( \Delta P \) and \( \Delta P_s \) are the pressure drops by the drag reducing solution and by the solvent respectively based on the same flow rate in the same pipe. If the drag ratio is less than one, the fluid is drag reducing. The percent drag reduction, \( \%DR \), can be defined by:

\[
\%DR = 100(1 - DR) \tag{4}
\]

From equations 1-4, one can also write:

\[
\frac{f}{f_s} \cdot \%DR = 100 \left(1 - \frac{f}{f_s}\right) \tag{5}
\]

where \( f \) and \( f_s \) represent the friction factors of the solution and the solvent respectively at the same flow rate. A fluid is drag reducing if the \( \%DR \) values are greater than zero, and the greater the value, the more effective it is.

Newtonian fluids in a turbulent pipe are known to follow the von Karman equation:

\[
f^{1/2} = 4.0 \log_{10} \left( \frac{N_{Res} f^{1/2}}{10} \right) - 0.4 \tag{6}
\]

The \( N_{Res} \) in the equation is the solvent Reynolds number defined by:

\[
N_{Res} = \frac{\rho_s VD}{\mu_s} \tag{7}
\]

where \( \rho_s \) is the solvent density and \( \mu_s \) is the solvent viscosity. Thus fluids with data points lying below this line in a \( f \) vs. \( N_{Res} \) chart are drag reducing.
3.3 Maximum Drag Reduction Asymptote

Different asymptotes of maximum drag reduction (or minimum friction) have been proposed by a number of researchers, most of which are in a power-law form. For example, Castro and Squire [1967] studied two different molecular weights of polyethylene oxide and reported the following equation:

$$f = 1.40N_{Re}^{-2/3}$$  \hspace{1cm} (8)

A maximum drag reduction asymptote with a form similar to the von Karman equation (eq. 6) was first given by Gills and Pettit [1967] from correlating the drag reduction data for polyethylene oxide aqueous solutions. Their equation is:

$$f^{-1/2} = 17.4 \log_{10}(N_{Re}^{1/2}) - 27.0$$  \hspace{1cm} (9)

A better known equation of the same form was proposed by Virk et al. [1970b] by correlating drag reduction data of different polymers in both water and organic solvents [Virk et al., 1970b; Virk, 1971] from a number of sources:

$$f^{-1/2} = 19.0 \log_{10}(N_{Re}^{1/2}) - 32.4$$  \hspace{1cm} (10)

According to Virk [1975a], for shear thinning solutions, Reynolds numbers based on apparent wall viscosity are preferred in using this equation. Virk [1970b, 1975a] also proposed an asymptote in a power-law form:

$$f = 0.58N_{Re}^{-0.58}$$  \hspace{1cm} (11)
which he suggested was valid for Reynolds numbers ranging from 4,000 to 40,000.

The drag reduction curves for most polymer solutions have been shown by a number of researchers to be located in a domain bounded by the von Karman line (eq. 6) and by Virk's maximum drag reduction asymptote (eq. 10). Although in some cases, drag reductions exceeding the asymptote have been reported [Hershey et al., 1975; Lee et al., 1974; Cho and Hartnett, 1982], the asymptote is still widely used as a reference curve by most drag reduction workers.

3.4 Mean Velocity Profile

The turbulent flow velocity profile for Newtonian fluids includes three zones, the viscous sublayer, the buffer layer, and the turbulent core [for example, see Brodkey, 1967]. For convenience, the outer wake region is not considered here [Granville, 1977; Huang, 1974]. These three zones are described by the following dimensionless velocity profiles:

1. Viscous sublayer (0 < y<sup>+</sup> < 5):
   \[ U^+ = y^+ \]  
   \( (12) \)

2. Buffer layer (5 < y<sup>+</sup> < 30):
   \[ U^+ = 5.0 \ln y^+ - 3.05 \]  
   \( (13) \)
3. Core region (30 < \( y^+ \)):

\[
U^+ = 2.5 \ln y^+ + 5.5
\]  
(14)

The dimensionless velocity, \( U^+ \), is defined as:

\[
U^+ = \frac{u}{U_\tau}
\]  
(15)

where \( u \) is the time average velocity in the mean flow direction at a distance \( y \) from the wall. \( U_\tau \) is the shear velocity (or friction velocity) defined by:

\[
U_\tau = (\tau_w/\rho)^{1/2}
\]  
(16)

The dimensionless distance, \( y^+ \), is defined as:

\[
y^+ = \frac{U_\tau y}{\nu}
\]  
(17)

where \( \nu \) is the kinematic viscosity of the solution.

For drag reducing fluids in the turbulent region, early researchers proposed a two-zone model to describe the velocity profile. Elata et al. [1966] suggested that a viscous sublayer (eq. 12) extends to a higher \( y^+ \) and intersects a line which shifts upwards from the Newtonian core (eq. 14). The two-zone model (eqs. 12 and 19), although useful in describing moderate drag reduction, is not adequate for the case of high drag reduction. Based on their maximum drag reduction asymptote (eq. 10), Virk et al. [1970b] mathematically derived a velocity profile of a semilogarithmic form (eq. 18). Virk [1971] later cited experimental evidence from the work of Seyer and
Metzner [1969] to support the existence of this "ultimate profile". Virk's three-zone model can be summarized as (also see Figure 2):

1. Viscous sublayer \((0 < y^+ < 11.6)\):
   \[
   U^+ = y^+ \quad (12)
   \]

2. Elastic sublayer \((11.6 < y^+ < y_e^+)\):
   \[
   U^+ = 11.7 \ln y^+ - 17.0 \quad (18)
   \]

3. Core region \((y_e^+ < y^+)\):
   \[
   U^+ = 2.51n y^+ + 5.5 + \Delta B \quad (19)
   \]

where \(\Delta B\) is an effective shift from the Newtonian law of the wall equation (eq. 14). The value \(y_e^+\) is obtained by solving eqs. 18 and 19:
\[
y_e^+ = \exp\left(\frac{\Delta B + 22.5}{9.2}\right) \quad (20)
\]

### 3.4 Diameter Effect and Scale-up Procedure

For Newtonian fluids, the effect of pipe diameter is completely absorbed in the Reynolds number, and the friction factor is a one-to-one function of Reynolds number. In laminar flow, the relationship between friction factor and Reynolds number is described by the simple expression:
\[
f = \frac{16}{N_{Re}} \quad (21)
\]
Figure 2. Dimensionless velocity profile for turbulent flow
and in turbulent flow, by the von Karman equation (eq. 10) or the Blasius equation:
\[ f = 0.079 \frac{N}{Re}^{-1/4} \]  

For purely viscous non-Newtonian fluids, Dodge and Metzner [1959] have proposed that for flow in the laminar region,
\[ f' = \frac{16}{N_{Re}'} \]  
and in the turbulent region (a chart of \( f' \) vs. \( N_{Re} \) was also provided in the same article):
\[ f'^{1/2} = \frac{4.0}{(n')}^{3/4} \log_{10} \left[ N_{Re} ' f' (n'/2) \right] - \frac{0.4}{(n')^{1.2}} \]  
The generalized Reynolds number, \( N_{Re} ' \), is defined by:
\[ N_{Re} ' = \frac{\rho V^{2-n} D^{n}}{K' 8^{n-1}} \]  

where \( n' \) and \( K' \) are the power-law index and consistency index respectively. Therefore, for a given purely viscous non-Newtonian fluid, the diameter effect is incorporated in the \( N_{Re} ' \).

In the case of drag reducing non-Newtonian fluids, a single \( f \) vs. \( N_{Re} \) curve can no longer describe the flow behavior in different sizes of pipe except for the case of maximum drag reduction. A number of efforts have been made to deal with the diameter effect as it is very important in scale-up. The scale-up methods can be classified into two categories: reduced variable
correlations and predictions based on velocity profile models [White and Hemmings, 1977].

Darby and Chang [1984] correlated the drag reduction data for both fresh and degraded polyacrylamide solutions in six different sizes of pipe. Based on an energy dissipation model, they proposed an equation relating drag ratio with Deborah number. The Deborah number was determined in a semi-empirical way and was shown to be a function of flow velocity, pipe diameter, solvent viscosity, and the viscoelastic properties of the solution. According to their method, the only information needed to predict drag reduction in a large pipe is the basic shear diagram of the solution. However, since the equation Darby and Chang [1984] derived was based on only one kind of polymer, and since most drag reducing polymer solutions are at such low concentrations that the viscoelasticity is not measurable, their model is of limited use. Whitsitt et al. [1969] suggested that, for a given polymer-solvent pair at a certain concentration, drag reduction is a unique function of wall shear stress (or shear velocity). They found the relationship held for pipe diameters ranging from 0.18 to 6 inches. Savins and Seyer [1977] found that a plot of percentage drag reduction against the solvent shear velocity calculated at the same flow velocity would give a better correlation. Sellin and Ollis [1983] examined the correlation method of Whitsitt et al. on their polyethylene oxide and polyacrylamide solutions and found the method did not provide satisfactory predictions.
A scale-up method based on the turbulent velocity profile was proposed by Granville [1977] who assumed the shift of the logarithmic velocity profile, $\Delta B$, is a function of the following parameters:

$$\Delta B = \Delta B(P, C, U_\tau \zeta / \nu)$$

(26)

where $P$ is the polymer type, $C$ the polymer concentration, and $\zeta$ the characteristic polymer dimension (e.g. radius of gyration). Huang [1974] studied the drag reduction of four types of commercial polymers under various conditions and concluded that $\Delta B$ depends on polymer species, temperature, and $U_\tau \zeta / \nu$. He also showed that $\Delta B$ increases with the square root of polymer concentration and is independent of pipe diameter. Accordingly, $\Delta B$ is expected to play an important role in the scale-up procedure. If one integrates the turbulent velocity profile across the pipe, the mean flow velocity is given by:

$$V = \frac{1}{\pi R^2} \int_0^R 2\pi (R - y) u \, dy$$

(27)

where $V$ is the mean velocity and $R$ is the pipe diameter,

or by:

$$V = \frac{2 U_\tau}{(R^+)^2}$$

(28)

where

$$R^+ = \frac{R U_\tau}{\nu}$$

(29)

and
\[ \Phi = \int_0^{R^+} (R^+ - y^+) U^+ dy^+ \] (30)

For drag reducing fluids, \( \Phi \) is a function of \( \Delta B \) and \( R^+ \) (or \( U_\tau \)). By using eqs. 28 and 29, the Reynolds number can be expressed as:

\[ N_{Re} = \frac{4 \Phi}{R^+} \] (31)

Using the definition of friction factor (eq. 2) together with eq. 16, the shear velocity, \( U_\tau \), can be expressed as:

\[ U_\tau = \frac{\nu}{R} \frac{N_{Re}}{f^{1/2}} \] (32)

which leads to

\[ R^+ = 8^{-1/2} N_{Re} f^{1/2} \] (33)

Equations 31 and 33, together with a turbulent velocity profile, are the basis for the scale up procedure. Since \( \Phi \) in eq. 30 is a function of \( \Delta B \) and \( R^+ \), from eq. 31, \( N_{Re} \) can also be expressed as a function of \( \Delta B \) and \( R^+ \). Combining eqs. 31 and 33, and eliminating \( R^+ \) from the equations, one obtains a relationship between \( f \) and \( N_{Re} \) with \( \Delta B \) as a parameter:

\[ f = f (N_{Re}, \Delta B) \] (34)

For Newtonian fluids, \( \Delta B \) equals zero and an expression similar to the von Karman equation can be obtained. For a given drag reducing fluid, Granville [1977] assumed the \( \Delta B \) is only a function of \( U_\tau \zeta /\nu \) and is independent to pipe diameter. Therefore, in going from pipe diameter \( D_1 \) to \( D_2 \), we have:
where the subscripts 1 and 2 represent parameters for pipe 1 and pipe 2 respectively. For a given drag reducing fluid, $\zeta$ and $\nu$ are considered to be the same under the same shear stress in different sizes of pipes. As a result, we obtain:

\[
(U_\tau)_1 = (U_\tau)_2 \tag{36}
\]

or alternately by using eq. 32:

\[
\frac{(N_{\text{Re}} f^{1/2})_1}{D_1} = \frac{(N_{\text{Re}} f^{1/2})_2}{D_2} \tag{37}
\]

Equation 37 serves as a bridge between two pipes with different diameters.

Granville [1977] used Virk’s three-zone velocity model plus a velocity profile in the outer wake region to derive a relationship connecting $f$, $N_{\text{Re}}$, and $\Delta B$. In the case of moderate drag reduction for which the elastic sublayer can be neglected, Granville proposed a simple method, termed method of two loci, for the scale-up. It is most convenient to use a von Karman plot ($f^{1/2}$ vs. $N_{\text{Re}} f^{1/2}$) for scale-up. Each measured point in pipe 1 plotted in von Karman coordinates, $(f^{1/2}, N_{\text{Re}} f^{1/2})_1$, corresponds to a certain $U_\tau$ and $\Delta B$ combination. In scaling from pipe 1 to pipe 2, this point (point 1) has a corresponding point in pipe 2 (point 2) with the same $U_\tau$ and $\Delta B$ values. Point 2 can be located by finding the intersection of the constant $\Delta B$ line where point 1 is located and the constant $N_{\text{Re}} f^{1/2}$ line whose
value is determined by eq. 37. For moderate drag reduction, the constant $\Delta B$ lines are simply a family of straight lines parallel to the von Karman line. By doing this point by point, the predicted drag reduction curve can be obtained. Although the method of two loci has proven successful in scale-up of drag reducing behavior for moderate changes of pipe diameter [Sellin and Ollis, 1983; Havlik, 1984], it can only be used for drag reducing flows in which the turbulent core dominates the pipe cross-section since the elastic sublayer was ignored. Sellin and Ollis [1983] found the method didn’t give good predictions in going from small pipes with diameters less than 5 mm to 50 mm diameter pipes. They also pointed out the method can not give satisfactory results for good drag reducers. The elastic sublayer was considered by Matthys and Sabersky [1982] who used an iteration method in treating the diameter effect. Granville [1984] later refined his scale-up method of two loci by including the elastic sublayer in the new graphical procedure. The new method is similar to the old one except the constant $\Delta B$ lines are no longer straight lines parallel to the von Karman line. Rather, they curve downwards near the elastic sublayer region and are determined by eqs. 31 and 33, along with the turbulent velocity profile.
3.6 Micelle Formation and Shape Transformation

At very dilute solutions, ionic surfactants act as normal electrolytes in water. As the surfactant concentration is increased, the unfavorable contact between the nonpolar part of the surfactant molecule and water causes an increase in the free energy of the system. In order to reduce this contact while retaining the polar part of the molecule in an aqueous environment, micelles are formed. Early researchers believed micelles were spherical [Reychler, 1913; Adam, 1925]. McBain [1944] suggested that there were two forms of micelles, one being a spherical micelle containing less than 10 surfactant molecules, and the other being a lamellar shaped micelle. Now it is generally agreed that micelles formed at or slightly above the CMC are spheres or oblate ellipsoids [Tanford, 1974; Tartar, 1955].

In fact, the micellar structure in the surfactant solutions depends on the free energy of different interactions inside the micelles and between the micelles. It can be written as:

\[ G_{\text{total}} = G_{\text{inter}} + G_{\text{intra}} \]

where \( G_{\text{total}} \), \( G_{\text{intra}} \), and \( G_{\text{inter}} \) stand for free energy of the whole system, that contributed by intramicellar interactions, and that contributed by intermicellar interactions, respectively. The intramicellar interaction term, \( G_{\text{intra}} \), consists of the following contributions:

1. Interactions between surfactant hydrophobic chains in the
same micelle (van der Waals forces)

2. Interactions between surfactant headgroups, including both electrostatic and steric effects

3. Interactions of surfactant chains and headgroups with water

4. Interactions between surfactant chains and the nonpolar parts of counter-ions

5. Interactions between surfactant headgroups and the hydrophilic parts of counter-ions, including both electrostatic and steric effects

The intermicellar term, $G_{\text{inter}}$, includes the following:

1. Electrostatic repulsions between charged micelles

2. Steric hindrance by other micelles

3. Van der Waals attraction forces between micelles

4. Chemical forces such as hydrogen bonding between micelles

5. Repulsions between micelles due to solvent mediated forces

In order to explain the shape transition between micelles, the surface area taken up by each surfactant headgroup in each geometric shape of micelle needs to be discussed first. Assuming that it takes N spheres to form a rod with both ends capped by hemispheres, and it takes M rods to form a plate with four half-cylindrical ends, then between the spheres and rod, we have the following relationship:
\[ N \left( \frac{4\pi r^3}{3} \right) = \pi r^2 \ell + 2 \left( \frac{2\pi r^3}{3} \right) \]  

(38)

or

\[ \ell = \frac{4}{3} (N-1)r \]  

(39)

where \( r \) is the radius of a sphere or rod, and \( \ell \) is the length of the rod.

The ratio of the surface of a rod, \( S_r \), to that of \( N \) spheres, \( NS_s \), is given by:

\[ \frac{S_r}{NS_s} = \frac{2\pi r \ell + 4\pi r^2}{N \left( 4\pi r^2 \right)} \]  

(40)

Inserting eq. 39 into eq. 40, we have:

\[ \frac{S_r}{NS_s} = \frac{2N + 1}{3N} \]  

(41)

Thus for the same number of surfactant molecules to pack in a rod results in a reduction of \( 1/3 \) of the surface area when compared to their packing in \( N \) spheres (where \( N \gg 1 \)). The same considerations can be applied between rod and plate:

\[ M(\pi r^2 \ell + \frac{4}{3} \pi r^3) = 2rW_1W_2 + 2\pi r^2 \ell \]  

(42)

or

\[ \frac{W_1W_2}{2r} = \frac{(M-2)\pi r \ell + \frac{4}{3}M\pi r^2}{2r} \]  

(43)

where \( W_1 \) and \( W_2 \) are the length and width of the plate. The ratio of the surface area of a plate, \( S_p \), and that of \( M \) rods, \( MS_r' \), is calculated by:
Inserting eq. 43 into eq. 44, we have:

\[
\frac{S_p}{MS_r} = \frac{2 W_1 W_2 + 4\pi r l}{M(2\pi r l + 4\pi r^2)}
\]

(44)

Thus when \( M \) is large and \( l \gg r \), a reduction of \( 1/2 \) in surface area is obtained in going from \( M \) rods to one plate.

For dilute solutions \( G_{\text{inter}} \) is less important than \( G_{\text{intra}} \). Without added salts the repulsions between charged headgroups favor the formation of spherical micelles while the greater exposure of hydrocarbon chains to water favors the formation of rod-like micelles. Since the concentration is low, the former factor overpasses the latter, and the micelles formed are spherical in shape. As concentration increases, the number of spheres also increases which raises the importance of \( G_{\text{inter}} \). When the system energy gained due to the electrostatic and steric effects between micelles as well as to the increased hydrocarbon-water contact exceeds that caused by the intramicellar charge repulsions, a sphere-to-rod transition is necessary. The concentration at which this occurs is called the CMC_{II}. For cetyltrimethylammonium bromide (CTAB) solutions, this corresponds to a concentration of 0.3 M or 10% by weight [Ekwall et al., 1971; Gotz and Heckmann, 1958]. A further increase in concentration results in continuous lengthening of the rod-like micelles until a certain concentration is
reached, where a second structure, liquid crystal, appears. There are four well-defined liquid crystal phases described in the literature, namely, lamellar, hexagonal, inverse hexagonal, and cubic phases [Tiddy, 1980; Lindman, 1985]. Forces between micelles in the liquid crystal phase are balanced by van der Waals attraction forces, electrostatic forces, and hydration forces (repulsion forces between bonded water on micellar surface). For CTAB solution, a hexagonal array consisting of rod-like micelles is formed at concentrations above 0.71 M (26%) [Ekwall et al., 1971]. The phase transition of surfactant systems can be summarized as follows:

increasing concentration —►

<table>
<thead>
<tr>
<th>surfactant ions</th>
<th>spherical micelles</th>
<th>rod-like or disk-like micelles</th>
<th>liquid crystal</th>
</tr>
</thead>
</table>

(isotropic phase) ▵  anisotropic phase

3.7 Micellar Geometric Packing Constraints

A simple criterion has been proposed by Israelachvili et al. [1976] for determining the shape of micelles under different conditions. They suggested that the free energy per surfactant molecule in the micelle, $\mu_N^0$, can be expressed by:

$$\mu_N^0 = \gamma a + \frac{A}{a} + g$$  (46)
where $\gamma$ is the interfacial free energy, $a$ the surface area taken by a surfactant headgroup, $A$ a constant, and $g$ the bulk free energy per surfactant. The first term on the right hand side is the energy contribution due to the hydrocarbon-water contact (interfacial tension) which is proportional to the area exposed to water. The second term includes the effect of electrostatic repulsions between charged headgroups, hydration forces, and steric headgroup interactions which are assumed to be inversely proportional to the area per headgroup. The last term on the right, $g$, is the self energy of the alkyl chain. Since the micellar core is considered as liquid-like, the last term is close to the free energy of a liquid hydrocarbon compound and is only a function of temperature and chain length. When each surfactant molecule in the micelle is in the most stable state, the minimum free energy is obtained by $\frac{\partial \mu}{\partial a} = 0$ through which we have:

$$\mu_{N, \text{min}}^0 = 2\gamma a_0 + g$$

(47)

where $\mu_{N, \text{min}}^0$ is the minimum free energy and $a_0 = (A/\gamma)^{1/2}$ is the optimal area taken up by a surfactant headgroup on the micelle surface.

Consider a spherical micelle in which all the surfactants are at the lowest energy level (that is, each one of the headgroups occupies an optimal area, $a_0$). The ratio of volume to surface area for the micelle can be expressed by:

$$\frac{N_0 v_0}{N_0 a_0} = \frac{4/3 \pi r^3}{4\pi r^2}$$

(48)
where $N_0$ is the aggregation number, $r$ the radius of the sphere, and $v$ the volume of each hydrophobic chain. Tanford [1972] used the X-ray data of Reiss-Husson and Luzzati [1964] to obtain the following equations:

$$v = (27.4 + 26.9n) \text{Å}^3 \text{ per hydrocarbon chain}$$

(50)

$$I_0 = (1.5 + 1.265n) \text{Å} \text{ per hydrocarbon chain}$$

(51)

where $n$ is the number of carbon atoms in the chain. Since $r$ is no greater than the length of a fully extended chain, $l_0$, we have:

$$\frac{v}{a_0 l_0} < \frac{1}{3}$$

(52)

This provides a criterion for formation of spherical micelles. Similarly, for rod-like micelles, we have:

$$\frac{v}{a_0 l_0} < \frac{1}{2}$$

(53)

Although the region $v/l_0 a_0 < 1/3$ is covered by both inequalities, the sphere is entropically favorable. Therefore, the condition for rod-like micelles to form is:

$$\frac{1}{3} < \frac{v}{a_0 l_0} < \frac{1}{2}$$

(54)

Similarly, for disk-like micelles:

$$\frac{1}{2} < \frac{v}{a_0 l_0} < 1$$

(55)
The dimensionless parameter, \( \frac{v}{a_0 \ell_0} \), is termed the "geometric packing parameter" and can be utilized to predict the shape of the micelle.
CHAPTER IV
EXPERIMENTAL

4.1 Flow Systems

Drag reduction experiments at high temperatures (up to 150°C) were performed in a circulation heating system whose schematic is shown in Figure 3. The test section was a 22.69 inches long stainless steel tube with a diameter of 0.243 inch. A smaller, 0.106-inch tube, which is 20.94 inches long, can replace it to study the diameter effect. To minimize heat loss in high temperature tests, the system was insulated by fiber glass material. The pump was an Oberdorfer bronze rotary gear pump (Model 11500), driven by a 2hp Vickers variable speed drive. The pumping rate was controlled by a Dayton SCR motor controller (Model 4Z377B) connected to the drive. A wire mesh strainer was installed on the pump suction line to prevent large particles from entering the pump. Another strainer was placed between the pump outlet and the test section entrance. A one gallon bellow-type accumulator was installed on the output line of the pump to dampen pressure fluctuations in the loop. Another two accumulators in the system,
Figure 3. Schematic of high temperature flow loop
each being four gallons in volume, also served for the same purpose. In addition, the accumulator located before the test section provides better thermal mixing of the test solution before the flow enters the test tube, and the one on the suction line can increase the suction head and thus prevent the occurrence of cavitation.

Fluid temperatures at the inlet and outlet of the test section were both measured by K-type thermocouples. High temperature runs were carried out using two 2000 watt heaters along with a 750 watt trimmer heater. The latter heater was connected to a temperature controller which controlled temperature to ± 1.0°C. Since the maximum sheath temperature for the heaters used was 350°F (177°C), the operating temperature in the heating system was confined to below 155°C. Pressure drops were measured by a Validyne differential pressure transducer (Model DP 15-52; pressure range = 0-200 psi). The pressure transducer was calibrated as follows. One end of the transducer was connected to the flow system, leaving the other end opened to the atmosphere. A precision gage which had previously been calibrated with a dead weight tester was then connected to the system. By adjusting the system pressure using nitrogen gas, a relationship between the transducer signal and the system pressure can be obtained. 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 given
speed and the water coming out from the opened end was 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 constructed.

Low temperature tests were carried out in a cooling loop shown in Figure 4. The test section of the system was a 48-inch long stainless steel tube with inside diameter of 0.243 inch. The system was equipped with a PolyScience chilling unit (Model KR-60A) which included a 1/2-hp compressor and a constant temperature circulator. A 50% ethylene glycol and 50% water mixture was used as the coolant. Heat was removed from the test system by the coolant passing through a stainless steel shell and tube heat exchanger. The refrigerating load was about 4200 Btu/hr at 5°F. The lowest temperature attainable in the test system was 2°C. The flow system was insulated with polyethylene foam to prevent heat from exchanging with the environment. Since the maximum temperature that the insulation material can sustain is 110°C, tests above this temperature could not be run in the cooling loop. The specifications of the pump and the measuring devices were the same as those in the high temperature loop.

A schematic of the 6-inch pipe system at Argonne National Laboratory is shown in Figure 5. The test section was a 60-foot long carbon steel pipe with inside diameter of 6.065 inches. The pipe was covered with fiber glass
Figure 4. Schematic of low temperature flow loop
Figure 5. Schematic of 6-inch pipe circulating system at Argonne National Laboratory.
to prevent heat loss. The system included two 3000-gallon stainless steel tanks serving as accumulators. However, only one of the tanks (the hot tank) was used in the tests. The flow was driven by a 50-hp centrifugal pump (Lincoln AC Motor) which had a maximum capacity of 1100 gallons per minute. Flow rates which were controlled by a valve on the output line of the hot tank were measured with a Polysonics Hydra ultrasonic flow meter (Model DHT-P). Three pressure taps were located along the test section. The pressure drops between taps 1 and 3 were measured by a Sensontac pressure transducer (Model 1018-2; pressure range = 0-1.0 psi). Another pressure transducer (Sensontac, Model A5; pressure range = 0-0.5 psi) was used to read the pressure differences across taps 2 and 3. The heat necessary for high temperature tests was provided by steam through a shell and tube heat exchanger.

4.2 Surfactant Solutions

Each surfactant solution used was comprised of two major ingredients: a quaternary ammonium surfactant and a counter-ion (see Figure 6). All the commercial surfactants tested and their chemical structures are summarized in Table 22 in APPENDIX A. The chain distributions of some of the surfactants, based on which surfactant molecular weights were calculated,
Figure 6. Chemical structure of cationic surfactants and aromatic counter-ions
are listed in Table 23. Shown in Table 24 are the counter-ions studied in this research and their chemical structures.

Test solutions were prepared according to the procedure described below. The surfactant was weighed in a one-liter beaker. One liter of distilled water was then added to the beaker and the mixing was provided by a magnetic stirrer. For some long chain surfactants such as Kemamine Q-2983C, Q-2803C and EX-300 which have poor solubilities in water at room temperature, hot water (Over 70°C) were used to dissolve the surfactants. The same is true for the surfactants supplied by Hoechst company, HABON and DOBON. The well-mixed surfactant solution was then slowly added to 20 liters of stirring distilled water in a 30-liter container lined with polyethylene. The counter-ion was prepared in a separate one-liter beaker. Most of the counter-ions used were in their acid form and had to be neutralized by an equivalent amount of NaOH. Counter-ions in salt form, such as sodium salicylate and sodium tosylate, easily dissolve in water. The counter-ion solution was added to the 30-liter container and enough distilled water was then added to make up a 30-liter solution. The prepared solution was mixed for 30 minutes by an electrically driven mixer and then loaded into the flow system.

The 5 mM/12.5 mM Ethoquad EX-300/NaSal solution tested in the 6-inch pipe system at Argonne National Laboratory was prepared as follows. Fifty pounds of NaSal was weighed and placed in a 200-gallon stainless steel
tank. About one hundred gallons of deionized water, previously preheated to 80°C in the test loop, was introduced to the tank. Mixing was then provided by a pneumatic mixer. While mixing continued, 77 pounds of Kemamine EX-300 (75% active) was added to the tank. Another one hundred gallons of deionized water was then added to make a 200 gallon solution. The 75 mM/187.5 mM Kemamine EX-300/NaSal concentrate solution was left over the weekend and injected into the flow loop by a pump through the bottom of the 3000-gallon tank. While pumping continued, an equivalent amount of water was removed through the overflow line on the top of the tank. The diluted solution was then circulated at a pumping rate of 700 gpm for one hour before the measurements were made.

4.3 Drag Reduction Tests

For both the heating and the cooling loops, the prepared solution was fed into the system through the opening located above the accumulator on the suction line. After the accumulator and the suction line were filled up, the pump was run at low speed to drive the solution into the rest of the loop. About 1/4 of the accumulator on the suction line was left unfilled which was then purged with nitrogen to minimize any possible interactions between surfactant solution and oxygen. The pressure of the system was adjusted to 15 psig with nitrogen. The fluid was heated to 50°C and allowed to circulate
for 2 hours at that temperature. Pressure drops at different times under a constant flow rate were recorded to monitor any possible changes during the circulation. This was to ensure that an equilibrium for the solution was reached before any data were taken. For most of the surfactant systems studied, only minor changes were observed during the circulation. In some cases, particularly for solutions containing the Ethoquad Series of surfactants from Akzo Chemicals, the drag reduction of the solutions was found to increase with time. For these solutions, the variations of pressure drop with time at constant flow rate was closely tracked until an equilibrium reading was obtained. This will be discussed in detail in Section 5.8, "Effect of Preshearing". A higher circulation temperature (80°C) was needed for the surfactants with poor solubility at low temperature. Examples include long chain surfactants (C_{22}), DOBON, HABON, and the surfactant systems containing binuclear aromatic counter-ions (e.g. 3-hydroxy-2-naphthoate) or multiple substituted benzoates (e.g. 5-chlorosalicylate).

For the tests at a given temperature, each time the flow rate was altered the solution was circulated for five minutes before the stable reading was recorded. When the test was switched to a new temperature, the solution was allowed to circulate at the new temperature for at least one hour before any flow data were taken. After all the tests for a given solution were completed, the solution was drained with the aid of compressed air. The system was then filled with tap water. With the heater turned on, the
water was allowed to circulate at medium high speed until a temperature of 120°C (100°C for the low temperature loop) was reached. The system was then completely drained and replaced with fresh water. The flushing process was repeated at least five times to ensure the removal of any surfactant residue.

4.4 Data Processing

From the flow rates measured, fluid velocities in the test section can be obtained. The Reynolds numbers were calculated based on solvent properties. Water densities at temperatures from 0 to 250°C, as cited from Perry’s Chemical Engineers' Handbook, are tabulated in Table 25 in APPENDIX C. Viscosities of water from 0 to 100°C, also obtained from the same source, are listed in Table 26. Since the temperature range studied in this research also covered temperatures from 100 to 150°C, water viscosities in that range, which are not provided by the above literature, had to be properly estimated. The following equation, which is valid for water temperatures from -10 to 160°C [Makhija and Stairs, 1970], was used to calculate the viscosities of water from 100 to 150°C:

\[
\log_{10} \mu_w = -1.5668 + \frac{230.298}{T - 146.797}
\]  \hspace{1cm} (56)
where $\mu_s$ is the water viscosity in centipoise and $T$ the temperature in K. The average percentage error for the equation was reported to be 0.51%. In order to calculate the wall shear stresses, the measured pressure drop should be corrected for entrance and kinetic losses. The entrance loss can be represented by:

$$\Delta P_{\text{ent}} = K_1 \rho_s \left( V_1^2 - V_2^2 \right)/2 \quad (57)$$

where $V_1$ is the velocity at the test tube, $V_2$ is the velocity in the pipe before the test tube, and $K_1$ is an empirical constant. By using a mass balance, the equation can also be written as:

$$\Delta P_{\text{ent}} = K_1 \left( \frac{1 - \beta^2}{2} \right) \rho_s V_1^2 \quad (58)$$

where $\beta$ is the ratio of the cross-sectional area of the test tube to that of the pipe before the test tube. McMillan [1970] suggested that a $K_1$ value of 0.8 be used. The kinetic loss takes the following form:

$$\Delta P_{\text{k}} = K_2 \rho_s V_1^2 \quad (59)$$

For turbulent flows, a $K_2$ value of 0.5 was recommended [McMillan, 1970; Stapleton, 1983]. Both the $\Delta P_{\text{ent}}$ and $\Delta P_{\text{k}}$ are proportional to the kinetic energy per unit volumetric flow rate in the test tube. In the present work, the losses were incorporated into one term which was assumed to be of the form:

$$\Delta P_{\text{loss}} = K \rho_s V_1^2 \quad (60)$$
The constant, $K$, was empirically determined from the flow data of deionized water and was assumed to be constant for all fluids tested. The values of $K$ for the 0.243- and 0.106-inch tubes in the heating loop were found to be 0.69 and 0.71 respectively. The data for deionized water in the 0.243- and 0.106-inch tube flows, corrected with the above $K$ values, are shown in Figure 67 in APPENDIX D. For the 0.243-inch tube in the cooling loop, a $K$ value of 0.49 was obtained. The flow data of deionized water in this system are shown in Figure 68. With the corrected pressure drops, the Fanning friction factors for the test solutions can then be calculated using eq. 2. The percentage drag reduction, DR\%, is obtained using eq. 5 with the friction factor of the drag reducing fluid and that calculated by the von Karman equation (eq. 6) for the solvent at the same flow rate. In general, the repeatability of the drag reduction data for the surfactant systems studied was excellent as illustrated in Figure 70 and Table 27 in APPENDIX E. In Figure 70, the drag reduction data for a 5 mM/12.5 mM Arquad S-50/NaSal solution are presented. The test was carried out in such a way that the flow rate was first varied from low to high. When the highest tested flow rate was reached, the solution was allowed to be sheared continuously for 10 minutes and then the flow rate was decreased stepwise. As the data show, the drag reducing capability of the solution was reversible. Another test on the same solution was made in which the flow rate was randomly varied. The percent drag reduction results
from four different measurements at a specific flow rate were within \( \pm 1\% \) (Table 27).

In the 6-inch pipe system, the deionized water was tested at 173°F (78.3°C) and 198°F (92.2°C). The results shown in Figure 69 (APPENDIX D) indicate that at low flow rates the data points lie slightly above the von Karman line, but at high Reynolds numbers the friction factors become unusually high. This is probably due to roughness inside the pipe which increases the skin friction. In addition, there were three Victaulic couplings along the test section which can also increase the friction of the flow. To give a conservative estimate of the drag reduction effectiveness in this system, calculations of percentage drag reduction were based on the von Karman equation rather than the deionized water data.
5.1 Effect of Temperature

Figure 7 shows typical drag reduction curves for a surfactant solution in a 0.243-inch pipe flow at various temperatures. The solution was a tetradecyltrimethylammonium bromide/sodium salicylate (TTAB/NaSal) mixture with concentration of 5 mM and 12.5 mM respectively. Shown in the same figure are the von Karman line which describes the Newtonian fluid in turbulent flow and the maximum drag reduction asymptote given by Virk [1970]. The figure is presented as friction factor vs. solvent Reynolds number. Reynolds number based on solvent density and viscosity is frequently used in drag reduction studies so that drag reduction can be immediately seen as data below the von Karman line. Data points for Reynolds numbers less than $10^4$ can not be measured because of limitations of the equipment. For temperatures between 5 to 50°C, the friction factor at each temperature first decreases with increasing Reynolds number until a certain point is reached, then increases rapidly until it approaches the von
Figure 7. Flow data for a 5 mM/12.5 mM solution of TTAB/NaSal plotted as friction factor vs. solvent Reynolds number.
Karman line. The same data are plotted as percent drag reduction vs. solvent Reynolds number in Figure 8, in which maximum drag reduction up to 67% is seen at temperatures from 5 to 40°C. At 50°C, drag reduction started to decrease, and at 60°C no drag reduction was observed. For temperatures at and below 2°C, phase separation was observed during the test, and the originally transparent solution became cloudy. Drag reduction was also lost in this case.

In order to define the effective temperature range of drag reduction, a 50% cut-off was arbitrarily chosen. The effective temperature in this research has been defined as the temperature at which more than 50% of drag reduction is observed in flow through a 0.243-inch tube at Reynolds numbers from 10,000 to 500,000. For the 5 mM/12.5 mM TTAB/NaSal solution, the effective temperature range according to this definition is from 5 to 40°C. In order to characterize drag reduction effectiveness, a critical wall shear stress, $\tau_{wc}$, was taken at the point where percent drag reduction dropped to 50% in the 0.243-inch tube. It is believed this critical shear stress is a better criterion for evaluating drag reducing efficiency than the critical stress taken at the lowest point of the $f - N_{Re}$ curve as commonly used by other researchers. The reasons are given below. First, the existence of a $\tau_{wc}$ indicates that drag reduction greater than or equal to 50% can be observed. Second, for Newtonian turbulent flow, the friction factor is approximately proportional to $N_{Re}^{0.25}$ (Blasius equation). Accordingly, the wall shear
Figure 8. Flow data for a 5 mM/12.5 mM solution of TTAB/NaSal plotted as %DR vs. solvent Reynolds number.
stress at 50% drag reduction should be roughly proportional to $V^{1.75}$. Thus, higher critical shear stresses reflect higher flow rates that surfactant drag reducers can reach before losing their drag reducing capabilities. The following example shows the inadequacy of using the conventional critical wall shear stress to evaluate drag reduction effectiveness. Assuming that there are two $f - N_{Re}$ curves both of which show their minimum friction factors at the same Reynolds number, but with the $f$ value of one curve being twice that of the other curve. Drag reduction of the latter is apparently more effective than the former. However, critical wall shear stress calculated in the conventional way indicates the opposite order. In this work, unless otherwise noted, the critical wall shear stress stands for the wall shear stress taken at 50% drag reduction. The conventionally defined critical shear stress will be used solely in Section 5.6, "Effect of Pipe Diameter".

Changes in micellar characteristics explain the effect of temperature. In Figure 9 the phase diagram for an aqueous surfactant solution is plotted in terms of surfactant concentration and temperature. Three curves are shown in the diagram. The solubility curve describes the temperature dependence of concentration, that is temperatures below which separation occurs. The CMC curve is the minimum concentration needed to form spherical micelles. When the concentration is lower than the CMC, surfactants exist as individual molecules. The CMC curve is usually a weakly increasing function
Figure 9. Surfactant characteristics in terms of concentration and temperature
of temperature. In the concentration region between the CMC and the CMC_{II}, micelles of spherical shape are formed. For concentrations above the CMC_{II}, rod-like micelles dominate. The temperature at which the solubility curve intercepts the CMC curve is called the Krafft point temperature, a temperature below which micellization does not occur. The formation of rod-like micelles in the surfactant solution is a necessary condition for drag reduction to take place [Ohlendorf et al. 1984, 1986a]. As can be seen from the figure, for a fixed surfactant concentration, rod-like micelles can only be present in a certain temperature range. The upper critical temperature is determined by the so-called micellar shape transition temperature (the CMC_{II} curve) above which all the micelles transform into spheres, and no drag reduction can be observed. The lower temperature limit is controlled by the solubility curve of the surfactant solution. The length of the rod-like micelles has been shown to decrease with increasing temperature [Ohlendorf et al., 1984, 1986a, 1986b]. This is attributed to the increased thermal motion of the surfactant alkyl chains caused by the rising temperature. Ohlendorf et al. [1984, 1986a] found that the critical wall shear stresses for the cetyltrimethylammonium and the tetradecyltrimethylammonium salicylate (CTASal and TTASal) systems were a decreasing function of temperature. Accordingly, they concluded that the critical shear stress, and thus the drag reducing efficiency, is mainly determined by the micellar length. The drag reduction of alkyltrimethylammonium salts in the presence
of 1-naphthol was studied by Elson and Garside [1983]. Their results show that, although the critical wall shear stress decreased with increasing temperature for the CTAB/1-naphthol system, it increased with temperature for the ETAB (C_{22})/1-naphthol system. For all the surfactant solutions studied here including the TTAB/NaSal system, the critical shear stress first increases with increasing temperature until a maximum is reached, then decreases as temperature is further increased. Since the tested temperature ranges in our studies were much broader than those of the above authors, it is very likely that the trends observed by these workers were only a part of the entire $\tau_{wc}$ vs. temperature curve. In the case of the TTAB/NaSal solution, our result shows the temperature at which the maximum $\tau_{wc}$ occurs, as listed in Figure 8, is at 10°C while the temperature range for TTASal (corresponding to 1:1 molar mixture of TTAB and NaSal) studied by Hoffmann et al. [1986a] was from 15 to 45°C, on the high temperature side of the $\tau_{wc}$-temperature curve. It is therefore no surprise that the $\tau_{wc}$ values they observed decreased with increasing temperature. Further support of our results was supplied by the drag reduction study recently made by Steiff et al. [1991] on alkyltrimethylammonium salts with salicylate and 3-hydroxy-2-naphthoate as additives. Their results show a dependence of critical wall shear stress on temperature similar to the results obtained here.
Although the length of the rod-like micelles indeed plays an important role in drag reduction of surfactant solutions, it is apparently not the only factor that can determine their effectiveness. Other factors such as solution viscosity and micellar strength are also believed to interplay. Let us speculate how the micellar structures change when the temperature is altered and how these changes are expected to affect the drag reducing capability. When the system temperature is slightly above the precipitation temperature, micelles are very long and they probably are able to form an entangled network. Drag reduction is expected to occur when these long micelles and the network they formed start to interact with turbulent eddies. It is well known that, for a given polymer species at a certain concentration, high molecular weight polymers are more effective than low molecular weight ones. Similarly, for a given surfactant solution, the longer the micelles are, the more effective they should be in producing drag reduction. On the other hand, drag reducing effectiveness is adversely affected by the high relative viscosity of the solution at low temperatures compared to high temperatures. As the temperature is increased, micelles become shorter, but their number increases. If the rod-like micelles are still long enough to interact with the flow or the network structure can still be formed by these shorter but more numerous of micelles, drag reducing ability can be retained. When the factors attain the best compromise at a certain temperature, maximum critical wall shear stress is observed. Further increase in
temperature results in a decrease in drag reduction efficiency. Above a certain high temperature, either the micelles are too short to form an effective network in the flow field, or micelles of spherical shape are dominant in the solution and drag reduction is lost. The stiffness of the rod-like micelles, which probably increases with decreasing temperature, is also believed to have some influence on drag reduction performance. However it is not clear whether the effect is positive or negative.

For each surfactant system, there exists an effective temperature range within which drag can be obtained. (We have arbitrarily selected the 50% cut-off to be the standard as mentioned earlier.) This range is primarily determined by the nature of the surfactant and the counter-ion species. It is also affected by the concentrations of both the above components. These factors will be discussed in the following sections.

5.2 Effect of Chemical Structure of Surfactant

5.2.1 Hydrophobic Chain

5.2.1.1 Effect of Chain Length

Drag reduction for a homologous series of alkyltrimethylammonium salts with different chain lengths was studied. The solutions tested
contained 5 mM of surfactant and 12.5 mM of salicylate as counter-ion. The role of the counter-ion will be discussed in detail in Section 5.3. Table 1 shows the critical shear stress for various solutions tested at different temperatures. It should be borne in mind that each number in the table, regardless of its magnitude, indicates that more than 50% of drag reduction was observed in the Reynolds number range studied \((10^4 \text{ to } 5 \times 10^5)\) in a 0.243-inch tube flow. The magnitude of the number represents a measure of the flow rate beyond which effective drag reduction is lost. In some systems, drag reduction less than 50% was observed. This usually happened when the upper or the lower temperature limit was approached. The designation, "M", for moderate is for drag reduction between 20 to 50%. For effective drag reducers such as those listed in Table 1, this criterion is generally not needed since the drag reduction usually decreases below 20% if the temperature is further increased or decreased by 10°C. However, for those surfactant solutions which exhibit only moderate drag reduction (below 50%), which will be discussed in Section 5.2.3, "Mixed Surfactant Systems", and in Section 5.3, "Effect of Chemical Structure of Counter-ion", the M designation is useful. In addition, the letter "N" has been used to designate the conditions when drag reduction was lower than 20%.

From Table 1, one can clearly see the presence of a maximum \(\tau_{wc}\) (in bold figures) at a specific temperature which depends on the surfactant species. The longer the surfactant chain, the higher the temperature at
<table>
<thead>
<tr>
<th>Surfactant</th>
<th>Hydrophobic Chain</th>
<th>T(°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>2  5 10 15 20 30 40 50 60 70 80 90 100 110 120</td>
</tr>
<tr>
<td>Arquad 12-50</td>
<td>C_{12}H_{25}</td>
<td>N 160 150 N N - - - - - - - - -</td>
</tr>
<tr>
<td>TTAB</td>
<td>C_{14}H_{29}</td>
<td>N 240 240 220 190 150 M N - - - - - - - - -</td>
</tr>
<tr>
<td>Arquad 16-50</td>
<td>C_{16}H_{33}</td>
<td>- - M 190 220 300 - 190 130 45 N - - - - - - - - -</td>
</tr>
<tr>
<td>CTAB</td>
<td>C_{16}H_{33}</td>
<td>- N 200 320 320 280 - 230 170 110 N - - - - - - - - -</td>
</tr>
<tr>
<td>Arquad 18-50</td>
<td>C_{18}H_{37}</td>
<td>- - - - N 220 220 230 230 220 200 160 M - - - - - - - - -</td>
</tr>
<tr>
<td>Kemamine Q-2983C</td>
<td>C_{22}H_{43}</td>
<td>- - - - - - - - 90 160 280 220 200 160 49</td>
</tr>
</tbody>
</table>

\(^a\) Surfactant / NaSal = 5 mM / 12.5 mM
\(^b\) N: %DR < 20%; M: 20% < %DR < 50%
which the maximum $\tau_{wc}$ occurs. An important piece of information revealed in Table 1 is that the effective temperature range shifts upwards as the surfactant chain length is increased. The upper temperature limit for drag reduction is controlled by the rod-to-sphere transition. It is known that surfactants with longer chains have a greater tendency to form rod-like micelles and hence have lower CMC$_{II}$ values than the shorter chains [Ohlendorf et al. 1984, 1986a]. This is due to a greater proneness for long chain surfactants to avoid the energetically unfavorable hydrocarbon-water contact. As temperature rises, Brownian motions of the surfactant hydrophobic chains get stronger. On the other hand, chains in the micellar core are held together by the van der Waals forces which increase with increasing chain length [Pilpel, 1954]. As a result, rod-like micelles of long chain surfactants have a more stable structure at high temperatures than do the short chain ones. The low temperature stability of rod-like micelles is primarily determined by the solubility of the surfactant, which explains the increase of the lower temperature limit with increasing alkyl chain length. The results in Table 1 show that, as the chain length is increased from C$_{12}$ to C$_{22}$, the effective temperature range increases from 5-10°C to 60-120°C. In district heating systems, working fluid temperatures as high as 120°C or above are sometimes required. Drag reduction at such high temperatures can be achieved by combining erucyltrimethylammonium chloride (C$_{22}$) with sodium salicylate. Surfactants with chain lengths longer than C$_{22}$ are
expensive and difficult to synthesize, but should give even higher upper
temperature limits. For those systems requiring drag reduction at
temperatures higher than 120 °C, other surfactant solution formulae are
needed. This will be discussed in Section 5.3.4.4, "Multiple substituents", and
Section 5.3.4.5, "Binuclear counter-ions".

Before we close this section, another interesting finding is worth
mentioning. When the results in Table 1 are examined, one finds that the
critical shear stresses for CTAB are higher than those of Arquad 16-50
(CTAC). The CTAC surfactant is composed of 12% C_{14}, 75% C_{16}, 11% C_{18}, and
1% C_{20} and the average chain length is calculated to be 16.02, being almost
exactly the same as that of CTAB. Thus, both surfactants have similar
chemical structure except the anion of the former is bromide while that of
the latter is chloride. Bromide ions are known to be more effective in
promoting micellar growth than chloride ions [Dorshow et al., 1983, Nicoli et
al., 1984]. This has been attributed to the smaller hydration radius of
bromide ions which enables them to penetrate into the electric double layer
(Stern layer) more easily and neutralize the surfactant charges more
effectively [Bunton and Nicoli, 1985]. The difference in micellar size for
CTAB and CTAC solutions can probably account for the difference in their
critical shear stresses. Another factor which can affect the $\tau_{wc}$ value is the
presence of alcohol in the CTAC sample. The commercial CTAC sample
contained 50% isopropyl alcohol which corresponds to a concentration of 26
mM in the prepared solution. Alcohols with carbon number less than five have been shown to reduce micellar size [Candau and Zana, 1981]. The isopropyl alcohol in CTAC is believed to be at least partly responsible for the different results observed with the two solutions. It was also noticed that CTAC has a slightly higher lower temperature limit than CTAB. This is probably due to the difference in Krafft point temperature of these two surfactant solutions.

5.2.1.2 Effect of Unsaturated Chain

The effect of incorporating one or more cis- double bonds into the surfactant hydrophobic chain on drag reduction was studied. Both Arquad 18-50 and Arquad S-50 are single chain trimethylammonium salts. The hydrophobic chain of Arquad 18-50 is primarily a saturated C_{18} chain (>90%, see Table 23 in APPENDIX A). The Arquad S-50 is a product made from soybean oil. It is a mixture of 16- and 18-carbon chain surfactants with the following chain distribution: 17% C_{16}, 12% C_{18}, 55% C_{18}" (oleyl), and 14% C_{18}" (linoleyl) and the average carbon number of the chain is 17.7 (Table 23). The oleyl chain is an unsaturated chain with one double bond located between the 9th and the 10th carbons, while the linoleyl chain has two double bonds between the 9th and 10th, and between the 12th and 13th carbons respectively [Fessenden and Fessenden, 1982]. A comparison of the results
for Arquad 18-50 and Arquad S-50 surfactants is shown in Table 2. It is seen that the upper temperature of Arquad 18-50 is about 10°C higher than that of Arquad S-50. This is probably due to the higher content of C_{16} in the latter surfactant. The most interesting finding is the remarkable drag reducing capability of Arquad S-50 at low temperatures. As the data show, the saturated Arquad 18-50 could only go down to 30°C. At 20°C, phase separation was noticed. On the other hand, effective drag reduction was observed for Arquad S-50 at a temperature as low as 2°C. In addition, the temperature at which maximum $\tau_{wc}$ occurs is 20°C lower than that of Arquad 18-50. The discrepancy can not be explained by the higher C_{16} content of the former surfactant, since even for Arquad 16-50 (primarily C_{16}), the lower temperature limit is only 15°C. Although surfactants with mixed chain lengths can also extend the lower temperature limit, this effect is most significant when the difference in chain length is large as will be seen in Section 5.2.3, "Mixed Surfactant Systems". The only factor which can explain the lower temperature drag reduction is the increased solubility due to the chain unsaturation.

Researchers have likened the Krafft point, the temperature below which micellization can not occur, to the freezing point of ordinary substances [Tsujii et al., 1980; Elson and Garside, 1983]. It is well known that the saturated alkanes usually have much higher freezing temperatures than the unsaturated alkenes because the former can form ordered zigzag
Table 2

Effect of Chain Unsaturation on Critical Wall Shear Stress\(^a\) (N/m\(^2\))

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>Chemical structure</th>
<th>T((^\circ)C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>2</td>
</tr>
<tr>
<td>Arquad 18-50</td>
<td>(C_{18}H_{37}N(CH_3)_3)</td>
<td>-</td>
</tr>
<tr>
<td>Arquad S-50</td>
<td>Soya-N(CH_3)_3</td>
<td>123</td>
</tr>
</tbody>
</table>

\(^a\) Surfactant / NaSal = 5 mM / 12.5 mM
\(^b\) N : %DR < 20% ; M : 20% < %DR < 50%
chains that can fit compactly together. For example, the freezing point of octadecane \( \text{C}_{18}\text{H}_{38} \) is 28°C. With one double bond between the 9th and 10th carbon, 9-octadecene \( \text{C}_{18}\text{H}_{36} \) has a much lower freezing point at -30.5°C \((\text{CRC Handbook of Chemistry and Physics, 49th edition, 1968-1969})\). In the case of the Arquad S-50 surfactant solution, the disorderly arranged unsaturated chains increase the difficulty in forming solid complex soap and therefore delay the phase separation. This finding is important in that most of the surfactant drag reducers lose their effectiveness below room temperature. In district cooling systems, operating temperatures lower than 5°C are sometimes needed. As shown in Table 1, for surfactants with saturated alkyl chains, only Arquad 12-50 \( \text{C}_{12} \) and TTAB \( \text{C}_{14} \) exhibit effective drag reduction at a temperature as low as 5°C, but no further. Also, the upper temperature for Arquad 12-50 is lower than the return temperature (usually > 15°C) for district cooling systems. Thus this surfactant is not suited for use in low temperature systems. The unsaturated Arquad S-50, on the other hand, can not only provide a wide temperature range (2 to 80°C), but also high critical shear stresses at these temperatures and is therefore a promising candidate for low temperature applications.
Three surfactant solutions each with two hydrophobic chains were tested. They were Arquad 2C-75, Kemamine Q-2802C, and Arquad DMHTB-75.

The Arquad 2C-75 is a surfactant with two 12-carbon chains. Two solutions were prepared, one being a 5 mM Arquad 2C-75 solution, the other being a 5 mM/5 mM mixture of Arquad 2C-75/NaSal solution. It was noticed that the former solution was transparent while the latter appeared cloudy. Both solutions were tested in the flow system at temperatures ranging from 10 to 50°C. The results are shown in Figure 10. For clarity only data obtained at two temperatures are presented. As can be seen neither of the solutions exhibited any drag reduction.

Israelachvili et al. [1976, 1985] have proposed a geometric packing constraint model to explain the micellar shape under different conditions. They suggested the micellar shapes that surfactant molecules can pack into are determined by the packing parameter, \( N_g = \frac{v}{a_o \ell_o} \), where \( v \) and \( \ell_o \) represent the volume and the length of the surfactant chain, and \( a_o \) is the area taken up by each surfactant headgroup on the micelle surface. The micelles are predicted to be spheres when \( N_g < 1/3 \), rods when \( 1/3 < N_g < 1/2 \), and disks when \( 1/2 < N_g < 1 \). Using equations 50 and 51 in CHAPTER III proposed by Tanford [1972], one can calculate the volume and length of
Figure 10. Flow data for 5 mM Arquad 2C-75 solutions

<table>
<thead>
<tr>
<th>SYM</th>
<th>T(°C)</th>
<th>NaSal(mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>o</td>
<td>10</td>
<td>-</td>
</tr>
<tr>
<td>▲</td>
<td>30</td>
<td>-</td>
</tr>
<tr>
<td>+</td>
<td>10</td>
<td>5</td>
</tr>
<tr>
<td>*</td>
<td>30</td>
<td>5</td>
</tr>
</tbody>
</table>

\[
\begin{align*}
\text{C}_{12}\text{H}_{25} & \\
\text{N} & \\
\text{C}_{12}\text{H}_{25} & \text{CH}_3
\end{align*}
\]

\[
\begin{align*}
\text{C}_{12}\text{H}_{25} & \\
\text{CH}_3 & \\
\text{N} & \\
\text{C}_{12}\text{H}_{25} & \text{CH}_3
\end{align*}
\]

\[
\text{Cl}^-
\]

\[
D = 0.243\ \text{IN.}
\]
the C\textsubscript{12} chain to be 350.2 \text{Å}\textsuperscript{3} and 16.68 \text{Å} respectively. The surface area, \(a_0\), for CTAB and SDS surfactant solutions has been suggested by Israelachvili [1985] to be 62 \text{Å}\textsuperscript{2} in low salt and 45 \text{Å}\textsuperscript{2} in high salt content solutions. A value of 62.1 \text{Å}\textsuperscript{2} has been reported by Tartar [1955] for TTAB in water. Van De Sande and Persoons [1985] reported the area per headgroup for a 0.0119 M dodecyldimethylammonium bromide in a 1.5 M NaBr aqueous solution to be 51 \text{Å}\textsuperscript{2}. These values are reasonably close to those proposed by Israelachvili et al. which will be used for the calculations. It should be noted that, in calculating the parameter, \(N_g\), for Arquad 2C-75 twice the volume of a C\textsubscript{12} chain should be used since both C\textsubscript{12} chains are embedded in the micellar core.

The \(N_g\) values obtained are 0.68 for the 5 mM Arquad 2C-75, and 0.93 for the equimolar mixture of Arquad 2C-75/NaSal. Both values indicate the micelles formed in these solutions are disk shaped. A surfactant with two C\textsubscript{22} chains, the Kemamine Q-2802C, was also tested. For the equimolar Kemamine Q-2802C/NaSal solution, it was found that when the test temperatures exceeded 60\,°C, the pressure drop of the flow was much higher than that of water. After the solution was completely drained and the system flushed with water, the high friction factor lasted for about twenty seconds, and then returned to the value of water. Also noticed was that large particles were found in the drained solution. It is therefore believed that a different structure was formed above 60\,°C, which blocked the test section or the
pressure taps. For this solution, only data at 50°C were used. The results presented in Figure 11 indicate no drag reduction as well. Similar calculations for the $N_g$ values give 0.68 and 0.47 respectively for 5 mM Kemamine Q-2802C solutions with and without the presence of 5 mM NaSal. Therefore the model again predicts the presence of disk-like micelles, which is consistent with the experimental results. Aqueous solutions containing a double chain surfactant, dodecyloctyldimethylammonium bromide (DODABr), were studied by Hoffmann et al. [1985b] using a number of different techniques. They found that the micelles in the solutions are anisometric from the results of electrical conductivity and light scattering experiments. Since the viscosities of the solutions were very low, the micellar shape should be disk-like rather than rod-like. In addition, the solutions became turbid and separated into two phases as the surfactant concentration was increased. One of the phases was seen to exhibit birefringence and a lamellar phase was found under a polarized microscope.

Interesting results were obtained with Arquad DMHTB-75 surfactant solutions. The surfactant also contains two hydrophobic groups, one being a hydrogenated tallow group (a mixture of $C_{16}$ and $C_{18}$), the other being a benzyl group. The chemical structure of the surfactant is provided in the upper left of Figure 12. A 5 mM/5 mM mixture of Arquad DMHTB-75/NaSal solution surprisingly showed drag reduction at temperatures from 10 to 50°C. This means rod-like micelles are present in the above temperature range. The
Figure 11. Flow data for 5 mM Kemamine Q-2802C solutions
Figure 12. Drag reduction data for a 5 mM/5 mM Arquad DMHTB-75/NaSal solution
model of Israelachvili et al. is now used to examine this case. The length of the tallow chain is taken as the shortest dimension of the micelles (the radius of the sphere and rod, and one half the thickness of the disk). Based on a 0.3:0.7 mixture of C_{16}C_{18} (see APPENDIX A), the volume and length of the tallow chain are estimated to be 495.5 Å$^3$ and 23.5 Å respectively by Tanford's equations. The volume of a benzyl group can be estimated to be the sum of a benzene and a methylene group (-CH$_2$-). The size of the methylene group is 26.9 Å$^3$ as can be directly obtained from the coefficient in Tanford's equation. We couldn't find the volume of a benzene molecule in the literature. However, since the micellar center has been widely accepted to be liquid-like [Wennerstrom and Lindman, 1979], it seems to be a reasonable approach to calculate the benzene molecular volume from its molecular weight and liquid density. A calculated value of 148 Å$^3$ was used as the volume occupied by each benzene ring in the micelles. In order to make a comparison, the volumes of various alkanes are also calculated using both equation 50 and the density data at 20°C (CRC Handbook of Chemistry and Physics, 49th edition, 1968-1969). The results are listed in Table 3. As can be seen the volumes for alkanes calculated by two different methods are reasonably close. If the area occupied by each surfactant headgroup is again chosen as 45 Å$^2$ (in the presence of salicylate), the packing parameter calculated is equal to 0.63. Thus the model predicts the micelles in Arquad DMHTB-75/NaSal solution are disk shaped. This is contrary to our drag
Table 3

Estimated Molecular Volume ($\text{Å}^3$/molecule) for Some Organic Compounds

\[
v = \frac{\rho}{M_w N_A} \times 10^{24} \quad v = (27.4 + 26.9n)
\]

<table>
<thead>
<tr>
<th>Chemical</th>
<th>$M_w$</th>
<th>$\rho$ (cm$^3$)</th>
<th>$v$ ($\text{Å}^3$/molecule)</th>
<th>$v$ ($\text{Å}^3$/molecule)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dodecane</td>
<td>170.34</td>
<td>0.7487 (20°C)</td>
<td>378</td>
<td>350</td>
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<tr>
<td>Tetradecane</td>
<td>198.40</td>
<td>0.7627 (20°C)</td>
<td>432</td>
<td>404</td>
</tr>
<tr>
<td>Hexadecane</td>
<td>226.45</td>
<td>0.7733 (20°C)</td>
<td>486</td>
<td>458</td>
</tr>
<tr>
<td>Octadecane</td>
<td>254.50</td>
<td>0.7768 (28°C)</td>
<td>544</td>
<td>512</td>
</tr>
<tr>
<td>Benzene</td>
<td>78.11</td>
<td>0.8787 (15°C)</td>
<td>148</td>
<td>-</td>
</tr>
</tbody>
</table>
reduction results which predict that the micelles are rod-shaped. One possible explanation could be the steric effect caused by the bulky benzyl groups located near the surface of the micelles. They tend to push away the surfactant headgroups in the neighborhood, which results in an increase in the surface area occupied by each headgroup (\(a_0\)). This results in a decrease in \(N_g\) and makes the formation of rod-like micelles possible. However, it should be noted that the use of the model by Israelachvili et al. to predict micellar shape is only an approximation. The model only considers the intramicellar interactions while ignoring the intermicellar interactions which can become important when the surfactant concentration is high. In addition, the applicability of the prediction model on solutions containing aromatic counter-ions is questionable in that the counter-ions can insert into the micellar surface and interact with the surfactants in micelles (Section 5.3.2). This interaction as well as the steric effect caused by the counter-ions were not considered by the model either.

Upon investigating the effect of excess NaSal on drag reduction of Arquad DMHTB-75 surfactant solution, we observed a very unusual result which is illustrated in Figure 13. The effective temperature range for the 5 mM/12.5 mM mixture of Arquad DMHTB-75/NaSal spans from 10 to 90°C, with the upper temperature limit being 50°C higher than a 5 mM/5 mM mixture (Figure 12). This is not altogether surprising, however, since the upper temperature limit is strongly affected by the amount of counter-ion
Figure 13. Drag reduction data for a 5 mM/12.5 mM Arquad DMHTB-75/NaSal solution
present in the solution. The effect of counter-ion concentration will be further discussed in a later section (5.4.1). Interestingly enough, the percent drag reduction remains constant over a wide range of flow rate at temperatures from 10 to 50°C. At temperatures from 70 to 90°C, the flow behavior is similar to that usually seen in other drag reducing surfactant systems. It is also noted that, when compared with the equimolar data in Figure 12, the maximum drag reduction is lower. This behavior was also noticed for drag reducing surfactant solutions with binuclear aromatic salts as counter-ions. It will be further discussed in Section 5.4.1, "Effect of Counter-Ion Concentration".

5.2.2 Hydrophilic Headgroup

5.2.2.1 Pyridinium Headgroup

The drag reduction of cetylpyridinium chloride (CPyC) was investigated to compare with that of cetyltrimethylammonium chloride (CTAC). CPyC and CTAC are surfactants with a common hydrocarbon tail and counter-ion, but with different polar heads. A 5 mM/12.5 mM mixture of CPyC/NaSal was tested and the results are shown in Figure 14. The $\tau_{wc}$ values at different temperatures are also listed in the figure. A comparison between these $\tau_{wc}$ values and those of CTAC/NaSal system listed in Table 1 indicates that the
Figure 14. Drag reduction data for a 5 mM/12.5 mM CPyC/NaSal surfactant solution
two surfactant solutions are similar in their drag reducing abilities. They both show almost the same effective drag reducing temperature range, with the CPyC system being slightly better at 10°C. Both solutions have their maximum $\tau_{wc}$ values at 30°C. In fact, their CMC's are also very close, with the CMC of CPyC being 0.90 mM at 25°C and that of CTAC being 1.3 mM at 30°C [Rosen, 1978]. In the case of CPyC, the pyridine group can be considered to be a nitrogen surrounded by small alkyl groups [Rosen, 1978], while in CTAC, the nitrogen is bonded to three methyl groups. Therefore it is not surprising that these two surfactants have very similar drag reducing behavior. It is noted that the $\tau_{wc}$ values for CPyC are in general higher than those of CTAC. This can probably be attributed to the planar structure of the pyridinium headgroup which makes the charge center (nitrogen) easier to be approached by counter-ions.

5.2.2.2 Hydroxyethyl Groups Substituted in the Headgroup

When the surfactant headgroup becomes more hydrophilic, interactions between the surfactant polar group and water are increased through hydrogen bonding. Accordingly, the micelles formed should be more stable at low temperatures since the increased interaction with water tends to keep the surfactants from precipitating. Ethoquad 18/12 and 18/13-50 are surfactants with the same alkyl chain ($C_{18}H_{37}^{-}$) as Arquad 18-50. However,
their headgroups are more hydrophilic than that of the latter since two or three methyl groups on the nitrogen atom are replaced by hydroxyethyl groups ($-\text{C}_2\text{H}_4\text{OH}$). Solutions of Ethoquad 18/12/NaSal and Ethoquad 18/13-50/NaSal, each being a 5 mM/12.5 mM mixture, were tested for drag reduction. The results, together with those for Arquad 18-50/NaSal system, are presented in the first three entries of Table 4. It was found that the effective drag reducing temperature range was the same for these three surfactant solutions. They all are effective in the range of 30 to 90$^\circ$C. The temperature at which the maximum $\tau_{wc}$ occurs is 50-60$^\circ$C. From the results listed, it seems that the substitution of hydroxyethyl groups for methyl groups does not effectively reduce the lower temperature limit as would be expected. However, it was noticed during the tests that the Ethoquad 18/13-50 solution exhibited good drag reduction at 20$^\circ$C, which lasted for 5 hours before it started to drop and finally reached the level of solvent after 10 hours of continuous running. In contrast, the Arquad 18-50 solution began to precipitate 30 minutes after the temperature was reduced to 20$^\circ$C. Therefore, the substituted hydroxyethyl groups indeed have some effect in improving the low temperature performance. However, since the lower temperature limit is also strongly affected by the hydrophobic chain length especially when the chain is long like that in the present surfactants, the improvement is not substantial. The most interesting feature of the surfactants with substituted hydroxyethyl groups is that they show an
<table>
<thead>
<tr>
<th>Surfactant</th>
<th>Chemical Structure</th>
<th>T(°C)</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
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<tr>
<td>Arquad 18-50</td>
<td>C&lt;sub&gt;18&lt;/sub&gt;H&lt;sub&gt;37&lt;/sub&gt;- N(CH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt;</td>
<td>2</td>
<td>5</td>
<td>10</td>
<td>20</td>
<td>30</td>
<td>40</td>
<td>50</td>
<td>60</td>
<td>70</td>
<td>80</td>
</tr>
<tr>
<td>Ethoquad 18/12</td>
<td>C&lt;sub&gt;18&lt;/sub&gt;H&lt;sub&gt;37&lt;/sub&gt;- N(CH&lt;sub&gt;3&lt;/sub&gt;)(C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;OH)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>340</td>
<td>370</td>
<td>370</td>
<td>390</td>
<td>-</td>
<td>190</td>
<td>110</td>
<td>N</td>
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<tr>
<td>Ethoquad 18/13-50</td>
<td>C&lt;sub&gt;18&lt;/sub&gt;H&lt;sub&gt;37&lt;/sub&gt;- N(C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;OH)&lt;sub&gt;3&lt;/sub&gt;</td>
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<td>410</td>
<td>410</td>
<td>-</td>
<td>320</td>
<td>230</td>
<td>150</td>
<td>N</td>
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<td>10</td>
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<td>410</td>
<td>490</td>
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<td>Ethoquad 0/13-50</td>
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<td>480</td>
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<td>200</td>
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<td>160</td>
<td>90</td>
<td>-</td>
<td>50</td>
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</tbody>
</table>

**Table 4**

Effect of Hydroxyethyl Substituents on Critical Wall Shear Stress<sup>a</sup> (N/m<sup>2</sup>)
Table 4 (continued)

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>Chemical Structure</th>
<th>T(°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>2 5 10 20 30 40 50 60 70 80 90 100</td>
</tr>
<tr>
<td>Ethoquad R/12-75</td>
<td>Rapeseed-N(CH₃)(C₂H₄OH)₂</td>
<td>- - - - 530 400 350 300 250 190 130 30</td>
</tr>
<tr>
<td>Ethoquad R/12-75</td>
<td>Rapeseed-N(CH₃)(C₂H₄OH)₂</td>
<td>230 230 220 220 220 210 - - - - -</td>
</tr>
<tr>
<td>Arquad T-50</td>
<td>Tallow-N(CH₃)₃</td>
<td>- - - - 290 270 230 200 130 M N -</td>
</tr>
<tr>
<td>Ethoquad T/13-50</td>
<td>Tallow-N(C₂H₄OH)₃</td>
<td>340 340 370 370 450 410 350 280 170 M - -</td>
</tr>
</tbody>
</table>

a Surfactant/counter-ion = 5 mM/12.5 mM
b Ethoquad R/12-75 / NaSal = 5 mM/7.5 mM
c N : %DR < 20%; M : 20% < %DR < 50%
increasing $\tau_{wc}$ as the number of the hydroxyethyl groups is increased from 0 to 3. It has been shown by Geer et al. [1971] in their studies of decylammonium salts that the aggregation number of the surfactant decreased when the protons on the nitrogen atom were sequentially replaced by functional groups such as methyl and ethyl groups of increasing size. Geer et al. attributed this to the increasing steric hindrance for counter-ions to approach the charge center. If the magnitude of $\tau_{wc}$ reflects only the length of the rod-like micelles, our experimental results appear to exhibit a totally reversed trend. However, the $\tau_{wc}$ value is also determined, as we argued earlier, by a number of other factors such as solution viscosity, stiffness of the rod, and most importantly, the strength of the micelles. The explanations given below will be on the basis of micellar strength. One explanation is that hydrogen bonds are formed between hydroxyethyl groups on adjacent headgroups. They form an outer layer outside the micellar core which tends to screen out any possible penetration by water. Through the formation of this structure, rod-like micelles are greatly stabilized. Hence, drag reducing ability is greatly enhanced. The formation of such a structure is not possible by substituted ethyl groups which, although large enough to approach other ethyl groups in the neighborhood, can not form hydrogen bonds between each other. This is probably why, as shown by the results of Geer et al. [1971], the micellar size is smaller for the surfactants with ethyl substituents. Another possible explanation is that, since the hydroxyethyl
since the hydroxyethyl groups are so extended that they can reach the carboxylate groups on the salicylate counter-ions, hydrogen bonds are formed between the hydrophilic headgroups and the salicylates. In this manner the negative charges on the counter-ions can be effectively delocalized. As will be shown in a later section, the charge delocalization effect is a very important factor in determining the stability of rod-like micelles and thus the drag reducing effectiveness. It is worth mentioning that the size of the hydroxyethyl groups does create some steric hindrance in the early stage of forming rod-like micelles. This is seen from the long period of time (hours instead of seconds) the solutions took to attain good drag reduction, as will be discussed in Section 5.8, "Effect of Preshearing".

Since the introduction of hydroxyethyl groups causes an increase in drag reducing capability at all temperatures, and since the major barrier to extend the lower temperature limit comes from the saturated long alkyl chain, it is interesting to examine surfactants with both hydroxyethyl substituents and unsaturated hydrophobic tails. A 5mM Ethoquad O/12 surfactant solution in the presence of 12.5 mM NaSal was tested. The surfactant contains two hydroxyethyl groups on its headgroup, and most importantly, about 75% of the hydrophobic chain is unsaturated C\textsubscript{18} chain (oleyl and linoleyl groups, see APPENDIX A). The test results are shown in entry 4 of Table 4. Another surfactant with a common hydrophobic chain but three hydroxyethyl groups on the nitrogen atom, Ethoquad O/13-50, was
also studied, and the results are listed in entry 5 of Table 4. As seen from the data, these two surfactant solutions exhibit excellent drag reduction particularly at low temperatures. As the results of Ethoquad 18/12 and Ethoquad O/12 are placed side by side, one finds the lower temperature limit is reduced from 30 to 2°C by increasing the unsaturation of the chain. The temperature where maximum $\tau_{wc}$ appears shifts from 60 to 10°C. Also noticed is that, at temperatures above 40°C, the saturated Ethoquad 18/12 is a better drag reducer with a slightly higher upper temperature limit probably due to the stronger micellar structure formed by the saturated alkyl chains. At temperatures below 40°C, the Ethoquad O/12 is superior. Similar results are obtained when Ethoquad 18/13-50 and Ethoquad O/13-50 are compared. In addition, as would be expected, increasing the number of substituted hydroxyethyl groups results in an increase in $\tau_{wc}$ values at all temperatures tested. Therefore in this study, one sees a cooperative effect of hydroxyethyl group and unsaturated chain in enhancing low temperature performance. The former improves the hydrophilicity of the headgroup, while the latter lowers the precipitation temperature.

Tests were also carried out using two other surfactants with hydroxyethyl groups, Ethoquad R/12-75 and Ethoquad T/13-50. The former contains unsaturated mixed chains of $C_{18}$, $C_{20}$, and $C_{22}$, and the latter contains both saturated and unsaturated mixed chains of $C_{16}$ and $C_{18}$. They both have good drag reducing capability at temperatures down to 2°C as shown in
Table 4. It is worth noting that, from the above discussion, although the chain unsaturation seems to be more important in determining the lower temperature limit for drag reduction, the hydroxyethyl groups can play an important role particularly when the surfactant chain length is long. For example, it was found the flow behavior of the Arquad R-50 surfactant was very unstable at temperatures lower than 25°C. While the solution was drag reducing, it was impossible to obtain any steady state data as the readings jumped up and down continuously. For this reason, the results shown in entry 6 of Table 4 do not include the information for temperatures below 30°C. The bizarre behavior observed at low temperatures is probably due to the high content of long chain surfactants in the rapeseed mixture which have a strong tendency to separate from water below 30°C. However, when two hydroxyethyl groups are introduced into the surfactant, the Ethoquad R/12-75 is an excellent drag reducer in the low temperature range.

5.2.3 Mixed Surfactant Systems

The drag reducing behavior of two mixed cationic surfactant systems was investigated. The systems studied were dodecyltrimethyl-ammonium chloride/erucyltrimethylammonium chloride (DTAC/ETAC), and dodecyltrimethylammonium chloride/cetyltrimethylammonium chloride.
(DTAC/CTAC). The DTAC, CTAC, and ETAC are surfactants containing hydrophobic chains of $C_{12}$, $C_{16}$, and $C_{22}$ respectively.

When a small quantity of short chain surfactant is mixed with a long chain surfactant, both the effective drag reducing temperatures and the critical wall shear stress at each temperature change dramatically. This is demonstrated in Figure 15. A 3.75 mM/12.5 mM solution of ETAC/NaSal exhibited effective drag reduction at temperatures ranging from 70 to 120°C. When 1.25 mM DTAC was added in the above solution, the effective temperature range of drag reduction extended significantly on the low temperature side. As seen in Figure 15, drag reduction greater than 50% was obtained at temperatures from 2 to 110°C. Also the temperature at which the maximum $\tau_{wc}$ occurs shifts from 90 to 50°C. From an entropical point of view, it is unlikely that DTAC and ETAC can each form pure micelles in the solution containing both of them. In a separate test, it was noted that a 1.25 mM/12.5 mM solution of DTAC/NaSal showed no drag reduction over a very wide temperature range. Accordingly, if pure micelles of DTAC and ETAC are formed, there shouldn’t be any drag reduction which can be observed at temperatures between 2 and 50°C. Thus, the experimental results indicate that the mixed micelles are causing the drag reduction.

The drag reduction of the DTAC/ETAC system was further investigated by keeping the total surfactant concentration constant (5 mM), while varying the ratio of the two surfactants in the mixed solutions. The
Figure 15. Effect of short chain surfactant on the critical wall shear stress at various temperatures. Salicylate in both solutions was 12.5 mM.
concentration of NaSal was unchanged, being equal to 12.5 mM in all the mixed systems tested. The results are shown in Figure 16, plotted as effective temperature vs. mole fraction of DTAC. The region enveloped by the two curves are the temperatures at which drag reduction greater than 50% was observed. We first focus on the left hand side of the graph. As seen in the figure, a remarkable reduction in the lower temperature limit can be obtained by replacing a portion of the long chain ETAC by the short chain DTAC. For example, as the mole fraction of DTAC was increased from 0 to 0.15, the lower temperature limit was extended from 60 to 2°C, but the upper temperature limit dropped by only 5°C. Note that the lower temperature limit observed is lower than the lowest temperature that can be reached by either of the pure surfactants. A reasonable explanation can be given on the basis of mixed micelle structure. In order to minimize hydrocarbon-water contact, both the long chain and short chain surfactant molecules in a mixed micelle must position their polar groups on the micellar surface which leaves cavities in the core which must be filled by bending and twisting the long alkyl chains. This leads to a less-ordered alignment in the micellar core. As mentioned earlier, if the surfactant chains can line up in order, phase separation occurs at a higher temperature. On the other hand, a more irregularly arranged core structure, such as that for unsaturated surfactants, tends to delay the precipitation temperature. This explains the unusually low temperatures for the mixed systems. Such a disarranged core
Figure 16. Effective drag reducing temperature range for DTAC/ETAC mixed surfactant system. Total surfactant concentration was 5 mM. Salicylate concentration was 12.5 mM. Dashed line at 2°C is the lowest temperature attainable in test system.
structure also brings down the upper temperature limit due to the weaker van der Waals forces maintaining the rod-like structure at high temperatures. In the case of the DTAC/ETAC system, the reduction in upper temperature limit is not significant until the mole fraction of DTAC reaches 0.33. At a DTAC mole fraction of 0.625, while the lower temperature limit can still be maintained at 2°C, the highest temperature for drag reduction to occur is only 20°C. Figure 17 presents the critical wall shear stress as a function of temperature for various mole fractions of DTAC in the DTAC/ETAC mixture. As seen in the figure there is a consistent shift of the maximum $\tau_{wc}$ from high to low temperature as the mole fraction of DTAC increases. The 25:75 DTAC/ETAC mixture exhibits both a fairly high $\tau_{wc}$ and a broad temperature range.

We now turn to the right hand part of Figure 16. In the absence of ETAC, the short chain DTAC solution has an effective temperature range of 5 to 10°C. When a small quantity of DTAC was replaced by ETAC, the solution became a less efficient drag reducer. Since percent drag reduction in these mixed solutions was less than 50%, they can not be shown in Figure 16. In order to see the changes of effectiveness with composition, the maximum percent drag reduction as a function of temperature for DTAC mole fraction from 1 to 0.625 is listed in Table 5. An explanation is provided as follows. When a small amount of long chain ETAC is present in a DTAC solution, the formation of individual pure micelles is again not entropically favorable. The
Figure 17. Temperature dependence of critical wall shear stress for various mole fractions of DTAC in DTAC/ETAC. X is the mole fraction of DTAC in DTAC/ETAC mixture. Total concentration of mixed surfactant was 5 mM. Salicylate concentration was 12.5 mM.
<table>
<thead>
<tr>
<th>DTAC mole fraction</th>
<th>T(°C)</th>
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<th>4</th>
<th>5</th>
<th>7</th>
<th>10</th>
<th>20</th>
<th>30</th>
</tr>
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<td>-</td>
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<td>-</td>
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<td>32</td>
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<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
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<td>-</td>
<td>8</td>
<td>-</td>
<td>5</td>
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<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.75</td>
<td>25</td>
<td>-</td>
<td>20</td>
<td>-</td>
<td>15</td>
<td>5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.625</td>
<td>58</td>
<td>-</td>
<td>58</td>
<td>-</td>
<td>57</td>
<td>52</td>
<td>38</td>
<td></td>
</tr>
</tbody>
</table>

\[ a \] Total surfactant concentration = 5 mM; NaSal concentration = 12.5 mM
long chain molecules can exist in the mixed micelle either by twisting their chains in the core which is dominated by the short chain molecules, or by inserting part of their tails into the core while leaving some portion in the water phase. In both cases, the structure of the rod-like micelles is not energetically stable due to the hydrocarbon-water interaction. Even if rod-like micelles are formed, they are believed to be weak in structure and can not induce good drag reduction. As the mole fraction of ETAC reaches 0.125 (mole fraction of DTAC = 0.875), the maximum drag reduction observed was only 10%. Drag reduction increased again as the concentration of ETAC exceeded a certain level probably because the skeleton of the core (the radius of the rod) is now determined by the long chain surfactant.

The drag reduction of the DTAC/CTAC ($\text{C}_{12}/\text{C}_{16}$) mixed surfactant system was also studied and the effective temperature range is shown in Figure 18. Similar results were observed as for the DTAC/ETAC system. Both upper and lower temperature limits decrease with increasing amounts of short chain surfactant. However, unlike the DTAC/ETAC system, significant drag reduction for the DTAC/CTAC system can still be seen at mole fractions of DTAC from 0.75 to 0.95. As noted earlier, when the mole fraction of the short chain surfactant is high, incomplete penetration of the long chain surfactants into the micellar core can cause the free energy of the system to rise due to hydrocarbon-water interaction. For the DTAC/CTAC mixture, however, the difference in the alkyl chain lengths between the two
Figure 18. Effective drag reducing temperature range for DTAC/CTAC mixed surfactant system. Total surfactant concentration was 5 mM. Salicylate concentration was 12.5 mM. Dashed line at 2°C is the lowest temperature attainable in test system.
surfactants is much smaller than in the DTAC/ETAC mixture. Therefore, the reduced amount of hydrocarbon exposed to water in the former is believed to be responsible for the retention of good drag reducing ability at high DTAC concentrations in DTAC/CTAC mixtures. The critical wall shear stress for the DTAC/CTAC system at various mixing ratios is plotted as a function of temperature in Figure 19.

To summarize, the present study demonstrates the feasibility of using mixed cationic surfactants to change the effective drag reducing temperature range. By properly choosing the surfactant species and mixing ratios, it is possible to reduce the lower temperature limit significantly while not reducing the upper temperature limit markedly. For flow systems requiring both heating and cooling functions, the 0.25:0.75 mixture of DTAC/ETAC appears to be a good candidate because of its remarkably broad temperature range (2 to 115°C). In addition, most high temperature drag reducers separate into two phases upon standing at room temperatures, which can lead to clogging in the pipelines when the system is not being run. For these cases, the use of mixed surfactants provides a promising alternative.

5.3 Effect of Chemical Structure of Counter-Ion

As noted earlier, at a certain temperature, rod-like micelles can only be present when surfactant concentration is higher than the CMCII (see Figure
Figure 19. Temperature dependence of critical wall shear stress for various mole fractions of DTAC in DTAC/CTAC. X is the mole fraction of DTAC in DTAC/CTAC mixture. Total concentration of mixed surfactant was 5 mM. Salicylate concentration was 12.5 mM.
9). The CMC strongly depends on the surfactant species, the presence of salts and temperature. Without the addition of foreign salts, the CMC is usually very high. For example, it is 10% by weight (about 0.3 M) for cetyltrimethylammonium bromide (CTAB) in aqueous medium [Ekwall et al., 1971; Gotz and Heckmann, 1958]. The major barrier preventing sphere-to-rod transition at low surfactant concentration is the electrostatic repulsions between the neighboring charged headgroups. Since spheres provide the largest surface area-to-volume ratio, the mean spacing between headgroups in a sphere can be larger than that in a rod. This is why the micelles are sphere-shaped in dilute solution.

5.3.1 Inorganic Counter-Ion

The addition of electrolytes has been reported to induce sphere-to-rod transition [Anacker and Ghose, 1963, 1968; Ford et al. 1966; Nicoli et al., 1984]. Since the anions can travel to the micelle surface and neutralize the positive charges, which results in a reduction of the effective size of the ionic atmosphere, the shape transformation is possible (Figure 20). It has been shown by Dorshow et al. [1983; Nicoli and Dorshow, 1985] that the minimum NaBr concentration required to induce rod-like micelles in a CTAB solution (0 - 50 mM) is 0.05 - 0.1 M. Nicoli et al. [1981] have reported that the length of the micelles in a 4 mM/0.2 M solution of CTAB/NaBr is 200 A at 60°C and
Figure 20. Sphere-to-Rod transition by adding inorganic salts
increases to 1200 Å as temperature is lowered to 20°C. Using cryo-TEM (transmission electron microscope) technique, Ness and Moth [1988] were able to observe the long, tortuous rod-like micelles in a 1.4 mM/0.5 M solution of CTAB/NaBr. In our study, a 5 mM CTAB solution in the presence of 0.2 M potassium bromide (KBr) was prepared. The concentration of KBr was chosen to ensure the formation of rod-like micelles in the solution. Drag reduction measurements show that the solution behaves like a Newtonian fluid at temperatures from 30 to 60°C. The result supports our early hypothesis. That is, the presence of rod-like micelles, although necessary, is not a sufficient condition for drag reduction to take place. One might suspect that there is a minimum micelle length below which rod-like micelles are unable to induce drag reduction. However, Ohlendorf et al. [1984] have observed good drag reduction for a 2000 ppm (4.75 mM) cetyltrimethylammonium salicylate solution from 65 to 45°C at which micellar length was only 120 - 190 Å. It is believed that, to show drag reduction, micellar strength is a very crucial factor. Electrolytes can induce rod-like micelles by screening the positive charges on the surfactant headgroups, but they do not provide any strong binding forces between surfactant molecules in neighboring layers. When high shear stress is imposed, the rod-like micelles can be broken up at any point along the micelle contour and hence be too short to induce drag reduction.
5.3.2 Aromatic Counter-Ion

Aromatic salts such as sodium salicylate (NaSal) are known to be able to induce viscoelasticity in cationic surfactant solutions [Gravsholt, 1976; Wan, 1968]. It has been shown that these aromatic compounds, when dissolved in surfactant solutions, tend to adsorb at the micelle-water interface with their hydrophilic parts (e.g. -COO\(^-\), -SO\(_3\)\(^-\)) pointing to water, with the hydrophobic portion (e.g. benzene ring) inserting into the micelle [Rao et al. 1987; Bunton and Cowell, 1988; Bachofer and Turbitt, 1990]. Although it is generally agreed that the aromatic counter-ions are located at the surface rather than in the core [Eriksson and Gillberg, 1966; Lindblom et al., 1973; Wennerstrom and Lindman, 1979; Gonzalez et al., 1984], it is not clear how they arrange themselves at the micellar surface. In the study of micellar properties of cetylpyridinium salicylate (CPySal) solutions, Kalus et al. [1982] proposed a rod-like micelle model in which they suggested the salicylate ions are "sitting in the same layer with the pyridinium rings". A similar model was also proposed recently by Murray [1989]. Both models are shown in Figure 21. It is believed that the most plausible adsorption position for aromatic counter-ions should be in between surfactant headgroups on adjacent layers as suggested in Figure 22 where the toluate ion has been used for illustration. There are two major reasons to support this model. First, with such an arrangement, the electron-rich phenyl ring can provide the most efficient
Figure 21. The alignments of aromatic counter-ions at the surface of a rod-like micelle proposed by Kalus et al. [1982] (left), and by Murray [1989] (right)
Figure 22. Sphere-to-Rod transition by adding aromatic salts
contact with the positively-charged surfactant headgroups, which lowers the system energy. Second, it has been shown that the micellar size increases upon continuous addition of aromatic compounds [Hoffmann et al., 1981a]. Since the radius of the rod-like micelles is virtually unchanged, being approximately equal to the length of a fully stretched hydrophobic chain [Kalus et al., 1982], the micelles must grow along the axial direction. Only the "sandwich structure" in Figure 22 can satisfactorily explain the role the aromatic counter-ions play in lengthening the rod. With such a structure, the π electrons on the phenyl ring can not only effectively neutralize the positive charges on the headgroups, but also provide strong binding forces between surfactant molecules on the neighboring stacks. As a result, the micellar structure can be greatly strengthened.

A drag reduction study for a 5 mM/12.5 mM mixture of CTAB/NaSal was carried out, and the results are shown in Figure 23. The selection of relative concentrations of surfactant and counter-ion will be discussed in Section 5.4, "Effect of Concentration". As can be seen, effective drag reduction can be obtained at temperatures ranging from 10 to 70°C. This example demonstrates the superiority of aromatic salts over inorganic salts in producing effective drag reduction.

It is interesting to see how drag reducing effectiveness can be affected by having both inorganic and aromatic counter-ions in the surfactant solution. Figure 24 shows the effect of adding various amounts of KBr on the
Figure 23. Drag reduction data for a 5 mM/12.5 mM CTAB/NaSal surfactant solution.
Figure 24. Drag reduction data for 5mM/12.5 mM CTAB/NaSal solutions at various KBr concentrations. The data were obtained at 50°C.
drag reduction of a 5 mM/12.5 mM CTAB/NaSal solution at 50°C. Bromide ions, which cannot compete with salicylate ions for positions at the micellar surface, surprisingly improve the percent drag reduction at both high and low Reynolds number regions. The $\tau_{wc}$ values as a function of temperature are tabulated in Table 6 for two 5 mM/12.5 mM CTAB/NaSal solutions with and without the presence of 0.2 M KBr. The results show that in all the temperature ranges studied, the $\tau_{wc}$ values are higher for the solution with KBr than those for the solution without KBr.

Using both light scattering and electric birefringence techniques, Hoffmann et al. [1982] have shown that an increase in the NaCl concentration in CPySal solution results in a considerable increase in micellar length which they attributed to the change in intermicellar interaction energy by the added NaCl. Since surfactant and salicylate in the solution are on an equimolar basis in the work of the above authors, it is very possible that not all the salicylate ions are bonded to the micelles due to their partition equilibrium between water and the micelles. Therefore, the micelles are still weakly charged. The addition of NaCl further reduces the micellar charge density and results in micellar growth.

In our study, a 1:2.5 molar ratio of CTAB/NaSal was used. At such a high mole ratio of counter-ion to surfactant, the micelles should have been totally neutralized [Shikata et al., 1988a], or negatively charged [Bunton, 1973; Bunton et al., 1973; Olsson et al., 1986; Rehage and Hoffmann, 1988a, 1988b]. It is hard to see how bromide ions can affect micellar growth in this case.
Table 6
Effect of KBr on Critical Wall Shear Stress (N/m²) of CTAB/NaSal Solution

<table>
<thead>
<tr>
<th>KBr (M)</th>
<th>2</th>
<th>5</th>
<th>10</th>
<th>15</th>
<th>20</th>
<th>30</th>
<th>50</th>
<th>60</th>
<th>70</th>
<th>80</th>
</tr>
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<td></td>
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<td>300</td>
<td>330</td>
<td>350</td>
<td>310</td>
<td>-</td>
<td>200</td>
<td>M</td>
</tr>
</tbody>
</table>

a CTAB/NaSal = 5 mM/12.5 mM
b N: %DR < 20%; M: 20% < %DR < 50%
One possibility is that the ionic strength was increased by the addition of electrolyte, which results in an increase in the flexibility of the micelles [Hoffmann et al., 1984b; Olsson et al., 1986]. It has been shown by Radin [1974] that, in fiber suspensions, flexible fibers are more effective for drag reduction at equal aspect ratios. Thus based on the effectiveness of polymers and fibers in drag reduction, a more flexible conformation seems to be more effective in interacting with turbulent eddies. Another possibility is that, if the micelles are negatively charged, potassium ions rather than bromide ions are responsible for the growth of the micelles. Robb and Smith [1974] used pulsed NMR to study counter-ion binding to alkyl sulfate (an anionic surfactant) micelles and reported the order of decreasing binding as: Cs$^+$ > Rb$^+$ > Na$^+$ > Li$^+$, which is also the order of increasing hydrated size of the cations. The light scattering results by Benedek [1985] also showed that the length of the rod-like micelles in SDS (an anionic surfactant) solutions in the presence of different metal ions decreased in the order: Rb$^+$ > Cs$^+$ > K$^+$ > Na$^+$ > Li$^+$. If the increase in drag reduction here is caused by the presence of K$^+$, changing the cation species from K$^+$ to Cs$^+$ should make drag reduction even better. Unfortunately, further investigations were not made. It is also seen from Table 6 that the lower temperature limit is reduced by more than 5°C by the addition of KBr. This can be interpreted as follows. The binding capability of bromide is inferior to that of salicylate. However, it increases with decreasing temperature, which can be seen from the high growth rate.
of CTAB micelles at low temperatures [Nicoli et al., 1981; Dorshow et al., 1983]. At temperatures below, say, 20°C, bromide ions can probably replace some of the salicylate ions bonded on the micelles, especially when the concentration of the former is much higher than the latter (200 mM vs. 12.5 mM). The resulting reduced lower temperature limit can be interpreted in two ways. First, a decrease in the ratio of salicylate to surfactant usually causes a decrease in the lower temperature limit for drag reduction (see Section 5.4.1, "Effect of Counter-Ion Concentration"). Second, if we consider the micelles at low temperatures as formed by mixed counter-ions (salicylate and bromide ions), this also results in a depression of the lower temperature limit (see Section 5.3.5, "Mixed Counter-Ion Systems").

5.3.3 Effect of Anionic Functional Group

The effects of aromatic counter-ions with different anionic functional groups on the drag reduction effectiveness of Kemamine Q-2983C surfactant solutions were investigated. The counter-ions studied were benzoate (C₆H₅-COO⁻), benzenesulfinate (C₆H₅-SO₂⁻), and benzenesulfonate (C₆H₅-SO₃⁻). The results in Table 7 suggest that the benzenesulfonate is the most effective counter-ion for drag reduction since it requires the least concentration to show the greatest effect. The benzoate only exhibited a maximum of 30% drag reduction at 50 and 60°C when its concentration in the solution was
Table 7

Critical Wall Shear Stress (N/m²) of Kemamine Q-2983C Surfactant\textsuperscript{a} Solutions with Counter-Ions Having Different Anionic Groups

<table>
<thead>
<tr>
<th>Counter-Ion</th>
<th>Counter-Ion concentration (mM)</th>
<th>T(°C)</th>
</tr>
</thead>
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<tr>
<td></td>
<td></td>
<td>30</td>
</tr>
<tr>
<td>[\text{CO}_2^-]</td>
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<td>N\textsuperscript{b}</td>
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<td>12.5</td>
<td>60</td>
</tr>
<tr>
<td>[\text{O}^-]</td>
<td>12.5</td>
<td>N</td>
</tr>
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</table>

\textsuperscript{a} Surfactant/counter-ion = 5 mM/12.5 mM
\textsuperscript{b} N : %DR < 20% ; M : 20% < %DR < 50%
12.5 mM. As the concentration was increased to 16.5 mM, drag reduction effectiveness was increased. A further increase of concentration to 25 mM (surfactant/counter-ion = 1/5) shows even better drag reduction, with more than 50% at temperatures from 40 to 60°C. The benzenesulfinate appears to be the least effective counter-ions with no drag reduction found even when the surfactant to counter-ion ratio was 1/3.3. Viscosity measurements on TTAB solution in association with the above three counter-ions were performed by Totten et al. [1986] who reported the following increasing order in promoting solution viscosity: benzoate < benzenesulfinate < benzenesulfonate. Thus, the benzenesulfonate appears to be the most effective in promoting both viscosity and drag reduction, but the order between benzoate and benzenesulfinate is reversed. It is believed that, in order to have rod-like micelles of strong structure, both the surfactants and counter-ions in the micelle must be maintained at some low energy level. A sulfonate group is more stable than a carboxylate or a sulfinate group because the negative charge of the anion is dispersed over three oxygens instead of two. Therefore the micelles formed with the presence of benzenesulfonates are more stable than with the other two counter-ions. This charge delocalization effect was found to play a significant role in producing drag reduction as will be seen in many other cases. The use of phenoxide (C₆H₅-O⁻) as counter-ion was also tested and the result is also
shown in Table 7. As expected, it is unable to induce drag reduction since the negative charge is only dispersed on one oxygen atom.

5.3.4 Effect of Substituent Groups and Substituted Sites

The introduction of certain substituent groups onto the phenyl ring of benzoate or benzenesulfonate can dramatically alter their capabilities as effective counter-ions for drag reduction. The effect depends on both the nature of the substituent and their substitution positions.

5.3.4.1 Hydrophobic Substituents

Salicylate (2-hydroxy-benzoate) is formed by replacing a proton next to the carboxylate group on benzoate by a hydroxyl group (-OH). It has been long been noticed that this aromatic compound can significantly increase the viscosity of cationic surfactant solutions [Wan, 1968; Gravsholt, 1976]. For example, Totten et al. [1986] reported an approximately 6000-fold increase in viscosity when salicylate was added to a 0.2 M TTAB solution on a 1:1 molar basis. In contrast, the same dosage of benzoate can only increase the solution viscosity by 18 times [Totten et al., 1986]. Apparently, the hydroxyl group plays an important role in the formation of rod-like micelles. In order to study the effect of the hydroxyl group position on the phenyl ring on the
effectiveness of the counter-ion for drag reduction, salicylate and its two geometric isomers, 3- and 4- hydroxybenzoates as counter-ions were investigated. Drag reduction results of Kemamine Q-2983C surfactant solutions in the presence of each of these counter-ions are shown in the first three entries of Table 8. It is seen that the effectiveness of the counter-ion is reduced when the hydroxyl group is moved from the \textit{ortho} to the \textit{meta}, then to the \textit{para} position with respect to the carboxylate group. This is interpreted as follows. The stability of the rod-like micelles, which is a prerequisite for drag reduction to take place, depends on the stability of both the surfactants and the counter-ions in the micelles. By inserting themselves halfway into the micellar surface, salicylate and benzoate ions can both find the best environment for their hydrophobic part (phenyl ring) and hydrophilic part (carboxylate group). However, the former is a more effective counter-ion because hydrogen bonds can be formed between the neighboring carboxylate (-COO\textsuperscript{-}) and hydroxyl (-OH) groups, through which the negative charge is dispersed. This charge delocalization greatly stabilizes the counter-ions on the micellar surface and hence the structure of the micelle they form. Hydrogen bonds formed between the -OH groups on the salicylate ions with water also help to stabilize the micelles, but the effect is not as great as charge delocalization. This is seen from the result of 3-hydroxybenzoate whose -OH group also has the ability to form hydrogen bonds with water but the micellar structure is much weaker as seen from the
<table>
<thead>
<tr>
<th>Counter-Ion</th>
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<th>20</th>
<th>30</th>
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<tr>
<td>2-OH benzoate (salicylate)</td>
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<td>-</td>
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<tr>
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<td>-</td>
<td>N</td>
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</table>

Table 8
Critical Wall Shear Stress (N/m$^2$) of Kemamine Q-2983C Surfactant$^a$
Solutions with Counter-Ions Having Different Hydrophilic Substituents

$^a$
Table 8 (continued)

<table>
<thead>
<tr>
<th>Counter-Ion</th>
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</thead>
<tbody>
<tr>
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<td>10</td>
</tr>
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<td>4-OH benzenesulfonate</td>
<td>-</td>
</tr>
<tr>
<td>2-NH₂ benzenesulfonate</td>
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</tr>
<tr>
<td>4-NH₂ benzenesulfonate</td>
<td>-</td>
</tr>
</tbody>
</table>

Kemamine Q-2983C/counter-ion = 5 mM/12.5 mM
N: %DR < 20%; M: 20% < %DR < 50%
drag reduction results. Another advantage of the intramolecular hydrogen bonding between -COO$^-$ and -OH groups is that the planar characteristic of the chelation structure can partly reduce the steric hindrance from neighboring surfactant headgroups and produce a closer contact between the ring current and the headgroups. The orientation of the salicylate ion at the micellar surface is plotted in Figure 25. The position of the proton next to the carboxylate group should be addressed. Rao et al. [1987] studied the CTAB/NaSal system using the proton NMR technique and found that, as compared with pure salicylate in water, the chemical shift signal of this proton moved downfield (or became more unshielded) when CTAB was present in the solution, while the other three protons moved upfield (or became more deshielded). A deshielded signal means the environment of the protons is changed into a more nonpolar one (than water), while an unshielded signal means the nature of the environment is unchanged. This indicates that only three protons are located under the micellar surface. The remaining one, along with the -COO$^-$ and -OH groups, should stay in the water phase as shown in Figure 25.

When the -OH group is moved to the meta position, the formation of intramolecular hydrogen bonding is no longer possible. The inability to delocalize the charge is believed to be responsible for the less stable micellar structure and thus for the ineffectiveness in promoting drag reduction. This is demonstrated by the results shown in Table 8 where the upper
A. salicylate  E. 4-aminobenzoate  
B. 3-hydroxybenzoate  F. 2-nitrobenzoate  
C. 4-hydroxybenzoate  G. 4-nitrobenzoate  
D. 2-aminobenzoate  

Figure 25. Orientational binding for counter-ions with different hydrophilic substituents
temperature limit of the Kemamine Q-2983C/3-hydroxybenzoate (about 50°C) is much lower than that of salicylate in the same surfactant solution (120°C). It should be noted that the loss of drag reducing capability of the salicylate at low temperatures does not necessarily mean its interaction with surfactants has decreased. Instead, at low temperatures, the interactions are so strong that a solid complex soap is formed by the surfactant and the counter-ion, which is seen from the cloudiness of the solution. The NMR studies by Rao et al. [1987] showed that the 3-hydroxybenzoate orients itself by having both the -COO⁻ and -OH groups tilting 60 degree toward the micellar surface (Figure 25). Based on the orientations of salicylate and 3-hydroxybenzoate ions, Rao et al. [1987] proposed a bead-string model in which they suggested the viscoelasticity of the surfactant solution with salicylate as counter-ion does not originate from the formation of rod-like micelles, rather, it is caused by strings of spherical micelles. This claim is similar to that proposed earlier by Tanford [1972] except in their model Rao et al. suggested the linkages between spherical micelles are provided by salicylate ions through ionic bonding between the -COO⁻ group on one micelle and the surfactant headgroup (-N(CH₃)₃⁺) on another micelle (Figure 26). According to Rao et al. [1987], the salicylate is able to induce viscoelasticity because its -COO⁻ group extends outwards which provides a favorable position to make contact with other micelles. In the case of 3-hydroxybenzoate, its -COO⁻ group is seated close to the headgroup of the
Figure 26. Bead-String Model by Rao et al. [1987]
neighboring surfactant on the same micelle where it is neutralized, and thus loses its bridging ability. Rao et al. suggested that all the evidence from flow birefringence, electric birefringence, and small angle neutron scattering experiments being used to support a rod-like micelle model cannot disprove the existence of bead-stringed micelles for these techniques are unable to distinguish a rod from a bead string. Recently, this bead-string model has been questioned by Bachofer and Turbitt [1990] who pointed out that the 4-hydroxybenzoate and 4-nitrobenzoate both can direct their -COO⁻ groups away from micellar surface but cannot produce any viscoelasticity when combined with CTAB solution. Here, direct evidence is provided to show the inadequacy of the model by Rao et al. So far, all the viscoelasticity studies using 3-hydroxybenzoate as counter-ion have been performed in CTAB surfactant solutions [Gravsholt, 1976; Rao et al., 1987; Bachofer and Turbitt, 1990]. Indeed, our results showed that solutions containing CTAB and 3-hydroxybenzoate are not viscoelastic. However, a 5 mM/12.5 mM mixture of Kemamine Q-2983C and 3-hydroxybenzoate was found to be viscoelastic and drag reducing. If the bead-string model of Rao et al. were correct, the unfavorably tilted -COO⁻ group on 3-hydroxybenzoate should not be able to serve as a bridge between spherical micelles and consequently the viscoelastic properties cannot be seen, which is contrary to our finding. It is believed that the formation of rod-like micelles is still the best explanation for the occurrence of viscoelastic properties. To the best of our knowledge,
the ability of 3-hydroxybenzoate to promote surfactant viscoelasticity has never been reported in the literature. The reason that 3-hydroxybenzoate can produce viscoelasticity in Kemamine Q-2983C solution but not in CTAB is that the former surfactant has a longer alkyl chain (C_{22} vs. C_{16} in CTAB). It was mentioned earlier that the 3-hydroxybenzoate is a less effective counter-ion than salicylate because the intramolecular chelation structure, through which rod-like micelles can be greatly stabilized, cannot be formed. (Recall that it is necessary to have some potent factors which can override the unfavorable electrostatic repulsions between headgroups before rod-like micelles can be formed.) However, this disadvantage is compensated for by the greater tendency to form rod-like micelles when the surfactant alkyl chain length is increased. As a result, drag reduction can occur in Kemamine Q-2983C/3-hydroxybenzoate systems.

With 4-hydroxybenzoate as counter-ion in surfactant solution, it is impossible to have both the -COO^- and -OH groups sticking out into water, and still keep the phenyl ring in the micelle. To obtain maximal hydrophobic interaction, the -OH group has to be kept away from water and confined in an oily region (see Figure 25). This is not energetically favorable for formation of rod-like micelles but is possible for spherical ones. Since the surface of a spherical micelle is less covered by the solvated surfactant headgroups than a rod-like one, water has a better opportunity to penetrate several angstroms deep into the micellar surface [Menger, 1979, 1984], and
interacts with the embedded -OH groups. Indeed, our light scattering result (see APPENDIX F) shows that the micelles in the CTAC/4-hydroxybenzoate solution are spheres with diameter of about 5 nm, corresponding to twice the extended alkyl chain length plus twice the thickness of the hydration layer [Kalus et al., 1982].

Drag reduction results using 2- and 4-aminobenzoates as counter-ions in Kemamine Q-2983C solution are shown in entries 4 and 5 of Table 8. Like salicylate, intramolecular hydrogen bonds can also form between the -COO\(^-\) and the NH\(_2\) groups on the 2-aminobenzoate ion. However, the strength of the NH---O hydrogen bond in 2-aminobenzoate is weaker than the strength for OH---O in salicylate, with the bond dissociation energy for the former being 2 kcal/mole while for the latter it is 5 kcal/mole [Fessenden and Fessenden, 1982]. As a result, the charge delocalization ability for 2-aminobenzoate through the chelation structure is weaker than that for salicylate. This explains the relative effectiveness of these two counter-ions in promoting drag reduction as shown in Table 8. Totten et al. [1986] have reported that the ability of ortho-substituted benzoates to increase solution viscosity of TTAB is in the following order: SH < NH\(_2\) < OH, which is consistent with our drag reduction results. Derivatives of benzenesulfonate with hydroxyl and amino substituents were also used as counter-ions in Kemamine Q-2983C solution and the drag reduction results are shown in the
last three entries of Table 8. When compared to 2-aminobenzoate, the 2-
aminobenzenesulfonate appears to be a more effective counter-ion (broader
effective temperature range and greater drag reduction). The reason for this
result has been discussed in Section 5.3.3.

Interesting results were obtained when drag reduction of Kemamine Q-
2983C with nitrobenzoates as counter-ions were investigated. Since a -NO₂
group is hydrophilic in nature, at first it was thought an ortho-substituted
benzoate would show drag reducing capability while a para- one would not.
However, contrary results were obtained. This is explained as follows.
Although a -NO₂ group next to the -COO⁻ group has great advantage in
making contact with water, it is so bulky that its unshared electron pairs on
the two oxygen atoms interfere with the the electron cloud of the -COO⁻
group (see Figure 25). This is contrary to the rule of charge delocalization
according to which stable rod-like micelles can not form. When the -NO₂ is
seated at the para position, it has to stay in a hydrophobic environment
(micellar interior) in order to keep the -COO⁻ group in water. This is not
energetically favorable either. However, since the -NO₂ group is a very
strong, electron-withdrawing group (only slightly weaker than the NR₃⁺
group, where R is an alkyl group [Morrison and Boyd, 1983]), it helps to
disperse the negative charge on the counter-ion and hence stabilize the
micelle. We see from this example that the importance of charge
delocalization exceeds that of hydrophilic interaction. Drag reduction,
although not too great, was observed (entry 7 of Table 8). It is worth mentioning that Bachofer and Turbitt [1990] reported no viscoelasticity for either 2- or 4-nitrobenzoate in CTAB solution. Again, this is due to the energetically unfavorable conditions for these two counter-ions to form rod-like micelles in CTAB. However, in a solution of longer chain surfactant (C_{22}), the driving force for rod-like micelle formation is increased from the surfactant side. This is why drag reduction can be obtained in the latter.

To summarize, counter-ions with a hydrophilic substituent can stabilize the rod-like micelle structure if the substituent is located at the *ortho* or *meta* site of a -COO$^-$ group where good hydrophilic interaction is possible. The *ortho* substituent has an even greater effect if it can form intramolecular hydrogen bonding with the -COO$^-$ group. Like the *ortho* and *meta* substituted benzoates, the *para* substituted benzoate can also provide good hydrophobic interaction by plugging the phenyl ring into the micelle but at the price of losing the hydrophilic interaction. This disadvantage can only be overridden if the charge delocalization effect can be strengthened (for example, by a strong electron-pulling substituent, or by further introducing an -OH or -NH$_2$ group at the *ortho* position).
5.3.4.2 Hydrophobic Substituents

When a methyl group (-CH₃) is brought onto the phenyl ring of a counter-ion, the hydrophobicity of the counter-ion increases. The 3- and 4-methylbenzoates (or m- and p-toluates) can provide their best hydrophobic contact by inserting the methyl group into the micelle, which greatly stabilizes the counter-ion. This orientation is supported by the results of Bachofer and Turbitt [1990] who used the proton NMR technique to study the orientational binding of substituted benzoates at micellar surfaces. They found that, in the presence of CTAB, the chemical shift signals of the two protons next to the -COO⁻ group on 3- and 4-methylbenzoates were more deshielded, while those of the other two protons are more shielded. This indicates that the aromatic rings of both the counter-ions are partially embedded in the micelle with their -COO⁻ groups pointing outwards (Figure 27). Bunton et al. [1973] studied the orientation of 4-methylbenzenesulfonate (p-tosylate) in CTAB solution and also reached a similar conclusion. Drag reduction results of Kemamine Q-2983C surfactant solutions with 2-, 3-, and 4-methylbenzoates as counter-ions are listed in Table 9. The solutions with 3- or 4-methylbenzoate as counter-ions both exhibit drag reduction in the same temperature range, 30 to 80°C. It is interesting to note that the temperature at which maximum $r_{wc}$ occurs for 3-
Figure 27. Orientational binding for counter-ions with different hydrophobic substituents
<table>
<thead>
<tr>
<th>Counter-Ion</th>
<th>T(°C)</th>
<th>20</th>
<th>30</th>
<th>40</th>
<th>50</th>
<th>60</th>
<th>70</th>
<th>80</th>
<th>90</th>
<th>100</th>
<th>110</th>
<th>120</th>
<th>130</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-CH₃ benzoate</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-</td>
<td>N</td>
<td>N</td>
<td>N</td>
</tr>
<tr>
<td>3-CH₃ benzoate</td>
<td>N</td>
<td>84</td>
<td>140</td>
<td>120</td>
<td>110</td>
<td>N</td>
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<td>-</td>
<td>-</td>
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<tr>
<td>4-CH₃ benzoate</td>
<td></td>
<td>27</td>
<td>64</td>
<td>98</td>
<td>120</td>
<td>130</td>
<td>110</td>
<td>M</td>
<td>N</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<td>-</td>
<td>N</td>
<td>M</td>
<td>N</td>
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<tr>
<td>4-Cl benzoate</td>
<td></td>
<td>290</td>
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<td>280</td>
<td>270</td>
<td>270</td>
<td>260</td>
<td>240</td>
<td>210</td>
<td>190</td>
<td>N</td>
<td>N</td>
<td>N</td>
</tr>
<tr>
<td>4-OCH₃ benzoate</td>
<td></td>
<td>M</td>
<td>M</td>
<td>-</td>
<td>36</td>
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<td>N</td>
<td>N</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

a  Kemamine Q-2983C/counter-ion = 5 mM/12.5 mM
b  N : %DR < 20%; M : 20% < %DR < 50%
and 4-methylbenzoate systems are 50°C and 70°C respectively. The 3-methylbenzoate seems to have better drag reducing capability at low temperatures (below 70°C) than the 4-methylbenzoate. This can be attributed to the fact that the methyl group in the latter isomer can provide the best interactions with the surfactant chains, while in the former it can not fit in so well. Therefore, the latter isomer is more effective at high temperatures because it can help to form micelles with stronger structures. Low temperature performance favors the 3-methylbenzoate since the micellar structure is slightly disrupted by the side methyl group. If one recalls that a methyl group is a weakly electron-releasing group, one sees two opposing factors in determining the stability of the counter-ions. The increased hydrophobic interactions between methyl groups and surfactant chains tends to favor the formation of rod-like micelles, but the electron-releasing characteristic of the methyl group tends to oppose it. The observed drag reduction as compared to that in the Kemamine Q-2983C/benzoate system, implies the former effect is greater.

For 2-methylbenzoate in the surfactant solution, Bachofer and Turbitt [1990] found by NMR study that the counter-ion does penetrate into the micelle to seek the best environment for its phenyl ring. However, since the methyl group is seated close to the micellar surface (Figure 27), the resulting structure is unstable, and drag reduction was not found for this solution.
Drag reduction studies for Kemamine Q-2983C with three geometric isomers of chlorobenzoate were also made. It has been pointed out by Underwood and Anacker [1985] that the partition coefficient of chlorobenzene, based on the distribution between n-octanol and water, was five times that of benzene. Therefore a chlorine substituted on benzoate can also improve the hydrophobicity of the counter-ion. Gravsholt [1976] showed that the 3- and 4-chlorobenzoates can induce viscoelasticity in CTAB solutions while the 2- isomer cannot. This is in accordance with our drag reduction results shown in Table 9. Orientation of 3-chlorobenzoate at the micellar surface has been reported by Rao et al. [1987] who concluded from their NMR measurements that the counter-ion plugs halfway into the micelle leaving two protons and the -COO\(^-\) group in water. Since the chlorine is an electron-withdrawing group, it helps to stabilize the counter-ion which makes the 3- and 4-chlorobenzoate even better counter-ions for drag reduction than the 3- and 4-methylbenzoate, as seen in Table 9. This charge delocalization effect also affects the capability of 2-chlorobenzoate in forming rod-like micelles. When compared to 2-methylbenzoate in Kemamine Q-2983C solution, which did not show any drag reduction, 2-chlorobenzoate in the same surfactant solution exhibited about 20% drag reduction at 50\(^\circ\)C.

The 4-methoxylbenzoate is a counter-ion with a methoxyl group (-OCH\(_3\)) substituted at the para position. When combined with Kemamine Q-2983C, drag reduction was also observed (Table 9). However, it is a less
effective counter-ion than 4-methylbenzoate since the methoxyl group, with
the presence of an oxygen atom, is less hydrophobic than the methyl group.
The difference also lies in the the electron-releasing ability of the two
counter-ions, for which the former is much stronger than the latter
[Fessenden and Fessenden, 1982].

An interesting study was made using phenylacetate as counter-ion in
Kemamine Q-2983C solution. The chemical structure of the counter-ion is
similar to that of benzoate except the -COO⁻ group does not directly bind to
the phenyl ring, rather, it is linked to the ring through a methylene group (CH₂⁻). A 5 mM/12.5 mM mixture of Kemamine Q-2983C/phenylacetate
solution was tested and no drag reduction was found. Since the benzoate
itself is not very effective at the same concentration (see Table 7), it was
decided to increase the hydrophobic characteristic of the counter-ion by
introducing a chlorine at the para position to see whether any drag reduction
could be obtained. When a mixture of 5 mM Kemamine Q-2983C and 12.5
mM 4-chlorophenylacetate was first prepared, it was found that the solution
was water-like. However, after standing for 24 hours, it became viscoelastic.
This is in contrast to most of the surfactant solutions we studied which
showed viscoelasticity as soon as surfactant and counter-ion were brought
together. This is believed to be due to the bulky -CH₂-COO⁻ group which
creates some steric hindrance during the association between surfactants
and counter-ions. It is believed that the phenyl ring, like other aromatic
counter-ions, inserts halfway into the micelle since this is the position to produce the greatest interactions between the $\pi$ electrons and the surfactant headgroups. The methylene group, therefore, is forced to stay in the water. This unfavorable hydrocarbon-water contact, as would be expected, raises the system energy and makes the micellar structure less stable. The drag reduction results are presented in Figure 28. Also shown in the same figure is the chemical structure of the counter-ion. The effect is significant when the drag reduction data are compared with Kemamine Q-2983C/4-chlorobenzoate system (Table 9). It is seen that the effective temperature range, as compared to that of the Kemamine Q-2983C/4-chlorobenzoate solution, moves to a lower temperature region. The upper temperature limit of the present system is 60 - 70°C lower. The lower temperature limit for a 5 mM/12.5 mM Kemamine Q-2983C/4-chlorobenzoate solution is not available (lowest temperature tested was 30°C for this solution), but for a 5 mM/7.5 mM solution it is 20°C. For the present solution, more than 50% drag reduction can still be observed at 5°C. At 2°C, a maximum drag reduction of 43% was found. Thus we have found another way to enhance drag reduction performance at low temperatures.

To sum up, good drag reduction can be obtained if the counter-ion used is a benzoate (or benzenesulfonate) substituted by a hydrophobic group at the para or meta position. The effectiveness of the substituent in decreasing order is: Cl > CH$_3$ > OCH$_3$. A decrease in hydrophobicity of the counter-ion
Figure 28. Drag reduction data for a 5 mM/12.5 mM Kemamine Q-2983C/4-chlorophenylacetate solution
by the exposure of a methylene group to water results in a reduction in both the upper and lower temperature limits.

5.3.4.3 The Size of the Hydrophobic Substituents

In order to study the size of the substituent on the effectiveness of the counter-ion, alkyl groups of different sizes were introduced into the para position of a benzenesulfonate. The drag reduction data of Kemamine Q-2983C in combination with each of these counter-ions are summarized in Table 10. It is noticed that the upper temperature increases by about 20°C on each addition of a methylene group on the substituent. The tosylate seems to have the best performance at low temperatures. As we proposed earlier, the loss of drag reduction at low temperatures does not mean the counter-ions fail to interact with the surfactants, rather, the observed phase separation suggests that the interactions are so strong that they co-precipitate with the surfactants. Therefore, the association capability of the counter-ion with surfactant should be judged from the upper temperature limit of the combined solution. An increase in the length of the alkyl group at the para site on the counter-ion increases the hydrophobic interaction between the surfactant chains and the alkyl groups, which helps to hold the micelle core more tightly and prevents water from getting in. The effect parallels that of increasing the surfactant chain length as described earlier.
<table>
<thead>
<tr>
<th>Counter-Ion</th>
<th>30</th>
<th>40</th>
<th>50</th>
<th>80</th>
<th>90</th>
<th>100</th>
<th>120</th>
<th>130</th>
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<tbody>
<tr>
<td>[O]SO₃⁻</td>
<td>60</td>
<td>110</td>
<td>110</td>
<td>M</td>
<td>N</td>
<td>-</td>
<td>-</td>
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<tr>
<td>CH₃[O]SO₃⁻</td>
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<td>240</td>
<td>210</td>
<td>-</td>
<td>140</td>
<td>M</td>
<td>N</td>
<td>-</td>
</tr>
<tr>
<td>CH₃CH₂[O]SO₃⁻</td>
<td>-</td>
<td>-</td>
<td>N</td>
<td>57</td>
<td>-</td>
<td>330</td>
<td>230</td>
<td>N</td>
</tr>
<tr>
<td>(CH₃)₃C[O]CO₂⁻</td>
<td>N</td>
<td>-</td>
<td>N</td>
<td>-</td>
<td>N</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

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*a* Kemamine Q-2983C/counter-ion = 5 mM/12.5 mM

*b* N : %DR < 20% ; M : 20% < %DR < 50%
As the alkyl substituent on the counter-ion turns even bigger, for example, in the case of 4-tert-butylbenzoate, no drag reduction was observed (Table 10). This result invites speculation. One possibility is that the bulky, branched tert-butyl group can not fit into the core as well as the straight chain groups. This is possible since when the group is introduced into the core, surfactant chains will be forced to move apart, which results in a decrease in van der Waals forces and a reduction in micellar strength. This can also result in an increase in spacing between the phenyl ring and the neighboring surfactant headgroups which raises the system energy. A second possibility is based on the work by Shick and Fowkes [1957] who found the straight chain additives are more efficient in depressing the surfactant CMC than the branched ones. Shick and Fowkes proposed that chemical compounds which can reduce surfactant CMC tend to stay in the outer portion of the core even though a lateral pressure at the interface tends to force them into the inner core. The pressure increases with the cross-sectional area of the molecule. Thus, with smaller cross-sectional area than the branched ones, straight chain molecules have a greater tendency to stay in the outer core portion, while the branched-chain ones are forced into the core. A third possibility is that the Kemamine Q-2983C/4-tert-butylbenzoate mixture has an extremely high effective temperature range beyond that we studied. This is also possible since the upper temperature limit increases with increasing number of methylene groups. From the data
shown in Table 10, the lower temperature limit of the 4-ethylbenzenesulfonate system is as high as 80°C. The lower temperature limit could be even higher if a large group such as tert-butyl group is present on the counter-ion. To test this third postulation, a shorter chain surfactant, CTAC (C_{16}), in combination with 4-tert-butylbenzoate was tested in the flow system. At temperatures ranging from 30 to 90°C, no drag reduction was observed. Since for a given counter-ion, changing surfactant chain length from C_{22} to C_{16} usually reduces the upper temperature limit by approximately 40°C, it is highly unlikely the 4-tert-butylbenzoate can be an effective counter-ion. The third possibility can therefore be ruled out.

5.3.4.4 Multiple Substituents

Two multiple substituted counter-ions were investigated. The 2,6-dihydroxybenzoate has a chemical structure similar to that of salicylate except an additional -OH group is introduced at the site next to the -COO\(^-\) group. The major reason to choose this counter-ion was based on charge delocalization considerations. The counter-ion was first combined with Arquad 12-50 (5 mM/5 mM) and tested in the flow loop. The results are presented in Figure 29. It is seen, when compared with the drag reduction results for a mixture of 5 mM/12.5 mM Arquad 12-50/NaSal in Table 1, the solution shows a reduced lower temperature limit (2°C vs. 5°C for the
Figure 29. Drag reduction data for a 5 mM/5 mM Arquad 12-50/2,6-dihydroxybenzoate solution
system with salicylate as counter-ion (Table 1). It also shows a slight increase in its upper temperature limit, which would be more pronounced if higher counter-ion concentrations were used. However, since the solution at 5 mM/5 mM concentration provided a satisfactory lower temperature limit, further tests using higher counter-ion concentration were not performed. The better performance at low temperatures can be attributed to the increased capability of forming hydrogen bonds with water. Drag reduction studies were also made using the same counter-ion in surfactant solutions with longer chain lengths. The results shown in Table 11 indicate the counter-ion is very effective in promoting drag reduction performance at high temperatures. A 5 mM/7.5 mM mixture of Ethoquad R/12-75 / 2,6-dihydroxybenzoate has an upper temperature limit of 110°C. By using 7.5 mM of the counter-ion in a 5 mM solution of Kemamine Q-2983C (C_{22}), drag reduction at a temperature as high as 130°C was obtained. It is worth noting that the upper temperature limit of the solution is very sensitive to the counter-ion concentration. For the Kemamine Q-2983C systems, an increase of the counter-ion concentration by 2.5 mM results in an increase in the upper temperature limit of 20°C. Temperatures even higher are possible if higher counter-ion concentrations (e.g. 12.5 mM) are used. The drag reduction results of a 5 mM Kemamine Q-2983C solution using a 7.5 mM/5 mM mixture of 2,6-dihydroxybenzoate and salicylate as counter-ion are also shown in Table 11. Compared with the solution without salicylate, the
Table 11

Critical Wall Shear Stress (N/m²) of Surfactant Solutions
with 2,6-Dihydroxybenzoate as Counter-Ion

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>Surfactant concentration (mM)</th>
<th>Counter-Ion concentration (mM)</th>
<th>T(°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>60</td>
</tr>
<tr>
<td>Arquad R/12-75</td>
<td>7.5</td>
<td>5.0</td>
<td>4</td>
</tr>
<tr>
<td>Kemamine Q-2983C</td>
<td>5.0</td>
<td>5.0</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>5.0</td>
<td>7.5</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>5.0</td>
<td>a</td>
<td>-</td>
</tr>
</tbody>
</table>

a Counter-Ion = (7.5 mM 2,6-dihydroxybenzoate) + (5 mM salicylate)

b N: %DR < 20%; M: 20% < %DR < 50%
mixed counter-ion system can provide an even higher upper temperature limit (140°C). The system will be further discussed in Section 5.3.5, "Mixed Counter-Ion Systems". The great stability observed for the 2,6-dihydroxybenzoate system at high temperatures is strongly related to the effective charge delocalization ability of this counter-ion. Additionally, the extra -OH group on each counter-ion probably plays some significant role in intermicellar interactions. To be more specific, it is speculated that the network in the solutions is not formed by the rod-like micelles merely through physical contacts (entanglements). In their viscoelasticity study of the CPySal system, Rehage and Hoffmann [1983] postulated that adhesion forces such as van der Waals forces or interfacial tension between the rods and the aqueous phase might also be responsible for the formation of the network. We inferred that hydrogen bonding formed between -COO⁻ and -OH groups on counter-ions located on different rod-like micelles helps to strengthen the network structure, which is particularly important when temperature is high. It is possible that such intermicellar hydrogen bonding also occurs in the systems with salicylate as counter-ion.

In Table 11, it is seen that the lower temperature limits for long-chained surfactant solutions are quite high. How to bring down the lower temperature limit while retaining the upper temperature limit at high levels is a very challenging problem. As noted in Section 5.2.3, a possible solution might be the use of mixed surfactant solutions.
Another multiple substituted counter-ion, 5-chlorosalicylate, was also studied. The counter-ion is formed by placing a chlorine opposite to the -OH group on the salicylate molecule, thus enhancing the hydrophobicity of the counter-ion. This counter-ion should show both the charge delocalization characteristic of salicylate, and the hydrophobic feature of 3-chlorobenzoate. Three equimolar mixtures of Arquad 16-50/5-chlorosalicylate, each at a different total concentration, were tested and the results are shown in Table 12. It is seen that this counter-ion is very effective in producing drag reduction. At a concentration as low as 2.5 mM/2.5 mM good drag reduction was obtained from 15 to 80°C. As the total concentration is increased, critical wall shear stress increases at all temperatures, accompanied by a reduction of the lower temperature limit. With an effective temperature range from 2 to 80°C, along with its high $\tau_{wc}$ values, the 5 mM/5 mM solution is also a very good candidate to be used in district cooling systems. Tests were also carried out on longer chain surfactant solutions with 5-chlorosalicylate as counter-ion. The results are presented in Table 13. For the 5 mM/5 mM Arquad 18-50/5-chlorosalicylate solution, drag reduction was observed from 30 to 90°C. Tests at temperatures lower than 30°C were not performed. However, judging from the high $\tau_{wc}$ value at 30°C, the solution should still be effective at lower temperatures. In a 5 mM/5 mM mixture of Kemamine Q-2983C/5-chlorosalicylate, effective drag reduction was found between 90 to 120°C. When the concentration of the counter-ion
### Table 12

Critical Wall Shear Stress (N/m²) of Arquad 16-50/5-Chlorosalicylate Solutions at Various Total Mole Concentration

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>Surfactant concentration (mM)</th>
<th>Counter-Ion concentration (mM)</th>
<th>T(°C)</th>
<th>2</th>
<th>5</th>
<th>10</th>
<th>15</th>
<th>20</th>
<th>30</th>
<th>50</th>
<th>70</th>
<th>80</th>
<th>90</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arquad 16-50</td>
<td>2.5</td>
<td>2.5</td>
<td></td>
<td>Mapult</td>
<td>11</td>
<td>13</td>
<td>16</td>
<td>19</td>
<td>16</td>
<td>14</td>
<td>N</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.75</td>
<td>3.75</td>
<td></td>
<td>36</td>
<td>19</td>
<td></td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>140</td>
<td>62</td>
<td>39</td>
<td>N</td>
</tr>
<tr>
<td></td>
<td>5.0</td>
<td>5.0</td>
<td>9</td>
<td>360</td>
<td>380</td>
<td></td>
<td>380</td>
<td>380</td>
<td>310</td>
<td>150</td>
<td>71</td>
<td>N</td>
<td></td>
</tr>
</tbody>
</table>

aN : %DR < 20% ; M : 20% < %DR < 50%
Table 13

Critical Wall Shear Stress (N/m²) of Surfactant Solutions with 5-Chlorosalicylate as Counter-Ion

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>Surfactant concentration (mM)</th>
<th>Counter-Ion concentration (mM)</th>
<th>T(°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>30</td>
</tr>
<tr>
<td>Arquad 18-50</td>
<td>5.0</td>
<td>5.0</td>
<td>170</td>
</tr>
<tr>
<td>Kemamine Q-2983C</td>
<td>5.0</td>
<td>5.0</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>5.0</td>
<td>12.5</td>
<td>-</td>
</tr>
</tbody>
</table>

\textsuperscript{a} N : %DR < 20% ; M : 20% < %DR < 50%
was increased to 12.5 mM, the whole temperature range shifts upwards by 
30°C, being in the range of 120 - 150°C. Tests at temperatures higher than 
150°C were not performed. Although the upper temperature is excellent, 
the lower temperature is too high for district heating uses. The solution 
might rely on using surfactants of mixed chain lengths to reduce the lower 
temperature limit.

5.3.4.5 Binuclear Aromatic Counter-Ions

Counter-ions with two aromatic rings, particularly derivatives of 
naphthalene, were studied. For comparison purposes, Table 14 lists the test 
results for 2-naphthalenesulfonate system together with the results for a 
solution using benzenesulfonate as counter-ion. The effective temperature 
ranges for the two systems are the same, both being 40°C. However, the 
counter-ion with the double ring structure is able to boost the temperature 
up by 30°C. If for both counter-ions, the sulfonate group (-SO_3^-) stays in the 
water phase, the naphthalenesulfonate with its second ring member appears 
to be able to provide deeper penetration into the micellar interior, which 
results in an increase in hydrophobic interaction. If this is only a part of the 
explanation, one should not forget that double-ring counter-ions can provide 
even stronger binding between neighboring surfactants than the single-ring 
ones, greatly enhancing the micellar strength. The drag reduction data in
<table>
<thead>
<tr>
<th>Counter-Ion</th>
<th>Counter-Ion concentration (mM)</th>
<th>T(°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>30</td>
</tr>
<tr>
<td>Benzenesulfonate</td>
<td>12.5</td>
<td>60</td>
</tr>
<tr>
<td>2-Naphthalene sulfonate</td>
<td>5.0</td>
<td>-</td>
</tr>
</tbody>
</table>

- **Surfactant concentration = 5 mM**
- **N : %DR < 20% ; M : 20% < %DR < 50%**
Table 14 are for a 5 mM/5 mM mixture of Kemamine Q-2983C/2-naphthalenesulfonate. In Section 5.4, "Effect of Concentration", the effects of increasing the concentration of binuclear counter-ion will be discussed.

For a given surfactant species, the orientational binding of substituent groups on single-ring aromatic counter-ions has been shown to affect the drag reduction behavior dramatically. For double-ring aromatic counter-ions, the effect is even greater. Three geometric isomers of hydroxynaphthoate were used as counter-ions in Arquad 16-50 surfactant solutions and tests were made to examine the effects. The results are shown in Table 15 where the chemical structure of the counter-ions are also presented. When compared to the Arquad 16-50/salicylate system (see Table 1), all three solutions showed higher effective temperatures. The solution with 1-OH-2-naphthoate as counter-ion exhibits an unusually high temperature range, from 80 to 110°C, while the other two solutions show almost the same range. Since all these three isomeric counter-ions are very similar in their chemical structure, their orientation at the micellar surface should be carefully examined. The first model proposed is presented in the upper part of Figure 30. For comparison purposes, the temperature range for each counter-ion system is also shown in the figure. The bond lengths between the two carbon atoms on which the -COO⁻ and -OH groups are bonded are also noted. In this model, all three counter-ions direct their -COO⁻ and -OH groups to
Table 15
Critical Wall Shear Stress (N/m²) of Arquad 16-50 with Hydroxynaphthoates as Counter-Ions

<table>
<thead>
<tr>
<th>T(°C)</th>
<th>30</th>
<th>40</th>
<th>60</th>
<th>80</th>
<th>90</th>
<th>100</th>
<th>110</th>
<th>120</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-OH-2-naphthoate</td>
<td>-</td>
<td>N&lt;sup&gt;b&lt;/sup&gt;</td>
<td>N</td>
<td>10</td>
<td>-</td>
<td>28</td>
<td>28</td>
<td>N</td>
</tr>
<tr>
<td>2-OH-1-naphthoate</td>
<td>65</td>
<td>83</td>
<td>92</td>
<td>86</td>
<td>-</td>
<td>38</td>
<td>N</td>
<td>-</td>
</tr>
<tr>
<td>3-OH-2-naphthoate</td>
<td>-</td>
<td>76</td>
<td>91</td>
<td>100</td>
<td>30</td>
<td>M</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

<sup>a</sup> Arquad 16-50/counter-ion = 5 mM/5 mM

<sup>b</sup> N : %DR < 20% ; M : 20% < %DR < 50%
Figure 30. Proposed binding models for hydroxynaphthoates
water, with each group at a 60° angle from the micellar surface. When 1-OH-2- and 2-OH-1-naphthoates are compared, there is hardly any difference between the bindings of the two which would enable one to explain the great differences in the observed temperature ranges. Therefore the model needs to be adjusted to the one shown in the lower part of Figure 30. The new model suggests that each counter-ion aligns at the surface with the -COO\(^-\) group pointing laterally outwards. This orientation has been shown by the NMR study of Rao et al. [1987] to be the orientation of salicylate ion at the micellar surface. We will try to interpret the relative micellar stability in terms of this model. When 1-OH-2- and 2-OH-1-naphthoates are placed side by side, they both can form intramolecular chelation which therefore cannot account for the discrepancy. However, it is noted that the former can penetrate more into the core. We have indicated earlier that deeper penetration tends to raise the effective temperature range. The present model is consistent with this. When 1-OH-2- and 3-OH-2-naphthoates are compared, both appear to provide the same degree of penetration. Then, what can possibly account for their differences in effective temperatures? For benzene, all carbon-carbon bond lengths are the same, being equal to 1.40 Å. In naphthalene however, the bond lengths are not all equal, as seen in Figure 30. It appears that the bond length between the two carbons to which the -COO\(^-\) and -OH groups are attached is shorter in the 1-OH-2-naphthoate than that in the 3-OH-2-naphthoate (1.36 Å vs. 1.40 Å). A shorter
distance between \(-\text{COO}^-\) and \(-\text{OH}\) groups results in a stronger hydrogen bond, which is believed to be responsible for the discrepancy between the two counter-ions. Finally, that the effective temperature range for 2-\text{OH}-1- and 3-\text{OH}-2-naphthoates are approximately the same can be explained by noting that the charge delocalization (stronger hydrogen bonding) favors the former while the penetration favors the latter.

5.3.5 Mixed Counter-Ion Systems

The drag reduction of mixed counter-ion systems was investigated. Figure 31 shows the effective temperature range of sodium salicylate/sodium tosylate (NaSal/NaTos) in CTAC aqueous solution. Figure 32 shows the \(\tau_{\text{wc}}\) values vs. temperature for this mixed counter-ion system as a function of NaTos mole fraction. Neither the NaSal/CTAC nor the NaTos/CTAC system is effective below 15°C. However, the mixed counter-ion systems are effective below that temperature. Comparing the chemical structure of salicylate and tosylate, the latter is able to penetrate deeper into the micellar surface due to the \(-\text{CH}_3\) group on its phenyl ring. The presence of the two kinds of counter-ions seems to provide different degrees of penetration into the micelles which results in disturbance of the regular micellar structure. This seems to gain some support from the drag reduction results for
Figure 31. Effective drag reducing temperature range for NaSal/NaOTo mixed counter-ion system. Total counter-ion concentration was 12.5 mM. Surfactant used was CTAC with concentration of 5 mM. Dashed line at 2°C is the lowest temperature attainable in test system.
Figure 32. Temperature dependence of critical wall shear stress for various mole fractions of NaOTo in NaSal/NaOTo. X is the mole fraction of NaOTo in NaSal/NaOTo mixture. Total counter-ion concentration was 12.5 mM. Surfactant used was CTAC with concentration of 5 mM.
Kemamine Q-2983C solution using a mixed counter-ion of salicylate and 2,6-dihydroxybenzoate (see last entry of Table 11). The lower temperature limit of this solution is much higher than that of the solution with salicylate alone as the counter-ion (60°C). Since the two counter-ions are different only in their hydrophilic part, it seems to be reasonable to assume that they provide the same degree of penetration into the micelle. It is therefore not surprising that the lower temperature limit can not be reduced by this combination. Since counter-ions can only slightly plug into the micellar surface, micellar core structure can be perturbed only to some extent. The effect of using mixed counter-ions to reduce the lower temperature limit is therefore not as great as using mixed surfactants, as is seen in Figure 31. Another possible explanation for the ability of mixed counter-ions to reduce the lower temperature limit was provided by Tsujii et al. [1980] who studied mixed anionic surfactants and found the Krafft points for some of these systems are lower than the pure components. For two component liquid mixtures, if the solids of the two components are totally immiscible, the freezing temperatures of the liquid mixtures are always lower than the pure substances. Usually a minimum freezing point, the eutectic point, can be found at a certain composition. Tsujii et al. [1980] suggested that, since the Krafft point is analogous to the freezing point of ordinary substances, a depression in the Krafft point indicates that the solid complexed soaps formed by the surfactant and these two counter-ions are immiscible.
The effective temperature range for another mixed counter-ion system, sodium salicylate/sodium 4-ethylbenzenesulfonate (NaSal/NaEbs), is shown in Figure 33. It was noted that, if only NaEbs was present in CTAC solution, the solution became cloudy at temperatures below 20°C. However, when 25% of the NaEbs was replaced with NaSal, the temperature at which cloudiness occurred decreased to 10°C. The $\tau_{wc}$ values for this mixed counter-ion system at different compositions are presented in Figure 34.

HABON, a commercial surfactant product, is a 1:1 compound of CTAB/sodium 3-hydroxy-2-naphthoate with the electrolytes removed by an ion exchange process. During the drag reduction study of HABON, we found an interesting phenomenon. HABON alone is an effective drag reducer in the temperature range from 40 to 100°C based on a 1500 ppm (about 2.83 mM) dosage. On the other hand, the effective temperature range for the CTAB/NaSal system is about 15 to 70°C. When 1500 ppm NaSal was added to a 1500 ppm HABON solution, the effective temperature range obtained was from 30°C (lowest temperature tests were made) to 100°C. The drag reduction results for this solution are presented in Figure 35. An unexpected result is that at 50°C there was almost no drag reduction observed. When the tests were carried out from high to low temperatures, it was noticed that the drag reduction began to drop at temperatures below 60°C until it was lost at 50°C. However, when the temperature was decreased to 40°C, good drag reduction was again observed, and the solution remained effective down
Figure 33. Effective drag reducing temperature range for NaSal/NaEbs mixed counter-ion system. Total counter-ion concentration was 12.5 mM. Surfactant used was CTAC with concentration of 5 mM. Dashed line at 2°C is the lowest temperature attainable in test system.
Critical Shear Stress (Pa)

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>12.5 mM. Surfactant used was CTAC with concentration of 5 mM.</th>
</tr>
</thead>
</table>

Figure 34. Temperature dependence of critical wall shear stress for various mole fractions of NaEbs in NaSal/NaEbs. X is the mole fraction of NaEbs in NaSal/NaEbs mixture.
Figure 35. Drag reduction data for a 2.85 mM/9.375 mM HABON/NaSal solution
to 30°C. Tests were not performed below this temperature. When the temperature was raised from 30 to 50°C, drag reduction was again lost and appeared again at 60°C. Most recently, a similar observation was reported by Kleuker et al. [1991] who studied the drag reduction of a commercial product, DOBAN-G (n-docosyldimethylpolyoxethylammonium 3-hydroxy-2-naphthoate) with excess salicylate as counter-ion. DOBAN-G itself is a saturated C\textsubscript{22} chain surfactant in the presence of an equimolar amount of 3-hydroxy-2-naphthoate counter-ion. Kleuker et al. found that the DOBAN-G/NaSal mixture was effective at temperatures from 40 to 130°C. However, after a few days of operation in their system, drag reduction in the range of 60 to 80°C was lost. A possible explanation is given below. Since the 3-OH-2-naphthoate is a counter-ion with double-ring structure, it has a greater binding ability with cationic surfactants than the single-ring counter-ions such as salicylate. In a surfactant solution containing both the counter-ions, for instance, a HABON/NaSal solution, they compete for the sites on the micellar surface. The 3-OH-2-naphthoate prevails because of its stronger associating ability, which is especially true at temperatures above the upper limit temperature of the salicylate system (70°C). This is probably still the case at 60°C at which the competition ability of salicylate is relatively weak. When the temperature was decreased to 50°C, 3-OH-2-naphthoate co-precipitates with the surfactant and drag reduction was lost. Below 50°C, the tendency for salicylate ions to associate with surfactant molecules
becomes strong enough (the maximum $\tau_{wc}$ appears at 30°C for a 5 mM/12.5 mM CTAC/NaSal system; see Table 1) to take away the surfactant from the solid surfactant/3-OH-2-naphthoate complex. As a result, rod-like micelles are again formed and drag reduction can be observed. It is also possible that, at temperatures below 40°C, micelles containing both the counter-ions are formed. The reason why the temperature "gap" didn't occur in the CTAC solution with Sal/Tos or with Sal/Ebs as counter-ion mentioned earlier, can be explained as follows. The difference between the binding ability of salicylate and tosylate, or between those of salicylate and 4-ethylbenzenesulfonate is not as great as that between salicylate and 3-OH-2-naphthoate, which makes the formation of rod-like micelles with both counter-ions involved much easier. Therefore, there isn't a particular temperature at which one counter-ion tends to co-precipitate with the surfactant while binding with the other counter-ion is still too "weak" to compete.

5.4 Effect of Concentration

5.4.1 Effect of Counter-Ion Concentration

When the concentration of the counter-ion in a surfactant solution is lower than that of the surfactant, the solution is usually not very effective in
reducing skin friction. This is illustrated in Figure 36, where the drag reduction results for a solution containing 5 mM Ethoquad O/12 and 3 mM NaSal (the mole ratio of counter-ion to surfactant, $\xi$, equals 0.6) are presented. The prepared solution was not as thick as other surfactant systems studied, but was still viscoelastic as recoil was observed when swirling the container. The results indicate that drag reduction only occurs in the low Reynolds number region. When the surfactant concentration was held at 5 mM while the counter-ion concentration was increased from 3 mM to 5 mM ($\xi = 1$), the drag reduction was only slightly improved (Figure 37), mainly at 20 and 30°C. As $\xi$ was raised to 1.5, a significant increase in drag reduction was observed. The effect is most obvious at relatively high temperatures as will be explained later. In Figure 38, it is seen the region where drag reduction occurs extended to much higher Reynolds numbers. A further increase of $\xi$ to 1.9 (Figure 39) and then to 2.5 (Figure 40) leads to even better drag reduction. However, it is noted that the drag reduction at low temperatures was gradually lost as $\xi$ was increased. The increase in drag reduction effectiveness by the addition of excess salicylate was also noticed by Rose et al. [1984; Rose and Foster, 1989] in their alkyltrimethylammonium salts/NaSal systems. Hoffmann et al. [1981] showed that the micellar length of CPySal solutions increased when excess was added to the solution. Their light scattering results indicated that the micellar size at 20°C increased rapidly with excess salicylate until $\xi$ reached 1.5 where
Figure 36. Drag reduction data for a 5 mM/3 mM Ethoquad 0/12 / NaSal solution ($\xi = 0.6$)
Figure 37. Drag reduction data for a 5 mM/5 mM Ethoquad O/12 / NaSal solution ($\xi = 1.0$)
Figure 38. Drag reduction data for a 5 mM/7.5 mM Ethoquad O/12 / NaSal solution ($\xi = 1.5$)
Figure 39. Drag reduction data for a 5 mM/9.5 mM Ethoquad 0/12 / NaSal solution ($\xi = 1.9$)
Figure 40. Drag reduction data for a 5 mM/12.5 mM Ethoquad 0/12 / NaSal solution ($\xi = 2.5$)
micelles grew to their maximum size. Further addition of salicylate led to a slight decrease, followed by a leveling off in micellar size. It is not yet clear what role the excess salicylate plays in affecting the drag reducing effectiveness of surfactant solutions. In fact, even the location of the excess counter-ions in surfactant solution is still a disputed matter. Two different theories have been proposed on counter-ion binding in cationic surfactant solution. Bunton et al. [1973] studied the binding of tosylate ions in CTAB solution by measuring the transport number of the mixture. The mixture was placed in a cell with two compartments divided by a porous disk. After current was applied for a few hours, the ion contents in both compartments were determined. Bunton et al. found that, with excess tosylate in the mixture, the CTA cations were transported to the anode, indicating that the micelles were negatively charged. The negative charge of the micelles in the presence of excess aromatic counter-ion was also corroborated by Olsson et al. [1986] who studied counter-ion binding by measuring the self-diffusion coefficients of micelles and counter-ions using the pulsed-field gradient NMR diffusion technique. They found that, for solutions with excess counter-ion, the percent counter-ion binding, which can be calculated from the diffusion coefficient data, was well over 100%. In one example provided by the authors, the counter-ion binding for a NaSal/CTASal solution with $\xi = 10$ was as high as 500%. Another theory was proposed by Shikata et al [1987, 1988a, 1988b] who suggested that the maximum binding of counter-ions at
the micellar surface can not exceed 100%. Judging from their NMR chemical shift results, they suggested that the excess salicylate in a CTAB/NaSal solution remains in the water phase. In their dynamic viscoelasticity experiments, Shikata et al. [1987] found that the plateau value for the storage modulus $G''$ is independent of the excess salicylate in the solution. Since the plateau value is directly related to the network density in the solution, they concluded that the excess salicylate does not affect the mesh size of the network. This was also supported by Clausen et al. [1991] who had similar observations in their studies of the viscoelastic properties of a similar system (CTAC/NaSal/NaCl). Clausen et al. also pointed out that the electron micrographs of the entangled network structure all looked similar for solutions with different amounts of excess salicylate. On the other hand, Shikata et al. [1987, 1988a, 1988b] and Clausen et al. [1991] found that the relaxation time of the surfactant solutions determined by dynamic viscoelasticity experiments was strongly affected by excess salicylate. Shikata et al. [1987] inferred that the salicylate ions in the water phase serve as catalysts which affect the scissioning and reforming rate and hence the relaxation time of the rod-like micelles.

We will first postulate where excess counter-ions reside in the surfactant solution. Then, an attempt will be made to explain how solution drag reduction is affected by excess counter-ions. It is believed that the percent counter-ion binding to micelles is strongly affected by the ability of
the counter-ion to interact with the surfactant (e.g. hydrophobicity, charge delocalization etc.), as well as by its solubility in water. In other words, the partition coefficient of the counter-ion between micelle and water plays an important role. Take the Ethoquad O/12 /NaSal system as an example. As the $\xi$ value was less than unity, the micelles are positively charged since the amount of salicylate is not large enough to neutralize all the micellar charges. As noted earlier, if the electrostatic repulsions between surfactant headgroups can be reduced, micelles would rather abandon their spherical shape and assume a long, rod-like one. However, if the micellar charge can not be sufficiently neutralized, the rod-like micelles formed will be short, and weak in their structure. This is probably the case in the solution with $\xi$ less than one. As $\xi$ was increased to one or slightly greater than one, micelles are still positively charged due to the partition of the counter-ions between micelles and water. Since NaSal is highly soluble in water, 100% binding will not be attained until a certain amount of excess salicylate is added (e.g. at $\xi = 1.5$). Further addition of salicylate results in a change in sign of the micellar charge. This is possible if the driving force for the counter-ions to associate with micelles is strong enough to overcome the electrostatic repulsions they might encounter during association. Since the aromatic counter-ions have a great tendency to find a hydrophobic environment for their phenyl rings, counter-ion binding exceeding 100% is attainable. Under such circumstances, the excess salicylate in the micelles can no longer be
packed into the positions shown in Figure 20. They must be located between surfactant molecules on the same layer (similar to that shown in Figure 19 except that the counter-ions should turn their flat sides to the neighboring surfactant headgroups). The binding process becomes more and more difficult as the micellar charge increases. Finally, a saturated binding (say, 150%) is reached at a certain $\xi$ value (say, at $\xi = 2.0$). Additional salicylate should all go to the water phase. These unbound salicylates (or "free salicylates"), as proposed by Shikata et al. [1987, 1988], can affect the reformation and scission rate of the rod-like micelles.

In turbulent flow, drag reduction occurs presumably due to the interaction of micelles or the network they form with the turbulent eddies. Rod-like micelles in the flow field are in a dynamic equilibrium state in which micelles are broken down and reform very quickly (the so-called fragmentation and coagulation processes [Zana, 1991]). At the same time, there are fast exchanges of surfactant molecules between micelles and water. The scission rate increases with the flow rate, and is balanced by the increasing reformation rate caused by the increasing collisions between the micelles. When a certain shear stress is exceeded, the reformation rate is exceeded by the scission rate. Micelles therefore become smaller and smaller and the network structure can no longer be retained. As a result, drag reduction is lost rapidly. The increase in drag reduction efficiency by adding salicylate can be attributed to two effects. First, the added salicylate
increases the percent counter-ion binding in the micelles. This results in a stronger micellar structure since the surfactants in the micelles are more tightly bound. Second, with high content of free salicylates, the water phase can provide an advantageous environment for the rod-like micelles which, when broken down, can find salicylates around and reconstruct themselves easily. An increase in reformation rate means a higher shear stress is needed to destroy the rod-like micelles and the secondary structure they form. Thus, the increase in critical wall shear with increasing salicylate concentration can be rationalized. The drag reduction of a few other surfactant systems with varying amount of salicylate as counter-ion were also studied and the results are presented in Table 16. The data clearly show that $\tau_{wc}$ increases with increasing salicylate concentration. Another interesting feature noted in Table 16 is that the upper and lower temperature limits both are shifted upwards by the increased amount of salicylate in the solution. It is seen that this does not hold for the Kemamine Q-2803C/NaSal system because when the salicylate concentration increases from 7.5 to 9.38 mM, drag reduction at temperatures from 50 to 80°C also increases. However, it should be noted that, for the 3 mM/7.5 mM Kemamine Q-2803C/NaSal solution, the maximum drag reduction (25-40%) in this temperature range appeared at the lowest Reynolds number (at about 30,000) in the tests performed. Therefore it is very possible that effective drag reduction can be obtained in the low flow rate region where our system
Table 16

Effect of Counter-Ion Concentration on Drag Reduction Effectiveness

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>Surfactant conc. (mM)</th>
<th>Counter-Ion conc. (mM)</th>
<th>ξ</th>
<th>T(°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>40 50 60 70 80 90 100 110 120 130</td>
</tr>
<tr>
<td>Kemamine</td>
<td>3.75</td>
<td>7.5</td>
<td>2.0</td>
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<td>2.5</td>
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Table 16 (continued)

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<tr>
<th>Surfactant</th>
<th>Surfactant conc. (mM)</th>
<th>Counter-Ion&lt;sup&gt;a&lt;/sup&gt; conc. (mM)</th>
<th>ξ</th>
<th>T(°C)</th>
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<td>40  50  60  70  80  90 100  110 120 130</td>
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<tr>
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<td>3.75 12.5 3.3</td>
<td>- N N 190 250 220 180 140 71 N</td>
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</table>

<sup>a</sup> Counter-Ion used was salicylate.

<sup>b</sup> N : DR% < 20% ; M : 20% < DR% < 50%
could not make measurements. The surfactant concentration in the tested solutions (3 mM), however, was too low to show good drag reduction at high flow rates. The increase in upper temperature limit can be attributed to two effects. First, an increase in reformation rate of rod-like micelles due to the increase of free salicylate is in part responsible for the rise. Second, the solubility of salicylate in water increases with increasing temperature, which causes dissociation of salicylate ions from the micellar surface and results in a decrease in micellar length. Increasing the amount of salicylate in the system helps to drive salicylate ions back to the micelles, which favors the long rod-like micelles and thus extends the drag reducing capability to high temperatures. The loss of drag reducing effectiveness at low temperatures (see also Figures 36-40) is probably due to a greater salting out effect caused by the increasing amount of free salicylate.

It is interesting to note that, for some surfactant solutions, an increase in counter-ion concentration can adversely affect the drag reduction effectiveness. This is illustrated in Figures 41 to 44 where the drag reduction data for Arquad 16-50 solutions in the presence of various amounts of 3-OH-2-naphthoate are shown. It is seen when $\xi$ was increased from 0.67 (Figure 41) to 1.0 (Figure 42), the effectiveness of drag reduction was greatly improved. However, a substantial decrease in the maximum percent drag reduction was observed as $\xi$ was raised to 1.5 (Figure 43). In Figure 43, it is interesting to note that, at temperatures below 80°C, the percent drag
Figure 41. Drag reduction data for a 3.2 mM/2.1 mM mixture of Arquad 16-50 and 3-OH-2-naphthoate ($\xi = 0.67$)
Figure 42. Drag reduction data for a 3.2 mM/3.2 mM mixture of Arquad 16-50 and 3-OH-2-naphthoate (ξ = 1.0)
Figure 43. Drag reduction data for a 3.2 mM/4.8 mM mixture of Arquad 16-50 and 3-OH-2-naphthoate ($\xi = 1.5$)
Figure 44. Drag reduction data for a 3.2 mM/8.0 mM mixture of Arquad 16-50 and 3-OH-2-naphthoate ($\xi = 2.5$)

% Drag Reduction

Solvent Reynolds Number

$D = 0.243$ IN.
reduction was almost unchanged for a very wide range of flow rates. A further increase of $\xi$ to 2.5 (Figure 44) led to an even greater drop in the drag reduction of the solution. The phenomenon is interpreted as follows. The partition coefficient of 3-OH-2-naphthoate ion (or other binuclear aromatic counter-ions) between micelles and water is very high due to its strong binding ability to micelles, and to its low solubility in water. For Arquad 16-50/3-OH-2-naphthoate solutions with $\xi$ less than or equal to one, the value of $\xi$ should be very close to the relative amount of counter-ion and surfactant in each micelle since almost all the counter-ions are associated with the micelles, leaving only trace amounts in water. It is therefore not surprising that a marked increase in drag reduction efficiency was observed when $\xi$ was raised from 0.67 to 1.0 since nearly all the added counter-ions were used to increase the micellar length. When $\xi$ is slightly above unity, 100% counter-ion binding is reached. It is interesting to plot the drag reduction data for the solution with $\xi = 1.5$ in von Karman coordinates ($f^{-1/2}$ vs. $N_{Res} f^{1/2}$). As seen in Figure 45, at low shear stresses (or low values of $N_{Res} f^{1/2}$), the data points at 40 and 60°C lie approximately on straight lines with slopes only slightly greater than that of the von Karman line. As a certain value of wall shear stress is exceeded, the friction factor increases ($f^{-1/2}$ decreases) rapidly due to the disruption of the micellar structure. For comparison purposes, Figure 45 also presents the data for $\xi = 1.0$ at 60°C (the dashed line) which lie on a much steeper straight line, and the data for $\xi = 2.5$ at 60°C (dotted
Figure 45. Drag reduction data for a 3.2 mM/4.8 mM mixture of Arquad 16-50 and 3-OH-2-naphthoate ($\xi = 1.5$) plotted in von Karman coordinates. The dashed line represents the data at $T = 60^\circ$C for a 3.2 mM/3.2 mM solution ($\xi = 1.0$). The dotted line represents the data at 60$^\circ$C for a 3.2 mM/8 mM solution ($\xi = 2.5$).
line) which lie on a line parallel to the von Karman line. For clarity, the drop in drag reduction at high shear stresses for the solution with $\xi = 1$ is not shown in the figure. Similar characteristics were reported by Virk [1975b] for the drag reduction of four different kinds of fiber suspensions. Berman [1978] also observed similar behavior in his drag reduction data for polyacrylamide and DNA in distilled-deionized water. All the above drag reducers are known to be rigid, and elongated in shape. It is therefore believed that the micelles in Arquad 16-50/3-OH-2-naphthoate solutions became less and less flexible as $\xi$ was increased, which reduced their effectiveness in decreasing skin friction. The rigidity could originate from two sources: electric repulsion and geometric packing. Olsson et al. [1986] suggested that when counter-ion binding reaches 100%, the rod-like micelles are most flexible since the resistance from electrostatic repulsions between surfactant headgroups in the same micelle is the least. When counter-ion binding exceeds 100% and continues to increase, micelles become more and more charged and they become less and less flexible. For Arquad 16-50/3-OH-2-naphthoate solution with $\xi = 1.5$, it is noted in Figure 45 that the solution at 100°C shows a different behavior from that at 60 and 80°C, being more analogous to that exhibited by solutions containing flexible polymers. This is explained by the dissociation of counter-ions from micelles at high temperatures due to the increased thermal motions and to the increased solubility of counter-ions in water. As a result, micelles become more flexible.
since fewer counter-ions are bound on the micelles. It should be noted that, since the 3-OH-2-naphthoate is a strong binding counter-ion, the micellar strength increases with increasing $\xi$ value despite the accompanying rigidness. This is seen in Figures 41-44 as higher shear stresses are needed to break down the micellar structure for solutions with higher $\xi$ values. Similar behavior was also observed for a 5 mM/12.5 mM Kemamine Q-2983C/ naphthalene-2-sulfonate solution as shown in Figure 46. With $\xi = 2.5$, no drag reduction was found at 80°C. At 90 and 110°C, drag reducing behavior is analogous to that exhibited by rigid polyelectrolytes or fibers. At 130°C, the solution behaves like flexible polymer solutions. If the concentration of counter-ion is reduced while that of the surfactant is held constant, drag reducing behavior of flexible micelles is again observed. This is illustrated in the same figure by the drag reduction data for $\xi = 1.0$ obtained at 100°C.

In the case of the Arquad 16-50/NaSal system, however, this behavior was not observed even when $\xi$ is large (e.g. $\xi = 2.5$). What could possibly account for this difference? Before this question is answered, one should first ask why the drag reduction behavior of all the surfactant solutions with $\xi$ less than one is always similar to that for solutions containing flexible polymers (e.g. Ethoquad O-12/NaSal system with $\xi = 0.6$ in Figure 36; also see the work by Elson and Garside [1983] on the CTAB/1-naphthol system). With $\xi$ less than one, the micelles should be positively charged and they are
Figure 46. Drag reduction data for a 5.0 mM/12.5 mM mixture of Kemamine Q-2983C and 2-naphthalenesulfonate (ξ = 2.5) plotted in von Karman coordinates. The dashed line represents the data at T = 100°C for a 5.0 mM/5.0 mM solution (ξ = 1.0).
supposed to be very stiff due to electrostatic repulsions between individual headgroups. To explain this, it is postulated that when a rod-like micelle is bent either by outer forces or by its own thermal motion, surfactant molecules around the bent portions are able to adjust their positions in order to relieve the stress build up. As a result, micelles are still flexible despite the fact that the charge density on the micellar surface is not zero. When counter-ion binding exceeds 100%, some of the counter-ions must bind to the positions between surfactants on the same layer. This increases the difficulty for surfactants to move since the molecules on the same layer are tightened up by the counter-ions between them. The difficulty of molecular movement increases with increasing binding ability of the counter-ions and thus increases the rigidity of the micelles. This is why, for $\xi$ greater than unity, the micelles in Arquad 16-50 solutions with 3-OH-2-naphthoate as counter-ion are more rigid than those in the same surfactant solutions with salicylate as counter-ion.

In addition to the electrostatic effect, the geometric packing of counter-ions in micelles is also believed to be a determining factor on micellar rigidity. The 3-OH-2-naphthoates are such bulky molecules that, when associated in micelles, the micelles are easily over-packed by them even when the $\xi$ value is not too great. The overpacking results in rigid micelles since surfactant chains inside the core have less space to move. Salicylate, on the other hand, is half as large as 3-OH-2-naphthoate and, most importantly,
salicylate only inserts halfway into the micellar surface (compare Figure 25 with Figure 30). It has been shown earlier in Section 5.2.1.3, "Bialkyl chain surfactants", that a 5 mM Arquad DMHTB-75 solution containing 12.5 mM salicylate also exhibited similar flow behavior (Figure 13). The drag reduction data of the solution plotted in von Karman coordinates is shown in Figure 47. The hydrophobic part of the surfactant includes a hydrogenated tallow chain and a benzyl group. In the solution with $\xi = 2.5$, micellar surfaces get crowded easily since some of the spaces near the micellar surface have already been taken by the bulky benzyl groups of the surfactant. Therefore, the micelles in the solution are quite stiff. If the concentration of salicylate is lowered, however, micelles become flexible again. This is shown in the same figure by a dashline representing the data for a 5 mM/5 mM mixture of Arquad DMHTB-75 and salicylate ($\xi = 1$) at 30°C.

5.4.2 Effect of Surfactant Concentration

As counter-ion concentration is held constant, an increase in surfactant concentration results in an increase in both the size and the number of micelles, which increases the drag reducing capability of the solution. The effect is demonstrated in Table 17 where the drag reduction results for a number of surfactant systems are presented. For the first three surfactant systems shown in the table, the critical wall shear stress is clearly seen to
Figure 47. Drag reduction data for a 5.0 mM/12.5mM mixture of Arquad DMHTB-75 and NaSal ($\xi = 2.5$) plotted in von Karman coordinates. The dashed line represents the data at $T = 30^\circ$C for a 5.0 mM/5.0 mM solution ($\xi = 1.0$).
Table 17
Effect of Surfactant Concentration on Drag Reduction Effectiveness

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>Surfactant conc. (mM)</th>
<th>Counter-Ion(^a) conc. (mM)</th>
<th>(\xi)</th>
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<th>40</th>
<th>50</th>
<th>60</th>
<th>70</th>
<th>80</th>
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<tr>
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<td>3.3</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<td>90</td>
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Table 17 (continued)

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<thead>
<tr>
<th>Surfactant</th>
<th>Surfactant conc. (mM)</th>
<th>Counter-Ion(^a) conc. (mM)</th>
<th>ξ</th>
<th>T(°C)</th>
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<td>2.13</td>
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<td>3.20</td>
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<td>0.67</td>
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\(^a\) Counter-ion used in Kemamine Q-2983C, Q-2803C, and EX-300 solutions was salicylate, while that in Arquad 16-50 was 3-OH-2-naphthoate.

\(^b\) N : DR% < 20% ; M : 20% < DR% < 50%
increase with increasing amount of surfactant. It is also noted that the lower temperature limits for the three systems decrease with increasing surfactant concentration. The reason is not very clear. One possible explanation is that, when more surfactant is added to the solution, the salicylate concentration in the water phase is reduced by associating with the surfactant, which results in a temperature delay in phase separation. It is interesting to note that the drag reduction effectiveness can sometimes decrease with an increase in surfactant concentration. This situation occurs for solutions in which the counter-ion concentration in the water phase is low. When more surfactant is added to the solution, new rod-like micelles can only be formed by extracting counter-ions from the existing micelles. Since the percent counter-ion binding in each micelle is reduced, the micellar strength is weakened. This is demonstrated by comparing the drag reduction results for two Arquad 16-50/3-OH-2-naphthoate solutions in the last two entries in Table 17. In a 2.13 mM/2.13 mM (ξ = 1) solution, nearly all the 3-OH-2-naphthoate ions are associated in the micelles due to their strong binding ability. The molar ratio of surfactant to counter-ion in each micelle is, as argued earlier, very close to unity. As the concentration of Arquad 16-50 is increased from 2.13 to 3.2 mM (ξ = 0.67), the average counter-ion binding in each micelle becomes less than one. This can result in both a weaker micellar structure and a smaller micellar size. As a result, the drag reducing effectiveness of the solution at high temperatures decreases.
5.4.3 Effect of Total Concentration

When the relative amount of surfactant and counter-ion is held constant, a change in both the surfactant and counter-ion concentrations results in an increase in drag reduction effectiveness. Shown in Table 18 are the results for three different surfactant systems in which the critical wall shear stress increases with increasing total concentration as the value of $\xi$ is held constant. A similar result was found previously by Zakin et al. [1971] in their CTAB/1-naphthol systems and by Ohlendorf et al. [1984, 1986] in their TTAB/salicylate and CTAB/salicylate systems. Another feature of the effect is that, as shown in Table 18, the effective temperature for drag reduction is broadened by the increase in total concentration. Effective drag reduction at both higher and lower temperatures was obtained. It appears that increasing the total concentration combines all the advantages of increasing the individual component alone: higher upper temperature limit, reduced lower temperature limit, and greater critical wall shear stresses.

5.5 Effect of Solution pH

It is known that the micellar properties for some nonionic surfactant solutions such as dodecyldimethylamine oxide (DDAO) can be strongly affected by the solution pH value [Ikeda et al., 1979]. For example, the CMC
Table 18
Effect of Total Concentration on Drag Reduction Effectiveness

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>Surfactant conc. (mM)</th>
<th>Counter-Ion&lt;sup&gt;a&lt;/sup&gt;</th>
<th>ξ</th>
<th>T(°C)</th>
</tr>
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</tr>
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</tr>
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<td>2.5</td>
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<td>5.0</td>
<td>12.5</td>
<td>2.5</td>
<td>-</td>
</tr>
</tbody>
</table>

<sup>a</sup> Counter-Ion used was salicylate
<sup>b</sup> N : DR% < 20%; M : 20% < DR% < 50%
of the DDAO aqueous solution was found to increase with decreasing pH of the solution. This is attributed to the increasing protonation on the amine groups of the surfactant, which makes the surfactant change from nonionic to cationic. Ikeda et al. [1979] also found that the influence of foreign salts on micellar aggregation number was more significant when the solution was in the acidic range. This, too, can be rationalized by the screening effect of salt on the micellar charges.

For cationic surfactant solutions, however, a change in solution pH should not alter the nature of the surfactant because protonation cannot occur. Therefore, any variation in micellar properties caused by the change of pH must originate from the effect of pH on the counter-ion characteristics. Generally speaking, for cationic surfactant solutions with substituted benzoates as counter-ions, a higher solution pH results in a greater degree of ionization of the counter-ions, which favors micellar growth since a greater neutralization of micellar charge can be attained. However, when the counter-ion has more than one functional group whose ionizations can be affected by the pH as for example in the case of salicylate, the situation is different. Totten et al. [1986] reported that an equimolar TTAB/NaSal solution became water-like as the solution pH exceeded 11.3. Under such a high pH value, both the hydroxyl and carboxylate groups on the salicylate are ionized, which makes it impossible to form intramolecular hydrogen bonds.
A loss in charge delocalization capability results in a decrease in the effectiveness of salicylate to induce sphere-to-rod transition.

The effect of pH on drag reduction was studied using three geometric isomers of phthalate, namely, phthalate, isophthalate, and terephthalate as counter-ions in Kemamine Q-2803C surfactant solutions. Unlike salicylate, phthalate contains two carboxylate groups which can be ionized or protonized more easily by change of solution pH. Menger et al. [1982] found that, when ortho, meta, or para phthalates were added to a decyltrimethylammonium bromide (DTAB) solution, an increase of bromide content in water was detected by a bromide selective electrode. The result indicates that the counter-ions, instead of staying in the water phase, bind on the micellar surface and replace the absorbed bromide ions there. From their light scattering results, Menger et al. [1982] found that the CMC's for DTAB solutions, measured at pH = 8-9, with phthalate (1,2-isomer) and with isophthalate (1,3-isomer) as counter-ion are similar, both being approximately half of that with terephthalate (1,4-isomer) as counter-ion. On the other hand, Bachofer and Turbitt [1990] found that an equimolar mixture of CTAC and phthalate (both with concentration of 10 mM) exhibited viscoelasticity while a mixture of CTAC and isophthalate did not. Stoichiometric equivalents of NaOH were used by the authors to prepare counter-ions from their acidic forms but the exact solution pH was not mentioned.
Drag reduction studies were made on Kemamine Q-2803C surfactant solutions with each of these three isomeric phthalates as counter-ion. When terephthalate was used as counter-ion, the solution exhibited no drag reduction at pH values ranging from 4.0 to 11.0. The result was expected since it is impossible to acquire the best hydrophobic interaction for the phenyl ring while still retaining both the -COO\(^-\) groups in a hydrophilic environment. With isophthalate as counter-ion, however, drag reduction was observed, the effectiveness of which was strongly dependent on the solution pH. Drag reduction results at 70°C for 5 mM/12.5 mM Kemamine Q-2803C/isophthalate solutions at different pH conditions are shown in Figure 48. It is seen that the effectiveness of drag reduction increases with decreasing pH. Examining the molecular structure of isophthalate, for high pH solutions in which both carboxylate groups are ionized, overlapping between the electron cloud of -COO\(^-\) groups in the same counter-ion is unlikely since they are located far apart from each other. However, the -COO\(^-\) groups are so extended that they can interfere with the -COO\(^-\) groups in the neighboring counter-ions (see the upper graph of Figure 49), whichdestabilizes the micellar structure. As the solution becomes acidic, one or both of the -COO\(^-\) groups on the counter-ion are protonized (the first dissociation constant, pK\(_1\), for isophthalic acid is 4.6 [CRC Handbook of Chemistry and Physics, 49th edition, 1968-1969]), and good drag reduction was obtained at pH = 4.2. Since intramolecular hydrogen bonds can not be formed because of the
Figure 48. Effect of solution pH on the drag reduction of a 5 mM/12.5 mM Kemamine Q-2803C/isophthalate solution. The data shown were measured at 70°C.
Figure 49. Proposed structure change for counter-ions in Kemamine Q-2803C/isophthalate solutions under the influence of the solution pH.
distance, other stabilizing factors must be involved in this process. A proposed structure is presented in Figure 49 where it shows that a string of counter-ions on the micellar surface are held together by intermolecular hydrogen bonds. By such an arrangement, negative charges on counter-ions are greatly delocalized and the formation of stable rod-like micelles is thus possible.

The drag reduction results for Kemamine Q-2803C/phthalate solutions under various pH conditions are shown in Figure 50. Again, one can see a pronounced effect of solution pH on drag reduction effectiveness. When inspecting the molecular structure of phthalate in Figure 51, it is clear that the inability to exhibit drag reduction in the high pH range is due to the instability brought about by the overlapping of the electron cloud of the two \(-\text{COO}^-\) groups on the same counter-ion. As pH is decreased, protonation of the \(-\text{COO}^-\) groups takes place. Two possible structures, as shown in the lower part of Figure 51, are proposed to explain the observed drag reduction. In one case, intramolecular chelation is formed through which charges can be delocalized. The two \(-\text{COO}^+\) groups on the same counter-ion probably need to tilt away from each other to avoid the possible interactions between their oxygen atoms (that is, the two carboxylate groups are not seated on the same plane). Another proposed structure is similar to the one suggested for isophthalate in which charges are delocalized through intermolecular hydrogen bonding. It is possible that both intra- and inter-molecular
Figure 50. Effect of solution pH on the drag reduction of a 5 mM/12.5 mM Kemamine Q-2803C/phthalate solution. The data shown were measured at 70\(^\circ\)C.
Figure 51. Proposed structure change for counter-ions in Kemamine Q-2803C/phthalate solutions under the influence of the solution pH.
hydrogen bonding are responsible for the observed drag reduction. Since more than one stable structure can be formed, the resulting rod-like micelles are expected to be stronger than those for solutions containing isophthalate. This is demonstrated in Table 19 where the critical wall shear stress at various temperatures for solutions containing phthalate and isophthalate at two different pH conditions is compared. The phthalate appears to be a more effective counter-ion than the isophthalate as indicated by the higher $\tau_{wc}$ values as well as a broader effective temperature range exhibited by the former.

5.6 Effect of Pipe Diameter

For drag reduction in surfactant systems, it was first shown by Savins [1967] that a critical wall shear stress exists above which drag reduction is lost rapidly. White [1967] found that the critical wall shear stress, taken at the point where minimum friction factor occurs on a $f$ vs. $N_{Re}$ curve, is independent of pipe diameter. This critical wall shear stress is hereinafter designated as $\tau_{wc}'$ to be distinguished from the one taken at 50% drag reduction ($\tau_{wc}$) which appeared in previous Sections. Two sizes of tubes were used in the drag reduction studies, one being 0.243 inch, the other being 0.106 inch in diameter. Typical drag reduction results from the two tubes are shown in Figure 52 where the data for a 5 mM/12.5 mM mixture of
Table 19

Effect of pH on the Drag Reduction of Kemamine Q-2803C Solutions\textsuperscript{a} with Phthalate or Isophthalate as Counter-Ion

<table>
<thead>
<tr>
<th>Counter-ion</th>
<th>Solution pH</th>
<th>T(°C) 30</th>
<th>40</th>
<th>50</th>
<th>60</th>
<th>70</th>
<th>80</th>
<th>90</th>
<th>100</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isophthalate</td>
<td>5.2</td>
<td>N</td>
<td>M</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>N</td>
<td>N</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>4.2</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>59</td>
<td>67</td>
<td>N</td>
<td>M</td>
</tr>
<tr>
<td>Phthalate</td>
<td>6.2</td>
<td>-</td>
<td>M</td>
<td>54</td>
<td>-</td>
<td>M</td>
<td>N</td>
<td>N</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>4.2</td>
<td>N</td>
<td>M</td>
<td>76</td>
<td>85</td>
<td>98</td>
<td>-</td>
<td>-</td>
<td>M</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Surfactant/Counter-ion = 5 mM/12.5 mM

\textsuperscript{b} N : DR\% < 20\%; M : 20\% < DR\% < 50\%
Figure 52. Effect of pipe diameter on the drag reduction of a 5 mM/12.5 mM Kemamine Q-2983C/4-chlorobenzoate solution
Kemamine Q-2983C/4-chlorobenzoate at 30, 50 and 70°C are presented. It is seen that, as tube diameter increases, the region where effective drag reduction occurs shifts to higher Reynolds numbers. This is consistent with the results obtained by other researchers [Ohlendorf et al. 1984, 1986; Bewersdorff and Ohlendorf, 1988] for similar surfactant systems. A number of surfactant solutions were studied in both test tubes. Shown in Figure 53 are the drag reduction results for Kemamine Q-2983C/NaSal solutions at various surfactant and counter-ion concentrations. The figure was plotted as $\tau_{wc}'$ measured in the 0.106-inch tube against that obtained in the 0.243-inch tube. Data points represented by the same symbol are the $\tau_{wc}'$ values of the same solution obtained at different temperatures. The data points do not fall far from the 45-degree line. Similar results for the $\tau_{wc}'$ values of a number of different surfactant systems obtained with both tubes are shown in Figure 54 where good agreement between $\tau_{wc}'$ values from both tubes is also seen.

It is interesting to see whether scale-up methods developed for drag reduction in polymer solutions can be applied to surfactant solutions. Granville's [1984] method of two loci was used to examine this. The scale-up method is based on the assumption that, for a given solution at a certain temperature, the velocity shift $\Delta B$ (eq. 19) is only a function of shear velocity and is independent of pipe diameter. The first step of the method is to construct the constant $\Delta B$ lines on a von Karman plot. In order to do this, a
Figure 53. Critical wall shear stress for Kemamine Q-2983C/NaSal solutions obtained from 0.106- and 0.243-inch pipes. Points with the same symbol represent data for the same solution taken at different temperatures.
<table>
<thead>
<tr>
<th>SYM</th>
<th>Surfactant</th>
<th>Counter-Ion</th>
</tr>
</thead>
<tbody>
<tr>
<td>○</td>
<td>18-50</td>
<td>salicylate</td>
</tr>
<tr>
<td>*</td>
<td>R/12-75</td>
<td>salicylate</td>
</tr>
<tr>
<td>△</td>
<td>S-50</td>
<td>salicylate</td>
</tr>
<tr>
<td>□</td>
<td>18/12</td>
<td>salicylate</td>
</tr>
<tr>
<td>▼</td>
<td>T-50</td>
<td>salicylate</td>
</tr>
<tr>
<td>+</td>
<td>Q-2983C</td>
<td>4-Cl-benzoate</td>
</tr>
</tbody>
</table>

Figure 54. Critical wall shear stress for various surfactant solutions obtained from 0.106- and 0.243-inch pipes. Points of the same symbol represent data for the same solution taken at different temperatures.
knowledge of the turbulent velocity profile is needed. Here, Virk's three-zone model (eqs. 12, 18, and 19) is used and the outer wake region is neglected. The procedure for constructing constant ΔB lines can be summarized as follows:

1. By employing the velocity profile (eqs. 12, 18, and 19) in eq. 30, the dimensionless mean velocity, $\bar{\phi}$, as a function of $R^+$ and ΔB is obtained.

2. At a given ΔB, for each Reynolds number assigned, an $R^+$ can be obtained from eq. 31 by an iteration process.

3. From eq. 33, the friction factor, $f$, can be obtained.

4. Continue steps 2 and 3 until the Reynolds numbers cover the entire region tested. A line for the given ΔB can be drawn.

5. Change the value of ΔB and repeat steps 2-4.

A more direct way to draw constant ΔB lines without going through the iteration process is described as follows. Since the test range of the wall shear stress in a small pipe is known, the range of $R^+$ can be calculated from eq. 29. Thus at a given ΔB, for each $R^+$ assigned (within the above range), one can calculate $\bar{\phi}$ by eq. 30, followed by calculating Reynolds number and the corresponding friction factor through eqs. 31 and 33. The calculated constant ΔB lines are shown in Figure 55. Complete information on constant ΔB lines, which covers Reynolds numbers from $10^4$ to $10^7$, is tabulated in Table 28 in APPENDIX G. The procedure for scale-up is described as follows. For each
Figure 55. Constant ΔB lines on a von Karman plot
point measured in the small pipe (point 1 in Figure 55), the value of $N_{Re}^{1/2}$, designated as $(N_{Re}^{1/2})_1$, can be calculated. Based on the same shear stress, the value of $N_{Re}^{1/2}$ at a corresponding point (point 2), $(N_{Re}^{1/2})_2$, can be obtained by eq. 37. The exact position of point 2 is determined by intercepting the vertical $(N_{Re}^{1/2})_2$ line with the constant $AB$ curve on which point 1 is located. The process is continued until all the data points from the small pipe are projected. Figure 56 shows a comparison between the data measured from a 0.243-inch tube for a 5 mM/12.5 mM mixture of Kemamine Q-2983C/4-chlorobenzoate, and the predicted results (dash line) from the 0.106-inch tube data. It is seen that the predictions match the data points fairly well. Another scale-up example is shown in Figure 57 where the experimental data and the prediction for a 5 mM/12.5 mM Arquad S-50/NaSal solution are presented. Good agreement is again obtained.

5.7 Field Test in a Circulation Heating System

In order to examine the feasibility of surfactant drag reducers in large scale pipe systems, a field test was carried out in a 6-inch pipe heating system at Argonne National Laboratory in 1989. Since drag reduction at high temperatures was required, the surfactant chosen was Kemamine EX-300 which is a quaternary ammonium surfactant with an unsaturated C_{22} chain. The headgroup of the surfactant contains two hydroxyethyl groups which,
Figure 56. Drag reduction data for a 5 mM/12.5 mM Kemamine Q-2983C/4-chlorobenzoate solution in a 0.243-inch pipe flow. The dashed lines are predicted from the 0.106-inch pipe data.
Figure 57. Drag reduction data for a 5 mM/12.5 mM Arquad S-50/NaSal solution in a 0.243-inch pipe flow. The dashed lines are predicted from the 0.106-inch pipe data.
together with the unsaturated chain, can provide good drag reduction at reasonably low temperatures. The counter-ion used was salicylate, an effective counter-ion. Tests on solutions with different concentrations of surfactant and counter-ion had been previously performed in a 0.243-inch tube system in the laboratory before the field test was made. It was found that a 5 mM/12.5 mM solution of Kemamine EX-300/NaSal was the best candidate for effective drag reduction at temperatures ranging from 30 to 120°C (see Table 17).

The test facility is shown in Figure 5. The preparation of solution and the test procedure have been described in detail in CHAPTER IV. The surfactant solution was tested at 175, 200, and 225°F (80, 93, and 107°C) and the results are shown in Figure 58. It is seen that approximately 70% drag reduction was obtained at Reynolds numbers ranging from 600,000 to 2,000,000, indicating the applicability of surfactant drag reducers in large scale systems. After the author finished the tests and left Argonne, recirculation was continued under a constant flow rate of 820 gpm ($N_{Re} = 1,344,100$) at 200°F and no change was observed in the effectiveness of the solution after 120 hours of circulation [Choi et al., 1989a]. To check whether the experimental data can be predicted by the data from a small tube, scale-up was made using the data from a 0.243-inch tube. The predicted drag reduction at 80°C is shown in Figure 58 by a dashline. As the experimental results and the prediction are compared, it is seen that the predicted drag
Figure 58. Drag reduction data for a 5 mM/12.5 mM Kemamine EX-300/NaSal solution in a 6-inch pipe system. The dashline represents prediction of drag reduction at 80°C from the data of a 0.243-inch pipe flow.
reduction, judged from the extension of the dashline, is about 10% lower than the measured data. It should be noted that there was some uncertainty about the measured data at high flow rates in the 6-inch pipe system. Both the pressure gradient and flow rate readings fluctuated quite a bit probably because the flow rates were close to the maximum flow rate allowed by the pump. However, even at such high flow rates, the wall shear stresses in a 6-inch pipe flow were still too low to be measured in the 0.243-inch tube system due to equipment limitations of the latter. In future studies, drag reduction in a 0.243-inch tube flow in the low shear stress region should be carried out. Nitrogen can be used to provide the necessary shear stresses in a once-through flow system.

5.8 Effect of Preshearing

An interesting phenomenon was found when surfactants with hydroxyethyl groups in their headgroups were studied. The drag reduction of these solutions at all temperatures tested was found to increase with time as illustrated in Figure 59 where the drag reduction results of a 3.75 mM/5.63 mM Ethoquad T/13-50/NaSal at 10°C are shown. After the first day of pumping, which lasted for about three hours, the system was shut down. On the next day, the drag reduction was surprisingly found to increase significantly. Drag reduction data were taken intermittently in the next ten
Figure 59. Time dependence of drag reduction for a 3.75 mM/5.63 mM Ethoquad T13-50/NaSal solution. The pump was shut down between measurements.
days. Between two consecutive tests, the pump was shut down. Results in Figure 59 indicate that most of the increase in drag reduction took place between the first and the second day of the test, and the increase rate slowed down after the 4th day. On the 11th day of the test, equilibrium appeared to be reached. This phenomenon was exhibited by all the Ethoquad series surfactants such as 18/12, O/12, T/13-50 etc., but was not shown by other surfactant systems tested. In a separate test, it was noticed that when the solution was left undisturbed for three weeks, no appreciable change in drag reduction effectiveness was observed. The effect can be attributed to the bulky hydroxyethyl groups which increase the steric hindrance for aromatic counter-ions to associate into micelles. Hoffmann et al. [1981, 1984, 1985] and Ohlendorf et al. [1986] found that, in Couette flow and in laminar pipe flow, the quaternary ammonium surfactant solutions exhibited rheopectic behavior when the shear rate exceeded a certain threshold value. They suggested that the micelles can grow to larger sizes in the shear flow. It is believed that the shearing process, particularly in a turbulent flow, increased the chances of contact between surfactants and counter-ions, which results in an increase in association rate. It was also found that the effect was especially great for surfactants with shorter chains such as Ethoquad T/13-50. This is probably because longer chain surfactants have a greater tendency to form rod-like micelles than the shorter chain ones and the micellization process for the longer chain surfactants is quicker.
When a 3.75 mM/5.63 mM Ethoquad T/13-50/NaSal solution was continuously circulated at a constant flow rate, drag reduction increased until a steady state was reached. This is shown in Figure 60 where the results were obtained at a Reynolds number equal to 61,500. After 26 hours of continuous shearing, the percent drag reduction reached a steady value of approximately 70%. In contrast, when a 5 mM/12.5 mM Arquad S-50/NaSal solution was continuously sheared at the same flow rate, 67% drag reduction was obtained when the pumping was started and the value was virtually unchanged for 53 hours, which indicates that stable micelles were formed in the solution as soon as the solution was prepared. As suggested above, the increase in drag reduction was due to the increasing interactions between surfactant molecules and counter-ions brought about by the shear flow. On the other hand, there are factors which can adversely affect the time dependence of drag reduction effectiveness of the surfactant solutions. For example, the surfactants can also interact with the metal parts of the flow system and with dissolved oxygen in the solution. In Figure 60, the percent drag reduction is seen to be unchanged from the 26th to the 45th hour after the shearing process was started. It will be shown in the next section that, after a few days of the test, this level of drag reduction for the solution can no longer be sustained. It started to drop gradually due to the reactions of surfactants with dissolved oxygen and with piping materials. As will be
Figure 60. Variations of DR% with time for a 3.75 mM/5.63 mM Ethoquad T/13-50/NaSal solution and a 5 mM/12.5 mM Arquad S-50/NaSal solution under continuous shearing at constant flow rate.
shown in the next section interactions associated with the latter have a
greater effect than with the former.

5.9 Effect of Corrosion Inhibitors

In district heating or cooling systems, corrosion caused by the working
fluid can be a serious problem. Corrosion is an electrochemical process,
which can be classified into two types by the nature of the chemical reaction:
hydrogen producing corrosion and oxygen reducing corrosion [Aastrup et al.,
1991]. Hydrogen producing corrosion is caused by the formation of hydrogen
atoms from their ionic form which can penetrate the metal. When these
atomic hydrogens combine into hydrogen molecules, a pressure is developed
inside the pipe material, which causes cracking or blistering [Perry et al.,
1963]. By raising the pH value of the working fluids to about 9.5-10.0, this
type of corrosion can be avoided [Aastrup et al., 1991]. On the other hand,
the oxygen reducing corrosion is due to the presence of oxygen dissolved in
water which, when contacted with metal materials, can cause corrosion.
Oxygen reducing corrosion can be minimized by preventing air from
contacting the aqueous solutions, and by removing the dissolved oxygen from
water. The former can be done by purging and blanketing the systems with
nitrogen and the latter can be attained by deaeration and by using corrosion
inhibitors. The presence of aggressive ions such as chlorides and sulfates can
also accelerate the corrosion process [Wieck-Hansen, 1991]. There are, in
general, two forms of corrosion for metals: general corrosion and localized
corrosion. The former is characterized by a uniform thinning and loss of
metal, and the latter is featured by attack at localized spots. Chloride ions
are specially involved in the latter type of corrosion [Smith, 1991] and should
be removed from the system.

The effect of corrosion inhibitors on drag reduction was investigated.
The objective of the study was to examine the compatibility between
commercial corrosion inhibitors and surfactants of the quaternary
ammonium type, and to study their influences on drag reduction
effectiveness. Two major types of corrosion inhibitors, oxygen scavenger and
passivator, were used in the studies. The oxygen scavenger may be a
hydrazine-based compound which has strong reactivity with oxygen. The
passivator, either organic or inorganic type, can pacify the metal surface and
prevent further corrosion [Fontana and Greene, 1978]. Four commercial
inhibitors for high temperature applications, as listed in the first four entries
of Table 20, were combined with a 5 mM/12.5 mM Kemamine EX-300/NaSal
solution separatively to check for compatibility. It was found that
precipitation occurred immediately when Dearborn 547 and 545 were added
to the solutions. Transparent granular crystals were observed in the solution
containing Dearborn 547 and a white, sticky precipitate was found in the
solution containing Dearborn 545. A loss of viscoelasticity was also observed
<table>
<thead>
<tr>
<th>Trade name</th>
<th>Supplier</th>
<th>Recommended dosage</th>
<th>Ingredient(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dearborn 547</td>
<td>Dearborn</td>
<td>0.01 gal per gal solution</td>
<td>Na₂NO₃, Na₂NO₂, Na₃BO₃, NaOH</td>
</tr>
<tr>
<td>Dearborn 545</td>
<td>Dearborn</td>
<td>0.01 quart per gal solution</td>
<td>Na₂MoO₄, Morpholine</td>
</tr>
<tr>
<td>Dearborn 519</td>
<td>Dearborn</td>
<td>100-500 ppm</td>
<td>N₂H₄, Morpholine</td>
</tr>
<tr>
<td>Dearborn BW-1500</td>
<td>Dearborn</td>
<td>100-500 ppm</td>
<td>Morpholine</td>
</tr>
<tr>
<td>Topcast 7375RM</td>
<td>Nalco</td>
<td>1200 ppm</td>
<td>NaNO₂, Na₂MoO₄</td>
</tr>
<tr>
<td>Nalco N-2819</td>
<td>Nalco</td>
<td>2000 ppm</td>
<td>NaNO₂, NaOH</td>
</tr>
<tr>
<td>Inhibitor 66P</td>
<td>Betz</td>
<td>3000 ppm</td>
<td>NaNO₂</td>
</tr>
<tr>
<td>Corr-Shield K7</td>
<td>Betz</td>
<td>5600 ppm</td>
<td>NaNO₂, Na₂HBO₃, Sodium metasilicate</td>
</tr>
<tr>
<td>Nalco 2593 Microbiocide</td>
<td>Nalco</td>
<td>40 ppm</td>
<td>5-chloro-2-methyl-4-isothiazolin-3-one; 2-methyl-4-isothiazolin-3-one</td>
</tr>
</tbody>
</table>
in both solutions. The Dearborn 547 inhibitor is a passivator type inhibitor whose active ingredients are borate \( \text{BO}_3^{3-} \), nitrate \( \text{NO}_3^- \), and nitrite \( \text{NO}_2^- \). It has been reported by Underwood and Anacker [1987] that the binding ability of nitrate ions to dodecyltrimethylammonium micelles is stronger than any halide ions, and the binding ability of nitrite ions is only slightly inferior to that of bromide ions. Bartet et al. [1980] and Gamboa et al. [1981] found that the association degree of nitrate with CTAB is greater than \( \text{Br}^- \), \( \text{SO}_4^{2-} \), \( \text{Cl}^- \), \( \text{HPO}_4^- \), \( \text{B}_4\text{O}_7^{2-} \), \( \text{AcO}^- \), \( \text{CO}_3^{2-} \), \( \text{OH}^- \), and \( \text{F}^- \). It is therefore believed that the precipitate formed in the solution containing Dearborn 547 was a solid soap of nitrate and nitrite. The Dearborn 545 is also a passivator type inhibitor whose active ingredient is molybdate \( \text{MoO}_4^{2-} \). Although the binding ability of the molybdate ion is not known, it is believed to be strong enough for the ion to compete with salicylate for surfactants. Dearborn 519 contains hydrazine \( \text{N}_2\text{H}_4 \) which is known to be an oxygen scavenger. The active ingredient of Dearborn BW-1500 is morpholine \( \text{C}_4\text{H}_9\text{NO} \), a nonaromatic heterocyclic amine, which serves as a passivator. Both the above inhibitors are compatible with the surfactant solutions. The Dearborn 519 was chosen as an additive in drag reduction studies at high temperatures.

Shown in Figure 61 are the drag reduction results of 5 mM/12.5 mM solutions of Kemamine EX-300/NaSal with and without the presence of Dearborn 519. At 60 and 80ºC, the inhibitor seems to have no effect on the
Figure 61. Effect of Dearborn 519 on the drag reduction of a 5 mM/12.5 mM Kemamine EX-300/NaSal solution.
drag reducing activity. It was surprising to find that the solution with inhibitor was more effective at 110°C than the one without. One possible explanation is that, at high temperatures, certain chemical reactions between surfactant and dissolved oxygen become important, which result in a reduction in the effective concentration of the surfactant. The addition of oxygen scavenger lowers the oxygen concentration and thus minimizes the reactions. Better drag reduction is therefore obtained. On the other hand, since acid anhydrides are able to react with ammonia or amines to form amides [Morrison and Boyd, 1982], it is believed that the amount of free salicylate in the solution was also reduced by reacting with hydrazine, which can result in a decrease in drag reducing effectiveness. However, since the amount of salicylate in the solution studied was in large excess (\(\xi = 2.5\)), the effect was not obvious. The influence of Dearborn 519 on the drag reduction of a 1500 ppm (3.2 mM) surfactant solution, HABON (cetyltrimethyl-ammonium 3-OH-2-naphthoate), was also studied and the results are shown in Figure 62. Here we see an obvious decrease of effectiveness by the addition of the corrosion inhibitor. As stated earlier in Section 5.4.1, "Effect of Counter-Ion Concentration", the 3-OH-2-naphthoates are counter-ions with such strong binding ability that, when combined with an equimolar quantity of surfactant (the \(\xi\) value of HABON is one), most of the ions are incorporated in the micelles. The addition of Dearborn 519 results in an extraction of the counter-ions from the micelles and hence reduces the drag
Figure 62. Effect of Dearborn 519 on the drag reduction of a 3.2 mM (1500 ppm) HABON solution.
reduction effectiveness of the solution. The degree of counter-ion binding in
the solution is therefore determined by the competition between the
surfactants and inhibitors (\(N_2H_4^+\)) for the counter-ions. Shown in Figure 63
are the drag reduction results of 1500 ppm (3.0 mM) DOBON solutions with
and without the presence of Dearborn 519. In this case, since the tendency
of forming rod-like micelles is greatly increased by the longer surfactant
chain, most of the counter-ions are retained in the micelle phase. The
inhibitor therefore had little effect on the solution effectiveness at all
temperatures studied, as seen in Figure 63.

The impacts of corrosion inhibitors on the effectiveness of surfactant
drag reducers at low temperatures were also investigated. The surfactant
system chosen was a 3.75 mM/5.63 mM (\(\xi = 1.5\)) Ethoquad T/13-50/NaSal
solution. Unlike most other surfactants studied, the counter-ion (anion) in
Ethoquad T/13-50 is acetate rather than chloride. The absence of the
chloride ions greatly reduces the rate of corrosion [Smith, 1991]. Four low
temperature corrosion inhibitors were studied and their major ingredients
and recommended dosages are listed in entries 5-8 of Table 20. The last
entry in this table is Nalco 2593 Microbiocide which was used together with
Nalco 7375RM in this study. As illustrated in Section 5.8, "Effect of
Preshearing", the 3.75 mM/5.63 mM Ethoquad T/13-50/NaSal solution
exhibited increasing drag reduction as the solution was sheared. The effect
of two different corrosion inhibitors on the variations of drag reduction with
Figure 63. Effect of Dearborn 519 on the drag reduction of a 3.0 mM (1500 ppm) DOBON solution
shearing time was studied and the results are presented in Figure 64 where, for comparison purposes, the dynamic shearing behavior for the solution without inhibitor is also presented. It was found that the solution containing 1200 ppm Nalco 7375RM (a dosage recommended by the company) exhibited decreasing drag reduction upon continuous shearing. The solution was prepared by first combining the surfactant and counter-ion, followed by adding Nalco 7375RM and then the Microbicide. It was noticed that white suspensions immediately appeared when the inhibitor was added, and they were dispersed upon stirring. If the Microbiocide was added first, no suspensions were observed. Therefore, it is believed that some reactions must have occurred between the components of the inhibitor ($\text{NO}_2^-$ and $\text{MoO}_4^{2-}$) and the surfactant. The observed gradual loss of drag reduction is likely caused by the competition between the inhibitors and the counter-ions for the surfactants in the solution, which reduced the effective surfactant concentration and decreased the rate of forming rod-like micelles. In his corrosion tests, Smith [1991] found that when the concentration of Nalco 7375RM was reduced by half, its ability to reduce the rate of corrosion was not affected. It was therefore decided to carry out the same experiment on the solution with 600 ppm Nalco 7375RM. The results are also shown in Figure 64 where it is seen the drag reduction at steady state was only slightly lower than that of the solution without the inhibitor. This can be explained by the lower content of inhibitor which can only interact with small portions
Figure 64. DR% vs. shearing time for 3.75 mM/5.63 mM Ethoquad T/13-50/NaSal solutions with different corrosion inhibitors.
of the surfactant. Interestingly enough, it was noted that the initial drag reduction was improved from 25% to 62% as the corrosion inhibitor was added. In addition, the time required to reach steady drag reduction was greatly shortened by the presence of the inhibitor as compared to that of the solution without (7 hours against 26 hours). It should be mentioned that, after all ingredients for each solution were combined together, the time for mixing and that for loading the solution into the system were strictly controlled so that they were approximately the same for all the solutions investigated in the dynamic studies. It was also found that, right after being prepared, the solution containing the inhibitor was more viscoelastic than the solution without. Therefore it seems that the presence of a small quantity of Nalco 7375RM, for some as yet not understood reasons, helped to induce the formation of rod-like micelles. One possible explanation is that the \( \text{NO}_2^- \) and \( \text{MoO}_4^{2-} \) ions in the inhibitor help to neutralize the micellar charges and thus favor micellization. Another corrosion inhibitor, Betz K7, was also combined with the same surfactant solution and the variation of drag reduction with time at constant flow rate was studied. The concentration used was 2800 ppm, half the dosage recommended by the supplier. The result shown in Figure 64 indicates a decrease in drag reduction effectiveness with time. The major ingredients in Betz K7 were \( \text{NO}_2^- \) and some other anions. According to the information provided by Betz Chemicals, the concentration of the active component (as \( \text{NO}_2^- \)) is 300 ppm for
a 2800 ppm solution. The percent by weight of NaNO$_2$ in Nalco 7375RM is approximately 20-40, corresponding to an active concentration of 80-160 ppm (as NO$_2$) in a 600 ppm solution. The higher NO$_2^-$ content in Betz K7 is apparently responsible for the decrease in drag reduction with shearing time.

A long term stability test on a 3.75 mM/5.63 mM Ethoquad T/13-50/NaSal solution was performed. It was shown in Figure 60 that the drag reduction of the solution reached an equilibrium value after 27 hours of continuous shearing in the flow system, and it stayed unchanged up to the 45th hour. The shearing was continued for another 14 days after the initial 45-hour run and drag reduction data were taken every three days. For the test on each day, the flow rate was altered to obtain drag reduction data at different Reynolds numbers. All measurements for each day were completed within one hour. The Reynolds number was then adjusted back to 61,300 and the system was kept running for another three days before the next test was carried out. It is seen in Figure 65 that the drag reduction started to decrease on the 5th day of continuous running. Between the 5th and the 8th day, there was a dramatic drop in drag reduction. The decrease slowed down after the 8th day and finally another equilibrium was reached. The loss of effectiveness during the shearing process was presumably due to the interaction of the surfactant solution with the metal parts of the flow system and the dissolved oxygen in the solution. Another stability test was carried out using the same solution in combination with Nalco 7375RM (600 ppm)
Figure 65. Variations of drag reduction with time for a 3.75 mM/5.63 mM Ethoquad T/13-50/NaSal solution under continuous shearing. After each day's measurements, the flow rate was maintained at Reynolds number = 61,300.
inhibitor and Nalco 2593 Microbiocide (40 ppm) were added. It has been shown earlier in Figure 64 that the solution reached an equilibrium value 7 hours after the continuous shearing was started. Following the same test procedure described above, drag reduction data were taken every three days after the initial 45-hour run and the results are shown in Figure 66. It is seen that drag reduction effectiveness was retained with the addition of the inhibitor. Only a slight decrease was observed 8 days after the continuous shearing was started. Since the Nalco 7375RM is a passivator-type inhibitor, the great improvement indicates that it was the interaction between surfactant and the metal parts of the system that was responsible for the decrease of drag reduction effectiveness. Reactions between surfactant and dissolved oxygen are also believed to occur but the rate was slow and the influence was only minor. The slight decrease observed in Figure 66 is probably due to this effect.

A number of low temperature corrosion inhibitors were added to the 3.75 mM/5.63 mM Ethoquad T/13-50/NaSal solutions separately and the equilibrium drag reduction for each solution was measured. Results are presented in Table 21. Among the inhibitors studied, Nalco 7375RM was the best since it only slightly reduced the critical wall shear stress. As the table shows, the influence of Nalco 7375RM was greatest for temperatures of 10°C or lower.
Figure 66. Variations of drag reduction with time under continuous shearing. The solution was a 3.75 mM/5.63 mM Ethoquad T/13-50/NaSal mixture containing 600 ppm Nalco 7375RM inhibitor and 40 ppm Nalco 2593 Microbiocide. After each day's measurements, the flow rate was maintained at Reynolds number = 61,300.
Table 21

Effect of Corrosion Inhibitor on the Drag Reduction of a 3.75 mM/5.63 mM Ethoquad T/13-50/NaSal Solution

<table>
<thead>
<tr>
<th>Corrosion inhibitor</th>
<th>Concentration (ppm)</th>
<th>T(°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>2</td>
</tr>
<tr>
<td>No</td>
<td>-</td>
<td>110</td>
</tr>
<tr>
<td>Topcast 7375RM&lt;sup&gt;a&lt;/sup&gt;</td>
<td>600</td>
<td>92</td>
</tr>
<tr>
<td>Nalco N-2819</td>
<td>2000</td>
<td>43</td>
</tr>
<tr>
<td>Inhibitor 66P</td>
<td>1500</td>
<td>51</td>
</tr>
<tr>
<td></td>
<td>3000</td>
<td>63</td>
</tr>
<tr>
<td>Topcast 7375RM&lt;sup&gt;a,b&lt;/sup&gt;</td>
<td>600</td>
<td>69</td>
</tr>
<tr>
<td>Topcast 7375RM&lt;sup&gt;a,c&lt;/sup&gt;</td>
<td>600</td>
<td>140</td>
</tr>
</tbody>
</table>

<sup>a</sup> The solution also contained 40 ppm Nalco 2593 Microbiocide

<sup>b</sup> Ethoquad T/13-50/NaSal = 3.75 mM/7.5 mM

<sup>c</sup> Ethoquad T/13-50/NaSal = 5.63 mM/5.63 mM
An attempt was made to make up this loss by increasing the concentration of surfactant or counter-ion. Two solutions were prepared. In one, the amount of salicylate was increased by 50% (from 5.63 to 7.5 mM) while the surfactant concentration remained unchanged. The test results for this solution are listed as entry 6 of Table 21. When compared to entry 2 in the same Table, the $\tau_{\text{Wc}}$ values of the solution boosted with salicylate are greater at temperatures above 10°C. However, at temperatures below 10°C, less effective drag reduction was obtained. The result is not surprising since it was shown in Section 5.4.1 that the effective temperature range tends to shift upwards with increasing amount of counter-ion in the system. The other test was made using a solution with 50% more surfactant (concentration changed from 3.75 to 5.63 mM) while the amount of counter-ion was held constant. The results are listed as entry 7 of the same table. The solution appeared to show better drag reduction at all temperatures studied. Therefore, a decrease in drag reduction effectiveness by the addition of corrosion inhibitors can be compensated for by adding more surfactant in the system.
The presence of rod-like micelles is a necessary condition for drag reduction to occur in cationic surfactant systems. The rod-like micelles can only exist in a certain temperature range and drag reduction is restricted to this range. The effective temperature range for drag reduction has been arbitrarily defined as the temperatures at which more than 50% of drag reduction is observed in flow through a 0.243-inch pipe at Reynolds numbers ranging from 10,000 to 500,000. To characterize drag reducing effectiveness, a critical wall shear stress has been defined as the stress taken at the point where DR% drops to 50%. The upper temperature limit for drag reduction is primarily determined by the rod-to-sphere transition temperature and the lower temperature limit by the solubility of the surfactant. Both temperature limits are strongly dependent on variables such as the chemical structures of surfactant and counter-ion, concentrations of surfactant and counter-ion, and solution pH.

The effective temperature range shifts upwards as the length of surfactant chain increases. In systems with salicylate as counter-ion, an
upper temperature limit of 120°C can be reached using a surfactant containing 22 carbons in the alkyl chain, and a lower temperature limit of 5°C can be obtained using a surfactant with 12 carbons.

By incorporating one or more double bonds into the surfactant chain, the lower temperature limit can be further reduced while the upper temperature limit is not significantly affected. This is presumably due to the disruption of micellar core structure, which reduces the temperature below which solid soap complex is formed.

Drag reduction at low temperatures can also be improved by introducing two or more hydroxyethyl groups in the surfactant headgroup. It was found that the critical wall shear stress at low temperatures increased with increasing number of hydroxyethyl groups. The presence of the hydroxyethyl groups alone does not seem to affect the lower temperature limit. However, with both the hydroxyethyl groups and the double bonds present in the surfactant structure, excellent drag reduction can be obtained at temperatures as low as 2°C.

The use of mixed surfactants can greatly enhance the drag reducing capability of surfactant solutions at low temperatures. The lower temperature limits of mixed solutions were found to be lower than those of their individual surfactant components. In the two mixed systems studied, drag reduction down to a temperature of 2°C (the experimental limit) was observed. The effect is explained by the disruption of the chain alignment in
the micellar core, and is most significant when a great difference in chain length exists between the surfactant components. Although the upper temperature limit of the mixed solution is also reduced, the loss can be minimized by properly choosing the mixing ratio. In the case of a 0.15:0.85 C_{12}/C_{22} mixed surfactant system with salicylate as counter-ion, an effective temperature range of 2 to 115°C was observed. The use of mixed surfactants provides a possible way of solving the clogging problem at lower temperatures in district heating systems caused by the low solubility of long chain drag reducers.

Aromatic acid salts are much more effective counter-ions for drag reduction than inorganic salts. The presence of inorganic counter-ions, however, can enhance the drag reducing efficiency of surfactant solutions containing aromatic counter-ions.

The effectiveness of counter-ions for drag reduction is strongly dependent on their chemical structures. Counter-ions which can disperse their negative charges by resonance structure or by forming inter- or intramolecular hydrogen bonds are effective in inducing drag reduction. Counter-ions with structures that have good hydrophobic and hydrophilic interactions with surfactants and with water respectively at micellar surfaces are also effective. In other words, the hydrophobic and hydrophilic groups on the counter-ions should be separated as far as possible to obtain good drag reduction.
The effectiveness of counter-ions with different anionic functional groups increases in the order: phenoxide < benzenesulfinate < benzoate < benzenesulfonate. The effectiveness of benzoate and benzenesulfonate can be greatly enhanced by replacing a proton at the *ortho* or *meta* position with respect to the carboxylate group by a hydrophilic substituent such as -OH or -NH₂. A counter-ion with an *ortho* hydrophilic substituent is more effective than one with a *meta* if an intramolecular hydrogen bond can be formed between the carboxylate group and the substituent. The effect of the *ortho* substituent group on the counter-ion effectiveness increases in the order: NO₂ < NH₂ < OH.

Good drag reduction can also be obtained if the counter-ion is a benzoate or benzenesulfonate substituted by a hydrophobic group such as CH₃ or Cl at the *meta* or *para* position. The effectiveness of the hydrophobic substituent in increasing order is: OCH₃ < CH₃ < Cl. For the same substituent group a counter-ion with a hydrophobic substituent at the *para* position is more effective at high temperatures than one with a substituent at the *meta* position. The opposite is true at low temperatures.

For counter-ions with an alkyl group at the *para* site, an increase in the alkyl length increases the effectiveness of the counter-ion. In the case of Kemamine Q-293C surfactant solutions with substituted benzenesulfonates as counter-ions, for example, the upper temperature was found to increase by about 20°C on each addition of a methylene group on the alkyl substituent at
the para site. If the alkyl group was a branched one such as a tert-butyl group, however, no drag reduction was found.

Drag reduction studies were performed on Kemamine Q-2983C solutions using counter-ions with multiple substituents. When 2,6-dihydroxybenzoate is mixed with a short chain surfactant (C\textsubscript{12}), drag reduction greater than 50% was obtained at temperatures down to 2°C. The improved drag reducing capability at low temperatures, as compared to the solution with salicylate, is probably due to the increased hydrophilicity of the counter-ion which delays the phase separation. On the other hand, when the surfactant is a long chain one, the effective temperature range moves to a higher upper limit. For a 5 mM/7.5 mM mixture of Kemamine Q-2983C/2,6-dihydroxybenzoate, an upper temperature limit of 130°C was obtained. It can be further increased if the concentration of the counter-ion is further increased. Another counter-ion studied was 5-chlorosalicylate which when combined with CTAC can also provide good drag reduction at temperatures down to 2°C. An upper temperature limit higher than 150°C can be obtained if the surfactant used is a Kemamine Q-2983C. However, the use of multiple substituted counter-ions in long chain surfactant solutions is usually accompanied by a loss of drag reduction at low temperatures.

Surfactant solutions with double ring counter-ions exhibit drag reduction to higher temperatures than those with only a single ring. Results
with three isomeric hydroxynaphthoates show that a higher upper temperature limit can be obtained if the counter-ion can penetrate deeper into the micelle, or stronger intramolecular hydrogen bonding can be formed.

As in mixed surfactant systems, the use of mixed counter-ions can also decrease the lower temperature limit of the surfactant solutions. This has been attributed to the different degrees of penetration provided by the different counter-ion species. For the two mixed counter-ion systems studied, lower temperature limits down to at least 2°C were obtained. When a great difference exists between the binding abilities of the two counter-ions used in the mixed system, a "temperature gap" at which no drag reduction is observed can be seen. This is explained by the competition between the counter-ions for the surfactants.

Both the concentrations of surfactant and counter-ion can affect the drag reducing effectiveness of the solution. In general, as the surfactant concentration is held constant, an increase in counter-ion concentration results in an increase in critical wall shear stress, particularly in the high temperature range. The effective temperature range was also found to shift to a higher level. For surfactant systems containing double ring counter-ions, however, drag reducing efficiency can be reduced by an excess of counter-ions. In this case, the rod-like micelles are believed to become more rigid with increasing concentrations of counter-ions in the solution. For surfactant systems with \( \xi \) greater than unity, as the counter-ion concentration is held
unchanged, increasing the surfactant concentration increases the critical wall shear stress at all temperatures. While the upper temperature limit is not substantially affected by the increased surfactant, the lower temperature limit is greatly reduced. When the mole ratio of surfactant and counter-ion is held constant, increasing the total concentration of the solution results in a rise in the upper temperature limit and a reduction in the lower temperature limit.

For solutions with phthalate or isophthalate as counter-ion, the drag reduction effectiveness is strongly influenced by the solution pH. Results show that the effectiveness increases with decreasing pH. The effective temperature range was also found to be broader as the solution became more acidic. This has been attributed to the change in the counter-ion structure caused by the protonation effect.

Drag reduction for a number of surfactant solutions was studied in two different diameters of pipes. For a given surfactant solution, the critical wall shear stress taken at the lowest point of the friction factor curve is independent of the pipe diameter. For the first time, a scale up method developed for polymer drag reducers was used in surfactant systems. Good agreement between the predictions and the experimental data was found.

A successful field test was carried out in a 6-inch pipe circulation heating system at Argonne National Laboratory using a high temperature surfactant formulation developed in this research. Drag reduction as high as
70% was obtained at 80, 93 and 107°C, indicating the feasibility of using surfactant drag reducers in large scale heating systems.

For surfactants with hydroxyethyl groups in their headgroups, the drag reducing effectiveness increased with time of shearing. This is explained by the increased interactions between the surfactants and counter-ions in the flow field, which gradually overcomes the steric effect caused by the bulky hydroxyethyl groups during the association process.

The effect of corrosion inhibitors on the drag reducing behavior of surfactant solutions at both high and low temperatures has also been investigated. Inhibitors of the oxygen scavenger type can either increase or decrease the drag reduction effectiveness of the solution depending on the surfactant formula used. The increase can be explained by the removal of dissolved oxygen in the solution, which reduces chemical reactions between oxygen and surfactant. The inhibitors, however, can also react with the counter-ion in the system, which decreases the effective counter-ion concentration and thus lowers the effectiveness. The latter effect is not significant for solutions containing long chain surfactants, or for solutions with high ξ values.

Passivator type inhibitors were also found to reduce drag reduction effectiveness. This is attributed to interactions between surfactants and the anions of the inhibitors. The drag reducing capability at high temperatures can be greatly improved by increasing the amount of counter-ion, but that at
low temperatures is reduced. On the other hand, if additional surfactant is added, drag reduction at both low and high temperatures is significantly enhanced. Long term stability tests indicate that the 3.75 mM/5.63 mM Ethoquad T/13-50/NaSal solution in the presence of 600 ppm Nalco 7375RM inhibitor and 40 ppm Nalco 2593 Microbiocide is a promising candidate for use in district cooling systems.
CHAPTER VII
RECOMMENDATIONS

1. It is recommended that further studies on the drag reduction of mixed surfactant systems be performed. Research has been carried out on mixtures of Arquad 12-50 (C_{12}) and Arquad 16-50 (C_{16}) and of Arquad 12-50 and Kemamine Q-2983C (C_{22}). It is recommended that Kemamine Q-2983C be combined with decyltrimethylammonium chloride (C_{10}), or with Arquad 18-50 (C_{18}). In the former case, since the difference between the surfactant chain lengths is large, good drag reduction at low temperatures is expected if a small amount of C_{22} is replaced by C_{10}. In the latter case, since the difference in chain length is not too great, the upper temperature should not be affected too much but it is not clear how the lower temperature limit of the mixture would be affected. Mixed surfactant systems using counter-ions other than salicylate should also be investigated. Possible candidates are the highly effective counter-ions such as 4- or 5-chlorosalicylate, 4- or 5-methylsalicylate, and 2,6-dihydroxybenzoate. These counter-ions, when combined with long chain surfactants, are known to give drag reduction at extremely high temperatures but lose their effectiveness at low
temperatures. The question to be addressed is whether drag reduction at low temperatures can be obtained while that at high temperatures can be retained using mixed surfactants. Preliminary experiments have shown that the effective temperature range of mixed surfactant solutions containing these counter-ions are very sensitive to the mole fraction of the short chain surfactant and to the counter-ion concentration. Careful control of these variables is required. The preferred mixed surfactant systems consist of a short chain surfactant ($C_{10}, C_{12}$) and any surfactant of the following: Kemamine EX-300, Ethoquad R/12-75, Ethoquad R/13-50, Ethoquad O/12, Ethoquad O/13-50, and Ethoquad T/13-50.

2. It is recommended that birefringence experiments be carried out using a 5 mM/12.5 mM mixture of Arquad DMHTB-75/NaSal. The use of this solution serves two purposes. First, the solution was shown to exhibit good drag reduction at low shear rates which might be attainable in birefringence experiments. Second, since the solution is likely to contain rigid rod-like micelles, it will be interesting to see whether there is any difference between the birefringence built up by this solution and that by solutions containing flexible micelles such as a 5 mM/5 mM Arquad DMHTB-75/NaSal solution. Micelles in surfactant solutions containing double-ring aromatic counter-ions are also believed to be rigid if the $\xi$ value is greater than 1. Birefringence studies for these solutions are also recommended.
3. By combining static and dynamic light scattering techniques, the rigidity of micelles can be determined. It is recommended that light scattering experiments be carried out on the Arquad DMHTB-75/NaSal solutions at various NaSal concentrations.

4. According to the geometric packing model of Israelachvili et al. [1976], the micelles formed in solutions containing double chain surfactants such as Arquad 2C-75 and Kemamine Q2802C are disk-shaped. This should be further examined by light scattering measurements.

5. Multiple substituted benzoates such as 4-chlorosalicylate, 3- or 4-methylbenzoate, and hydroquinonesulfonate (2,5-dihydroxy-benzene-sulfonate) should be tested for their effectiveness in inducing drag reduction.

6. Both 3- and 4-chlorobenzoate have been shown to be effective counter-ions for drag reduction. It is recommended that other halide substituted benzoates such as 4-bromobenzoate and 4-iodobenzoate be used as counter-ions and their drag reduction studied.

7. The Kemamine Q-2983C surfactant solution with 4-nitrobenzoate as counter-ion was drag reducing while that with 2-nitrobenzoate was not. The discrepancy has been attributed to the steric effect of -NO₂ group in the latter counter-ion, and the strong electron-inducing effect of the -NO₂ group. It is recommended that solutions with 3-nitrobenzoate as counter-ion be tested.
8. The use of mixed counter-ions has been shown to reduce the lower temperature limit for drag reduction. The effect has been assumed to be partly due to the different degrees of penetration of the counter-ions into the micelles. It is recommended that drag reduction be studied on a Kemamine EX-300 surfactant solution using a mixed counter-ion of salicylate and 5-chlorobenzoate. The major purpose is to obtain drag reduction at high temperatures (over 150°C) and at reasonably low temperatures.

9. The drag reduction of CTAB solutions using CsBr/NaSal as mixed counter-ion should be performed to compare with that with KBr/NaSal. The major purpose is to find out whether the enhancement of drag reduction is due to the presence of Br⁻ or to the cations (K⁺, Cs⁺).

10. The "gap temperatures", at which drag reduction is not observed, for a HABON/NaSal solution has been interpreted as due to competition between the two different counter-ions in the solution. The phenomenon presumably occurs only when a large difference exists between the binding abilities of the two counter-ions. Since drag reduction tests for this solution at temperatures lower than 30°C were not performed (the solution at 30°C was still drag reducing), low temperature tests should be carried out in the low temperature loop.

11. Each of the following mixed counter-ion pairs should be combined with Kemamine Q-2983C and the drag reduction of the solution tested:
{salicylate, 3-OH-benzoate}, {salicylate, benzenesulfonate}, and {salicylate, 2-NH₂-benzoate}. Since the counter-ions in each pair are of relatively different binding abilities, a temperature gap phenomenon should be observed.

12. It is recommended that the drag reduction of a 5 mM/12.5 mM Arquad DMHTB-75/NaSal solution be studied in a 0.106-inch pipe. This is to study the flow behavior exhibited by rigid micelles in a pipe with different diameter.

13. Scale-up should be further tested using data from different sizes of pipes with larger diameter ratios.

14. It is recommended that a field test be carried out in a circulating cooling system (5 to 10°C). A prospective candidate is Ethoquad T/13-50 (1700 ppm or 3.75 mM) with salicylate (900 ppm or 5.63 mM) as counter-ion. The recommended corrosion inhibitor and microbiocide are 600 ppm Nalco 7375RM and 40 ppm Nalco 2593 respectively. Variations of drag reduction with time should be especially noted.

15. It has been shown that isophthalate and phthalate are effective counter-ions in Kemamine Q-2983C surfactant solutions when the solution pH is low. It is recommended that similar studies be carried out using 1,2- and 1,3-benzenedisulfonates as counter-ions.

16. It is recommended that drag reduction studies be made on the Armac and Ethomeen series of products from Akzo Chemicals. Surfactants in the former series are aliphatic amines and those in the latter are
ethoxylated amines, all being nonionic surfactants. Four Ethomeen surfactants, S/12, S/15, O/12, and T/13, are currently available in our laboratory. Preliminary tests on a 5 mM/12.5 mM solution of Ethomeen S/15/NaSal with a solution pH of 7 indicated that no drag reduction was observed at 30°C. Since protonation can occur in the acidic range, the surfactants are expected to become cationic and the formation of rod-like micelles in the presence of salicylate is possible.

17. It is recommended that light scattering studies be made on Kemamine Q-2983C solutions using 4-chlorophenylacetate as counter-ion. The solution was first found to be water-like right after preparation. As time went by, the undisturbed solution exhibited viscoelasticity. It would be very interesting to study the variations of micellar size with time in this solution including study of the micellar structure using an electron microscope. A number of samples from the same batch solution can be made and frozen rapidly at different times for electron micrograph studies.

18. The importance of the presence of π electrons in counter-ions in inducing sphere-to-rod transition can be investigated by comparing surfactant solutions containing benzoate and cyclohexane carboxylate and their derivatives. Flow tests probably are not suitable since benzoate itself is not an effective counter-ion. Light scattering experiments can be considered as the first priority.
19. It is recommended that electrokinetic or other transport experiments be used to determine the sign of the micellar charge in solutions containing excess counter-ions.

20. For some drag reducing surfactant solutions, the effective temperature range can be so wide that drag reduction tests must be performed in both heating and cooling systems in the laboratory. It is important to note that individual solutions should be made up to test in each system. This is because surfactants can be absorbed by the metal parts which reduces the effective surfactant concentration. Transferring solution from one system to the other is not recommended since a further reduction in surfactant concentration can occur.

21. The orientational binding for certain single-ring aromatic counter-ions on micelle surface has been investigated by a number of researchers using proton NMR techniques. It is recommended that proton NMR experiments be carried out to study the degree of penetration and the orientational binding of double-ring aromatic counter-ions such as 1- and 2-naphthlenesulfonates. The orientational binding for 3-hydroxy-2-naphthoate and its two isomers by NMR experiments is also very important since the results can probably explain the differences in their drag reducing effective temperature ranges (see Figure 30). NMR experiments are also recommended to be conducted on mixed counter-ion systems such as solutions containing salicylate and 3-hydroxy-2-naphtate.
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APPENDIX A

CATIONIC SURFACTANTS TESTED
Table 22
Cationic Surfactants Tested

<table>
<thead>
<tr>
<th>Trade name</th>
<th>Supplier</th>
<th>Chemical structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arquad 12-50</td>
<td>Akzo Chemicals Inc.</td>
<td>$C_{12}H_{25}-N(CH_3)_3Cl$</td>
</tr>
<tr>
<td>Tetradecyltrimethyl ammonium bromide</td>
<td>Aldrich Chemical Company, Inc.</td>
<td>$C_{14}H_{29}-N(CH_3)_3Br$</td>
</tr>
<tr>
<td>Arquad 16-50</td>
<td>Akzo Chemicals Inc.</td>
<td>$C_{16}H_{33}-N(CH_3)_3Cl$</td>
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<td>Hexadecyltrimethyl ammonium bromide</td>
<td>EM Science</td>
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<td>Tallow−$N(CH_3)_3Cl$</td>
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<td>Arquad S-50</td>
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<td>Soya−$N(CH_3)_3Cl$</td>
</tr>
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<td>$C_{22}H_{43}-N(CH_3)_3Cl$</td>
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<td>Rapeseed−$N(CH_3)(C_2H_4OH)_2Cl$</td>
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<td>---------------------------</td>
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<td>Akzo Chemicals Co.</td>
<td>\text{C}<em>{18}\text{H}</em>{35}–N((\text{C}_2\text{H}_4\text{OH})_3\text{Ac})</td>
</tr>
<tr>
<td>Ethoquad 18/13-50</td>
<td>Akzo Chemicals Co.</td>
<td>\text{C}<em>{18}\text{H}</em>{35}–N((\text{C}_2\text{H}_4\text{OH})_3\text{Ac})</td>
</tr>
<tr>
<td>Ethoquad R/13</td>
<td>Akzo Chemicals Co.</td>
<td>Rapeseed–N((\text{C}_2\text{H}_4\text{OH})_3\text{Ac})</td>
</tr>
<tr>
<td>Cetylpyridinium chloride</td>
<td>Aldrich Chemical Company, Inc.</td>
<td>\text{C}<em>{16}\text{H}</em>{33}–N((\text{C}_5\text{H}_5)\text{Cl})</td>
</tr>
<tr>
<td>Arquad 2C-75</td>
<td>Akzo Chemicals Co.</td>
<td>\text{C}<em>{12}\text{H}</em>{25}\text{N}(\text{CH}_3)_2\text{Cl}</td>
</tr>
<tr>
<td>Arquad DMHTB-75</td>
<td>Akzo Chemicals Co.</td>
<td>Hydrogenated Tallow \text{C}<em>{6}\text{H}</em>{5}\text{CH}_2\text{N}(\text{CH}_3)_2\text{Cl}</td>
</tr>
<tr>
<td>Kemamine Q-2802C</td>
<td>Witco Chemical Co.</td>
<td>\text{C}<em>{22}\text{H}</em>{45}\text{N}(\text{CH}_3)_3(3-\text{OH}-2-naphthoate)</td>
</tr>
<tr>
<td>HABON</td>
<td>Hoechst</td>
<td>\text{C}<em>{16}\text{H}</em>{33}–N((\text{CH}_3)_3(3-\text{OH}-2-naphthoate)</td>
</tr>
<tr>
<td>DOBON</td>
<td>Hoechst</td>
<td>\text{C}<em>{22}\text{H}</em>{45}–N((\text{CH}_3)_3(3-\text{OH}-2-naphthoate)</td>
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Table 23
Carbon Chain Distribution of Some Cationic Surfactants

<table>
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<tr>
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<th>Arquad 12-50</th>
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<th>Arquad S-50</th>
<th>Arquad 18-50</th>
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<td>1</td>
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<tr>
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<td>27</td>
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<td>55</td>
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<td>-</td>
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<td>C_{22 }</td>
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<td>-</td>
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</tr>
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<td>C_{22}'</td>
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Table 23 (continued)

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<th>Ethoquad 18/12</th>
<th>Ethoquad R/12-75</th>
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<th>Kemamine Q-2803C</th>
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</tr>
<tr>
<td>$C_{16'}$</td>
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<tr>
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<td>30</td>
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</tr>
<tr>
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<td>-</td>
<td>6</td>
</tr>
<tr>
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<td>-</td>
<td>10</td>
<td>6</td>
<td>-</td>
</tr>
<tr>
<td>$C_{22}$</td>
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<td>-</td>
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<tr>
<td>$C_{22'}$</td>
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<td>-</td>
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APPENDIX B

COUNTER-IONS TESTED
<table>
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<tr>
<th>Trade name</th>
<th>Supplier</th>
<th>Chemical structure of counter-ion</th>
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</thead>
<tbody>
<tr>
<td>Benzoic acid</td>
<td>EM Science; J. T. Baker Chemical Co.</td>
<td>C₆H₅-COO⁻</td>
</tr>
<tr>
<td>Sodium salicylate (Sodium 2-hydroxybenzoate)</td>
<td>MCB Manufacturing Chemists, Inc.</td>
<td>2-(OH)C₆H₄-COO⁻</td>
</tr>
<tr>
<td>3-Hydroxybenzoic acid</td>
<td>Aldrich Chemical Company, Inc.</td>
<td>3-(OH)C₆H₄-COO⁻</td>
</tr>
<tr>
<td>4-Hydroxybenzoic acid</td>
<td>Aldrich Chemical Company, Inc.</td>
<td>4-(OH)C₆H₄-COO⁻</td>
</tr>
<tr>
<td>Anthranilic acid (2-Aminobenzoic acid)</td>
<td>Aldrich Chemical Company, Inc.</td>
<td>2-(NH₂)C₆H₄-COO⁻</td>
</tr>
<tr>
<td>4-Aminobenzoic acid</td>
<td>Aldrich Chemical Company, Inc.</td>
<td>4-(NH₂)C₆H₄-COO⁻</td>
</tr>
<tr>
<td>2-Nitrobenzoic acid</td>
<td>Aldrich Chemical Company, Inc.</td>
<td>2-(NO₂)C₆H₄-COO⁻</td>
</tr>
<tr>
<td>4-Nitrobenzoic acid</td>
<td>Aldrich Chemical Company, Inc.</td>
<td>4-(NO₂)C₆H₄-COO⁻</td>
</tr>
<tr>
<td>o-Toluic acid (2-Methylbenzoic acid)</td>
<td>Aldrich Chemical Company, Inc.</td>
<td>2-(CH₃)C₆H₄-COO⁻</td>
</tr>
<tr>
<td>m-Toluic acid (3-Methylbenzoic acid)</td>
<td>Aldrich Chemical Company, Inc.</td>
<td>3-(CH₃)C₆H₄-COO⁻</td>
</tr>
<tr>
<td>p-Toluic acid (4-Methylbenzoic acid)</td>
<td>Aldrich Chemical Company, Inc.</td>
<td>4-(CH₃)C₆H₄-COO⁻</td>
</tr>
<tr>
<td>4-tert-Butylbenzoic acid</td>
<td>Aldrich Chemical Company, Inc.</td>
<td>(CH₃)₃C₆H₄-COO⁻</td>
</tr>
<tr>
<td>p-Anisic acid (4-Methoxybenzoic acid)</td>
<td>Aldrich Chemical Company, Inc.</td>
<td>4-(OCH₃)C₆H₄-COO⁻</td>
</tr>
<tr>
<td>Trade name</td>
<td>Supplier</td>
<td>Chemical structure of counter-ion</td>
</tr>
<tr>
<td>--------------------------------</td>
<td>---------------------------------</td>
<td>---------------------------------------</td>
</tr>
<tr>
<td>2-Chlorobenzoic acid</td>
<td>Aldrich Chemical Company, Inc.</td>
<td>$2-(\text{Cl})\text{C}_6\text{H}_4\text{-COO}^-$</td>
</tr>
<tr>
<td>3-Chlorobenzoic acid</td>
<td>Aldrich Chemical Company, Inc.</td>
<td>$3-(\text{Cl})\text{C}_6\text{H}_4\text{-COO}^-$</td>
</tr>
<tr>
<td>4-Chlorobenzoic acid</td>
<td>Aldrich Chemical Company, Inc.</td>
<td>$4-(\text{Cl})\text{C}_6\text{H}_4\text{-COO}^-$</td>
</tr>
<tr>
<td>Phenylacetic acid</td>
<td>Aldrich Chemical Company, Inc.</td>
<td>$\text{C}_6\text{H}_4\text{CH}_2\text{-COO}^-$</td>
</tr>
<tr>
<td>4-Chlorophenylacetic acid</td>
<td>Aldrich Chemical Company, Inc.</td>
<td>$4-(\text{Cl})\text{C}_6\text{H}_4\text{CH}_2\text{-COO}^-$</td>
</tr>
<tr>
<td>2,6-Dihydroxybenzoic acid</td>
<td>Aldrich Chemical Company, Inc.</td>
<td>$2,6-(\text{OH})_2\text{C}_6\text{H}_3\text{-COO}^-$</td>
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<tr>
<td>5-Chlorosalicylic acid</td>
<td>Aldrich Chemical Company, Inc.</td>
<td>$2-(\text{OH})-5-(\text{Cl})\text{C}_6\text{H}_3\text{-COO}^-$</td>
</tr>
<tr>
<td>Potassium acid phthalate</td>
<td>Mallinckrodt, Inc.</td>
<td>$1-(\text{COOH})\text{C}_6\text{H}_4\text{-2-}(\text{COO}^-)$</td>
</tr>
<tr>
<td>Phthahlic anhydride</td>
<td>Aldrich Chemical Company, Inc.</td>
<td>$\text{C}_6\text{H}_4\text{-1,2-}(\text{COO}^-)_2$</td>
</tr>
<tr>
<td>Isophthalic acid</td>
<td>Aldrich Chemical Company, Inc.</td>
<td>$\text{C}_6\text{H}_4\text{-1,3-}(\text{COO}^-)_2$</td>
</tr>
<tr>
<td>Terephthalic acid</td>
<td>Aldrich Chemical Company, Inc.</td>
<td>$\text{C}_6\text{H}_4\text{-1,4-}(\text{COO}^-)_2$</td>
</tr>
<tr>
<td>Benzenesulfonic acid, sodium salt</td>
<td>Aldrich Chemical Company, Inc.</td>
<td>$\text{C}_6\text{H}_5\text{-SO}_3^-$</td>
</tr>
<tr>
<td>Aniline-2-sulfonic acid (2-Aminobenzenesulfonic acid)</td>
<td>Aldrich Chemical Company, Inc.</td>
<td>$2-(\text{NH}_2)\text{C}_6\text{H}_4\text{-SO}_3^-$</td>
</tr>
<tr>
<td>Sulfanilic acid (4-Aminobenzenesulfonic acid)</td>
<td>Mallinckrodt Chemical Works</td>
<td>$4-(\text{NH}_2)\text{C}_6\text{H}_4\text{-SO}_3^-$</td>
</tr>
<tr>
<td>Trade name</td>
<td>Supplier</td>
<td>Chemical structure of counter-ion</td>
</tr>
<tr>
<td>------------------------------------------------</td>
<td>---------------------------------</td>
<td>-----------------------------------</td>
</tr>
<tr>
<td>p-Toluenesulfonic, acid, sodium salt</td>
<td>Aldrich Chemical Company, Inc.</td>
<td>(4-(CH_3)C_6H_4-\text{SO}_3^-)</td>
</tr>
<tr>
<td>(Sodium tosylate)</td>
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<td></td>
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<tr>
<td>4-Ethylbenzenesulfonic acid</td>
<td>Aldrich Chemical Company, Inc.</td>
<td>(4-(C_2H_5)C_6H_4-\text{SO}_3^-)</td>
</tr>
<tr>
<td>Benzenesulfinic acid</td>
<td>Aldrich Chemical Company, Inc.</td>
<td>(C_6H_5-\text{SO}_2^-)</td>
</tr>
<tr>
<td>Phenol</td>
<td>EM Science</td>
<td>(C_6H_5-\text{O}^-)</td>
</tr>
<tr>
<td>1-Hydroxy-2-naphthoic acid</td>
<td>Aldrich Chemical Company, Inc.</td>
<td>(1-(OH)C_{10}H_{7}-2-(\text{COO}^-))</td>
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<tr>
<td>2-Hydroxy-1-naphthoic acid</td>
<td>Aldrich Chemical Company, Inc.</td>
<td>(2-(OH)C_{10}H_{6}-1-(\text{COO}^-))</td>
</tr>
<tr>
<td>3-Hydroxy-2-naphthoic acid</td>
<td>Aldrich Chemical Company, Inc.</td>
<td>(3-(OH)C_{10}H_{6}-2-(\text{COO}^-))</td>
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<tr>
<td>2-Naphthalenesulfonic acid</td>
<td>Aldrich Chemical Company, Inc.</td>
<td>(C_{10}H_7-\text{SO}_3^-)</td>
</tr>
<tr>
<td>Potassium bromide</td>
<td>Allied Chemical</td>
<td>(\text{Br}^-)</td>
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APPENDIX C

PHYSICAL PROPERTIES OF WATER
### Table 25
Density of Water from 0 to 250°C

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<td>9679 9711 9741 9769 9796 9821 9844 9866 9887 9905</td>
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</tr>
<tr>
<td>4</td>
<td>1.000 0000 9999 9996 9992 9986 9979 9970 9960 9947 9934</td>
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<tr>
<td>5</td>
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<td>7282 7194 7105 7014 6921 6826 6729 6632 6583 6432</td>
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<td>6331 6228 6124 6020 5915 5805 5696 5586 5474 5362</td>
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<tr>
<td>38</td>
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Table 25 (continued)

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<th>Volume</th>
<th>Temp., °C</th>
<th>Density</th>
<th>Volume</th>
<th>Temp., °C</th>
<th>Density</th>
<th>Volume</th>
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<td>1.01207</td>
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<tr>
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<td>0.99815</td>
<td>1.00186</td>
<td>21</td>
<td>0.99823</td>
<td>1.00177</td>
<td>51</td>
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</tr>
<tr>
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<td>0.99815</td>
<td>1.00186</td>
<td>22</td>
<td>0.99823</td>
<td>1.00177</td>
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</tr>
<tr>
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<td>1.00186</td>
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<td>0.99823</td>
<td>1.00177</td>
<td>53</td>
<td>0.98807</td>
<td>1.01207</td>
</tr>
<tr>
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<td>1.00186</td>
<td>24</td>
<td>0.99823</td>
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Table 26

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APPENDIX D

FLOW DATA OF DEIONIZED WATER
Figure 67. Flow data of deionized water in 0.106- and 0.243-inch pipes in high temperature flow loop.
Figure 68. Flow data of deionized water in a 0.243-inch pipe in low temperature flow loop.
Figure 69. Flow data of deionized water in a 6-inch pipe system at Argonne National Laboratory

\[ D = 6.065 \text{ IN.} \]

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Reynolds Number

von Karman line
APPENDIX E

REPEATABILITY OF THE DRAG REDUCTION DATA
Figure 70. Drag reduction for a 5 mM/12.5 mM Arquad S-50/NaSal solution.

- The flow rate was increased stepwise.
- The flow rate was decreased stepwise.
Table 27

Repeatability\(^a\) of the Drag Reduction Data\(^b\) for a 5 mM/12.5 mM Arquad S-50/NaSal Solution

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\(^a\) The flow rate was randomly varied

\(^b\) The test was carried out at 30°C in a 0.243-inch tube
APPENDIX F

QUASI-ELASTIC LIGHT SCATTERING RESULTS
Figure 71. Quasi-Elastic light scattering result of a 5 mM/12.5 mM Arquad 16-50/4-OH-benzoate solution. The result indicates that the micelles are spherical in shape and are quite monodispersed.
APPENDIX G

\( f^{1/2} \) VS. \( N_{Re} \) AT VARIOUS \( \Delta B \) VALUES
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