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DRAG REDUCTION OF NON-IONIC SURFACTANTS IN AQUEOUS SYSTEMS

BY

JEN-LIN CHANG, 1944-

A THESIS

Presented to the Faculty of the Graduate School of the

UNIVERSITY OF MISSOURI-ROLLA

In Partial Fulfillment of the Requirements for the Degree

MASTER OF SCIENCE IN CHEMICAL ENGINEERING

1972

Approved by

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ABSTRACT

The use of polyoxyethylene alcohol non-ionic surfactants as drag reducing additives in aqueous systems was investigated. Significant drag reduction was obtained with suitable combinations of one percent Alfonic 1214 and salts at 30°C such that the surfactant was near or above its upper critical solubility temperature. Maximum drag reduction was observed at the cloud point. Relative viscosity values also peaked at this point. No upper critical shear stress was attained up to wall shear stresses of 2,000 dynes/cm² with one percent Alfonic 1214 solutions at their cloud points.

At a fixed temperature, the salt concentration required to reach the cloud point is sensitive to the nature of the anion, but is less sensitive to the nature of the cation. Some sensitivity to pH was also observed. The cloud point is not sensitive to the concentration of the surfactant at concentrations below one percent.

At 0.5 percent Alfonic 1214, upper critical shear stresses were observed even with solutions at their cloud points. The mechanical degradation is only temporary, however, and drag reduction ability is regained when the shear stress is lowered.

ACKNOWLEDGEMENT

The author wishes to thank Dr. Jacques L. Zakin for his suggestions and assistance throughout the entire investigation.

The author also wishes to thank Drs. Gary L. Bertrand and Raymond L. Venable for their helpful comments. The generosity of the donors of the surfactants is appreciated.

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LIST OF SYMBOLS

D	diameter of pipe
f	friction factor
g_c	gravitational conversion factor
L	length of pipe
N_{Re}	Reynolds number
ΔP	pressure drop over the length, L
V	bulk mean velocity of fluid flowing in pipe
v	local velocity of fluid flowing in pipe
y	distance between two layers of fluid
τ	shear stress
μ	viscosity of fluid
η_R	relative viscosity, ratio of solution viscosity to that of solvent

I. INTRODUCTION

The addition of small amounts of certain materials to fluids undergoing turbulent flow causes a reduction in pressure drop called drag reduction. (Polymer solutions, soap solutions, and solid suspensions) in liquids and gases have all demonstrated this phenomenon.

Polymer solutions, which have been the most widely studied as drag reducers, are subject to irreversible mechanical degradation which has limited their use in many applications. The aqueous soap solutions studied thus far lose their drag reducing character at high shear stresses such as in pumps, but quickly regain it at lower stresses so that mechanical degradation is not a limitation. However, conventional alkali soaps precipitate in the presence of calcium and other ions and the complex soap systems previously studied are very expensive and degrade chemically in a few days. The solid suspensions studied so far require high concentrations of additive. Thus, there is a need to find a cheap, commercially available additive, which can be used in impure aqueous systems and which provides good drag reducing properties along with chemical and mechanical stability.

This study was aimed at exploring the possibilities of using commercial non-ionic detergents as drag reducers. Since a previous investigation had shown that solution viscosity correlated with drag reducing ability, viscosity measurements were used for screening formulations for the turbulent drag reducing experiments.

II. REVIEW OF LITERATURE

A. Classification of Fluids

Fluids are classified into two types by rheologists according to the behavior of their viscosity coefficients at a given temperature and pressure. These are Newtonian and Non-Newtonian fluids.

1. Newtonian Fluids

Newtonian fluids are defined as those for which the viscosity coefficient, μ , is constant in the laminar region^{*},

$$\tau = - \mu \frac{dv}{dy} \quad (1)$$

The negative sign is required as momentum is transferred in the direction of the negative velocity gradient.

2. Non-Newtonian Fluids

A non-Newtonian fluid is any fluid for which μ is a function of the shear stress, extent of deformation, or the velocity gradient. Polymer solutions are typical non-Newtonian fluids except at very dilute concentrations.

B. Flow of Fluids in Smooth Round Pipes

There are two major flow regions in ordinary tube flow: the laminar region and the turbulent region. In laminar flow, fluid

^{*}All symbols are defined in the Symbols section.

layers slide over each other and there is no macroscopic mixing. As flow rate increases, the flow becomes less stable and more turbulent and the velocity at a point fluctuates about a mean value. Adjacent portions of the fluid become mixed due to the motion of turbulent eddies.

The Fanning friction factor, f , is defined as:

$$f = \frac{D \Delta P / 4L}{\rho V^2 / 2g_c}$$

For Newtonian fluids in laminar flow, the friction factor is inversely proportional to Reynolds number:

$$f = \frac{16}{N_{Re}} \quad (3)$$

For the turbulent region, Von Karman proposed that the friction factor could be expressed in the form of:

$$1 / \sqrt{f} = A \log(N_{Re} \sqrt{f}) - C \quad (4)$$

where $A = 4.0$ and $C = 0.40$ are universal constants evaluated from the turbulent pipe flow data of Nikuradse [1].

Metzner and Reed [2] defined a generalized Reynolds number for non-Newtonian fluids:

$$N_{Re'} = \frac{\rho D^{n'} V^{2-n'}}{g_c K' 8^{n'-1}}$$

where n' and K' are defined by the equation for laminar tube flow:

$$\frac{\Delta P D}{4L} = K' \left(\frac{8V}{D} \right)^{n'}$$

In laminar flow the friction factor-generalized Reynolds number relationship has the same form as for Newtonian fluids:

$$f = \frac{16}{N_{Re}'} \quad (5)$$

For turbulent flow, Dodge and Metzner [3] obtained:

$$1/\sqrt{f} = \frac{4.0}{(n')^{0.75}} \log(N_{Re}' f^{(1-n'/2)}) - \frac{0.40}{(n')^{1.2}} \quad (6)$$

which reduces to equation (4) when $n' = 1$.

C. Drag Reduction

The phenomenon of drag reduction in turbulent flow was first observed in World War II in the flow of aluminum soaps added to gasoline [4]. In 1948 Toms reported the same phenomenon for the turbulent flow of polymethyl methacrylate in monochlorobenzene [5].

Drag reduction was defined by Savins [6] as the ~~increase in pump-ability of a fluid caused by the addition of a small amount of another substance to the fluid.~~ He defined the drag ratio as:

$$D_R = \frac{(\Delta P)_{\text{solution}}}{(\Delta P)_{\text{solvent}}}$$

or

$$D_R = \frac{f_{\text{solution}}}{f_{\text{solvent}}}$$

where $(\Delta P)_{\text{solution}}$ is the pressure drop for the solution and $(\Delta P)_{\text{solvent}}$ is the pressure drop for the solvent at the same flow rate. So drag reduction occurs when $D_R < 1$.

The friction factor ratio is defined as:

$$\text{Friction Factor Ratio} = \frac{(\Delta P)_{\text{solution}}}{(\Delta P)_{\text{pv}}}$$

or

$$= \frac{f_{\text{solution}}}{f_{\text{pv}}}$$

where f_{pv} is the friction factor of a non-drag reducing (purely viscous) fluid having the same rheological character as the solution and is calculated from equation (6) for the same mean velocity. The friction factor ratio is a more fundamental variable than the drag ratio as it compares the drag reducing solution with one having the same viscous behavior as itself rather than the solvent. The friction factor ratio is always less than or equal to the drag ratio.

In plotting friction factor against Reynolds number, it is often convenient to use solvent viscosity in computing the Reynolds number. In this type of plot, drag reduction begins at the point where the solution curve crosses the von Karman curve and continues below it in the turbulent region.

1. Drag Reduction in Polymer Solutions

Drag reduction in polymer solutions has been investigated by a large number of investigators [7].

Hershey [8] found that the amount of drag reduction in turbulent flow is dependent on the size and conformation of the polymer molecules. The effect of an expanded conformation of the polymer molecules in solution or of higher molecular weight is to increase drag reduction. Drag reduction increases with decreasing tube diameter at the same concentration and Reynolds number but when data are compared at the same velocity, the diameter effect is small.

At low concentrations drag reduction begins at a critical shear stress following transition and normal behavior in the turbulent region. Increase in polymer concentration lowers the critical shear stress. For a given size tube, a concentration is reached where the critical shear stress is in the laminar region and no transition zone is observed. Liaw [9] defined solutions having this behavior as "concentrated" and those showing a normal transition region before becoming drag reducing as "dilute". The critical concentration for "concentrated" behavior increases with tube diameter.

The amount of drag reduction at any set of flow conditions increases with concentration until an optimum is reached. Further increase in concentration causes a decrease in drag reduction as the effect of increased viscosity becomes dominant. Friction factor ratios continually decrease until an asymptotic value of about 0.25 is reached [9].

Polymer solutions are sensitive to mechanical degradation at high shear stresses. Liaw suggested that the absolute rate of molecular degradation may be the same for all concentrations of polymer at a given wall shear stress so that degradation of dilute solutions has a more noticeable effect on the drag reduction than degradation of concentrated solutions.

The mechanism for turbulent drag reduction is not fully understood. Many explanations and theories of drag reduction have been suggested. Most of these depend on the viscoelastic characteristics of the solutions [7].

2. Drag Reduction in Soap Solutions

a. Soaps in Organic Solvents

Drag reduction of soap solutions in organic solvents was studied by Radin [11], Lee [12], McMillan [13] and Baxter [14].

Lee investigated the drag reduction of dilute (but well above the critical micelle concentration) aluminum soaps in hydrocarbon solution. He observed that high relative viscosity in aluminum disoap-hydrocarbon systems are generally associated with good drag reduction to high Reynolds number (solvent) and high upper critical wall shear stresses. Hydrogen-bonding additives speed up the dispersion of aluminum disoaps in toluene. The additives also speed up the loss of drag reducing ability with age of low concentration soap solutions. Dilute solutions show apparent upper critical wall shear stresses (τ_{WC}) above which mechanical degradation occurs. Degradation may also occur after long

time shearing at stresses below the apparent upper critical shear stress.

McMillan studied the effects of solution aging, shear degradation, make-up temperature, and testing temperature of aluminum disoaps in hydrocarbon solution. Diameter and concentration effects were similar to those observed in polymer solutions. He concluded that drag reduction was caused by the presence of large soap micelles dispersed in the solvent. He interpreted his results in terms of an equilibrium model. From both drag reduction data and light scattering data, he concluded that a minimum concentration for stability exists in non-aqueous aluminum disoap solutions. Below this concentration, a metastable structure exists in solution. The metastable structure may be broken down either by high shear or by aging or by a combination of both. Above it, the aluminum disoap exists as an association colloid in dynamic equilibrium. It may be broken down by shear stress but slowly reforms upon standing. Hence, he concluded that no permanent degradation occurs in higher concentration solutions.

Pilpel [15] found that with the addition of one mole of water to one mole of alkoxide soap there is considerable increase in viscosity. Further addition of water causes a lowering of viscosity.

Zakin [16] observed that differences in the water content of dilute aluminum disoap solutions gave differences in the extent of drag reduction and in their aging characteristics.

b. Soaps in Aqueous Solutions

Savins [17,18] made a thorough study of drag reduction in aqueous soap solutions (anionic type). By adding from 3.5 to 10 percent KCl

to 0.2 percent sodium oleate in water, he obtained drag reductions ranging from 45 to 82 percent at a fixed shear stress. Solution pH also affected drag reduction. Diameter and concentration effects were similar to the polymer solutions. Savins explained that in his aqueous solution initially spherical micelles were rearranged into cylindrical micelles due to the influence of the electrolytes. The cylindrical micelles formed a network of interlaced rod-like elements.

Savins noted that at a critical wall shear stress, independent of tube diameter, the solutions suddenly lost their drag reducing ability. This was interpreted as happening because the breakdown of micelles was faster than their reformation leading to a steep return to purely viscous pressure drop behavior. He also observed that the sudden loss of drag reduction ability can be regained by lowering the flow rate (shear stress). No permanent degradation was noticed even after 88 hours of continuous shearing at high flow rates.

White [19] obtained results similar to Savins with a 500 ppm equimolar system of cetyltrimethylammonium bromide and 1-naphthol in water.

D. Characteristics of Micelles

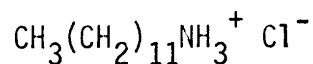
It is believed that micelles cause the viscoelastic character which is associated with drag reduction in both aqueous and non-aqueous soap solutions. Some of the properties of micelles will be discussed here.

The molecules of a surface-active agent possess two regions of chemical structure. One is a hydrocarbon chain, the hydrophobic region

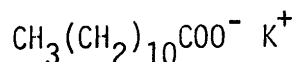
of the molecule; and the other a water-soluble group, the hydrophilic region. There exist two moieties in one compound; one of which has an affinity for the solvent and the other of which is antipathetic to it. These properties are responsible for the micellization.

Surfactants can be divided into five types [20]:

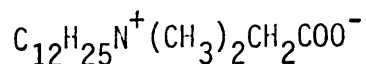
1.) Cationic: the cation of the compound is the surface-active species, e.g., Dodecylamine hydrochloride:



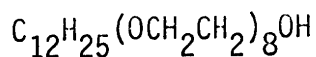
2.) Anionic: the anion is the surface-active species, e.g., Potassium laurate:



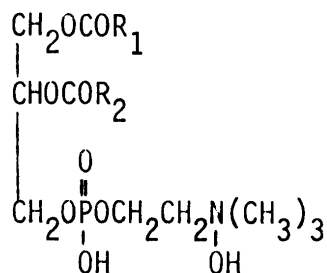
3.) Ampholytic: can behave as either an anionic, non-ionic, or cationic species, depending upon the pH value of the solution, e.g., N-dodecyl-N:N-dimethylbetaine:



4.) Non-ionic: the water soluble moiety of this type can contain hydroxyl groups or a polyoxyethylene chain, e.g., 8-polyoxyethylene dodecanol:



5.) Naturally occurring compounds: can contain portions similar to one or more of the above types. Phosphatides are surface active agents, e.g., Lecithin:



When the surfactants are dissolved in a solvent at high concentrations, aggregations of like molecules form. They are called micelles. In aqueous solutions, the micelle structure of surface-active agents is such that the hydrocarbon chains are inside, remote from the solvent, and the polar head groups are on the outside of the particles. In non-aqueous solvents, micelles have a reverse structure with the polar head groups of the monomer present in the center of the micelle and the hydrocarbon chains extending into the solvent. Water molecules may be present in the center of the micelle.

At very low concentrations the ionic surface active agents behave like any other strong electrolyte, approaching the behavior of an ideal dilute solution. There is a large interfacial energy between the hydrocarbon chain and water. This large interfacial energy will be minimized as far as possible by a curling up of the chain. Progressive addition of monomer to water thus increases the excess free energy of the system*. As more and more solute is added to the solution, there are three ways in which the excess free energy can be reduced. One of these is adsorption at the interface between air and solution, with the hydrocarbon chain remote from the water, so that the high energy

*Excess free energy of the system is the total free energy of the system minus the free energy of an ideal solution of the same composition.

of the hydrocarbon/water interface is lost. Another is self-association, or formation of small aggregates containing a small number of soap monomers. However, the surface has only a limited area and self-association can not prevent the increase of free energy with concentration. Thus, as concentration increases a point will be reached where micelle formation begins in the solution. The concentration at which this occurs is the critical micelle concentration (CMC).

Non-ionic detergents, for which no work is expected to be done against the electrostatic repulsions between similarly charged polar head groups, form micelles at lower CMC than ionic ones [20]. It should be realized that micelles, when formed are not indestructable [20]. They must be considered as structures capable of rapid breakdown, and hence of rapid formation. Micelles form and break down faster at higher temperatures than at lower ones.

Factors affecting CMC and micelle size in aqueous systems are [20]:

a.) Hydrocarbon chain length and structure: CMC decreases as the hydrocarbon chain length increases because the loss of hydrocarbon/water interfacial energy is larger for longer chains. Lengthening of the hydrocarbon chain generally causes an increase in the micelle size.

b.) Nature of the polar head group: the more ionized groups present in the surfactant, the higher the CMC, due to the increase in electrical work to form the micelle as the number of groups increases.

c.) Effect of additives: the addition of salts decreases the CMC of ionized detergents, presumably because the screening action of the simple electrolytes lowers the repulsive forces between the polar head groups, and less electric work is required in micelle formation. The micelle size increases with increased salt concentration, due to the reduction in electrical repulsion affecting the balance of forces upon which the size of the micelles depends.

Bailey and Callard [21] showed that the theoretical effect of the addition of salts to water solutions of poly (ethylene oxide) should be to lower the upper temperature limit for solubility. The amount of lowering should depend on the concentration of the salt and the valences of the ions. Small radius ions should be more effective in salting out the polymer than large ions. Their experimental results using various salts with this polymer confirmed all their deductions except that concerning ionic strength. Certain anions appear to be quite selective in salting out; cations are less selective. They noted that the order of effectiveness of salting out poly (ethylene oxide) from water resembled the "Hofmeister Series" for proteins. Polyethylene alcohols (non-ionic surfactants) should follow the same behavior in aqueous solution.

Becher [22] has shown that the aggregation number of 8-polyoxyethylene lauryl alcohol was increased from 310 to 856 as salt concentration increased from 0.3N to 0.5N Na_2SO_4 . He has suggested, in qualitative terms, that the micelle of the non-ionic agent is not truly non-ionic, but possibly possesses a small positive charge arising from hydronium ion formation to form a positive double layer. Schick [23]

has suggested that the effect of the salt additive in changing the nature of the water structure would be reflected in a decrease in the hydration of the polyoxyethylene chain. This increases their hydrophobicity and consequently their tendency to micellize, i.e., lowers CMC and increases aggregate size above CMC.

Unfortunately, too little is known at present about the actual nature of the hydration of the polyoxyethylene chains.

d.) Effect of temperature: in general, the micellar weight of ionic compounds decreases slightly with temperature. For non-ionics, Balmbra, et al. [24] using homogeneous compounds, found that increase in molecular weight with temperature was strictly exponential for the hexaoxyethylene glycol derivatives of n-decanol, n-dodecanol, and n-hexadecanol.

Elworthy and McDonald [25] have found that the logarithm of the micellar weight versus temperature curves for hepta-, octa-, and nonaoxyethylene glycol ethers of n-hexadecanol exhibit a break at a characteristic temperature, T_h , which they interpreted as corresponding to a marked change in hydration and solvation properties.

e.) Effect of solubilization: surfactant micelles in aqueous solutions can incorporate large quantities of water-insoluble substances into their structure without a second phase appearing. This phenomenon is called solubilization. The solubilized substance lies either in the interior of a spherical or rod-like micelle or in a thick layer between the hydrocarbon ends of a lamellar micelle. In general, the CMC decrease is much smaller than that caused by addition of salts.

1. Shape of Micelles

In very dilute solutions of surfactants, Mukerjee [27], Elworthy and McDonald [25], and Elworthy and Macfarlane [28] have suggested that the micelles are spherical from a study of transport viscosity properties of different surfactant solutions.

The high level of hydration for polyoxyethylene-containing non-ionics is believed to be due to the arrangement of the polyoxyethylene chains in the micelle [29], which are believed to have the conformation of an expanding spiral (a cone shape), the base of the cone being at the outside of the micelle. This structure provides space for trapping of water molecules in the mesh of polyoxyethylene chains, as well as hydration by hydrogen-bond formation between water molecules and ether oxygens of the polyoxyethylene chains.

Increasing the concentration of detergent has a pronounced effect on micelle shape [30]. Spherical, cylindrical and rod-like models have all been suggested in order to explain the experimental data from light scattering and viscosity measurements.

2. Cloud Point of Non-ionic Surfactants in Aqueous Solutions

Non-ionic surfactants have both an upper and a lower temperature limit for solubility. As temperature is raised for a non-ionic dissolved in water, a point is reached where the solution becomes turbid. This is known as the cloud point. The micellar weight is increased by the elevation of temperature. The increase in micellar weight becomes more and more marked as the cloud point is approached [31]. As temperature is further increased, the micelle becomes larger

and larger until a surfactant-rich phase separates, presumably as the result of dehydration of the hydrophilic ether linkages in the chain leading to an increase in the hydrophobic nature of the chain [31]*. Bailey and Callard [21] showed that increasing the propylene content of copolymers of ethylene and propylene oxide which increased the hydrophobicity, lowered the upper temperature limit of solubility. Above the cloud point, the concentration of the surfactant is low in the co-existing water-rich phase because there are few micelles present.

The cloud point is insensitive to the concentration of the surfactant, but is highly influenced by the presence of additives. Electrolytes depress the cloud point in proportion to their concentrations, because of their dehydrating effect on the ether linkages. An electrolyte of lower lyotropic number depresses the cloud point more effectively [32].

*Elworthy and McDonald [25] concluded from viscosity and vapor pressure measurements that the amount of hydration increases with temperature below T_h , a temperature which is below the cloud point.

III. EXPERIMENTAL

A. Materials

1.) Non-ionic surfactants used were:

Trade Name	Donated by	Chemical Formula
Brij 30	Atlas Chemical Co.	$C_{12}H_{25}(OCH_2CH_2)_4OH$
Brij 35	Atlas Chemical Co.	$C_{12}H_{25}(OCH_2CH_2)_{23}OH$
Brij 92	Atlas Chemical Co.	$C_{18}H_{37}(OCH_2CH_2)_2OH$
Brij 96	Atlas Chemical Co.	$C_{18}H_{37}(OCH_2CH_2)_{10}OH$
*Alfonic 1012-60	Continental Oil Co.	$C_{10.3}H_{21.6}(OCH_2CH_2)_{5.51}OH$
**Alfonic 1214-60	Continental Oil Co.	$C_{12.8}H_{26.6}(OCH_2CH_2)_{6.72}OH$

2.) Solvents

The distilled water used was steam condensate. A small amount of volatile amine is charged to the boilers to prevent scaling but conventional chemical analysis does not detect amine in the condensate. Analysis of the water (tap) used is shown in Table 1. Toluene was ACS Reagent grade.

3.) Salts

The salts used are listed in Table 2.

*Alfonic 1012 is a mixture of 85 percent saturated C_{10} hydrocarbon and 15 percent C_{12} hydrocarbon with 60 percent (by weight) of polyoxyethylene.

**Alfonic 1214 is a mixture of 60 percent saturated C_{12} hydrocarbon and 40 percent C_{14} hydrocarbon with 60 percent (by weight) of polyoxyethylene.

Table 1

Tap Water Analysis^{*}

pH = 7.8

<u>Cation or Anion</u>	<u>Concentration parts per million</u>
Sodium	3.6
Potassium	1.0
Calcium	51.2
Iron	0.4
Aluminum	0.01
Magnesium	0.-
Fluoride	0.9
Chloride	4.2
Nitrate	0.-
Bicarbonate	292.8
Silica	8.0
Sulfate	22.0

^{*}October 5, 1971, analysis supplied by Mr. L. Boulware,
City of Rolla.

Table 2

List of Salt Additives

<u>Salt</u>	<u>Formula</u>	<u>Formula weight</u>	<u>Weight percent dissolved salt in nominal 0.5N solution</u>
Calcium chloride	CaCl_2	110.99	2.70
Ferric chloride	FeCl_3	162.22	2.63
Potassium chloride	KCl	74.56	3.60
Potassium ferrocyanide	$\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$	422.39	4.40
Potassium fluoride	KF	58.10	2.83
Potassium iodide	KI	166.02	7.65
Potassium persulfate	$\text{K}_2\text{S}_2\text{O}_8$	260.31	6.35
Potassium phosphate	K_3PO_4	212.27	3.42
Potassium pyrosulfate	$\text{K}_2\text{S}_2\text{O}_7$	254.31	5.97
Sodium acetate	$\text{NaC}_2\text{H}_3\text{O}_2$	82.04	3.94
Sodium borate (tetra)	$\text{Na}_2\text{B}_4\text{O}_7$	201.27	4.78
Sodium chloride	NaCl	58.45	2.84
Sodium fluoride	NaF	42.00	2.05
Sodium iodide	NaI	149.92	6.98
Sodium molybdate	Na_2MoO_4	189.94	4.54
Sodium nitrate	NaNO_3	85.01	4.17
Sodium oxalate	$\text{Na}_2\text{C}_2\text{O}_4$	134.0	3.24
Sodium phosphate	Na_3PO_4	163.97	2.66
Sodium sulfate	Na_2SO_4	142.05	3.43
Sodium thiosulfate	$\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$	248.19	3.58

B. Preparation of Solutions

All the solutions were prepared by the same procedure. The 1.0 percent volumetric concentration solutions were made up by adding solvent to 10.0 ml of surfactant at room temperature to obtain a total volume of 1000 ml. The 1.0 percent by weight aqueous solutions were prepared by adding solvent to 10.0 grams of surfactant in a volumetric flask at room temperature to obtain a total volume of 1000 ml.

Salt solutions for viscosity measurements were all prepared by adding 10.0 ml of the surfactant solution to a flask containing the weighed amount of salt. Solutions used in turbulence measurements were made by adding 1500 ml of surfactant solution to the weighed salts. Salts dissolved readily in the surfactant solutions after stirring.

C. Viscosity Measurements

Viscosity measurements were made in a standard Cannon Ubbelohde size 50 viscometer in a constant temperature bath held at $\pm 0.02^\circ\text{C}$ of the test temperature. A stopwatch which was graduated to 0.1 seconds was used for measuring the efflux times.

D. Capillary Tube Flow System

Pressure drop measurements were made in a recirculation system. The system consisted of four components: pump, temperature control bath, capillary tube and pressure measuring devices as shown in Fig. 1. The system was described in detail by Hershey [8]. A Zenith metering gear pump driven by a Graham variable speed drive was used. The pump

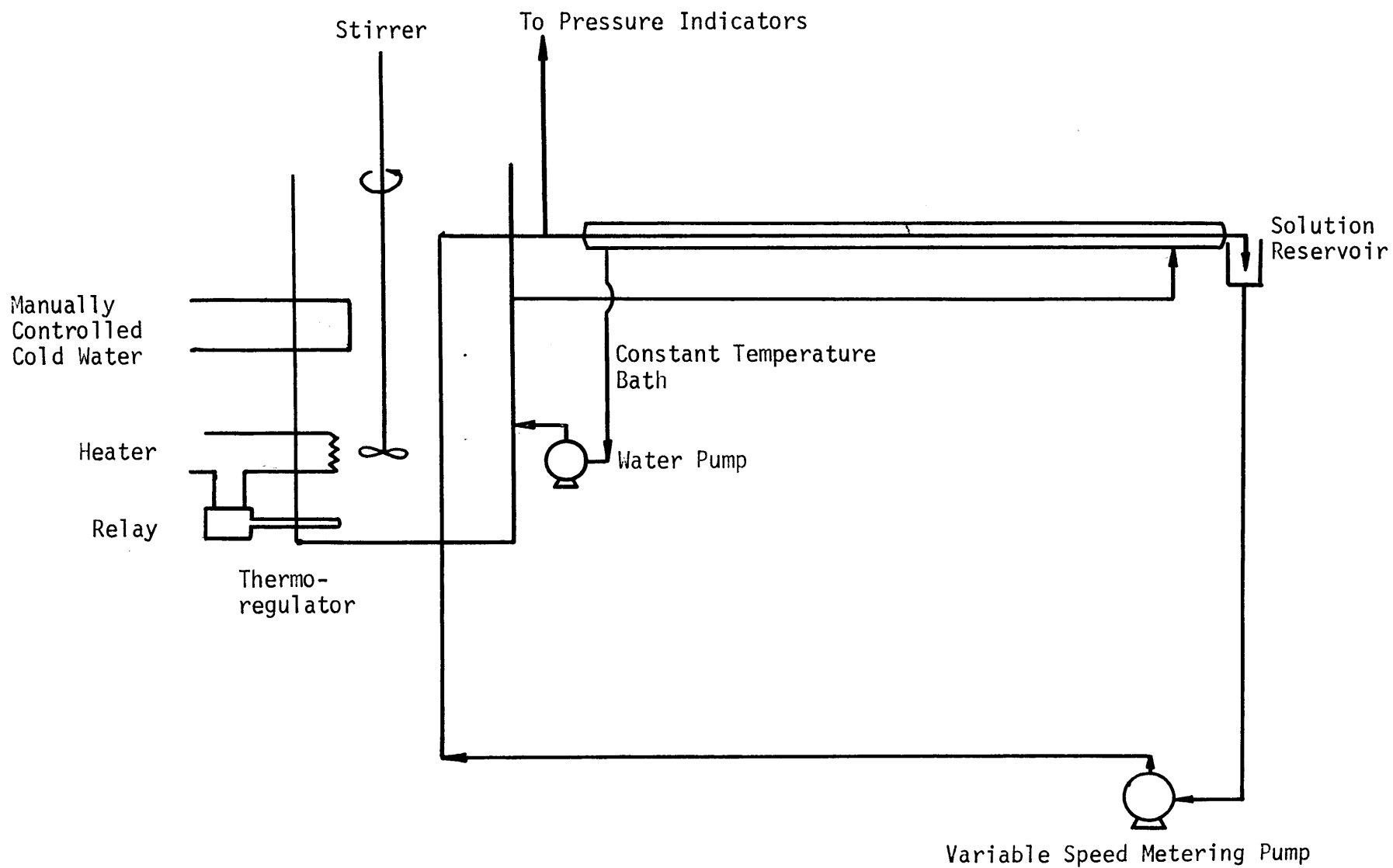


Figure 1. Capillary Tube System Schematic

has a maximum capacity of 500 ml/min. Nylon tubing (1/4 in. ID) was used to carry the fluid to the pump and from the pump to the capillary tube.

The temperature bath was controlled within $\pm 0.1^\circ\text{C}$ by means of a thermoregulator, heater and cooling water.

The test section was a 0.0326 inch ID stainless steel capillary tube mounted permanently in a 1/4 inch diameter copper water jacket. A 1/4 hp centrifugal water pump was connected to the water bath and circulated bath water to the water jacket to keep the capillary fluid temperature constant.

A mercury manometer, a process fluid manometer and pressure gauge (0-250 psi) were used to measure pressure drops. Flow rates were measured by collecting the test fluid in a graduated cylinder for from 60 to 120 seconds.

Fanning friction factors were computed from the measured pressure drops and flow rates. Densities of the solutions were taken to be that of the solvent. All pressure readings were corrected for the kinetic energy loss and viscous entrance effects using Bogue's empirical correction factor for total entrance loss [34]:

$$\Delta P_{\text{corrected}} = \Delta P_{\text{observed}} - \Delta P_{\text{entrance}}$$

$$\Delta P_{\text{entrance}} = C(\rho V^2 / 2g_c)$$

where $C = 2.16$ and $C = 1.0$ were used in the laminar and turbulent flow regions, respectively.

E. Cloud Point Measurements

The cloud point measurements on various surfactant-salt solutions were made in a test tube mounted in a beaker full of water. The water bath was slowly heated by a Bunsen flame. Temperature of the test solution was read with a thermometer used as a stirrer in the test tube. Readings could be made to $\pm 0.1^{\circ}\text{C}$.

IV. RESULTS

A. Relative Viscosities of Surfactant Solutions

The effects of aging, temperature, concentration and solvent on the relative viscosities of detergent solutions were investigated and the results are shown in Tables 3 and 4.

1. Effect of Solution Age

The results obtained in tap water for 0.5 and 1.0 percent by volume solutions of the surfactants listed in Table 3 show that aging has little effect on relative viscosity for periods up to three and a half days. These solutions tested after one hour showed little change after two days, solutions tested after 14 hours showed little change after 84 hours. Therefore, subsequent relative viscosity measurements were made at convenient times at least one hour after solution preparation.

2. Effect of Surfactant and Concentration

The relative viscosities were highest in the Brij 30 and the Alfonic 1012 and 1214 solutions in tap and distilled water at 30.0°C. The latter also had a very high value at 40.0°C. The 0.5 percent Brij solutions had lower relative viscosities in tap water at 30°C than the 1.0 percent solutions (Table 3), but values of η_{sp}/C were nearly independent of concentration for each Brij type.

Table 3

Effect of Aging on Relative Viscosity in Tap Water

Surfactant	Conc. (% vol)	Relative Viscosity of Surfactant Solution at 30.0°C after Hours of Aging						
		1	2	16	32	48	60	84
Brij 30	1.0			1.27 [*]		1.32 ^{***}		1.34
35	1.0			1.08 [*]				1.14
92	1.0		1.00			1.01		
96	1.0				1.15		1.13	
Alfonic 1012	1.0	1.20		1.20		1.20		
1214	1.0	1.25		1.24		1.24		
Brij 30	0.5	1.14	1.15	1.15 ^{**}		1.14		
35	0.5	1.04	1.04	1.05 ^{**}		1.05		
92	0.5	1.00		1.05				
96	0.5	1.05		1.05 ^{**}		1.04		

*14 hours

**18 hours

***45 hours

Table 4

Effect of Temperature on Relative Viscosity of Water Solutions of Surfactants with and without Additives

Surfactant	Conc. (% vol)	Relative Viscosity after 28 Hours							
		Tap Water		Distilled H ₂ O		0.5N NaCl in Distilled H ₂ O		0.5N Na ₂ SO ₄ in Distilled H ₂ O	
		30.0°C	40.0°C	30.0°C	40.0°C	30.0°C	40.0°C	30.0°C	40.0°C
Brij 30	0.5	1.14	1.13	1.12	1.11	1.14	1.11	1.18	1.14
35	0.5	1.05	1.03	1.05	1.02	1.10	1.11	1.10	1.10
92	0.5	1.00	1.02	1.00	1.01				
96	0.5	1.04	1.11	1.04	1.10	1.13	1.31	1.36	1.42
Alfonic 1012	1.0	1.20	1.06	1.18	1.05	1.18	1.08	1.14	1.10
1214	1.0	1.24	1.80	1.20	1.70	1.57	1.25	1.60	1.15

3. Effect of Temperature

The effect of a temperature rise from 30.0°C to 40.0°C on the relative viscosities of distilled and tap water solutions was small for Brij 30, 35, and 92. Brij 96 showed some increase with temperature and Alfonic 1214 showed a large increase but Alfonic 1012 showed a decrease.

4. Effect of Solvent

One percent solutions of Alfonic and Brij surfactants in toluene gave relative viscosities close to unity. No further work was done with hydrocarbon solvents.

B. Relative Viscosities of Aqueous Surfactant Solutions Containing Salt Additives

1. Effect of Various Salts

A number of salts were added to distilled water to determine their effect on the relative viscosities of one percent (volume) Alfonic 1012 and 1214 and one percent (weight) Brij 96 surfactant solutions at 30°C.

Relative viscosities one hour after preparation at 0.5N salt concentration are shown in Table 5. The Alfonic 1012 gave lower values than the 1214 for all of these solutions. High relative viscosities were observed for Alfonic 1214 with 0.5N sodium borate, 0.5N sodium phosphate, 0.5N potassium ferrocyanide, 0.5N potassium pyrosulfate, and 0.5N potassium phosphate, each of which contained multivalent anions.

Brij 96 gave a very high relative viscosity, 3.41 with 0.5N sodium thiosulfate.

Table 5

Relative Viscosity of Surfactant Solutions with Salts in Distilled Water at 30.0°C**

<u>Additive</u>	<u>Additive Concentration Normality</u>	<u>1.0%(vol) Alfonic 1214</u>	<u>1.0%(vol) Alfonic 1012</u>	<u>1.0%(wt) Brij 96</u>
Calcium chloride	0.5*	1.42		
	0.5	1.40		
Ferric chloride	0.15*	1.38		
	0.5*	1.70		
Sodium acetate	0.5*	1.57	1.18	
Sodium borate	0.8* (sat'd)	2.07	1.40	
	0.5	2.00		
Sodium chloride	0.5	1.57		1.31
Sodium fluoride	0.5*	1.49		
Sodium iodate	0.46 (sat'd)	1.53	1.17	
Sodium iodide	0.5	1.08		
Sodium molybdate	6.1* (sat'd)	1.93	1.15	

*tap water

**one hour after preparation

Table 5 (continued)

Relative Viscosity of Surfactant Solutions with Salts in Distilled Water at 30.0°C**

<u>Additive</u>	<u>Additive Concentration Normality</u>	<u>1.0%(vol) Alfonic 1214</u>	<u>1.0%(vol) Alfonic 1012</u>	<u>1.0%(wt) Brij 96</u>
Sodium nitrate	0.5	1.29		
Sodium oxalate	0.6***	1.61	1.13	
Sodium phosphate	0.3	1.43		
	0.5	2.15		
Sodium sulfate	0.5	1.60		1.97
Sodium thiosulfate	0.5	1.68	1.41	3.41
Potassium chloride	0.5	1.45		
Potassium ferrocyanide	0.5	2.10	1.29	
	0.5*	1.13		
Potassium fluoride	0.5	1.10		
	0.5*	1.21		
Potassium iodide	0.5	1.16		

*tap water

**one hour after preparation

***estimated value from solubility at 30.0°C saturated

Table 5 (continued)

Relative Viscosity of Surfactant Solutions with Salts in Distilled Water at 30.0°C**

<u>Additive</u>	<u>Additive Concentration Normality</u>	<u>1.0%(vol) Alfonic 1214</u>	<u>1.0%(vol) Alfonic 1012</u>	<u>1.0%(wt) Brij 96</u>
Potassium persulfate	0.4 (sat'd)*	1.54	1.23	
Potassium pyrosulfate	0.5	2.19	1.50	
Potassium phosphate	0.5	2.38		1.77

*tap water

**one hour after preparation

2. Effect of Salt Concentration

The normality of the salt additive was varied for the more effective salts to find the optimum salt concentration for viscosity increase at 30°C.

The results for one percent (volume) Alfonic 1214* are listed in Table 6. Maximum values of relative viscosity were obtained at 0.3N $\text{Na}_2\text{S}_2\text{O}_3$, 0.6N $\text{K}_2\text{S}_2\text{O}_7$, 0.5N $\text{K}_4\text{Fe}(\text{CN})_6$, 0.4N Na_2SO_4 , 0.9N NaCl, and 0.55N K_3PO_4 . Maximum relative viscosities at the optimum point ranged from 2.10 to 2.80.

The optimum salt concentrations for all salts except NaCl and K_3PO_4 were also measured at 0.5 percent (volume) Alfonic 1214. In all cases the optimum salt concentration for maximum relative viscosity was the same regardless of Alfonic 1214 concentration. Relative viscosities ranged from 1.33 to 1.41 indicating a much lower value of η_{sp}/C at this concentration than at one percent.

The results for one percent (weight) Brij 96 solutions are listed in Table 7. The optimum normality for NaCl was 1.5N, for Na_2SO_4 it was 0.7N, and for $\text{Na}_2\text{S}_2\text{O}_3$ it was 0.5N. The maximum relative viscosity values for Brij 96 with NaCl, Na_2SO_4 , and $\text{Na}_2\text{S}_2\text{O}_3$ were higher than for Alfonic 1214. A maximum for 0.5 percent (weight) Brij 96 with $\text{Na}_2\text{S}_2\text{O}_3$ was also observed at 0.5N, but the relative viscosity was 1.35.

Relative viscosities for 1.0 percent Alfonic 1214 with $\text{Na}_2\text{S}_2\text{O}_3$ and with NaCl at 40°C are also shown in Table 6. The relative viscosities are lower and the optimum salt concentration is lower than for 30°C.

*One percent (volume) Alfonic 1214 is about .98 percent (weight).

Table 6

Relative Viscosity of Alfonic 1214 Solutions in Distilled Water with Various Additives at 30.0°C*

<u>Additive</u>	<u>Normality of Additive</u>	<u>Relative Viscosity</u>		
		<u>0.5% (vol)</u>	<u>1.0% (vol)</u>	
Na ₂ S ₂ O ₃	0.1	1.15	1.39	
	0.2	1.29	1.72	1.15**
	0.25	---	1.81	1.19**
	0.3	1.33	2.20	1.18**
	0.35	---	1.92	1.16**
	0.4	1.26	1.87	
	0.5	1.15	1.68	
K ₂ S ₂ O ₇	0.1	1.13	1.34	
	0.2	1.13	1.52	
	0.3	1.22	1.64	
	0.4	1.23	1.77	
	0.5	1.25	2.15	
	0.6	1.41	2.33	
	0.7	1.36	1.92	
K ₄ Fe(CN) ₆	0.1	1.13	1.34	
	0.2	1.18	1.41	
	0.3	1.17	1.55	
	0.4	1.23	1.77	
	0.5	1.30	2.10	
	0.6	1.26	1.74	

*at least 1 hour after adding the salts

**40.0°C

Table 6 (continued)

<u>Additive</u>	<u>Normality of Additive</u>	<u>Relative Viscosity</u>		
		<u>0.5% (vol)</u>	<u>1.0% (vol)</u>	
Na ₂ SO ₄	0.1	1.11	1.37	
	0.2	1.20	1.55	
	0.3	1.28	1.75	
	0.35	1.26	2.34	
	0.4	1.39	2.80	
	0.45	1.24	2.03	
	0.5	1.22	1.58	
NaCl	0.3		1.40	
	0.4		1.53	
	0.5		1.57	1.25**
	0.6		1.77	1.26**
	0.7		1.98	1.30**
	0.8		2.31	1.27**
	0.9		2.92	1.18**
	1.0		2.46	1.13**
K ₃ PO ₄	0.3		1.68	
	0.4		2.21	
	0.45		2.21	
	0.5		2.38	
	0.55		2.68	
	0.6		2.10	
NaNO ₃	0.3		1.28	
	0.5		1.29	
	0.7		1.31	

*at least 1 hour after adding the salts

**40.0°C

Table 7

Effect of Additive Concentration on Relative Viscosity of 1.0% (wt)
Brij 96 Solutions in Distilled Water at 30.0°C

<u>Additive Concentration Normality</u>	<u>NaCl</u>	<u>Na₂SO₄</u>	<u>Na₂S₂O₃</u>	<u>Na₂S₂O₃ (0.5%)</u>
0.2	1.11		1.73	
0.3		1.48	3.28	
0.4	1.27	1.68	3.32	1.30
0.5	1.31	1.97	3.41	1.35
0.6	1.32	2.53	2.86	1.29
0.7		3.36	2.58	
0.8		2.73		
0.9	1.59			
1.3	3.02			
1.4	3.36			
1.5	3.50			
1.6	3.12			

3. Effect of Salt Additive on Viscosity without Surfactant

Relative viscosities of 0.3N $\text{Na}_2\text{S}_2\text{O}_3$ (3.6% by weight) aqueous solutions at 30°C were 1.10 and 1.17, respectively. Solutions of 0.5N NaCl (2.8% by weight) and 1.0N NaCl (5.6% by weight) had relative viscosities of 1.03 and 1.16, respectively, at 30°C. Thus, all relative viscosity increases of surfactant solutions containing salt additives are the result of the effect of the surfactant and the contribution of the salt. Relative viscosities for surfactant solutions with additives could be computed on the basis of the salt solution viscosity instead of that of pure water. However, with the exception of the iodide solutions and the Brij 96 solutions with 1.3N NaCl or higher, all solutions of interest had salt concentrations below seven percent, with most below five percent. If the salt solution viscosity were used, changes in η_R would in most cases be less than 15 percent and no major change in ranking of additives would result. Therefore, the relative viscosities are listed based on the measured viscosity of water.

4. Effect of pH

In order to determine the effect of pH of the salt solutions on relative viscosity, 0.001N and 0.1N HCl and 0.001N and 0.1N NaOH were added to 0.5N NaCl solutions. The results are shown in Table 8.

The effect of added HCl and NaOH is to increase the viscosity of the aqueous NaCl solution slightly. The addition of 0.001N HCl to a one percent solution of Alfonic 1214 containing 0.5N NaCl causes little

Table 8

Effect of pH on Alfonic 1214 Solution

<u>Solution</u>	<u>Alfonic 1214 % (wt)</u>	<u>Relative Viscosity at 30.0°C</u>
0.5N NaCl	0.0	1.03
0.5N NaCl	1.0	1.57
0.5N NaCl + 0.001N HCl	0.0	1.11
0.5N NaCl + 0.001N NaOH	0.0	1.12
0.5N NaCl + 0.001N HCl	1.0	1.58
0.5N NaCl + 0.001N NaOH	1.0	1.70
0.5N NaCl + 0.1N HCl	0.0	1.10
0.5N NaCl + 0.1N NaOH	0.0	1.10
0.5N NaCl + 0.1N HCl	1.0	1.35
0.5N NaCl + 0.1N NaOH	1.0	1.73

change in viscosity, but additions of 0.1N HCl to this system gave a significant reduction in viscosity. The addition of 0.001N NaOH to a one percent solution of Alfonic 1214 containing 0.5N NaCl causes some increase in viscosity. However, the relative viscosity of this solution compared to the 0.5N NaCl plus 0.001N NaOH viscosity, 1.52, is about the same as the relative viscosity of the Alfonic 1214 solution plus 0.5N NaCl based on the 0.5N NaCl aqueous solution viscosity, 1.53 so that the addition of small amounts of alkali has little effect on the surfactant contribution to viscosity. Similar results were observed with 0.1N NaOH.

5. Effect of Temperature

Relative viscosities for 0.5 percent Brij 30, 35, and 96 and 1.0 percent Alfonic 1012 and 1214 in 0.5N NaCl solutions and in 0.5N Na_2SO_4 solutions are listed in Table 4 at 30°C and 40°C. The relative viscosities for all the Brij 30 and 35 solutions and the Alfonic 1012 solutions are low. These Brij solutions are not greatly affected by the salt or by temperature; Alfonic 1012 shows a drop in relative viscosity with NaCl but only a small effect with Na_2SO_4 . The 0.5 percent Brij 96 shows a large increase with temperature in the 0.5N NaCl solution and a smaller temperature effect but a high value of η_R with 0.5N Na_2SO_4 . Relative viscosity for the one percent Alfonic 1214 falls off with temperature for both the 0.5N NaCl and the 0.5N Na_2SO_4 .

Relative viscosities for 1.0 percent Alfonic 1214 with NaCl and $\text{Na}_2\text{S}_2\text{O}_3$ at 40°C are listed in Table 6. At this temperature, which is

well above the cloud point for all the solutions tested, relative viscosities are low and there is no sharp maximum in relative viscosity.

6. Effect of Aging

Alfonic 1214 solutions containing 0.3N and 0.5N Na_2SO_4 at 0.5 percent (volume) and 1.0 percent (volume) surfactant were tested at times varying from two hours to 120 hours. In this time period no significant changes in relative viscosity were observed.

C. Cloud Points of Surfactant Solutions

The addition of some of the salts to some of the surfactant solutions caused a loss of clarity of the solution and in some cases haze was observed. Cloud point measurements were made on a few of these to compare the temperature at the start of precipitation with relative viscosity-temperature trends reported in Tables 4 and 6. The results are listed in Table 9.

Alfonic 1012 has a cloud point at 34°C, Alfonic 1214 at 42.1°C and Brij 96 at 57°C. The addition of salt to any of these solutions lowers the cloud point. Higher concentrations of salt cause increased lowering of the cloud point. About 0.3N $\text{Na}_2\text{S}_2\text{O}_3$ gives a cloud point close to 30°C for Alfonic 1214. In the one comparison made between salts, 0.5N Na_2SO_4 was more effective in lowering the cloud point of all three surfactants than 0.5N NaCl.

Table 9

Cloud Point Results

<u>Surfactant</u>	<u>Surfactant Concentration % (weight)</u>	<u>Concentration</u>	<u>Cloud Point °C</u>
Alfonic 1012	1.0	0	34
Alfonic 1012	1.0	✓ 0.5N Na ₂ SO ₄	27
Alfonic 1012	1.0	0.5N NaCl	29
Alfonic 1214	1.0	0	42.1
✓ Alfonic 1214	1.0	0.5N Na ₂ SO ₄	27.6
Alfonic 1214	1.0	✓ 0.1N Na ₂ S ₂ O ₃	37.1
Alfonic 1214	1.0	0.2N Na ₂ S ₂ O ₃	33.0
Alfonic 1214	1.0	0.3N Na ₂ S ₂ O ₃	29.8
Alfonic 1214	1.0	0.5N NaCl	34.5
Alfonic 1214	1.0	0.5N NaCl + 0.001N HCl	34.2
Alfonic 1214	1.0	0.5N NaCl + 0.001N NaOH	34.0
Brij 96	1.0	0	57
Brij 96	0.5	0	57
Brij 96	0.5	0.5N NaCl	49
Brij 96	0.5	0.5N Na ₂ SO ₄	42
Brij 96	1.0	1.0N NaCl	42

D. Drag Reduction of Surfactant - Salt Solutions

The effects of salt additives, surfactant concentration and mechanical degradation on the turbulent flow behavior of Alfonic 1214 and Brij 96 solutions were studied. All runs were made in a 0.0326 inch diameter tube.

1. Effect of Salt Additives

Plots of friction factor vs. solvent Reynolds number for one percent (volume) Alfonic 1214 in distilled water at 30°C at two aging times are shown in Figure 2 along with results for pure water. The solid lines on this graph and all subsequent graphs are the conventional friction factor - Reynolds number plots and are used for reference. The pure water data follow the laminar and von Karman lines closely. The data for the Alfonic solutions which had relative viscosities of 1.20 lie above both the laminar and turbulent lines with a transition region between them. The location of the transition region at N_{Re} (solvent) between 2,800 and 3,300 reflects the higher viscosity of these solutions compared with the solvent (water) viscosity used to compute N_{Re} (solvent). The data for the two solutions are in good agreement and indicate no aging and good repeatability of results.

Results for one percent (volume) Alfonic 1214 with varying amounts of Na_2SO_4 are shown in Figures 3 and 4. At 0.1N Na_2SO_4 the results are similar to those in Figure 2. However, at 0.2N Na_2SO_4 , the turbulent data lie closer to the von Karman line. At 0.3N, despite a relative viscosity value of 1.75, no transition region is observed and the solution shows "concentrated" drag reduction behavior, with a maximum

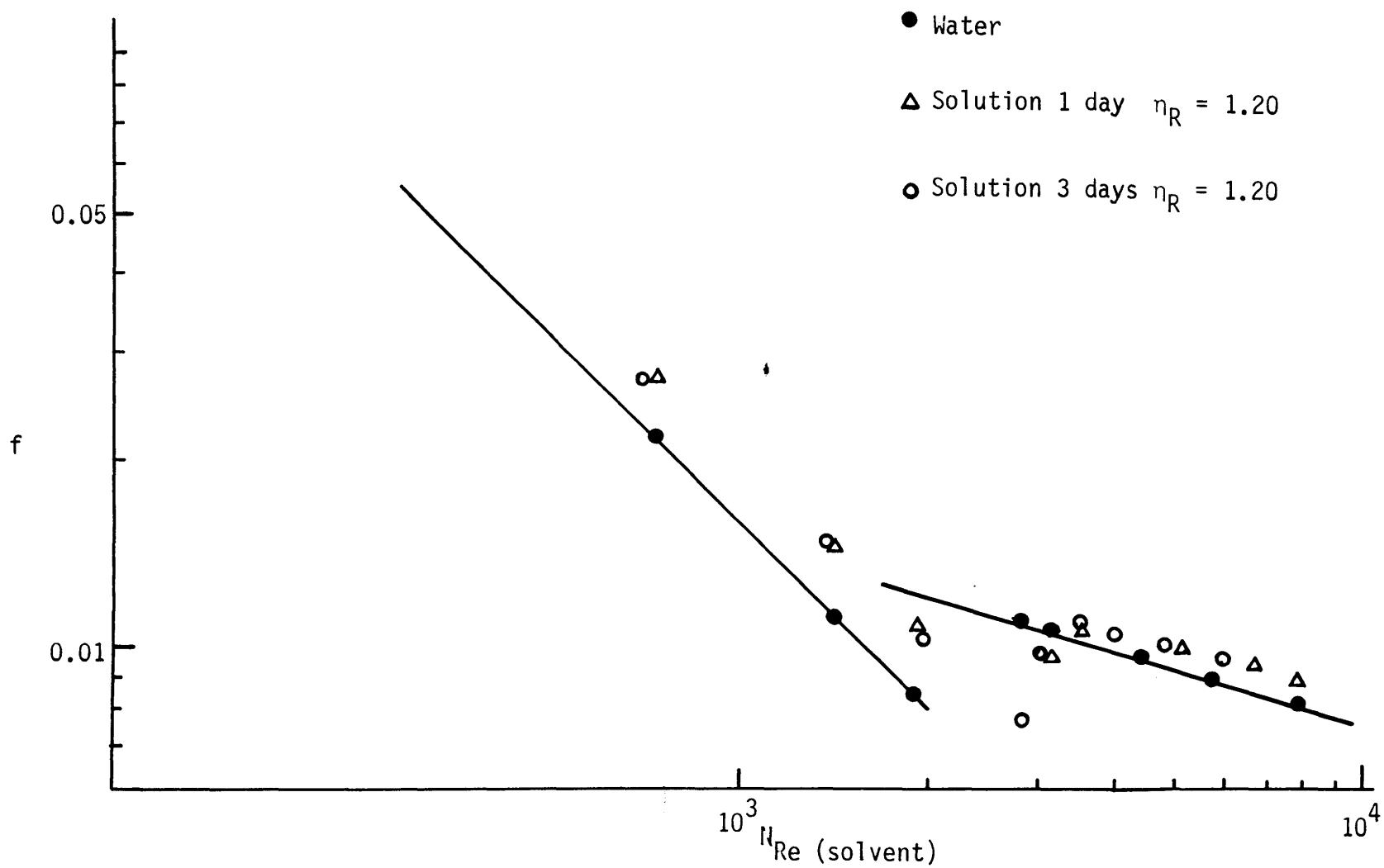


Figure 2. f vs. N_{Re} for 1.0% Alfonic 1214 Solutions at 30.0°C

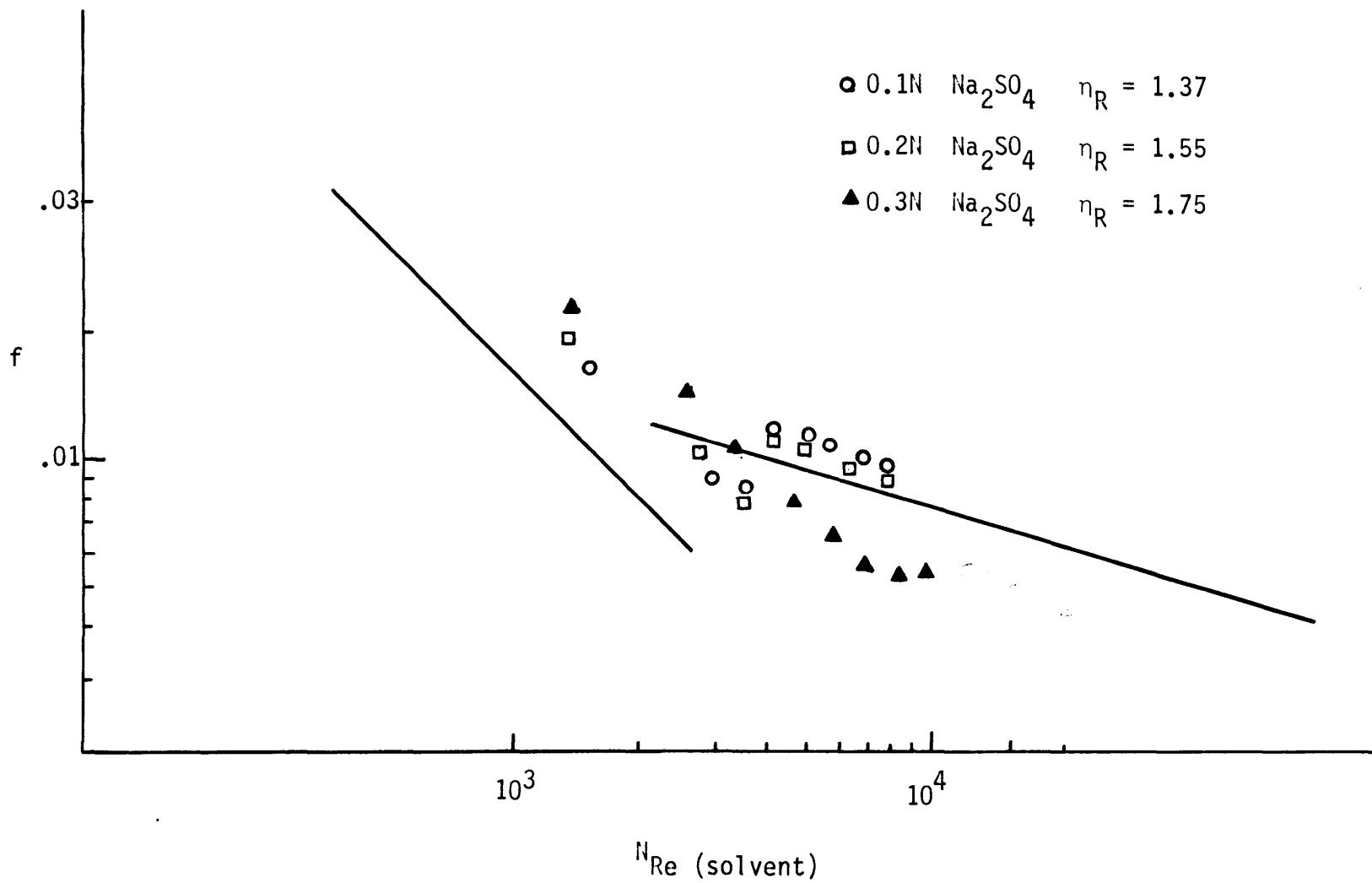


Figure 3. f vs. N_{Re} for 1% Alfonic 1214 Solutions with Na_2SO_4 at 30.0°C (low concentrations)

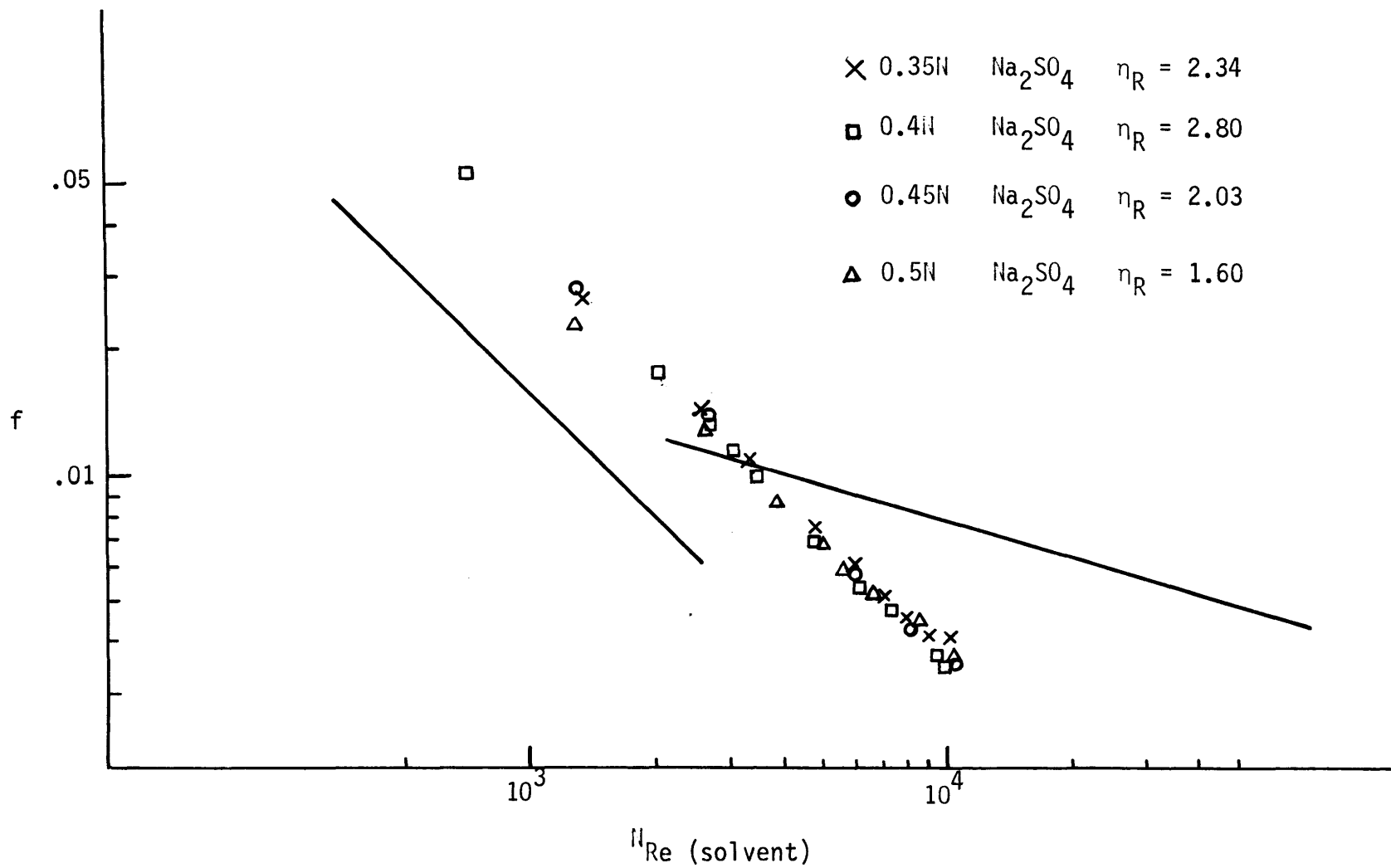


Figure 4. f vs. N_{Re} for 1% Alfonic 1214 Solutions with Na_2SO_4 at 30.0°C

drag reduction of 35 percent at a solvent Reynolds number near 8,000. At higher Reynolds numbers, the friction factor increases and less drag reduction is observed.

The trend to improved drag reduction with increasing Na_2SO_4 concentration continues to 0.4N Na_2SO_4 (Figure 4). At 0.35N Na_2SO_4 (relative viscosity = 2.34) maximum drag reduction is 49 percent and there is only a slight upturn in the last point ($N_{\text{Re}} \approx 10,000$). At 0.4N Na_2SO_4 (relative viscosity = 2.80) maximum drag reduction of 57 percent is seen and no upturn was observed suggesting that more drag reduction would be observed if higher flow rates could be achieved. At still higher salt concentrations (0.45N and 0.5N) the relative viscosity falls off rapidly but there is little change in the friction factor - Reynolds number results. Repeat runs on fresh solutions of 0.45N and 0.5N Na_2SO_4 gave results close to those shown.

Similar trends with salt concentration were observed on a series of one percent Alfonic 1214 solutions containing increasing amounts of K_3PO_4 (Figure 5) and $\text{Na}_2\text{S}_2\text{O}_3$ (Figure 6). Maximum drag reduction (over 50 percent) with no upturn in the data was obtained with 0.5N, 0.55N, and 0.6N K_3PO_4 . These correspond to relative viscosities of 2.38, 2.56, and 2.16.

The $\text{Na}_2\text{S}_2\text{O}_3$ data reach maximum drag reduction at 0.3N (over 55 percent) with some apparent decrease at 0.4N but over 55 percent at 0.5N.

Friction factor measurements made with 0.5 percent (weight) and 1.0 percent (weight) Brij 96 with 0.5N $\text{Na}_2\text{S}_2\text{O}_3$, the salt concentration for maximum relative viscosity, showed normal transition and no drag reduction.

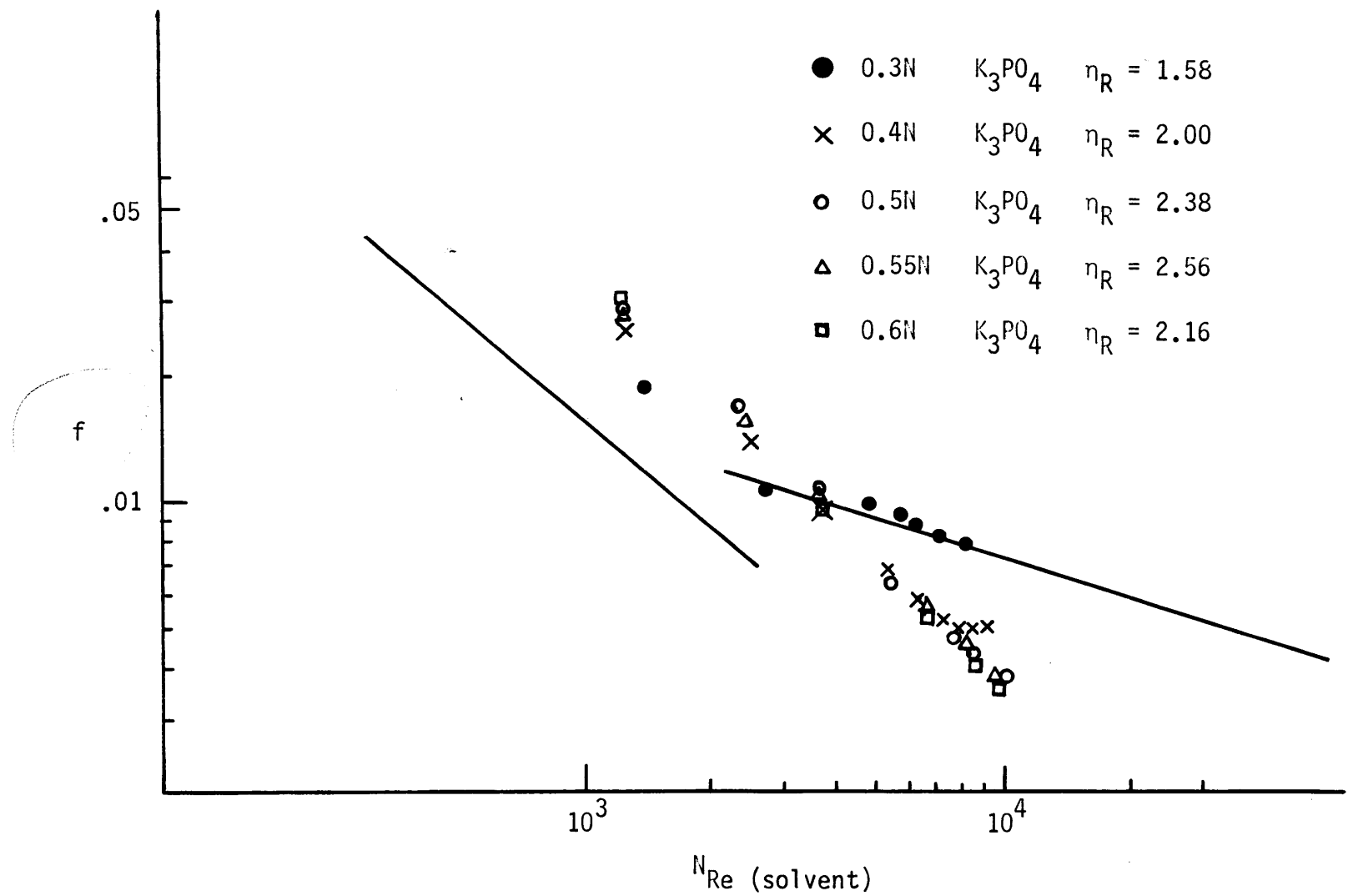


Figure 5. f vs. N_{Re} for 1% Alfonic 1214 Solutions with K_3PO_4 at 30.0°C

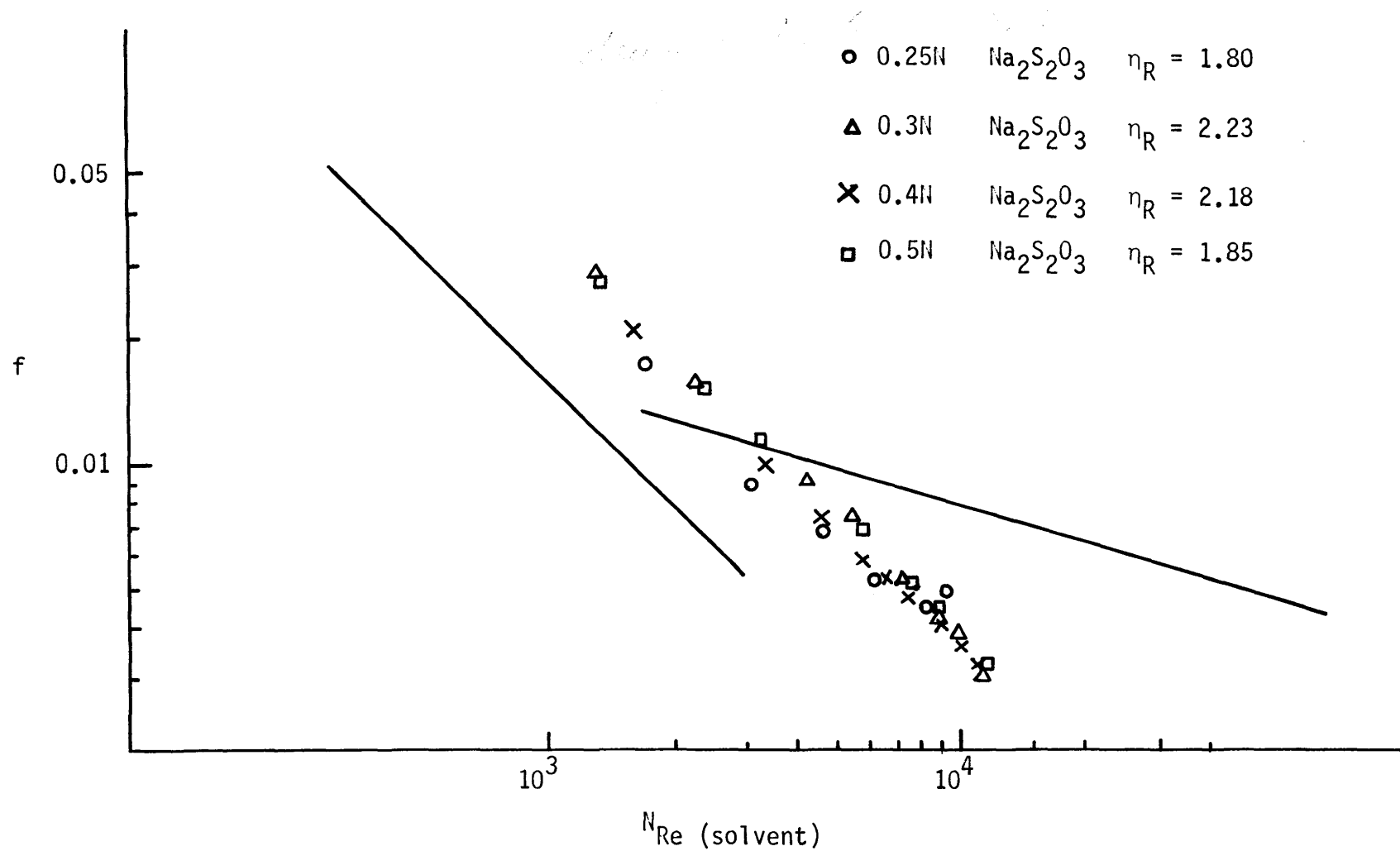


Figure 6. f vs. N_{Re} for 1% Alfonic 1214 Solutions with $\text{Na}_2\text{S}_2\text{O}_3$ at 30.0°C

2. Effect of Surfactant Concentration

Data for several 0.5 percent (volume) Alfonic 1214 solutions with 0.2N and 0.4N Na_2SO_4 are shown in Figure 7. The 0.2N Na_2SO_4 solution, like the 1.0 percent Alfonic 1214 with 0.2N Na_2SO_4 is not drag reducing. However, both 0.4N Na_2SO_4 solutions, one prepared by dilution of a 1.0 percent Alfonic 1214 solution and addition of more salt and the other prepared directly, are drag reducing. The diluted 0.4N Na_2SO_4 solution shows a maximum drag reduction of about 32 percent at a Reynolds number near 5,000 and then a gradual rise in friction factor indicating degradation at the higher shear stresses. The other 0.4N Na_2SO_4 solution is stable to a Reynolds number of over 6,000 and gives a maximum drag reduction of 47 percent.

Results for a 0.5 percent Alfonic 1214 with 0.3N $\text{Na}_2\text{S}_2\text{O}_3$ are also shown in Figure 7. The data follow the same trend as the 0.4N Na_2SO_4 solutions with a maximum drag reduction of 27 percent at a Reynolds number near 5,000 followed by degradation.

3. Effect of Mechanical Degradation

The more stable 0.5 percent Alfonic 1214 solution with 0.4N Na_2SO_4 was pumped at the maximum flow rate for about one hour and then rerun at successively decreasing Reynolds numbers (Figure 7). The results after mechanical shear are close to those of the fresh solution; that is, the degradation is reversible.

A one percent Alfonic 1214 solution with 0.4N Na_2SO_4 was tested in a similar manner. After one hour of pumping at the maximum flow

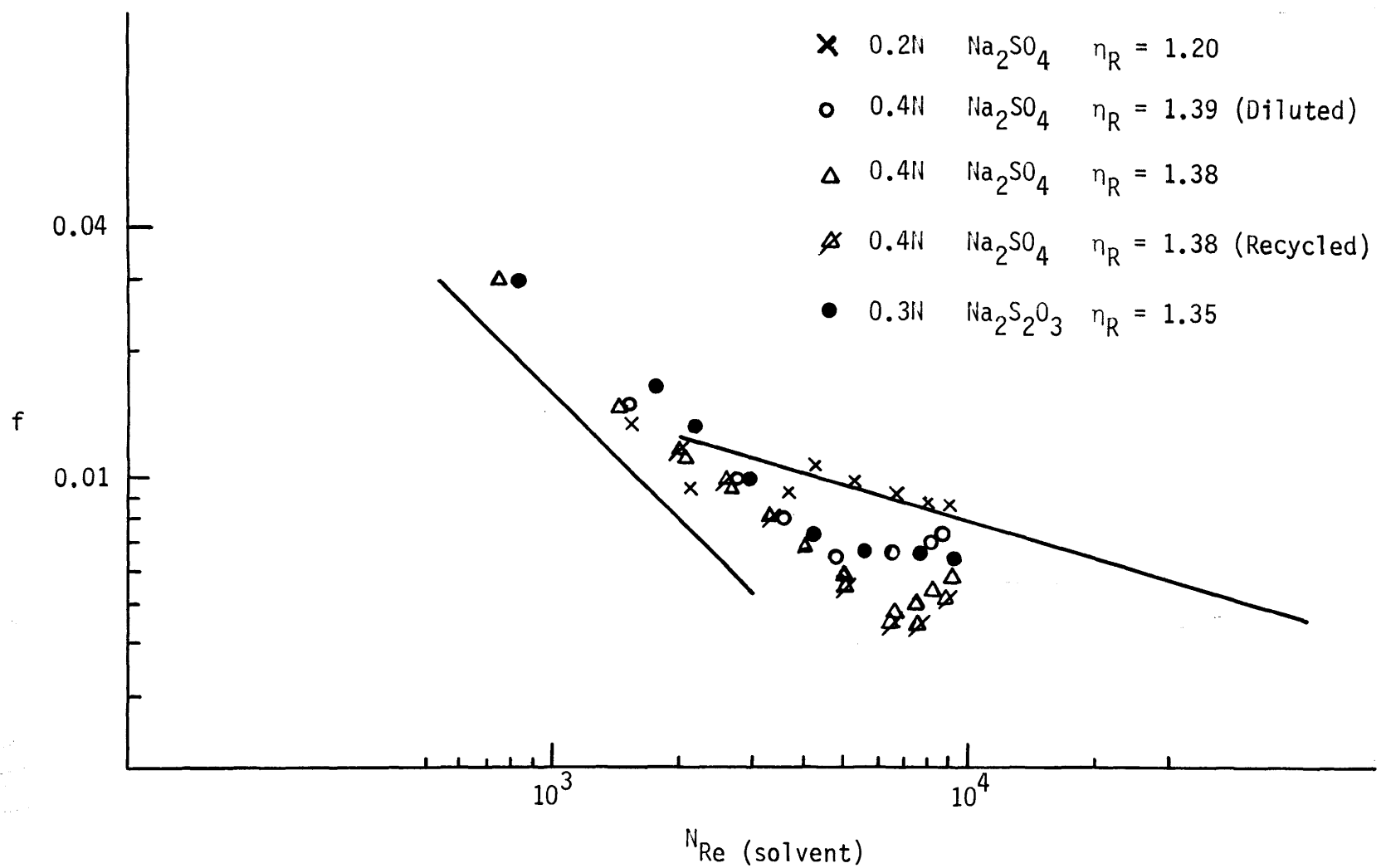


Figure 7. f vs. N_{Re} for 0.5% Alfonic 1214 Solutions with Na_2SO_4 and $\text{Na}_2\text{S}_2\text{O}_3$ at 30.0°C

rate, the flow rate was decreased. Little change in the friction factor - Reynolds number results was observed (Figure 8).

Similar experiments on one percent Alfonic 1214 solutions with 0.3N $\text{Na}_2\text{S}_2\text{O}_3$ and 0.5N $\text{Na}_2\text{S}_2\text{O}_3$ solutions are shown in Figure 8. The recycled samples give slightly improved drag reduction at 0.3N $\text{Na}_2\text{S}_2\text{O}_3$ and about the same results at 0.5N.

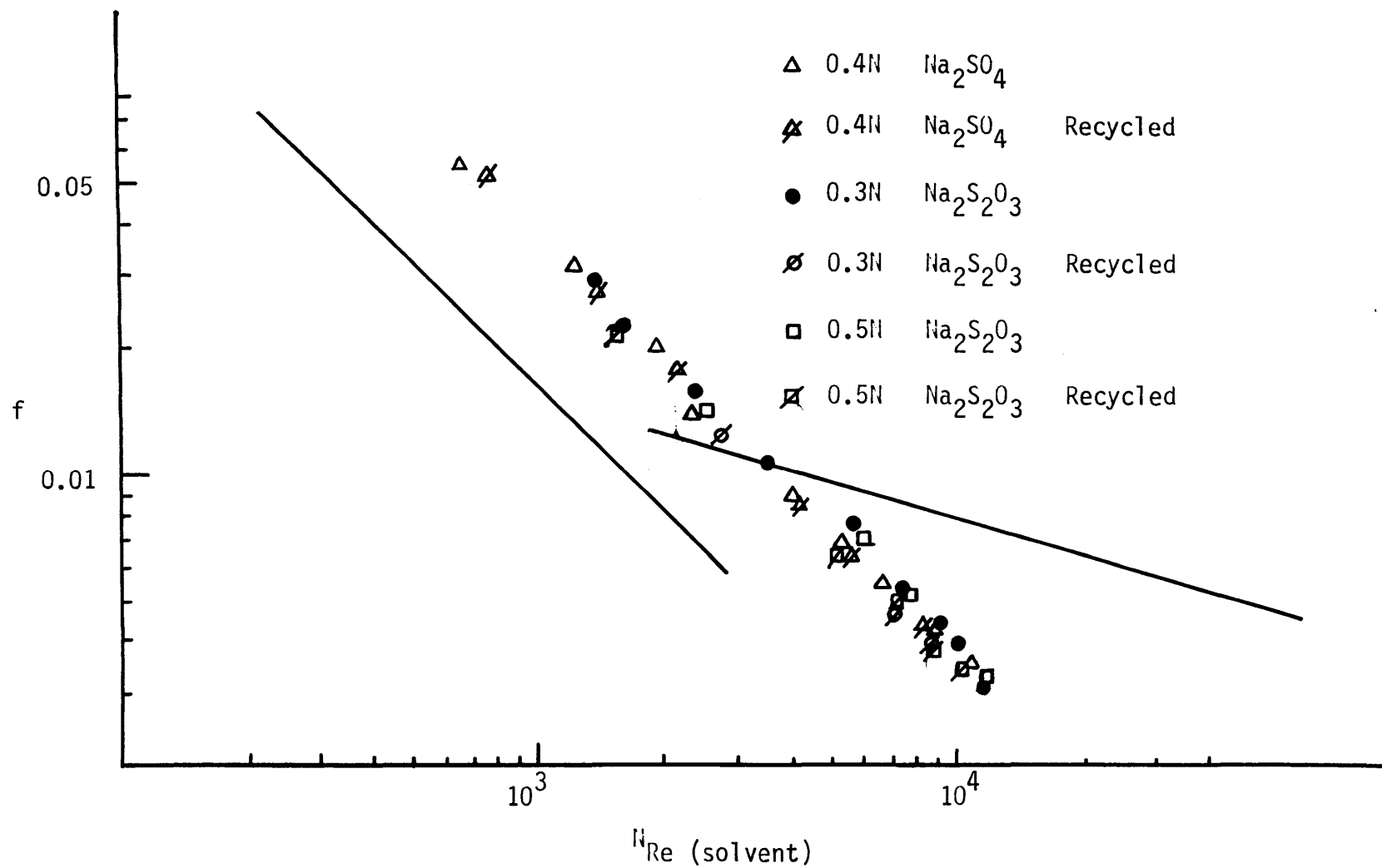


Figure 8. f vs. N_{Re} for 1% Alfonic 1214 Solutions with Na_2SO_4 and $\text{Na}_2\text{S}_2\text{O}_3$ at 30.0°C

V. DISCUSSIONS OF RESULTS

A. Relative Viscosities of Surfactant Solutions

The magnitude of the relative viscosity of the surfactant solutions is believed to be related to the size of the micelles [12]. The non-ionic surfactant, when dissolved in water, has the hydrophilic (polyethylene oxide) portion stretching out to the water and picks up water molecules while the micelles are forming.

The cloud point or maximum temperature at which the surfactant is soluble in water is lowered by the addition of electrolytes to the solution. The behavior of non-ionics is similar to cationic soaps in this respect. Pilpel [26] showed that ionic detergents have maximum viscosities at a particular concentration of electrolyte independent of the concentration of the surfactant. The viscosity maximum occurs just prior to coacervation and/or salting out of the soap (cloud point). This was observed here for all the solutions tested (Tables 6 and 7). Thus, the micelle size and relative viscosity grow until the cloud point is reached. At this point two phases begin to form. Further temperature rise results in a drop in the relative viscosity. Since Alfonic 1214 and 1012 and Brij 96 have cloud points above 40°C, their relative viscosity increased with temperature rise from 30°C to 40°C. The addition of salt lowers the cloud point (Table 9). In those cases in Table 4 where the salt solution had a cloud point above 40°C, the relative viscosity at 40°C was higher than at 30°C (see Brij 96 with 0.5N NaCl and 0.5N Na₂SO₄). In all cases where the cloud point was below 40°C, the relative viscosity at 40°C was less than at 30°C.

Alfonic 1214 with 0.3N $\text{Na}_2\text{S}_2\text{O}_3$ has a cloud point of 29.8°C, very close to the conditions at which maximum relative viscosity was observed. At lower salt concentrations the cloud point is higher and the micelles are smaller. At higher salt concentrations the cloud point is lower and much of the surfactant has separated into another phase.

Comparison of the relative effectiveness of different anions in salting out can be obtained by comparing relative viscosities of solutions having the same cation. Direct comparisons can not be made in all cases. However, from the results for 0.5N sodium salt solutions containing one percent of Alfonic 1214, the anions can be ranked as: phosphate > borate > thiosulfate > acetate = chloride > iodate > fluoride > nitrate > iodide. The iodide appears to have little effect. Corrections for differences in weight concentration could alter this ranking slightly. More serious errors may have been introduced by the choice of salt concentration (0.5N), as for some salts 30°C may be above the cloud point for this composition, that is, this salt composition may be above that for maximum relative viscosity at 30°C. This is the case for sodium thiosulfate and sodium sulfate (see Table 6). Further, the salts were not all completely dissociated so that comparisons were not necessarily made at the same anion concentration. In general it does appear that the multivalent anions are more effective than the monovalent ions; that is, ionic strength may be an important factor but the effect is not as great as would be expected if a flocculation mechanism were occurring. For the same degree of flocculation the concentration of divalent "counter"

ions is only one hundredth of that for monovalent ions, and the corresponding fraction for trivalent ions is one thousandth [23]. The mechanism here appears to be one of "salting out", and the anion effectiveness appears to be related to the lyotropic number — lower lyotropic numbers being most effective*. Similar effects have been reported by others [23,33].

Based on 0.5N potassium salts, the apparent order is:

phosphate > pyrosulfate > ferrocyanide > persulfate
> chloride > iodide > fluoride

Here too, multivalent anions are more effective than monovalent. Fluoride which was moderately effective in the case of sodium has little effect with potassium.

Only a few comparisons can be made for cations. Based on 0.5N chloride solutions, the apparent order is:

iron > sodium > potassium > calcium

Multivalent cations are not necessarily more effective than monovalent cations. Sodium is also more effective than potassium in fluoride solutions, but neither has much effect in iodide solutions. In phosphate solutions, where relative viscosity is very high, potassium appears to be a little more effective than sodium.

Bailey and Callard [21] found that anions were more selective than cations in salting out polyoxyethylene glycols. The cloud point of a high molecular weight polyglycol was sharply lowered at high concentration (0.1N) of hydroxyl ions, whereas it was raised in the presence

* A decrease in lyotropic number corresponds to a decrease in hydrated ionic radius [23].

of a high concentration (0.1N) of hydrogen ions. The addition of .001N HCl or .001N NaOH to 0.5N NaCl and 1.0 percent Alfonic 1214 had little effect on the cloud points observed here (Table 9), but there was a noticeable decrease in the relative viscosity of the acid solution. Addition of 0.1N HCl caused a large decrease in viscosity, presumably due to a rise in the cloud point temperature. Becher [22] found that molecules of low ethylene oxide content behave in a manner consistent with the existence of a small micellar charge. The greater selectivity of certain anions in increasing relative viscosities supports this hypothesis.

B. Drag Reduction

1. Effect of Salt Concentration

At low concentrations, drag reduction with Alfonic 1214 improved with increasing salt content until a maximum amount of drag reduction was obtained at about the same salt concentration as that for maximum relative viscosity. Further increase in salt concentration, however, had little effect on the drag reducing ability of the solutions in contrast to the observed lowering of relative viscosity.

This may be due to the existence of large micelles in the separated phase which are effective as drag reducers but have less effect on solution viscosity. This hypothesis is based on a comparison of 0.5N $\text{Na}_2\text{S}_2\text{O}_3$ with 1.0 percent Alfonic 1214 results in Figure 6 with 0.3N $\text{Na}_2\text{S}_2\text{O}_3$ results with 0.5 percent Alfonic 1214 in Figure 7. The former which is above the cloud point is far more effective even though

the latter is close to the cloud point. Thus, although the concentration of surfactant in the major phase is apparently lower for the 0.5N $\text{Na}_2\text{S}_2\text{O}_3$ solution, it is a more effective drag reducer. Either the remaining micelles in the major phase take on a size and/or shape which is much more effective at lower concentration in the presence of a large amount of electrolyte or, more likely, the surfactant micelles in the precipitated phase are effective as drag reducers.*

It is not understood why the 0.5 percent Alfonic 1214 with 0.4N Na_2SO_4 prepared by dilution from 1.0 percent and addition of more salt gives less drag reduction than the same composition solution prepared directly (Figure 7).

2. Effect of Mechanical Degradation

None of the 1.0 percent Alfonic 1214 solutions near or above their cloud point showed any critical shear stress above which drag reducing ability was lost at the shear stresses available in this equipment. At lower salt concentrations, where the tests were run well below the cloud point, critical shear stresses above which the solutions started to lose their drag reducing ability were observed (Figures 3 and 5). At 0.5 percent Alfonic 1214, upper critical shear stresses were observed even at the cloud point (Figure 7).

The 1.0 percent Alfonic 1214 solutions with 0.3N $\text{Na}_2\text{S}_2\text{O}_3$ (close to cloud point), with 0.5N $\text{Na}_2\text{S}_2\text{O}_3$ (above cloud point), and with

*It has also been suggested that the higher pressure and/or shear stresses present in the capillary tube in the turbulent measurements might raise the cloud point so that phase separation does not occur until near the tube exit.

0.4N Na_2SO_4 (close to cloud point) showed no degradation effects after extended pumping at the maximum shear stresses available in this equipment (Figures 6 and 8).

A similar run for a solution of 0.5 percent Alfonic 1214 with 0.4N Na_2SO_4 (close to cloud point) which exhibited a critical shear stress showed no loss in drag reducing ability at lower shear stress even when pumped for one hour above its critical shear stress (Figure 7).

Thus, for these solutions it appears that if any mechanical degradation of the micelle structure occurs, the micelles reform almost immediately and no permanent effects are observable. This is similar to the behavior of aqueous soaps as reported by Savins [17,18] and White [19] but is in contrast to the slow recovery of aluminum disoap micelles in hydrocarbon solutions [12,13].

The 1.0 percent Brij 96 with 0.5N $\text{Na}_2\text{S}_2\text{O}_3$ which had a relative viscosity of 3.41 gave no drag reduction. Apparently its critical shear stress is very low, lying in the laminar region.

VI. CONCLUSIONS

1. The addition of salts to aqueous solutions of non-ionic surfactants increases the relative viscosity of the solutions until a maximum is reached at a salt concentration (and temperature) corresponding to the upper solubility limit (cloud point) of the solution. At a fixed temperature, the salt concentration required to reach the cloud point is sensitive to the nature of the anion, less sensitive to the nature of the cation. The cloud point is not sensitive to the concentration of the non-ionic. Above the cloud point relative viscosity decreases.

2. The drag reducing ability of Alfonic 1214 solutions increases as the cloud point is approached, that is, as salt concentration increases. The best drag reduction is achieved at the cloud point. Further lowering of the cloud point by addition of salt has little effect on the drag reducing ability of the solution despite the decrease in relative viscosity.

3. At 0.5 percent Alfonic 1214 concentrations, mechanical degradation of micelles leads to a loss in drag reducing ability at high shear stresses. The micelles reform quickly at lower stresses and drag reducing ability is regained.

4. Brij 96 solutions with high relative viscosity show no drag reducing ability. This is apparently because the micelles are sensitive to degradation and break up at stresses attained in the laminar region.

5. Addition of 0.1N HCl causes a marked decrease in the viscosity of a one percent Alfonic 1214 plus 0.5N NaCl solution, presumably because of a rise in the cloud point temperature. Addition of

0.1N NaOH causes a smaller increase in solution viscosity of the same system, but there is no change in the Alfonic 1214 contribution to the viscosity.

VII. FUTURE WORK

The work of this thesis was exploratory and left a number of interesting and important questions unanswered. Experiments that will clarify some of them and lead to possible practical applications include:

1. Investigation of other non-ionic surfactants that may be more efficient as drag reducing additives for possible use in pipe flow or in blood at lower concentrations. In particular, surfactants effective in a salt environment similar to that of blood should be sought. Also, relative viscosity and degradation measurements should be made in salt-free systems near the cloud point.

2. Study of present systems and of new surfactant systems at higher shear stresses in both larger and smaller diameter tubes to see if they behave like drag reducing polymer solutions. This will require a pump or pumps capable of delivering higher volumetric flow rates and/or higher pressures.

3. Light scattering measurements on non-ionic - salt systems below and at the cloud point to determine the size and shape of the micelles.

4. Measurement of cloud points of systems showing good drag reduction above their cloud points under static pressures and/or shear stresses comparable to those present (at the wall) in the turbulent flow measurements. This will indicate whether there is a shift in the equilibrium conditions caused by static pressure or by partial degradation of the micelles due to shear. The high shear stress cloud point measurements might be done in a transparent Couette viscometer.

5. Study of other salt additives which might be more effective in promoting micelle structures useful for drag reduction. Combinations of small amounts of alcohol, which might dehydrate the surfactant, and small amounts of salt may be more effective than large amounts of salt alone.

6. Study the mechanical degradation of Brij 96 under shear stresses comparable to those in the flow experiments to substantiate the hypothesis that the micelles are fragile, degrading at wall stresses prevailing in the laminar region. This could be done by measuring relative viscosities of Brij solutions in a Couette viscometer at the comparable shear stresses, or in laminar flow in a smaller capillary tube.

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IX. VITA

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