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VISCOSITY OF MIXED SURFACTANTS

by

KHALED A. MANASRAH

A thesis submitted to the School of Graduate Studies
in partial fulfillment of the requirements for the
degree of
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ABSTRACT

This work is concerned with the measurement of viscosity of petroleum sulfonate-lignosulfonate solutions.

The influence of lignosulfonate Marasperse C-21 on the viscosity and phase behaviour of Petrostep-420 and Petrostep-465 was determined. The addition of Marasperse C-21 to Petrostep-420 and Petrostep-465 increased the viscosity of both Petrostep solutions in the presence or absence of sodium chloride. This increase in viscosity is accompanied by a specific pattern of phase behaviour which is represented as follows:

Isotropic → birefringent → phase separation → precipitate

The viscosity increase and the drop in specific conductivity suggest the involvement of a liquid crystalline structure in this region.

Screening the various lignosulfonates used in this study reveals that calcium or calcium-sodium based lignosulfonates increase the viscosity of Petrostep-420 and Petrostep-465.

Experiments on the effect of temperature on petroleum sulfonate-lignosulfonate solutions reveal that viscosity decreases with increasing temperature until a sudden increase in viscosity is recorded followed by a decrease.

CHAPTER 1

INTRODUCTION

The ever increasing demand for oil to fuel modern industry and the skyrocketing price of oil have brought a new urgency to the task of devising new methods of oil production. At the present time research into conversion of coal to oil and new technology may provide a long term solution to the shortfall in production. But, until these new methods are in full production, emphasis is being placed on the recovery of remaining oil in existing reservoirs which conventional methods cannot retrieve. New methods of oil recovery must not only be technically efficient but also cost efficient. Therefore, researchers are entering the field of enhanced oil recovery.

Primary and secondary recovery leave 60 to 70 percent of oil reserves virtually untapped. Tertiary recovery techniques such as surfactant flooding could recover most of this vast quantity of oil making these processes of prime interest to oil scientists. Various surfactants have been employed in tertiary oil recovery, the most commonly used of these being petroleum sulfonates.

The effectiveness of the surfactants to produce more oil is measured by its ability to lower interfacial tension. The reduction of interfacial tension has been achieved

through the addition of lignosulfonates to petroleum sulfonates.

One problem encountered with these surfactants is to achieve high sweep efficiency and low-mobility to eliminate viscous fingering. Adding lignosulfonates produces an increase in viscosity which has practical applications in enhanced oil recovery to overcome these problems.

In this study, the primary areas of investigation involve the effect of the addition of lignosulfonates on the viscosity of petroleum sulfonates Petrostep-420 and Petrostep-465, along with the accompanying structural changes of the solutions. In order to investigate these structural changes, specific conductivity measurements as well as measurements of viscosity were conducted. Also studied was the effect of temperature and salinity on viscosity of petroleum sulfonate-lignosulfonate solutions.

CHAPTER 2

LITERATURE REVIEW

STAGES OF OIL RECOVERY

Oil recovery from a reservoir incorporates three types of recovery operation:

1) Primary recovery
2) Secondary recovery
3) Tertiary recovery

2.1 PRIMARY OIL RECOVERY

Oil is normally found in the pores of certain underground formations under high pressure. Taber and Martin[1] estimated this reservoir pressure at several thousand psi. When a well is drilled, the release of the reservoir pressure forces the oil out. Release of this pressure is attributed to the expansion of the reservoir fluids caused by the presence of gas in the form of tiny bubbles inside the rock. The estimated production during this primary process is 15-20% of the oil in the reservoir [2].

2.2 SECONDARY RECOVERY PROCESS

When the reservoir pressure is not sufficient to force the oil out, the necessary pressure is built up by using an

external source, the injection of water or gas. Some authors[2,3] have referred to this process as waterflooding. An injection well is drilled as well as the production well. Fifteen to twenty percent of the oil in the reservoir may be extracted by this method. The method is rendered more efficient when the water is thickened in order to obtain high sweep efficiency.

2.3 TERTIARY OR ENHANCED OIL RECOVERY

By using the two recovery processes, primary and secondary recovery, sixty to seventy percent of total reservoir oil is left untapped. Morgan et al[4] estimated about 300 billion barrels of oil is left untapped in the U.S.A. after secondary oil recovery.

The current world wide demand for crude oil is so great that discovery of other means of recovery to tap previously unaccessible reserves at minimal cost has become top priority for scientists, and led to improve the efficiency of enhanced oil recovery.

The third stage of recovery employed is commonly called tertiary recovery. Taber et al[1] prefer to use the term enhanced oil recovery when referring to both secondary and tertiary recovery processes. It is their contention that enhanced recovery techniques are more effective when applied before waterflooding is used on a full scale.

After the completion of waterflooding, the remaining oil is trapped in the pore spaces of the rock in the swept

zones of the reservoir. This trapped oil becomes immobilized as a result of capillary forces and is left as isolated blobs or ganglia [3]. A diagram of trapped blob is depicted in Figure 2-1.

Morrow[5] estimated that 10^{11} blobs having an average volume of 10^{-6} cm^3 are present for each barrel of oil in a rock of 200 millidarcy permeability.

Enhanced oil recovery processes include:

1) Chemical flooding
2) Miscible displacement
3) Thermal recovery

2.3-1 Chemical Flooding Process

Chemical flooding itself is comprised of three different types of flooding:

1) Polymer flooding
2) Alkaline flooding
3) Surfactant flooding

Polymer flooding involves injecting water thickened by the dissolution of a high molecular weight polymer into the reservoir. This thickened water is also used in secondary recovery in order to increase the sweep efficiency. The thickened water is followed by drive water as shown in Figure 2-2. The addition of a polymer increases the viscosity of the injected water and increases the mobility ratio.

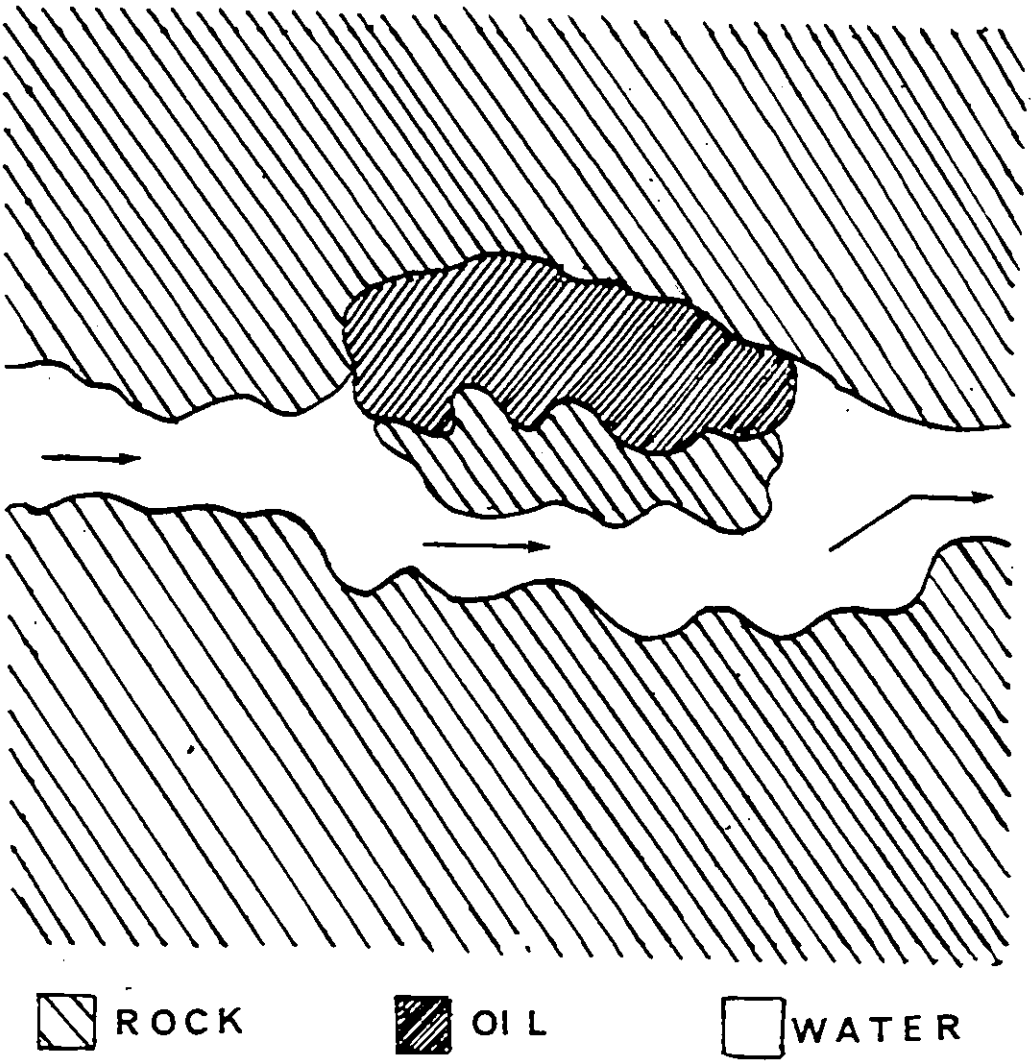


Figure 2-1: By-passed Ganglion of Residual Oil Trapped by Capillary Forces in a Pore Restriction

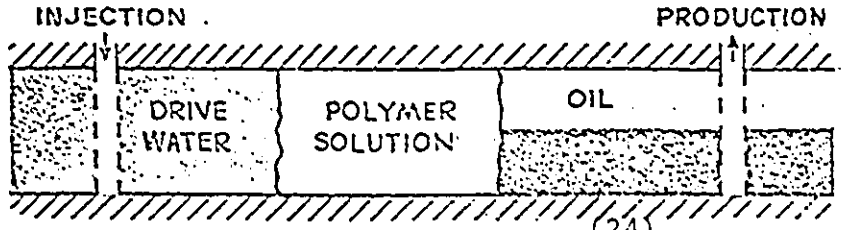


Figure 2-2: Polymer Flooding[24]

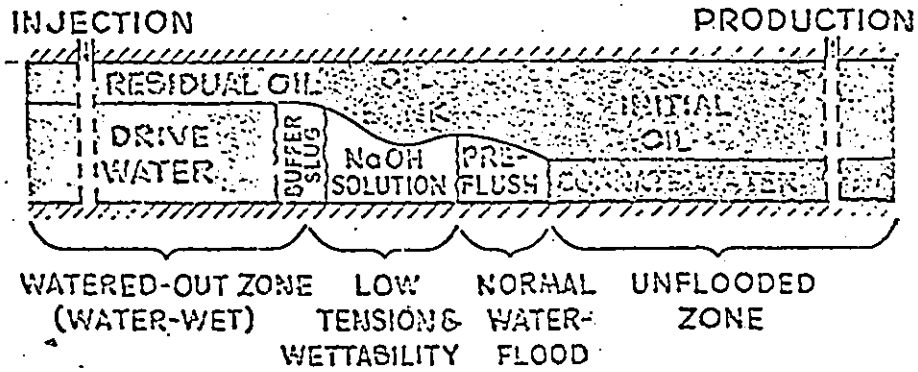


Figure 2-3: Alkaline Flooding[24]

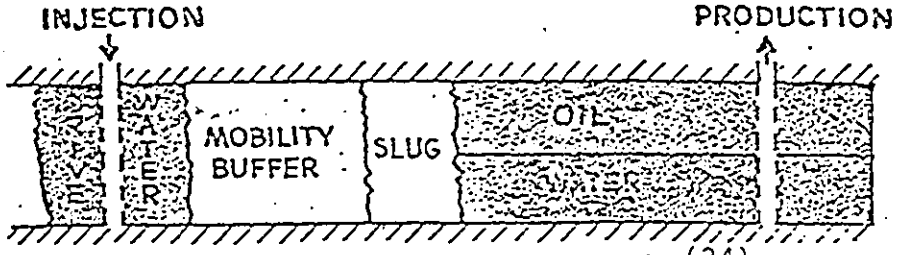


Figure 2-4: Surfactant Flooding[24]

In alkaline flooding, alkaline chemicals such as sodium hydroxide, sodium silicate and sodium carbonate are added to the injected water. This process helps reduce interfacial tension, emulsification of oil and formation of wettability reversal [6]. This process is illustrated in Figure 2-3.

Surfactant flooding is by far the most important process, in that, research is based on the improvement of surfactant efficiency in producing more oil. This process, briefly, consists of using water soluble surfactants of which the most widely used is petroleum sulfonates. It is usually followed by the injection of a polymer solution, and then drive water as shown in Figure 2-4.

In this process, either low concentrations of surfactant are used in the form of micellar solution or high concentrations of surfactants in conjunction with other components such as hydrocarbons, water, alcohol and salt, a combination known as microemulsion. In the low concentration process, about 3-20% pore volume is used while in the high concentration about 15-60% pore volume is used [2].

With surfactant flooding, the displacement of oil follows two configurations [2].

1) The "five spot" pattern, with four production wells at the four corners of a square and an injection well at the centre are drilled. This kind of arrangement is also followed in secondary recovery and is illustrated in Figure 2-5.

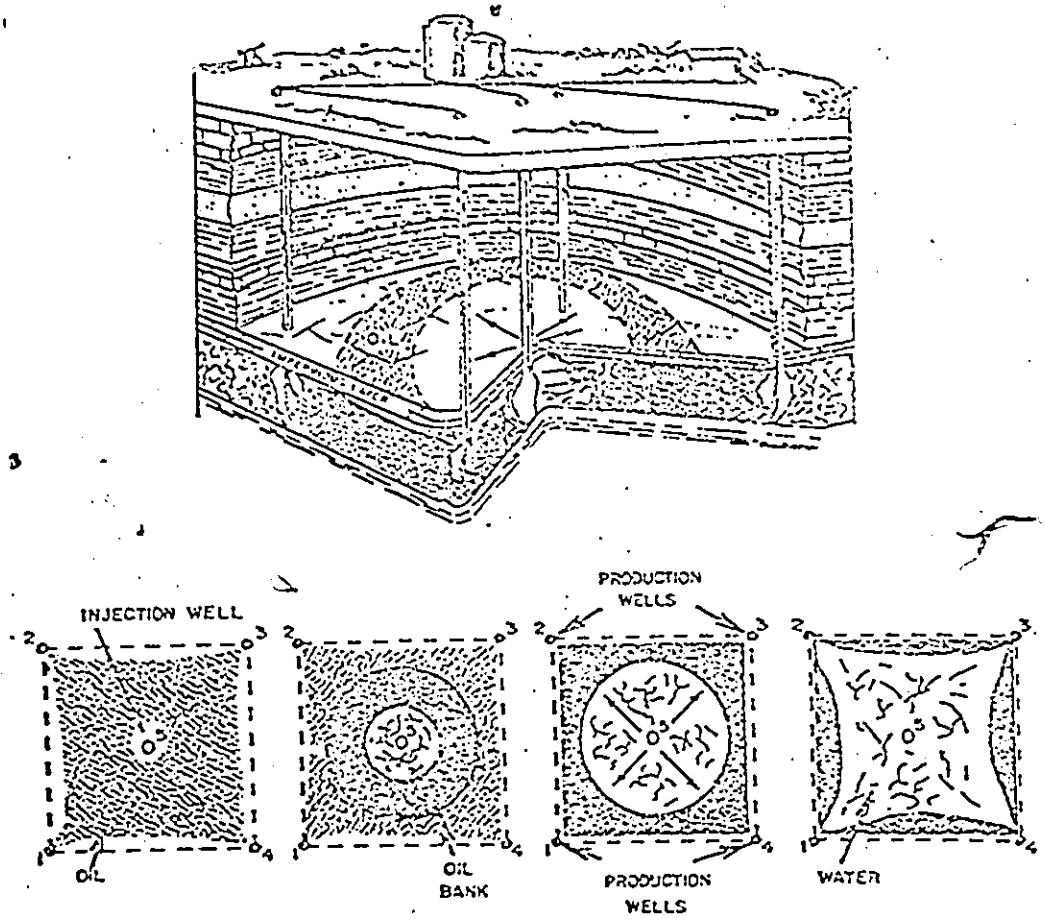


Figure 2-5: "Five Spot" Schème for Surfactant Flooding[2]

2) The "line drive" pattern placed production and injection wells in an alternate pattern. The five spot pattern is the more popular of the two [2].

In this process, one of two mechanisms is acting to produce more oil. Either, the oil is displaced from the rock's capillaries (immiscible displacement) or the oil is solubilized in the micelles of the surfactant. The first mechanism is more efficient and will be discussed in more detail.

2.3-2 Immiscible Displacement

As it has already been mentioned, after the water-flooding process, oil is trapped in rock capillaries in the form of ganglia.

Micellar flooding lowers the interfacial tension to mobilize the oil ganglion, to propogate and form an oil bank, and to minimize adsorption and degradation problems. The best designed micellar slug is that one which has the above characteristics and has high sweep efficiency to overcome viscous fingering.

Adding lignosufonate to petroleum sulfonate has been patented to act as a sacrificial agent in the adsorption of the surfactant [7]. The addition of lignosulfonate is also reported to produce ultra low tension between oil and the surfactant [8,9,10,11,12]. As will be shown in Chapter three, adding lignosulfonate produces high viscosity readings, therefore, lignosulfonate could be an ideal additive to

petroleum sulfonate.

The displacement efficiency of a slug is determined by its effects on the displaced phases. A surfactant slug, to be effective, must lower the interfacial tension, produce high sweep efficiency and increase the mobility ratio. To produce high displacement efficiency, the surfactant process may be conducted in the following manner [6]:

1) A preflush, which may contain: sodium chloride--to provide maximum compatibility between the water-flood reservoir and the micellar solution; or chelating agents--to reduce the concentration of the divalent ions in the reservoir fluid; or, to inactivate the clays present in the reservoir, it contains alkaline chemicals; or it contains all the above.
2) A slug of micellar fluid (3-10% PV) is injected.
3) A polymer solution is injected.
4) A drive water is also injected.

2.4 THE ROLE OF LOW INTERFACIAL TENSION IN OIL RECOVERY

Morgan et al [4] modelled the oil ganglion in a rock capillary as illustrated in Figure 2-6.

They simplified the model by assuming that the rock capillary is fully water wet (i.e., θ_1 and θ_2 are zero) and that the interfacial tension at both ends of the interface between oil and water is the same.

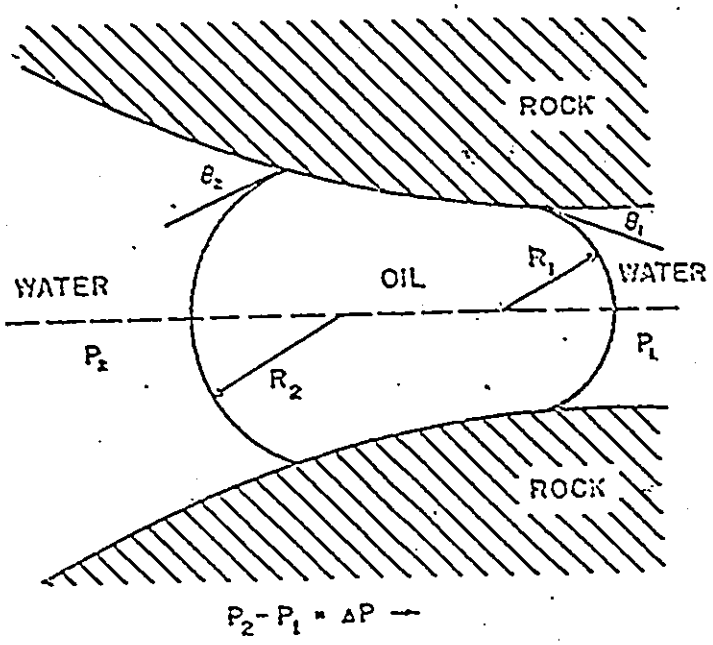


Figure 2-6: Model of Trapped Oil Ganglion(4)

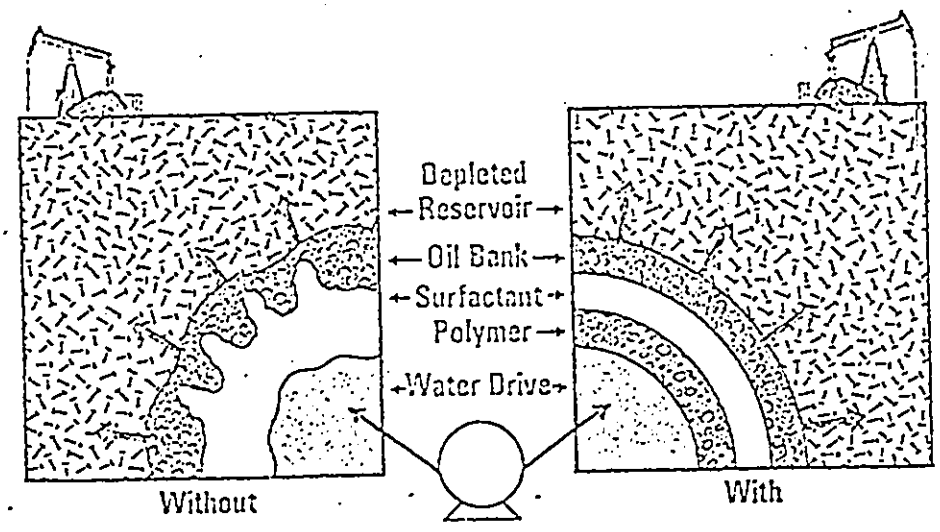


Figure 2-7: Sweep Efficiency (Mobility Control)(3)

The pressure required to move the oil ganglion should exceed the pressure difference as defined in the following equation:

$$\Delta P = P_2 - P_1 = 2\gamma\left(\frac{1}{R_1} - \frac{1}{R_2}\right) \qquad 2\text{-}1$$

where γ = Interfacial tension--dyne/cm

P_1 = Pressure in side 1 (water phase)--dyne/cm^2

P_2 = Pressure in side 2 (water phase)--dyne/cm^2

R_1, R_2 = Meniscus radii--cm

They suggested that to move the oil ganglion, the interfacial tension should be reduced to less than 0.1 dyne/cm, and probably to a lower value of 10^{-3} from its usual value of 10-30 dynes/cm.

Bansal and Shah[2] attributed this low value to the necessity to reduce the work of deformation for the oil droplet to emerge from the narrow neck of the capillary.

They explained, on the basis of capillary number, that γ should be reduced to approximately 10^{-3} dyne/cm to recover more oil, where the capillary number is defined as follows:

$$N_c = \frac{k\,\Delta P}{L\gamma} = \frac{\text{Viscous forces}}{\text{Capillary forces}} \qquad 2\text{-}2$$

where k = Permeability

ΔP = Pressure drop

L = Porous sample length

To mobilize the residual oil, the capillary forces must be overcome until viscous flow is sufficient. This condition led to the importance of viscous forces and bulk viscosity, in particular in enhanced oil recovery. Morgan et al[4] concluded that there is critical value for the capillary number of approximately 10^{-2} which must be exceeded before displacement of oil ganglia can occur. This value increases with the increase in the porous medium permeability.

2.5 EFFECT OF HIGH VISCOSITY IN CAPILLARY NUMBER INCREASE

Capillary number has been defined in another form, as follows:[14]

$$N_c = V\mu/\gamma\phi \qquad 2\text{-}3$$

where μ = Viscosity of the displacing fluid

V = Flow rate per unit cross sectional area

γ = Interfacial tension

ϕ = Porosity

From this relation, it may be deduced, that increasing the capillary number could be obtained by increasing either μ or V, or by decreasing capillary forces (decrease γ). V, the flow rate of the displacing fluid is limited by well spaces from 1 to 2 ft/day [4].

Morrow[5] concluded that complete recovery from the swept region could be achieved if the ratio of viscous to capillary forces is raised sufficiently. Capillary number of the order of 10^{-3} is necessary for efficient oil recovery. They suggested that this low capillary number could be achieved by either lowering the interfacial tension to low values of 10^{-2} to 10^{-3} dynes/cm or by increasing the viscosity of the displacing fluid. The increase in viscosity increases the viscous forces and could overcome the capillary forces and mobilize the residual oil from the rock capillaries.

2.6 MOBILITY RATIO AND SWEEP EFFICIENCY

Injecting surfactants in enhanced oil recovery to initiate and propogate an oil bank must provide both high displacement and high sweep efficiencies. In both secondary and tertiary recovery, the ability of the injected fluid to displace more oil is determined by its ability to sweep more of the reservoir area. Surfactant formulations display the ability to overcome capillary forces by reducing the interfacial tension between the injected fluid and the displaced fluid as well as having high sweep efficiency. The mobility must be reduced for the injected fluid to displace more oil. This is possible if the viscosity of the surfactant is increased to surpass that of the displaced fluid.

High sweep efficiency is more important in surfactant flooding than in waterflooding since small concentrations of surfactant are injected with which more area of the reservoir

must be contacted. Gilliland [3] defined areal sweep efficiency as "the fractional area of the reservoir that can be swept by surfactant."

Areal sweep efficiency is dependent on the viscosity of the injected fluid, and the arrangement of the injection, and producing wells, and the mobility ratio of the displaced and displacment fluid. Taber et al[1] demonstrate the importance of the mobility ratio in the following manner: If the injected fluid has a viscosity less than that of oil to be displaced, it tends to channel in the displaced fluid. Mungan[15] referred to this channelling as viscous fingering which causes the displacement front to spread, as illustrated in Figure 2-7.

The injected fluid will take the path of least resistance, therefore, it will enter the more permeable zones. In this way, few zones will be swept by the injected fluid. This leaves oil in the less permeable zones which remain unswept by the injected fluid. By increasing the viscosity of the injected fluid to surpass that of the oil, the injected fluid encounters more resistance entering the more permeable zones. Therefore, it will enter all zones more uniformly, and more zones will be swept by the injected fluid.

Viscosity also plays an important role as described by Burtch.[6]. He explained that capillary forces are overcome by low interfacial tension of the surfactant. The oil ganglion will be collected in the form of an oil bank. In the oil bank region the oil and water mixture behave in the porous media like a fluid with viscosity higher than either component (approximately 5 mPa·s). If the injected fluid has a viscosity

less than that of the oil-water bank, the surfactant will move faster through the porous media than the oil bank. To overcome this problem, the mobility ratio should be increased.

Mungan[15] described the displacement of oil by water in a piston-like manner. He neglected the capillary effects, for instance , the pressure in both the oil and the injected fluid are equal at any position in the porous medium. Let the length of the pore model be L and the displacement be at a position x where x < L. The flow in this system follows Darcy's Law for the thickened water and oil systems.

$$\frac{q}{A} = -\frac{k_w}{\mu_w} \cdot \frac{P_I - P_x}{x} = -\lambda_w \frac{P_I - P_x}{x} \qquad 2\text{-}4$$

$$\frac{q}{A} = -\frac{k_o}{\mu_o} \frac{P_x - P_L}{L - x} = -\lambda_o \cdot \frac{P_x - P_L}{L - x} \qquad 2\text{-}5$$

where q = Flow rate

A = Cross sectional area

k = Permeability

μ_w = Viscosity

P_I = Pressure at position I

P_x = Pressure at position x

λ_w = Mobility of displacing fluid

λ_o = Mobility of displaced fluid

subscript w = Displacing fluid system

subscript o = Oil system

Mobility ratio is defined as follows:

$$M = \text{Mobility ratio} = \frac{\text{Mobility of displacing fluid}}{\text{Mobility of displaced fluid}}$$

Since water or surfactant solution displaces oil, the mobility ratio is defined in the following formula:

$$M = \frac{k_w / \mu_w}{k_o / \mu_o} \qquad 2\text{-}6$$

where k_w = Absolute permeability of displacing fluid

k_o = Absolute permeability of displaced fluid

Burtch[6] has stated that the mobility ratio of the injected fluid to the displaced fluid will determine how much of the project pattern will be flooded. If the mobility of the displacing fluid is less than that of the displaced fluid, more oil will be displaced. Hence, if $\lambda_w < \lambda_o$ the mobility ratio is favorable.

Low mobility ratio will result in unfavorable rate of recovery. Therefore, the main objective in increasing the surfactant viscosity is to achieve a mobility ratio of less than 1 for good displacement of oil. From the definition of mobility, the ratio of permeability to viscosity, it may be seen that increasing the viscosity of the injected fluid will give it low mobility.

If M = 1, the oil and the injected fluid flow equally. But if the mobility ratio is greater than 1, the injection fluid will flow faster than the oil causing the formation of viscous fingering as shown in Figure 2-7. Therefore, this

will bring about low displacement efficiency and will leave large areas of the reservoir unswept because of the tendency of the mobile water to channel directly from the injection well to the production well.

Mungan[15] shows that if for some reason a finger has formed in the oil filled segment, and if the mobility ratio is favorable (i.e., $\lambda_o - \lambda_w > o$), then the velocity of the finger will decrease and the displacement front will catch up with the finger. However, if the mobility ratio is unfavorable (i.e., $\lambda_o - \lambda_w < o$), the finger will move faster than the displacement front yielding an early breakthrough of water causing much bypassing of the oil.

The idea behind the mobility ratio concept is to adjust the viscosity of the injected fluid to obtain low mobility in which fingering will not occur. Adding high molecular weight polymer to the surfactant is a frequently used method. The polymers used include mostly xantham gum or polyacrylamide. However, these polymers have high molecular weight, and they may be trapped in the capillary pores [16]. The use of lignosulfonate to adjust the viscosity of the surfactant might be of more practical use, since lignosulfonates have lower molecular weight than the polymers. Also, adding lignosulfonate, produces low interfacial tension [8,9,10,11]

2.7 DEFINITIONS

2.7-1 Viscosity

Viscosity is defined as[16] "a measure of the energy dissipated by a fluid in motion as it resists an applied shearing force". It is a measure of friction. Whenever a layer of fluid is made to move relative to another layer, as shown in Figure 2-8, a certain force per unit area is required to maintain a constant velocity gradient, and is defined by Newton's Law in the following form:

$$\frac{F}{A} = -\mu \frac{dv}{dy} \qquad 2\text{-}7$$

where $\frac{F}{A} = \tau$ = Shear stress

$\frac{dv}{dy} = \dot{\gamma}$ = Rate of shear

μ = Shear viscosity $= \frac{\tau}{\dot{\gamma}}$

The fluids which behave according to Newton's Law are known as Newtonian fluids. However, for many polymer melts and solutions, the shear stress and shear rate are not proportional over all ranges. These solutions are called non-Newtonian. Figure 2-9 shows the non-Newtonian behaviour when plotting τ against $\dot{\gamma}$ or μ against $\dot{\gamma}$.

Some materials shows an effect of shearing time on the viscosity. The viscosity may increase or decrease with time. If the effect is temporary and viscosity returns to its original value, the behaviour is called rheopexy, meaning that

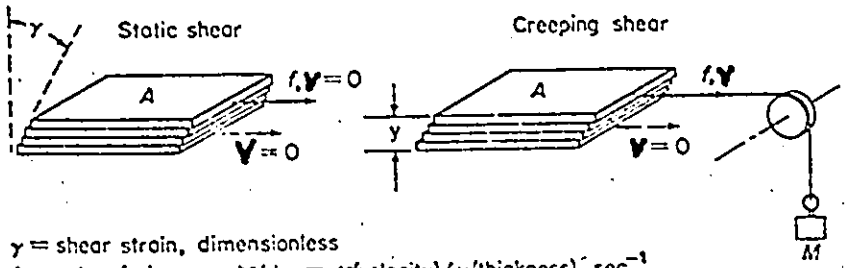


Figure 2-8: Viscosity in Laminar Unidirectional Flow[16]

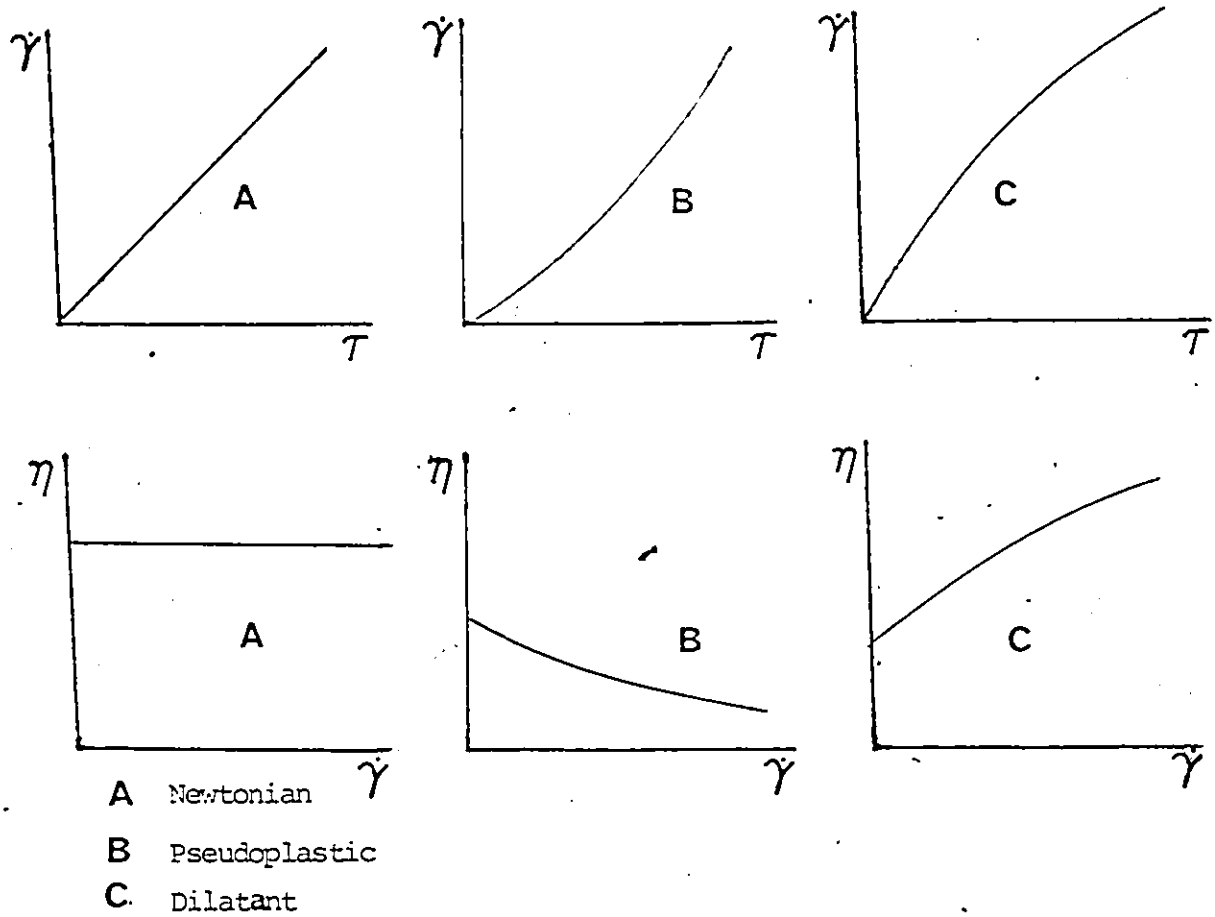


Figure 2-9: Newtonian and Non-Newtonian Behaviour of Fluids[29]

viscosity increases with time of deformation or thixotropy, meaning viscosity decreases with time of deformation. This type of behaviour is depicted in Figure 2-10.

Brown and Pinder[17] classify thixotropic materials into two types.

1) Thixotropic dispersions, viscosity decrease with shear to an equilibrium state, which is Newtonian.
2) False body dispersions, viscosity decrease with shear to an equilibrium state, which is pseudoplastic.

For liquid mixtures, the viscosity is correlated by different authors [18,19,20,21]. They showed that viscosity is dependent on the formulations and the types of constituents involved.

2.7-2 Viscosity and Resistance Factor[6]

The flow of injected solutions in porous media is defined by Darcy's Law.

$$\frac{Q}{A} = \frac{k}{\mu} \frac{\Delta p}{L} \qquad 2\text{-}8$$

where μ = Viscosity (mPa·s)

Since the viscosity of the injected surfactants or polymers is pseudoplastic, viscosity is expressed as a function of rate of shear. The viscosity of these solutions in porous media is greater (assuming $d_{pore} < d_{viscometer}$) than when measured by a viscometer. This viscosity is termed "effective

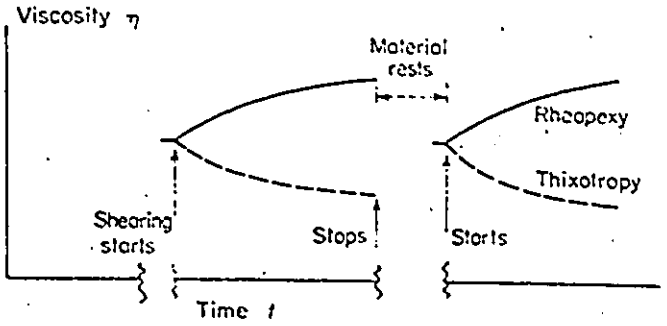
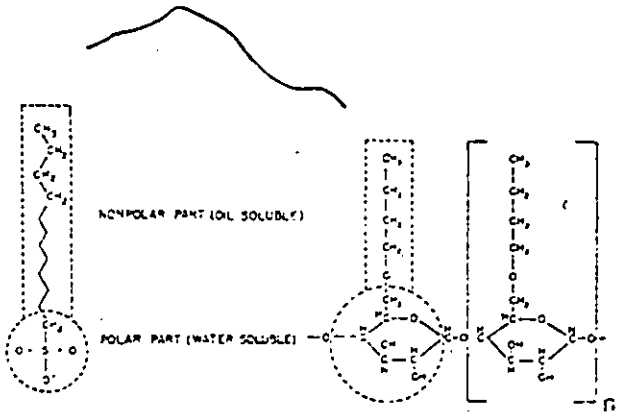


Figure 2-10: Schemetic Behaviour of Time-Dependent Viscosity which Increases (Rheopectic Behaviour) or Decreases (Thixotropic Behaviour) with Time during Shearing at a Steady Rate.(16)



Surfactant Polymer

Figure 2-11: The Structure of Surface-Active Molecules[2]

viscosity". The injected solution therefore, experiences a greater resistance to flow than measured by viscometer.

The efficiency of the solution is expressed in the following manner:

$$F_R = \frac{\mu(P - rock)}{\mu(W - rock)} \qquad 2\text{-}9$$

where F_R = Resistance factor

$\mu(P - rock)$ = Effective viscosity obtained by solving equation 2-8

$\mu(W - rock)$ = Viscosity of water at the same conditions

2.7-3 Permeability/Relative Permeability

Permeability is a physical property of the rock. It is a measure of the ease with which fluids flow through porous media expressed in Darcy's equation 2-8 .

Taber and Martin[1] stated that typical sandstones in the United States have permeabilities ranging from 0.001 darcy to 1.0 darcy or more.

Relative permeability is the effective permeability divided by a base permeability (absolute permeability k, which is the phase permeability of the porous medium). This ratio is known as the relative permeability.

2.7-4 Molecular Aggregates in Surfactant Solutions

Shah[22] defined the surfactant as that molecule which has two functional parts, a hydrophilic (water soluble) or

polar part and a lipophilic (oil soluble) or non-polar part. A polymer also can be surface-active if it has two functional groups, as illustrated in Figure 2-11.

When a surfactant is dissolved in water, it is adsorped at the air-water interface and also at interfaces between the solution and the adjacent phase(s).

Shah et al[2,22] considered the surfactant molecules as building blocks. When a surfactant is adsorbed, it tends to accumulate at the surface. Its concentration at the surface and the molecular interaction packing differ from those in the bulk as may be seen in Figure 2-12. Above a critical concentration, the surfactants forms aggregates called micelles. By increasing surfactant concentration various association structures can be formed as shown in Figure 2-13.

2.7-5 Liquid Crystals

Liquid crystals are those materials in which molecules hold a loosely held-together spatial geometry. The large groups of molecules in these liquids maintain their mobility. These liquid crystals fall into three categories[23]:

1) Smectic liquid crystals in which the molecules are arranged in precise layers.
2) Nematic liquid crystals in which the molecules are arranged in a less ordered manner than in type 1.
3) Cholesteric liquid crystals whose molecular layers are very thin. This name was derived because many of these compounds contain cholesterol.

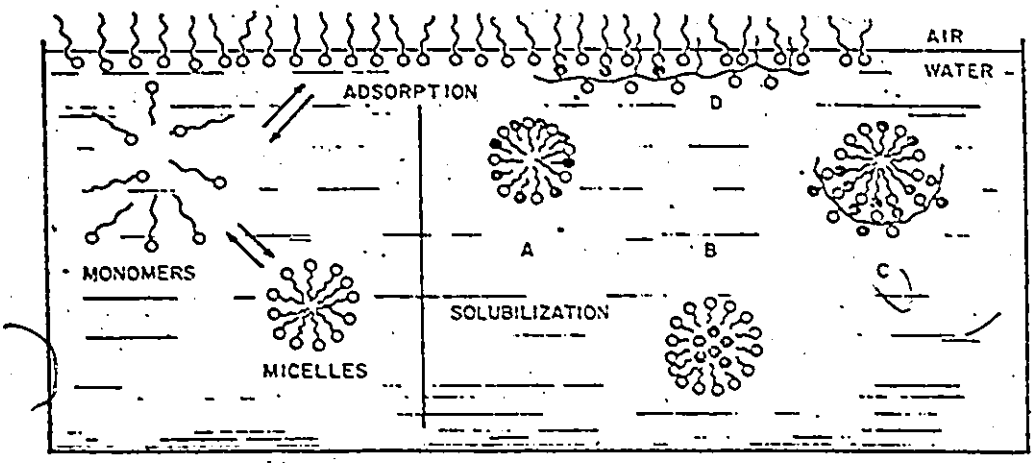


Figure 2-12: Adsorbing, Micelle Formation, Solubilization and Interaction at the Micelle Surface.(2)

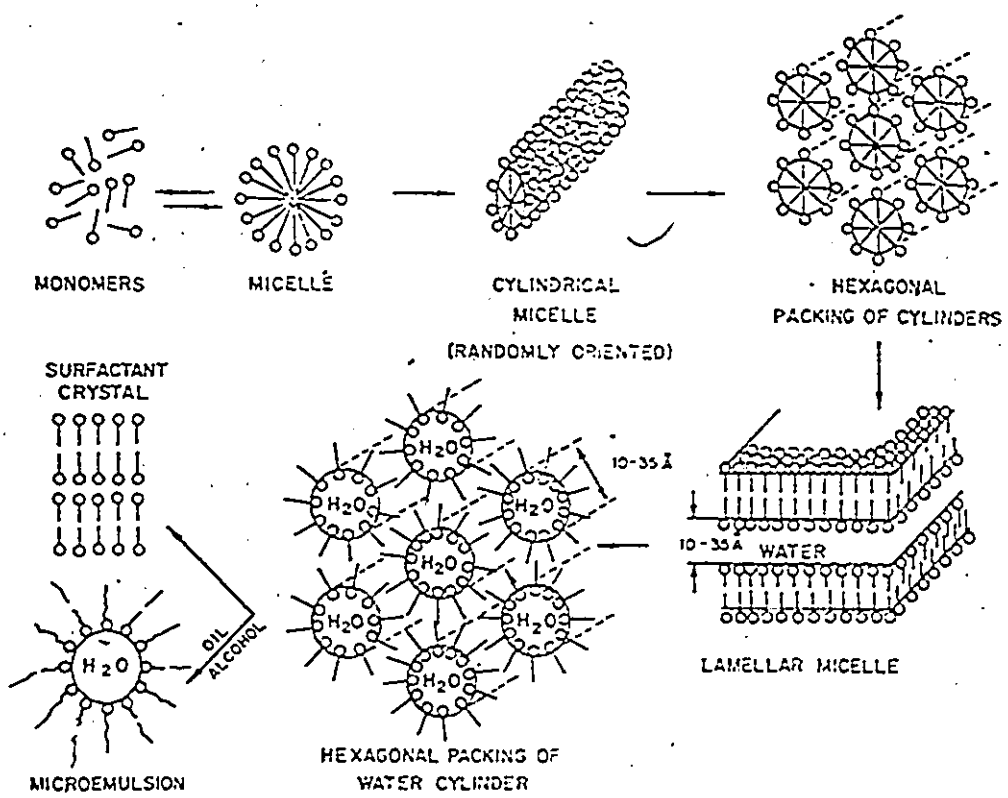


Figure 2-13: Structure Formation in Surfactant Solution(22)

CHAPTER 3

EXPERIMENTAL

3.1 MATERIALS

For the purpose of this study, two types of petroleum sulfonates were chosen, namely Petrostep-420®† and Petrostep-465®. Both are manufactured by Stepan Chemical Company in a tarry, semi-solid viscous form which is soluble in water. The specifications of these surfactants are shown in Table 3-1. Sodium alkyl aryl sulfonate was also used as a pure anionic surfactant supplied by Fisher Scientific Company.

Several lignosulfonates were investigated in this study, the principal of these being Marasperse C-21®; a sodium calcium based lignosulfonate manufactured by the American Can Company. It is supplied in a brown powder form. Among the other lignosulfonates studied were: sodium lignosulfonate Marasperse N-22®, Lignosol X2 U35®, Lignosol DP(105)® and Lignosol ORF #6B®, ammonium lignosulfonate Lignosol TSF® and a calcium lignosulfonate Lignosol SF®. Typical analysis of some of these lignosulfonates is shown in Table 3-2.

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†A superscript ® indicates a patented trademark.

Table 3-1

Specifications of Petroleum Sulfonates

Specifications	Petrostep-420	Petrostep-465
Equivalent weight	420	465
Sulfonate	59.1	57.5
Free oil	17.3	14.5
Water	19.5	24.9
Inorganic salt	4.1	2.8
Control number	484	558

Table 3-2

Typical Analysis of Lignosulfonates[27]

	Marasperse C-21	Marasperse N-22	Lignosol TSF	Lignosol SF
Chemical Data				
PH*	7.7	8.1	4.3	6.0
Total sulfur as S** (%)	6.1	6.5	6.8	5.2
Sulfate sulfur as S (%)	0.4	0.8	6.1	4.8
Ca (%)	4.0	0.6	0.2	6.1
Na (%)	2.1	6.7	-	-
Nitrogen as N (%)	-	-	3.9	-
Reducing bodies	1.3	0.8	5.0	4.5
Methoxyl (%)	8.8	8.1	7.6	7.2
Physical Data				
Color	Brown	Brown	Brown	Brown
Moisture (%)	6.0	6.0	6.0	6.0
Bulk density	46	43	28-32	28-32

*PH for Marasperses based on 3% solution while for Lignosols based on 27% solution.

**All percentages are weight percent

The source material of these lignosulfonates is lignin, the chemistry of which has been outlined by Bansal [25] and Ball [26]. Negative sulfonate groups on the surface of the particle and the presence of carboxylic and phenolic groups make them easily soluble in water [27]. These lignosulfonates are anionic polyelectrolytes having a molecular weight between 1,000-50,000 [28]. The structure of a section of lignosulfonates is shown in Figure 3-1.

Distilled water was used in the preparation of all of the solutions, and brine solutions were prepared with high purity sodium chloride supplied by Fisher Scientific Company. Calcium chloride supplied by Fisher Scientific Company was also used.

3.2 PREPARATION OF SOLUTIONS

The petroleum sulfonate stock solutions were prepared by weighing the surfactant to which was then added distilled water at room temperature. This stock solution was prepared on weight percent basis. The mixture was left to stand for two to three days after which period of time, the solution was stirred with a glass rod until the surfactant had completely dissolved. In the case of Petrostep-420, when the surfactant had completely dissolved, two layers appeared in the solution, a cloudy layer on the bottom and a clear layer on top. Before preparing a sample, the stock solution was shaken.

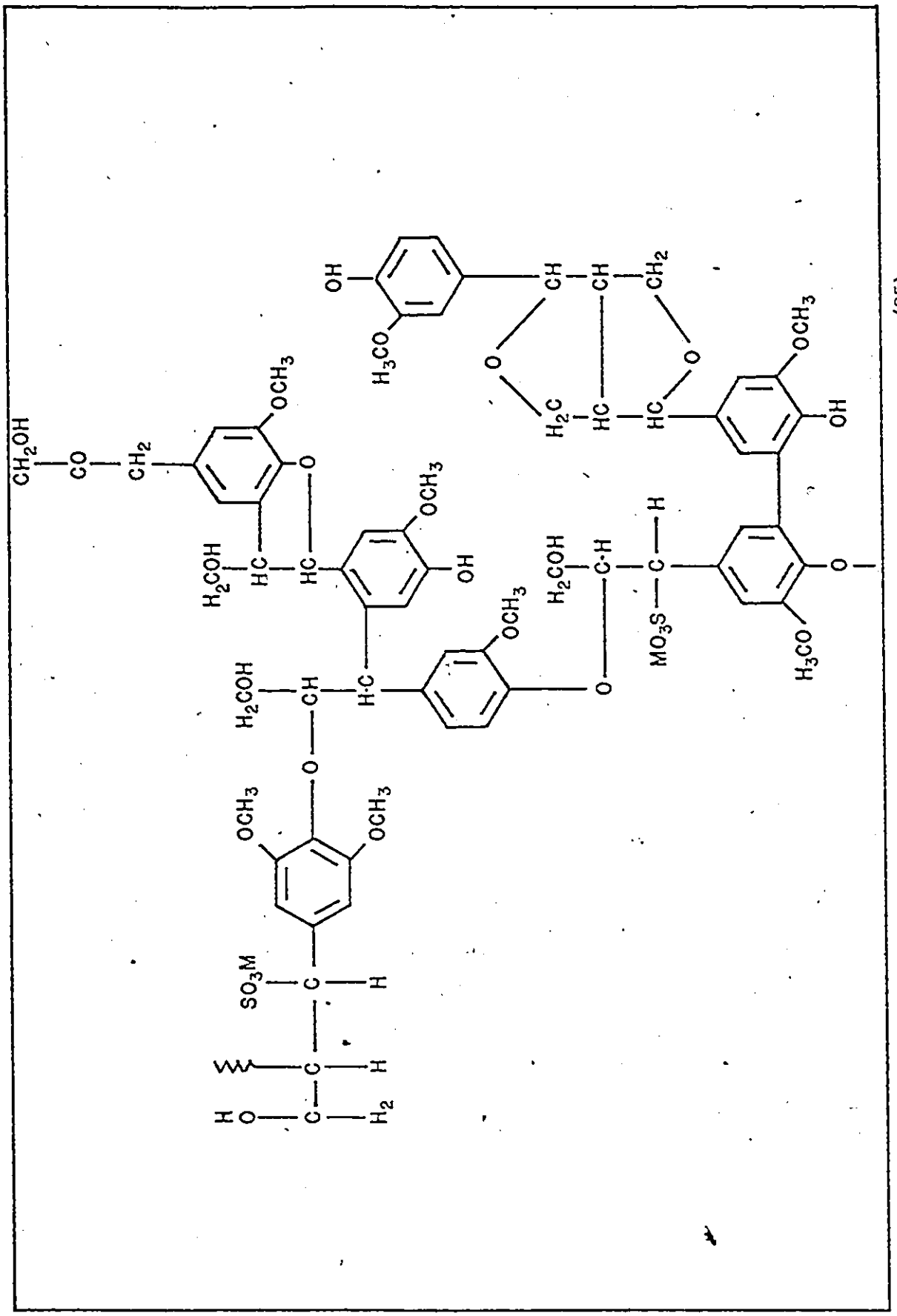

Figure 3-1: STRUCTURE OF A SECTION OF LIGNOSULFONATE (25)

Though, it is possible to dissolve the petroleum sulfonate more quickly by successive leaching with hot water, such a procedure yields non-reproducible viscosity measurements, as petroleum sulfonate has a complex structure. Dissolving it using hot water may affect this structure, thus producting this irreproducibility.

Similarly, lignosulfonate is also easily dissolved in water at room temperature. However, to dissolve it faster, it is weighed and small amounts are added each time, since it may agglomerate, otherwise, making it more difficult to dissolve.

Salt solutions were prepared in similar fashion, dissolving a weighed amount of salt in distilled water. It should be emphasized here that weight percent were used in all measurements.

To prepare the sample, petroleum sulfonate was added first, followed by lignosulfonate, distilled water, and, finally, NaCl solution. To measure the viscosity and specific conductivity, 30 gm. samples were prepared, then shaken for approximately 30 seconds, and left to stand overnight. The preparation and storage of samples were at an ambient temperature of 23-25°C, and the viscosity was measured at 25°C. After loading the viscometer with the sample, it was left to equilibrate at 25°C for approximately 10 minutes. The time interval between each measurement at different rotation speeds depends on the time needed for the reading to stabilize. For those solutions which were not thixotropic,

the time interval was usually around 5 minutes, starting at a rotation speed of 30 R.P.M.

3.3 PHYSICAL PROPERTIES MEASUREMENTS

3.3-1 Viscosity Measurements

Having allowed the sample to equilibrate for 10 minutes in a temperature controlled bath of 25°C, the viscosity was measured using a Brookfield viscometer and a Cannon-Fenske capillary viscometer.

Brookfield Viscometer

The Brookfield LV Synchro-lectric viscometer (provided with a set of four spindles), and the Brookfield U.L. Adaptor used in this study were supplied by Brookfield Engineering Laboratories Inc., U.S.A. This viscometer operates by measuring the torque necessary to overcome the viscous resistance to the induced movement [29]. It measures the force required to rotate a spindle in the fluid.

To detect the rheological properties of the samples, the viscosity is measured using the same spindle at different rotation speeds.

The U.L. Adaptor consists of a precision cylindrical spindle inside a stainless steel tube of known diameter.

The accuracy of this viscometer is within 1% of the full scale range employed and reproducibility of the measurements is within 2% of the full scale range. The U.L. Adaptor has

the following ranges:

R.P.M.	Range	Multiplying Factor(100 scale)
60	0 - 10	0.1*
30	0 - 20	0.2**
12	0 - 50	0.5
6	0 - 100	1.0

* Deduct 0.4 from reading before multiplying to correct for windage.

**Deduct 0.1 from reading.

The operation procedure is outlined in the instruction manual.[30]

Cannon-Fenske Viscometer

The Cannon-Fenske viscometer used in this study was supplied by Cannon Instruments Company, State College, PA. Operation instructions are outlined in the instruction manual [31]. The time for the solution to flow between two marks in the viscometer is recorded at a fixed temperature of 25°C, from which the kinematic viscosity may be determined. Knowing the cell constant of the viscometer, kinematic viscosity is then converted to absolute viscosity by multiplying it by the density of the solution. Extrapolation to 25°C was performed since the cell constants were obtained at higher temperatures.

3.3-2 Density Measurements

Density measurements were performed by using 25 ml. specific gravity bottles at ambient temperature of 23-25°C.

3.3-3 Specific Conductivity

Measurements of specific conductivity were made using the Reddick Zeta-Meter Electrophoresis cell supplied by Zeta-Meter Inc. with a cell constant of 65. Voltage was set at 65 volts to cancel out the cell constant in the following equation [32]:

$$S.C. = \frac{KI}{E} \text{ micromho/sec.}$$

where K = Cell constant (65)

I = Current (micro amps.)

E = Voltage (volts)

The current reading was therefore a direct measure of specific conductivity, according to the above equation.

3.3-4 Photomicrographs

Polarizing Microscope OPTIPHOT-POL with Photomicrographic attachment MICROFLEX-HFX, manufactured by Nikon was used.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 OBJECTIVES OF THE RESEARCH

Interfacial tension and bulk viscosity are the two most important properties of the surfactant solution in oil recovery. The use of lignosulfonates as an additive to petroleum sulfonates to reduce interfacial tension has been investigated by several researchers[8,9,10,11,12] in this field. An accompanying increase in bulk viscosity of the mixed surfactant solutions has been observed by Chiwetelu[9] but it has not been studied in any great depth.

The object of this research was to investigate the effect on viscosity of adding Marasperse C-21 to Petrostep-420 and -465, also to study phase behaviour in an attempt to deduce a mechanism for phase change. In addition, various lignosulfonates were screened to discover which show the greatest potential for producing an increase in viscosity. To accomplish these objectives, several parameters were investigated.

To begin, experiments were conducted to determine the effect on viscosity of adding Marasperse C-21 or NaCl to Petrostep-420 and -465. Further experiments consisted of adding both to the Petrosteps.

The order-of-mixing of the chemicals may produce a profound effect on the viscosity readings obtained. Therefore, experiments were conducted to determine if any such order-of-mixing effects were present.

The temperature of oil reservoirs also places certain constraints on the choice of surfactant formulations. Therefore, temperature effect was studied.

In order to understand and explain the structural changes involved with changes in the mixed surfactant formulations, viscosity and specific conductivity measurements were conducted. Aging as a possible factor involved in viscosity change was also investigated.

The results and discussion of these studies are outlined in the following sections.

4.2 ORDER-OF-MIXING

The stock solutions used in this study were prepared by mixing the chemicals specified below in the following order:

1) Petroleum sulfonate
2) Lignosulfonate
3) Distilled water
4) Brine solution

Since it must be borne in mind that the order in which chemicals are mixed together may have a profound effect on any subsequent measurements of viscosity, experiments were necessary to ensure that no such effect would occur.

Viscosity is influenced by the interaction of electrical double layers which in turn may be affected by the addition of NaCl to petroleum sulfonate or to a mixture of petroleum sulfonate and lignosulfonate. The interaction of these double layers, upon adding NaCl to petroleum sulfonate could be quite different to that of adding NaCl to a mixture of petroleum sulfonate and lignosulfonate [12]. When only petroleum sulfonate is present, NaCl affects petroleum sulfonates electric double layers. On the other hand, when NaCl is added to a mixture of petroleum sulfonate and lignosulfonate, NaCl interacts with not only petroleum sulfonate electric double layer, but also with lignosulfonate double layer.

Therefore, by changing the order of mixing, any effect may be estimated. The results of one such change in the mixing order are illustrated in Table 4-1. These results are for the system 4% Petrostep-420, 1.5% NaCl, and 1.4% Marasperse C-21.

As evidenced in this table, the experimentally observed order-of-mixing effect on viscosity was found to be insignificant.

Lorenz et al[33] have shown that higher saline concentrations may produce some effect on some of the petroleum sulfonates they used. It was found in their study that in experiments using petroleum sulfonates (Petrostep-420 and Petrostep-465) as the surfactants. The effect on viscosity measurements induced by changing the order-of-mixing were negligible. However, in the present study, sodium chloride

Table 4-1

Effect of Order-of-Mixing on the System

(4% Petrostep-420, 1.5% NaCl, 1.4% C-21)

Order of Mixing	Viscosity after one hour (mPa·s)		Viscosity after 24 hours (mPa·s)	
	12 R.P.M.	30 R.P.M.	12 R.P.M.	30 R.P.M.
Petrostep-420, brine, Marasperse C-21, water	15.85	14.34	20.45	18.64
Marasperse C-21, brine, Petrostep-420, water	15.90	14.88	21.05	18.82
Petrostep-420, Marasperse C-21, brine	15.70	14.62	20.85	18.78

was always added as the last ingredient, to ensure that no effect would be encountered. This same procedure was followed by Cayias et al[34] and by Margeson [12].

After leaving the samples overnight, the same phase behaviour was observed for all the samples and the effect on viscosity was insignificant.

4.3 EFFECT OF SALTS ON THE VISCOSITY OF PETROLEUM SULFONATES

The concentration of the two petroleum sulfonates, either Petrostep-420 or Petrostep-465, was fixed at 4%, with varying concentrations of sodium chloride.

These concentrations were selected on the basis of previous work by Chiwetelu [8].

This procedure was followed in order to observe the effect of salt on the viscosity of the petroleum sulfonates in the absence of lignosulfonate. The viscosity readings are depicted in Figures 4-1 and 4-2.

It should be emphasized at this point that the percent sodium chloride added does not include that sodium chloride which is already contained in the surfactant, as can be seen from Table 3-2.

As may be observed in Figure 4-1 for the system 4% Petrostep-420 at different sodium chloride concentrations, the increase in viscosity is a gradual one with the maximum viscosity value being recorded at 4.9 mPa·s at a stirring speed of 30 R.P.M.. A sharp decrease began above 2.8% NaCl

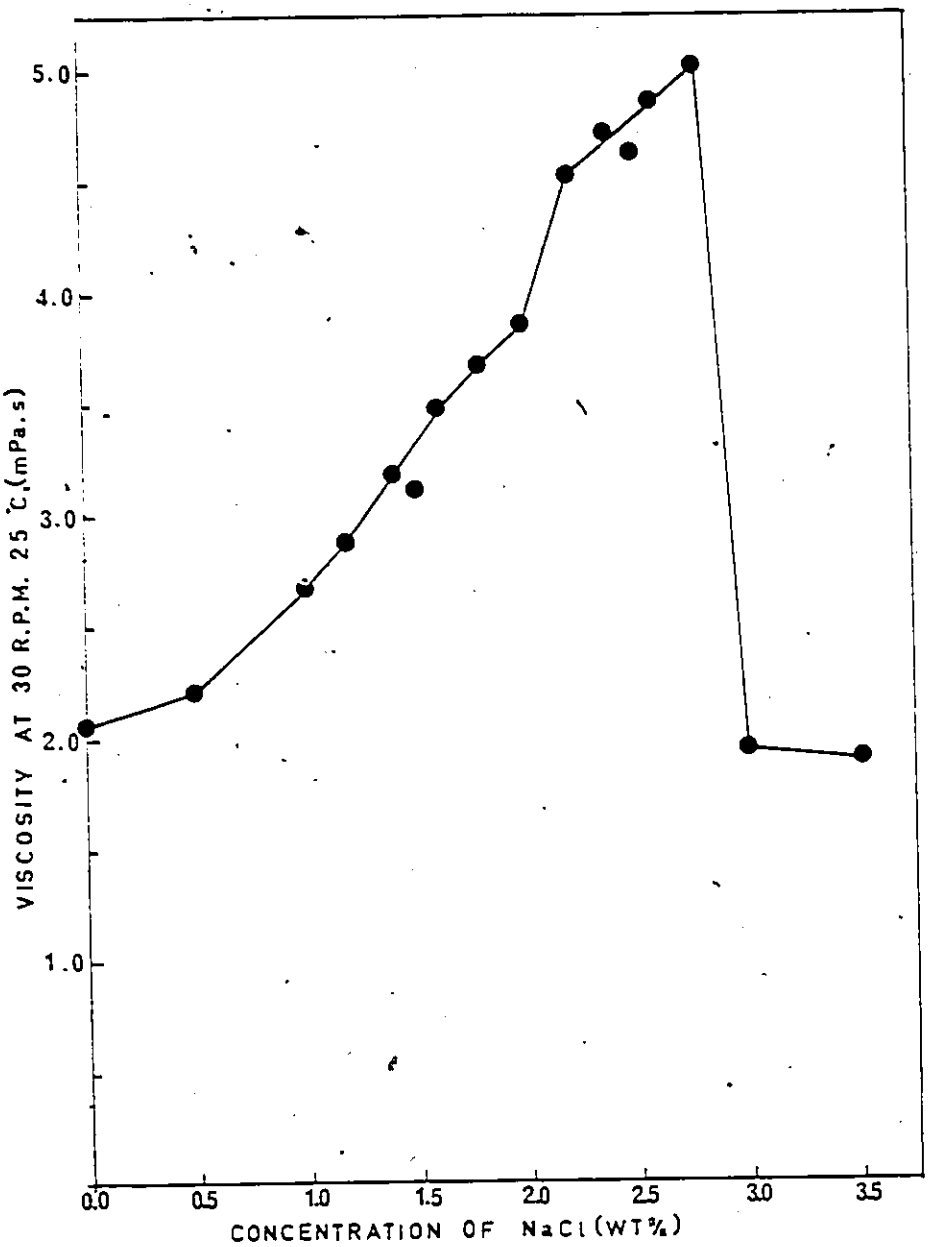

Figure 4-1: Effect of NaCl Concentration on Viscosity of System (4.0% Petrostep-420 + NaCl + 0.06 C-21)

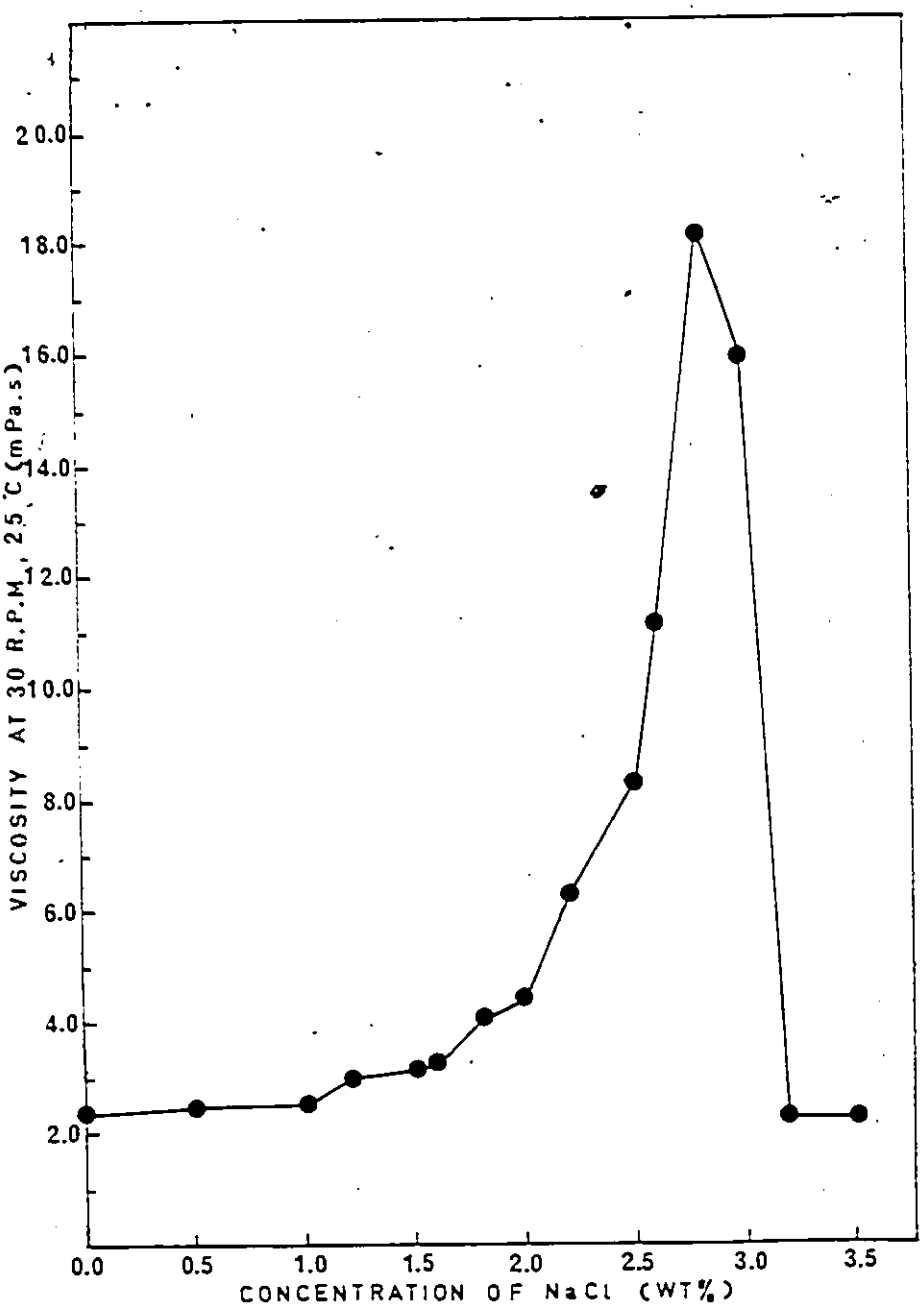

Figure 4-2: Effect of NaCl Concentration on Viscosity of System (4.0% Petrostep-465 + NaCl + 0.0% C-21)

and was recorded at 3.0% NaCl.

Comparing these results with those using Petrostep-465, Figure 4-2 records sharper increase in viscosity with a maximum increase being placed at 18.2 mPa·s at the same rotation speed. This maximum is recorded at sodium chloride concentration of 3.0% compared to 2.8% for Petrostep-420.

It should be noted here that the drop in viscosity is accompanied by the formation of a precipitate which settles to the bottom. The precipitate does not dissolve when shaken, but settles directly to the bottom when shaking has stopped.

The maximum viscosity recorded for Petrostep-465 was approximately 3.5 times greater than that recorded for Petrostep-420. The reason for this is not immediately apparent, but this might be because of the difference in the average molecular weight of the petroleum sulfonates.

The concentration of NaCl at which the breakdown in viscosity occurs is less for Petrostep-420 than Petrostep-465. This may be explained by comparing the properties of the two petroleum sulfonates. Petrostep-420 contains 4.1% organic salts, while Petrostep-465 contains 2.8% organic salts. This could very well be the reason for the difference in the concentration of NaCl at which precipitates were formed in each petroleum sulfonate. Therefore, one may conclude that the difference is accounted for by the Na^+ tolerance for both surfactants.

Vijayan et al[35] attributed the increase in viscosity to the presence of tight micelles. Increasing the concen-

tration of NaCl provides more binding ions which in turn cause the formation of more tightly packed micelle structures. This might be the case for the increase in viscosity as revealed from the present results.

Lorenz et al[33] predicted that the increase in viscosity might be due to the formation of discrete droplets of liquid crystals in a continuous brine phase. At higher concentration the crystalline particles will break, and the formation of precipitate is observed.

Also, a divalent salt ($CaCl_2$) was tried, to determine its effect on the viscosity of petroleum sulfonates. A precipitate was formed at very low concentration. Precipitate started forming after the addition of few drops of $CaCl_2$ solution. This happened with both petroleum sulfonates. Chou and Shah[36] attribute the difference between NaCl and $CaCl_2$ to their effectiveness in reducing the repulsion caused by the electric double layer. Mungan[15] attributed this kind of behaviour to the suppression of the electric double layer to a larger extent by the divalent cation than by the monovalent cation.

Figure 4-1 represents the viscosity readings using the Brookfield viscometer at a rotation speed of 30 R.P.M. In order to compare viscosity readings, these results are also reproduced in Figure 4-3 along with readings taken at 12 R.P.M. and also readings taken using the Cannon-Fenske capillary viscometer. From the graph it is apparent that the results obtained with the Cannon-Fenske viscometer agree qualitatively

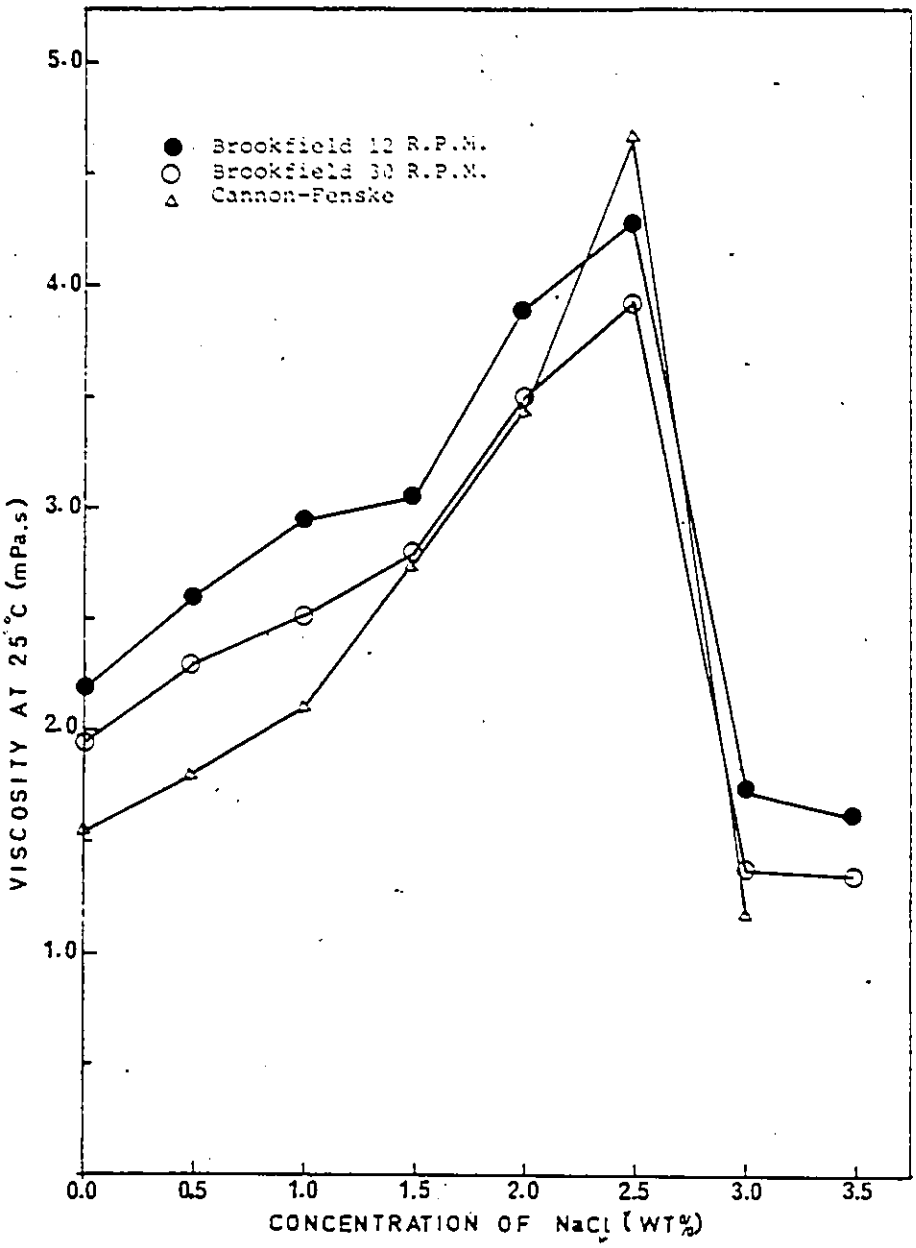

Figure 4-3: Comparison of Viscosity readings using Brookfield Viscometer at 30 and 12 R.P.M. and Cannon-Fenske Viscometer for System (4.0% Petrostep-420 + NaCl + 0.0%C-21)

with those obtained with the Brookfield viscometer, with some slight differences at low concentrations of NaCl. The results obtained at 12 R.P.M. suggest that the petroleum sulfonate solutions are pseudoplastic, the viscosity decreasing with an increase in shear rate.

4.4 PETROLEUM SULFONATES WITH LIGNOSULFONATE MARASPERSE C-21 (0.0% NaCl)

This section will examine the effect on viscosity of lignosulfonate Marasperse C-21 as an additive to petroleum sulfonate without adding sodium chloride. The experiments conducted to study this effect consisted of varying the Marasperse C-21 concentration for fixed Petrostep-420 concentrations. Upon adding the Marasperse C-21 to 4% petroleum sulfonate, the behaviour of the solution was readily observed, subsequent to having equilibrated overnight at an ambient temperature of 23-25°C. It was found that the phase behaviour of the solution is a function of the concentration of lignosulfonate Marasperse C-21.

At low concentration the solution is of a homogeneous, isotropic nature. With an increase in the concentration of Marasperse C-21, the solution becomes birefringent[†] and it is in this region where the sudden increase in viscosity was recorded. At a viscosity just below the maximum viscosity recorded, phase separation occurs. It is worthwhile noting

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[†]This nomenclature for the phase behaviour will be discussed in section 4-11.

that although no oil was added in the preparation of solutions, petroleum sulfonate does in fact contain free oil as is illustrated by Table 3-1. Consequently, we may conclude that the upper phase region is of an emulsion type as referred to by Margeson [12].

In the two-phase region, the upper region is clear and brown in colour registering low viscosity. The lower region on the other hand possesses a much higher viscosity. When the two layers are separated and are mixed with $CaCl_2$, a precipitate was observed to have formed in the lower phase region, while no precipitate was observed in the upper phase region. We may therefore conclude that the lower region was composed of most of the petroleum sulfonate used in the solution, since the addition of $CaCl_2$ to the petroleum sulfonates forms a precipitate as has been stated previously. We will now look at the two petroleum sulfonates separately to compare their respective behaviour.

4.4-1 4% Petrostep-420 & Marasperse C-21 (0.0% NaCl)

As may be seen in Figure 4-4 only a very slight increase in viscosity was obtained upon adding Marasperse C-21 up to a concentration of 1.0 wt% when a build up in viscosity began. With the increase in viscosity a two phase region began to form between 1.5 and 1.8 wt% Marasperse C-21. The maximum viscosity was recorded at 1.8% C-21 with a reading of 14.8 mPa·s. It is at a concentration of 2.0% lignosulfonate that the two phase region is clearly visible, the lower layer less in volume than

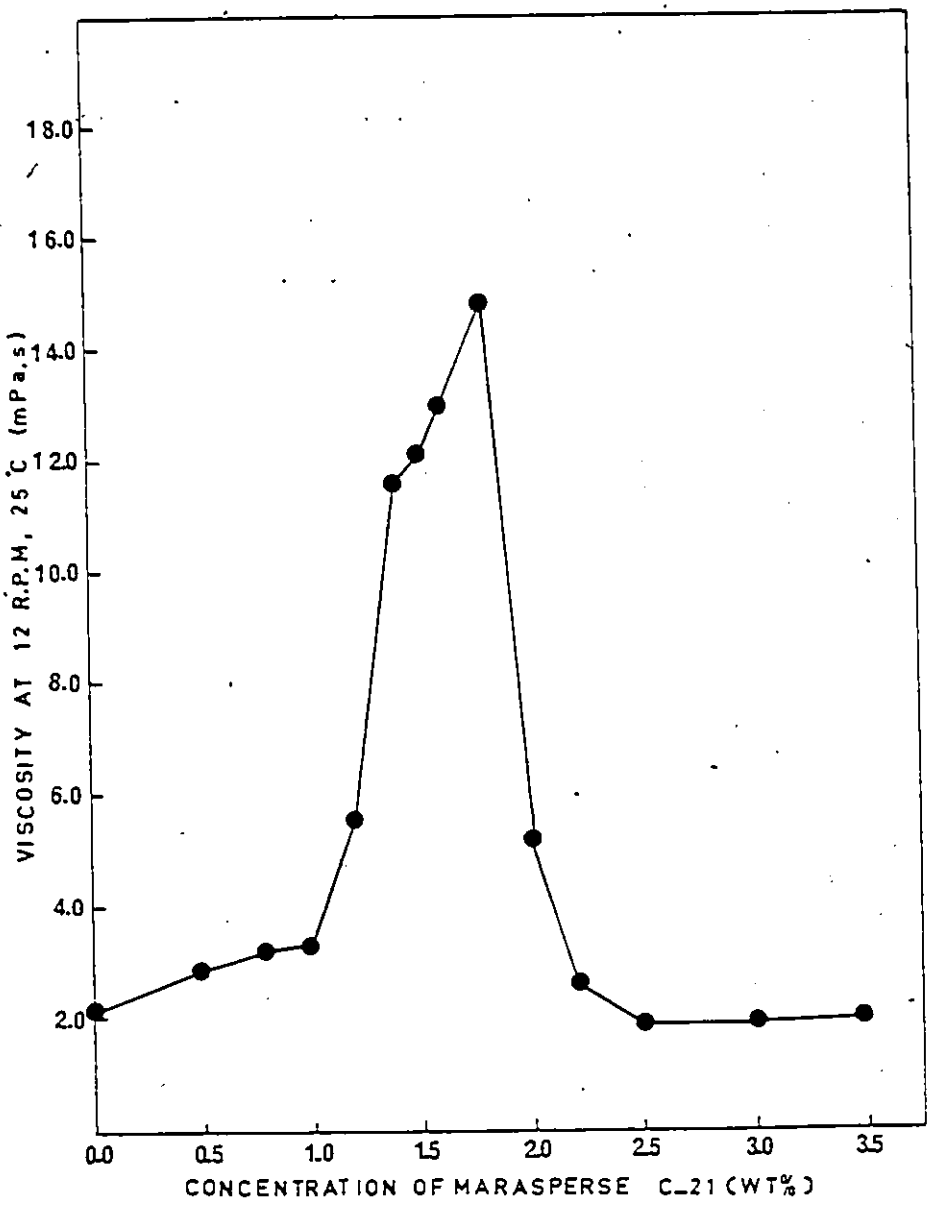


Figure 4-4: Effect of Marasperse C-21 Concentration on Viscosity of System (4.0% Petrostep-420 + C-21 + 0.0% NaCl)

the upper layer with a precipitate settling to the bottom. At 2.2 wt% the lower layer had completely disappeared accompanied with a sharp drop in viscosity.

Comparing this behaviour with that of NaCl alone, the maximum viscosity recorded here is three times greater than with NaCl alone. With NaCl the concentration at which the maximum viscosity was 2.8% NaCl while in this experiment maximum viscosity was recorded at 1.8% Marasperse C-21.

4.4-2 4% Petrostep-465 & Marasperse C-21 (0.0% NaCl)

In similar fashion to Petrostep-420, the viscosity of this system displayed the same behaviour below a concentration of 1.0% Marasperse C-21, as depicted in Figure 4-5 . A dramatic increase was recorded after 1.2% reading maximum of 16.4 mPa·s at 1.4% accompanied by the formation of a two phase region. The lower region began to decrease in volume at 1.5% C-21. As the volume decreased, a black precipitate settled to the bottom until at 1.6% Marasperse C-21 there remained no trace of the lower layer. Also noted was a sudden decrease in viscosity. Comparing this behaviour with that observed for Petrostep-465 with NaCl alone, the maximum viscosity recorded here is similar but the concentration of NaCl at which the maximum viscosity recorded was 3.0% compared to 1.4% Marasperse C-21 (0.0% NaCl).

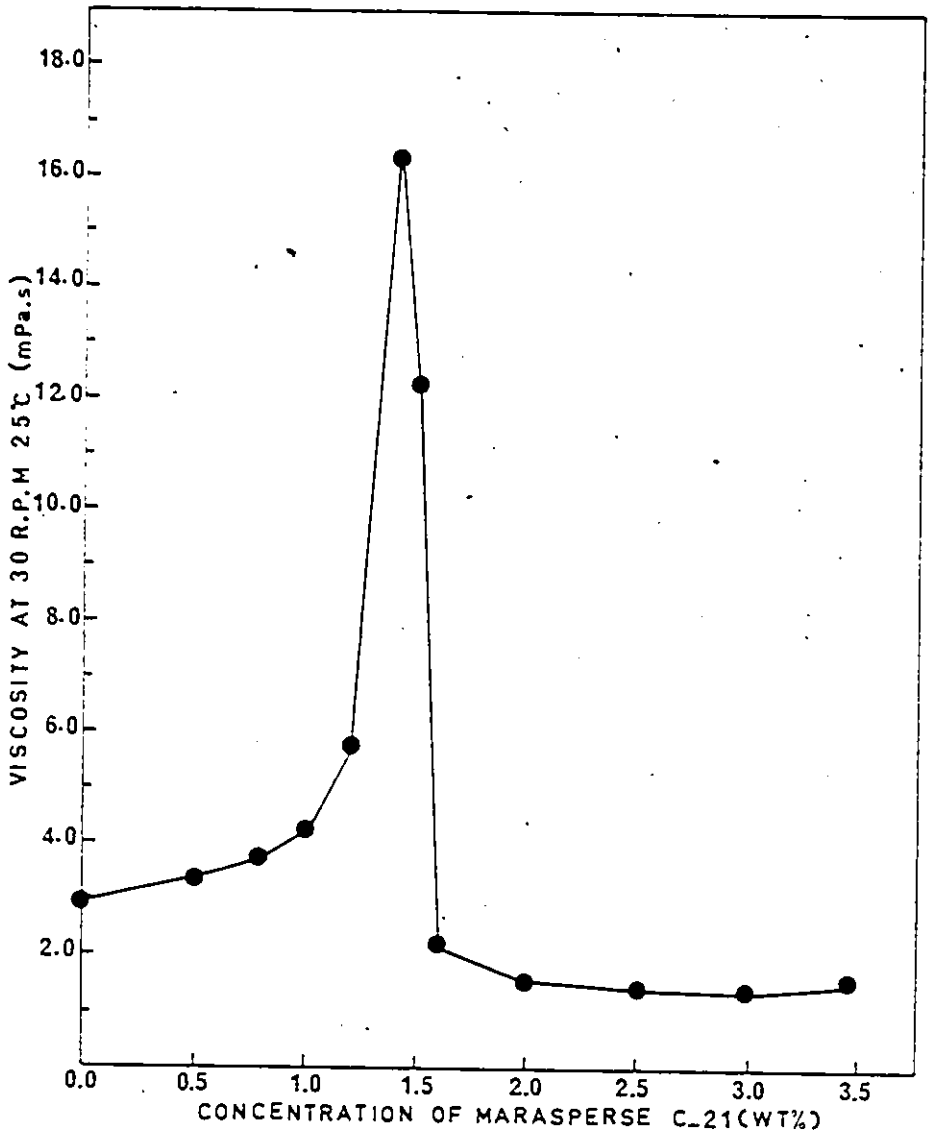


Figure 4-5: Effect of Marasperse C-21 Concentration on Viscosity of System (4.00 Petrostep-465 + C-21 + 0.0% NaCl)

4.4-3 Petrostep-420 and Petrostep-465 Compared

At concentrations of 1.0% Marasperse C-21 or less, both petroleum sulfonates displayed similar behaviour with little increase in viscosity. At higher concentrations of Marasperse C-21 and below the maximum viscosity obtained, they both display a two phase region. The bottom layer gradually dissipates with a corresponding presence of a precipitate until it has completely disappeared. This is accompanied by a decrease in viscosity. The most prevalent contrast to be revealed is the change in viscosity of the two systems, as observed by Figures 4-4 and 4-5.

The results of this study reveals that the viscosity of Petrostep-465 increased dramatically at 1.2% Marasperse C-21 reaching maximum at 1.4%. In contrast to this finding, such a dramatic rise in viscosity was not demonstrated in the case of Petrostep-420 solution. The increase in viscosity was, to be sure, more gradual, the maximum viscosity having been recorded at a higher concentration of Marasperse C-21: 1.8% C-21, to be specific, compared with 1.4% C-21 recorded for the Petrostep-465 system.

The concentration of Marasperse C-21 at which a precipitate was formed using Petrostep-465 is less than that for Petrostep-420, and this may lead to the conclusion that the Ca^{++} tolerance for Petrostep-465 is less than that of Petrostep-420. This is in accordance with the conclusion of Meister et al[37] that Ca^{++} tolerance increases logarithmically with the average equivalent weight of petroleum sulfonate. Also, by comparing

the results, it could be said that the crystalline liquid structure is formed faster with Petrostep-465 and with lesser range of concentration of Marasperse C-21 than for Petrostep-420. This may also be attributed to the difference in the average equivalent weight.

4.5 THE EFFECT OF MARASPERSE C-21 ON VISCOSITY AND PHASE BEHAVIOUR OF PETROLEUM SULFONATES IN THE PRESENCE OF 1.5% NaCl

Having investigated the effect of Marasperse C-21 and sodium chloride individually on the viscosity of Petrostep-420 and Petrostep-465, the attention is now turned to their combined effect. Various system formulations were studied. In each solution the concentration of petroleum sulfonate was fixed, beginning with 4% and descending to 1%. Sodium chloride concentration was fixed at 1.5% with varying concentrations of Marasperse C-21. The viscosity behaviour of the solutions is shown in Figures 4-7 and 4-8, and phase behaviour is depicted in Tables 4-2 and 4-3.

4.5-1 Petrostep-420

Figure 4-6 shows the viscosity of 4% Petrostep-420 against the concentration of Marasperse C-21 with rotation speed as the variable parameter. As may be seen in this graph, the behaviour is pseudoplastic. The behaviour of the viscosity, however, is identical at varying rotation speeds.

The viscosity at a rotation speed of 12 R.P.M. is

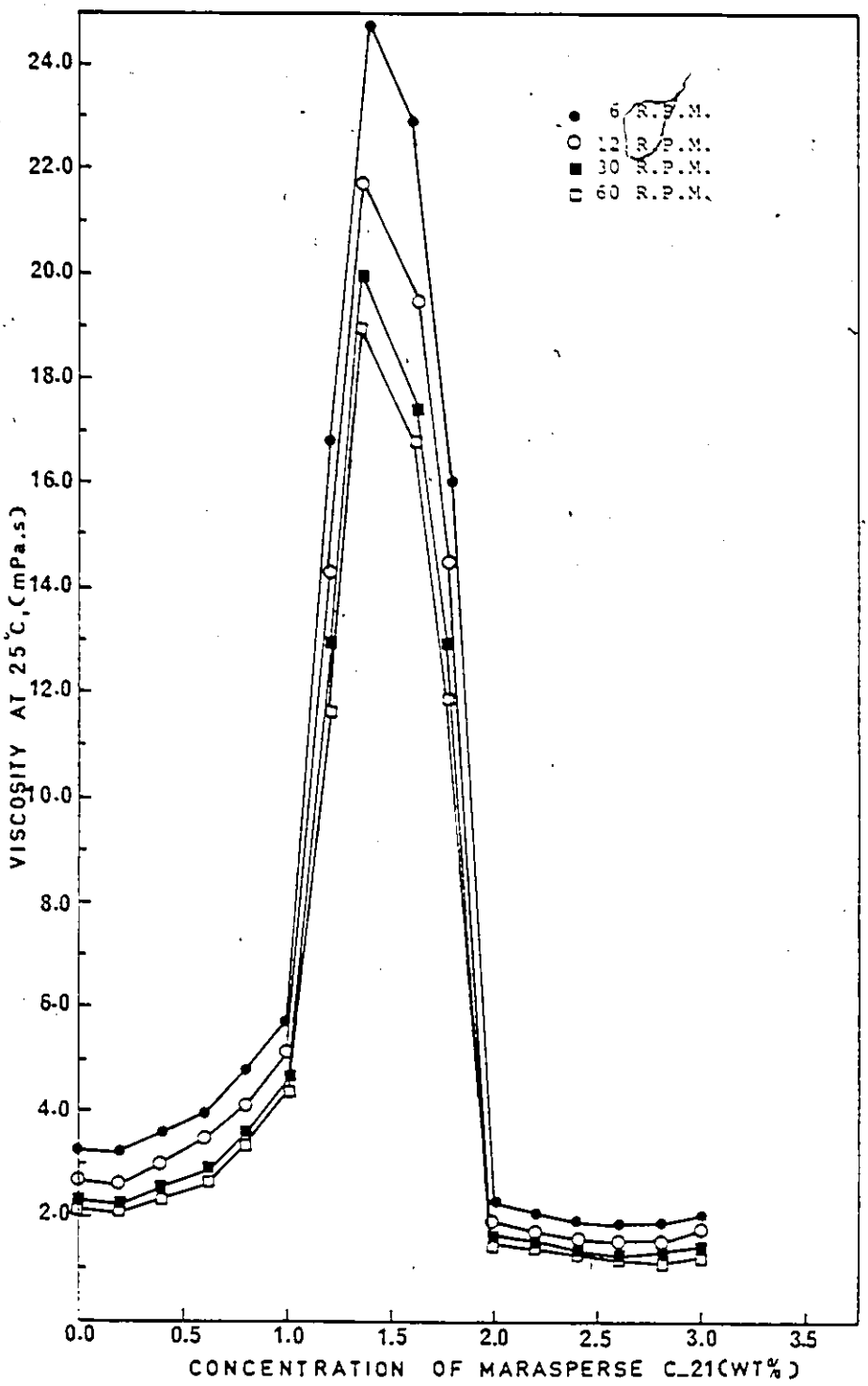


Figure 4-6: Effect of Marasperse C-21 Concentration on Viscosity of System (4.0% Petrosteb-420 + 1.5% NaCl + C-21) Using Brookfield Viscometer at Different Rotation Speeds

Table 4-2

Phase behaviour of surfactant solutions of varied Petrostep-420 concentration and Marasperse C-21 at 1.5% NaCl.

Petrostep-420 %	Marasperse C-21 %	Postulated phase behaviour
4	0 - 1.0	Isotropic
	1 - 1.4	Birefringent
	1.4 - 1.8	Two phases
	2.0 + up	Precipitate
3	0 - 0.8	Isotropic
	0.8 - 1.0	Birefringent
	1 - 1.4	Two phases
	1.6 + up	Precipitate
2	0 - 0.6	Isotropic
	0.6 - 0.9	Birefringent
	0.9 - 1.1	Two phases
	1.2 + up	Precipitate
1	0 - 0.3	Isotropic
	0.3 - 0.5	Birefringent
	0.5 - 0.7	Two phases
	0.7 + up	Precipitate

Table 4-3

Phase behaviour of surfactant solutions at varied Petrostep-465 concentration and Marasperse C-21 at 1.5% NaCl.

Petrostep-465 %	Marasperse C-21 %	Postulated phase behaviour
4.0	0 - 0.6	Isotropic
	0.6 - 0.8	Birefringent
	0.8 - 1.4	Two phases
	1.6 → up	Precipitate
3.0	0 - 0.4	Isotropic
	0.4 - 0.6	Birefringent
	0.6 - 1.2	Two phases
	1.2 → up	Precipitate
2.0	0 - 0.2	Isotropic
	0.2 - 0.4	Birefringent
	0.4 - 1.0	Two phases
	1.0 → up	Precipitate
1.0	0 - 0.2	Isotropic→Birefringent
	0.2 - 0.4	Two phases
	0.4 → up	Precipitate

reproduced in Figure 4-7. From this Figure, it is evident that the dramatic increase in viscosity began at 1.0% concentration of Marasperse C-21 reaching its apex of ≈ 21 mPa·s at 1.4%. Following this, the viscosity began to decrease sharply reading low viscosity at 2% C-21. Therefore, the phase behaviour may be described in the following manner.

At Marsperse C-21 concentrations of 0-1.0 wt%, isotropic micelles appear in the solution, the viscosity showing little increase. Following the isotropic region occurs the birefringent region in which the viscosity rises dramatically at 1.0 wt% concentration Marasperse C-21. The solution undergoes phase separation at the maximum viscosity recorded. With the volume increase of the upper layer region, the viscosity begins to decline until the lower phase region has completely disappeared. The lower phase region gradually begins to decrease in volume, and precipitate forms in its place and settles, as observed in Figure 4-9(a).

This phase behaviour is applicable to all of the systems, as may be seen in Table 4-1. However, in each system, the two phases began forming at lower concentrations of Marasperse C-21 with the decrease in Petrostep-420 concentration. As Table 4-4 indicates, there is no fixed ratio of Petrostep-420 to Marasperse C-21 at which the maximum in viscosity occurs.

The ratios of Petrostep-420 to lignosulfonate is shown in Table 4-4.

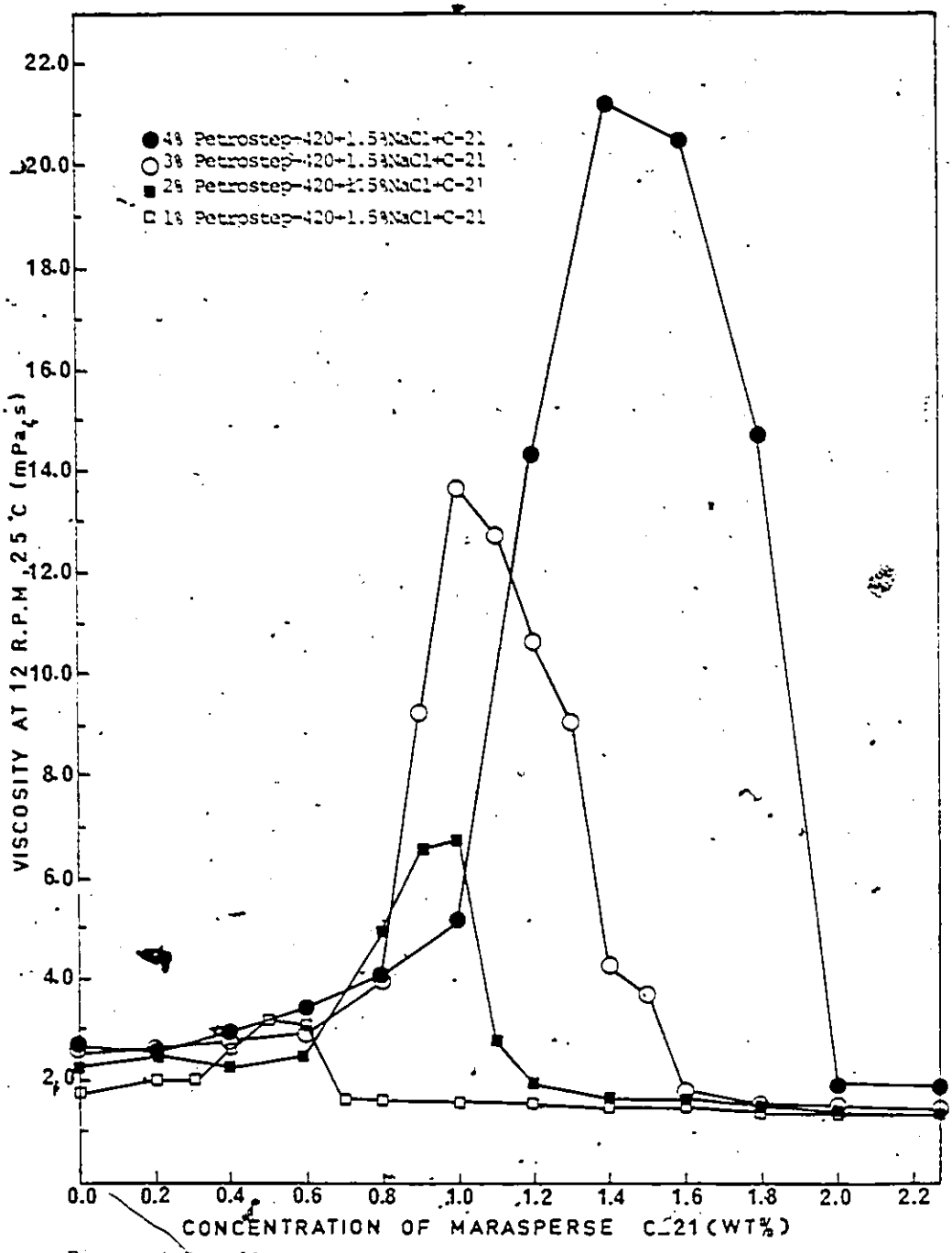


Figure 4-7: Effect of Marasperse C-21 Concentration on Viscosity of the Systems (Petrostep-420+1.5% NaCl + C-21)

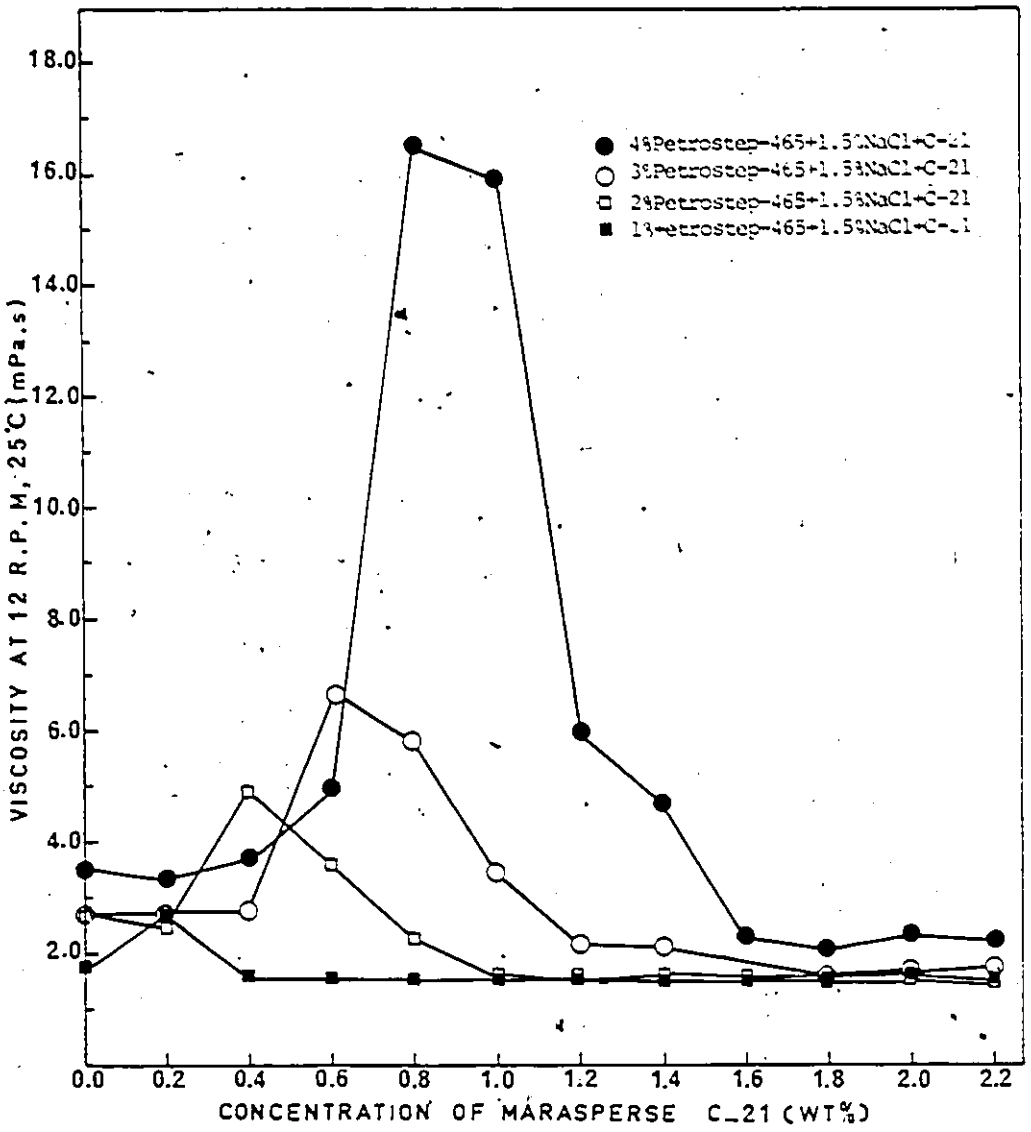


Figure 4-8: Effect of Marsperse C-21 Concentration on Viscosity of the Systems (Petrostep-465+1.5% NaCl + C-21)

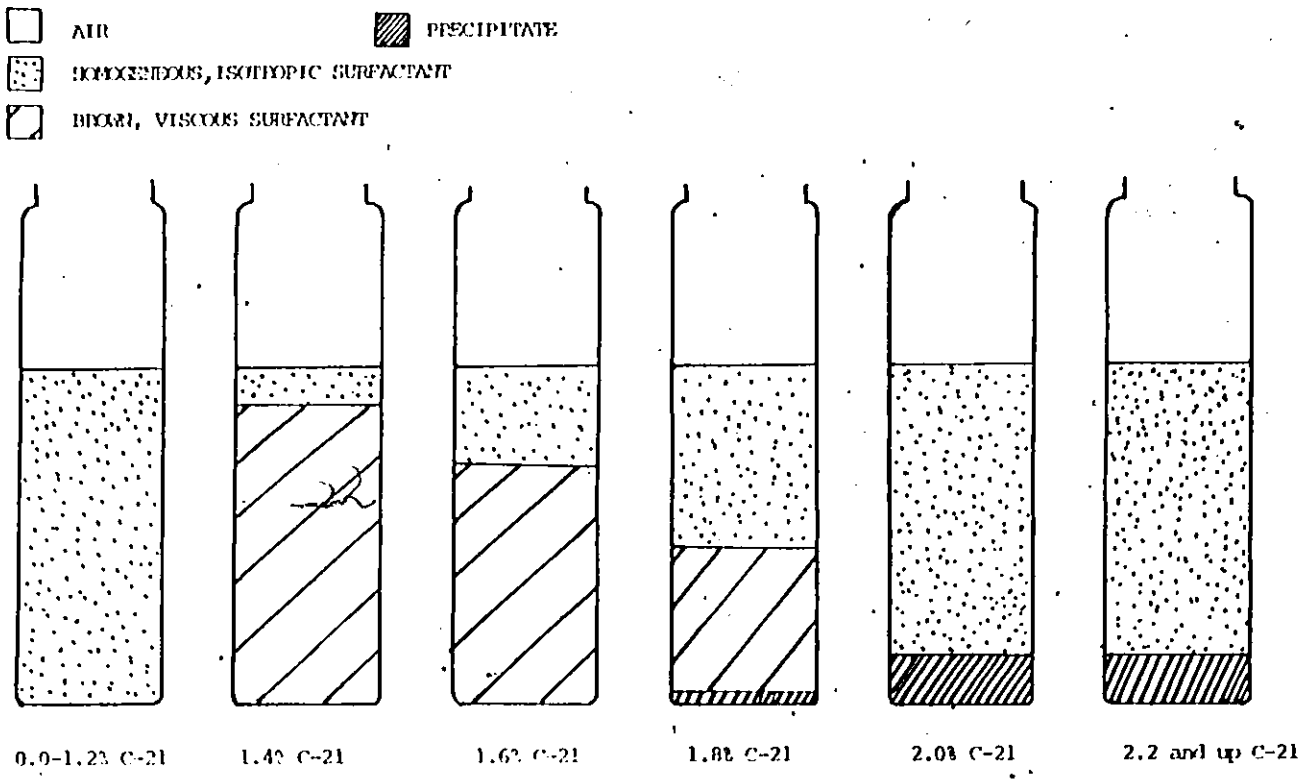


Figure 4-9(a) Representation of Homogeneous Surfactant and Separated Surfactant Solutions

Table 4-4

Petrostep-420/Marasperse C-21 Ratio
for Maximum Viscosity Recorded

Petrostep-420 Concentration %	Maximum Viscosity 12 R.P.M. (mPa·s)	Petrostep-420/ Marasperse C-21
4.0	21.75	4.0/1.4-1.6
3.0	13.65	3.0/1.0
2.0	6.70	2.0/0.8
1.0	3.20	1.0/0.5

From table 4-4, it may be concluded that as the concentration of Petrostep-420 increases, the maximum viscosity is recorded at successively higher concentrations of Marasperse C-21. Also significant is the revelation of increasingly higher maximum viscosities with the increase in Petrostep-420 concentration. This successive increase may be depicted, as shown, in Table 4-4.

The concentration at which precipitate began to form after phase separation is higher in relation to higher concentrations of petroleum sulfonate.

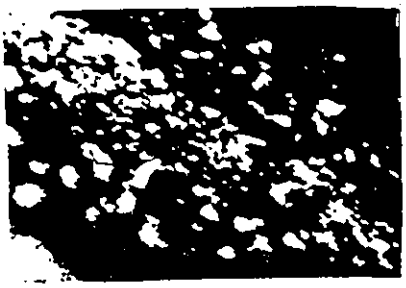
Photomicrographs were taken of the 4% Petrostep-420, Marasperse C-21, 1.5% NaCl; as shown in Figure 4-9(b). However, these microscope photos were not clear enough. Perhaps greater magnification would have produced more revealing photomicrographs.

0.0% C-21

0.4% C-21

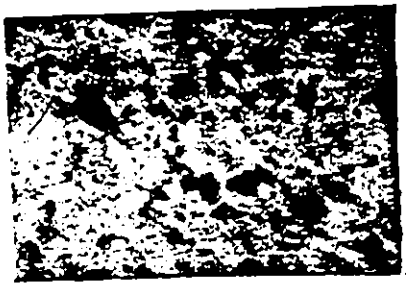
0.8% C-21

1.0% C-21



1.2% C-21

1.4% C-21



1.8% C-21 (Clear layer)

2.0% C-21 (Clear layer)

Figure 4-9(b): Photomicrographs for the System 4% Petrostep-420, 1.5% NaCl, Marasperse C-21 (Magnification 200X)

4.5-2 Petrostep-465

The viscosity readings for solutions containing Petrostep-465 are recorded in Figure 4-8 with phase behaviour indicated in Table 4-3 .

The viscosity of Petrostep-465 exhibits similar behaviour as that of Petrostep-420. The maximum viscosity recorded decreases with the decrease in Petrostep concentration at lower concentration of Marasperse C-21. This behaviour may be described, as shown in Table 4-5.

4.5-3 Comparison of Petrostep-420 and -465

From Figures 4-7 and 4-8, and Tables 4-2 and 4-3, it is apparent that Petrostep-420 and -465 exhibits the same phase behaviour in the following order,

Isotropic → Birefringent → Phase separation → Precipitation

It is also interesting to note that the maximum viscosity obtained increased with the increase in the ratio of petroleum sulfonate to Marasperse C-21. However, the results of this study show that Petrostep-465 produced lower maximum viscosities than for an equal concentration of Petrostep-420 at lower concentration of Marasperse C-21. For example, at 4% Petrostep-420, at a rotation speed of 12 R.P.M. the maximum viscosity ≈ 21 mPa·s at 1.4% Marasperse C-21. On the other hand, at the same concentration of Petrostep-465, the maximum viscosity recorded was much lower, in fact, registering ≈16 mPa·s at 0.8% Marasperse C-21 at the same rotation speed.

These results are depicted in Figures 4-7 and 4-8.

The concentration of C-21 in which a precipitate began to form was less for Petrostep-465 than for Petrostep-420. This may be accounted for by the difference in average equivalent weight which results in different Ca^{++} tolerance. Meister et al[37] discovered that calcium tolerance increases logarithmically with the decrease in the average equivalent weight of petroleum sulfonate.

The observation that Petrostep-465 required a lower concentration of Marsperse C-21 to effect an increase in viscosity may be explained by the lamellar crystalline structure forming faster as the average equivalent weight is increased. Therefore, less Marasperse C-21 could be accommodated in the free spaces of the surfactant. The size of the micelles accounts for the more rapid formation of the two-phase layers.

4.6 SPECIFIC CONDUCTIVITY OF MIXED PETROLEUM SULFONATE–LIGNOSULFONATE SOLUTIONS

To aid in the understanding of the structural changes accompanying the change in viscosity, specific conductivity measurements were taken along with viscosity measurements for various systems of mixed petroleum sulfonate and Marasperse C-21 with and without NaCl. The results of these measurements are depicted in Figures 4-10 and 4-11.

Table 4-5

Petrostep-465/Marasperse C-21 Ratio for Maximum Viscosity Recorded

Petrostep-465 Concentration %	Maximum Viscosity mPa.s (12 R.P.M.)	Petrostep-465/ Marasperse C-21
4	16.6	4.0/0.8
3	6.7	3.0/0.6
2	4.9	2.0/0.4
1	2.75	1.0/0.2

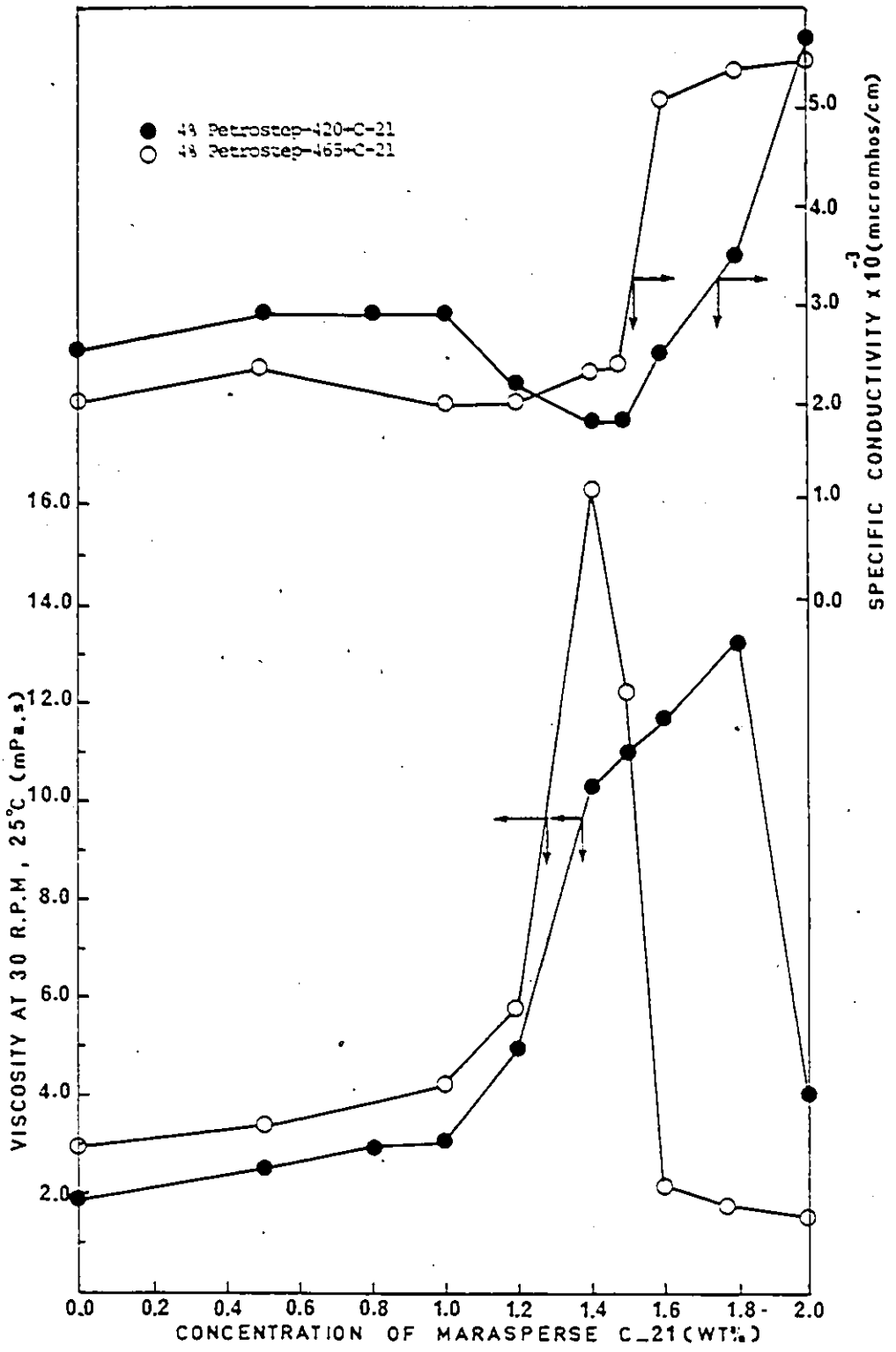


Figure 4-10: Viscosity and Specific Conductivity of Systems

(Petrostep-420 or 465 + Marasperse C-21 + 3.0% NaCl)

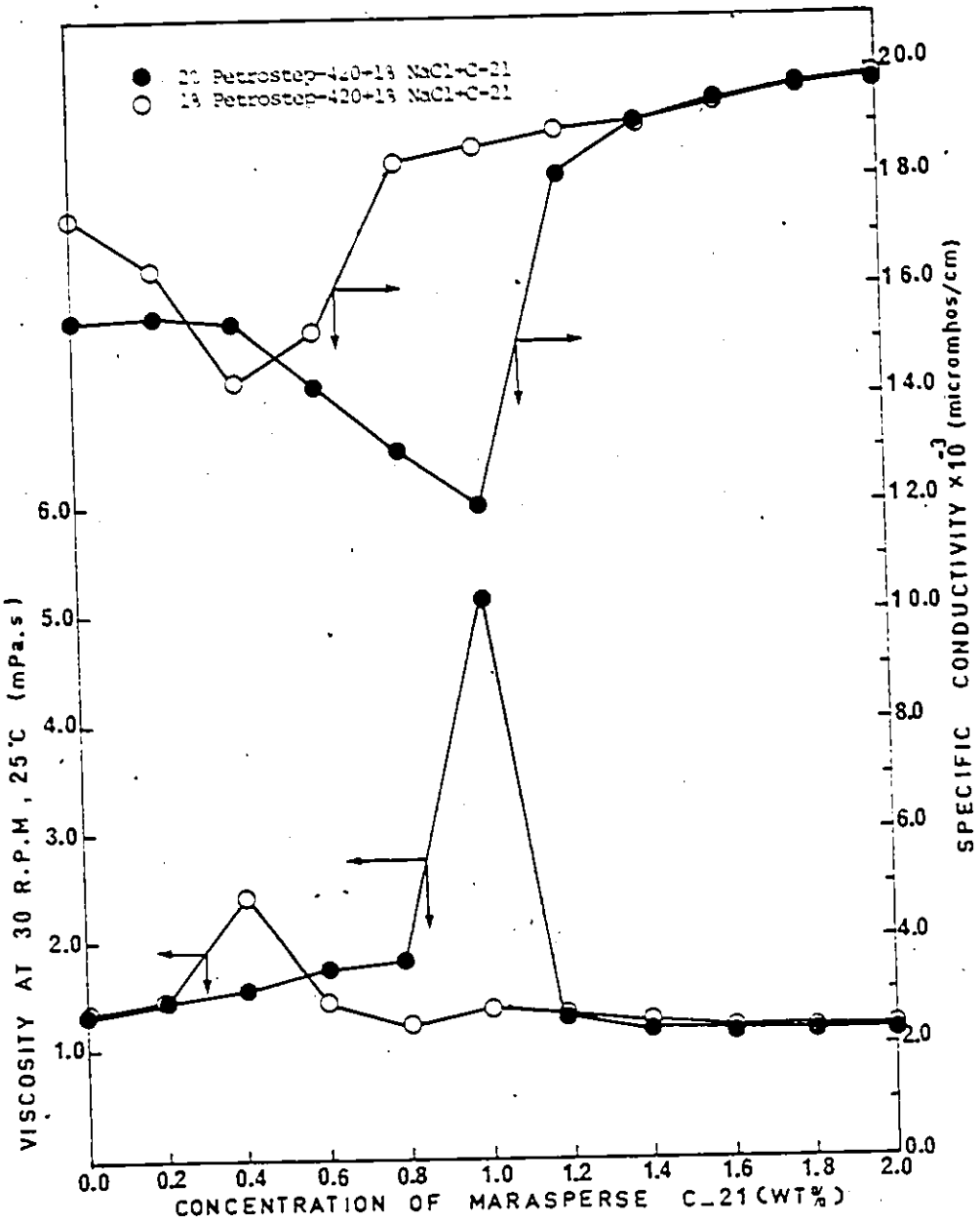


Figure 4-11: Viscosity and Specific Conductivity of Systems (Petrostep-420-1% NaCl+Marasperse C-21)

From these results, it is evident that specific conductivity exhibits little change up to the concentration of Marasperse C-21 where a sudden increase in viscosity is recorded. The specific conductivity began to decrease at this Marasperse C-21 concentration. Below the concentration of Marasperse C-21 where viscosity increases, it may be suggested that there is a loosely packed structure of micelles composed of ionized molecules. With the sudden increase in viscosity, specific conductivity decreases.

It is in this region that it has been suggested that the liquid crystalline structure is formed. The specific conductivity drops, where association of molecules occurs, to form the more tightly packed lamellar crystalline structure. Therefore, there are fewer free changed molecules in the solution. This effect is more clearly demonstrated with Petrostep-420.

At 4% Petrostep-420 without NaCl and 2% Petrostep-420 with NaCl, it may be concluded that along with an abrupt decrease in specific conductivity there is also a change in the structure of the micelles configuration at this concentration of Marasperse C-21.

Accompanying the formation of the two phases, there is an increase in specific conductivity. This finding agrees with the suggestion that with the decrease in the free space of the surfactant crystalline structure, the excess Marasperse C-21 is separated, forming an upper layer, and the surfactant-rich phase settles at the bottom. The upper layer containing the Marasperse C-21 is dissociated because of its poly-

electrolyte character. Hence, there are more charged molecules carrying the current. Above this concentration, with the formation of precipitate, the viscosity decreases and specific conductivity increases. This may be explained by the increase of free ion concentration as the surfactant is precipitated.

The difference in the specific conductivity readings of solutions with or without NaCl is accounted for by the dissociation of NaCl, which is responsible for the high specific conductivity readings.

It is believed that the region of abrupt change in viscosity and specific conductivity is the region of critical micelle concentration (c.m.c.). Vijayan et al[38] defined this as the concentration below which a minute amount of micelles is present. Above this concentration, all additional surfactant is found in the form of additional micelles.

4.7 EFFECT OF SALINITY ON THE VISCOSITY OF MIXED SURFACTANTS

In the results already discussed, the viscosity was measured at 1.5% NaCl. This concentration was fixed throughout all the previous experiments, because the previous researchers[8,9,10,11,12] used this particular salt concentration in their measurements of interfacial tension. To investigate further the effect of salinity on viscosity of these systems. Viscosity is now measured as a function of NaCl concentration in 4% Petrostep-420 and varying concentrations of Marasperse C-21. The results of this procedure

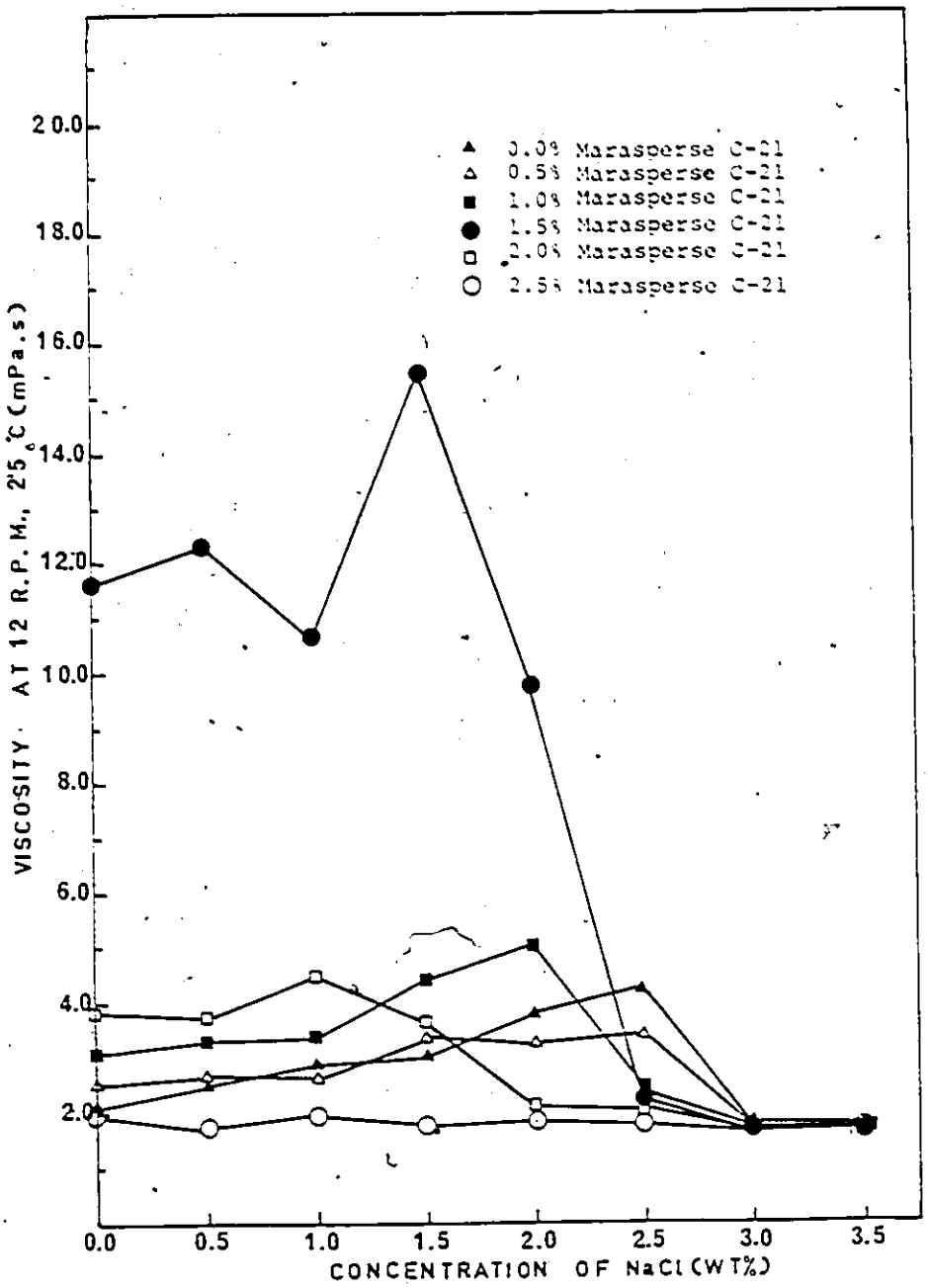


Figure 4-12: Effect of Salinity on Viscosity of Systems

(4% Petrostep-420 + C-21+NaCl)

are depicted in Figure 4-12.

From this Figure, it may be observed that as the concentration of Marasperse C-21 is increased, the viscosity reaches the maximum at decreasing concentration of NaCl. Subsequently, precipitate is formed at decreasing saline concentrations. At 2.5% Marasperse C-21 the viscosity remains relatively unchanged at all the concentrations of NaCl tested, the precipitate forming at a very low concentration of less than 0.5% NaCl.

For concentrations of 2.0% Marasperse C-21 and above, the viscosity is minimal with or without NaCl. With NaCl the precipitate is formed at a low concentration of NaCl. Increase in viscosity occurs at a concentration above 1.0% Marasperse C-21 with 1.5% NaCl as noticed in Figure 4-7. Comparing it with Figure 4-12, it is observed that the maximum in viscosity occurs between 1.5-2.0% NaCl for concentrations of Marasperse C-21 between 1.0-2%. Therefore, the choice of 1.5% NaCl in the previous experiments seems to be justified.

Bae and Patrick[39] reported that the maximum viscosity occurs at a saline concentration where there is a minimum of interfacial tension when they studied a blend of Petrostep-420 and -465.

4.8 OTHER TYPES OF LIGNOSULFONATES

Some other lignosulfonates were tested with NaCl and with both petroleum sulfonate Petrostep-420, -465, and NaCl. These

lignosulfonates are: Marasperse N-22, Lignosol SF, Lignosol X2 U35, Lignosol DP(105), Lignosol ORF #6B, and Lignosol TSF. The results are shown in Figures 4-13 and 4-14.

It is observed that the viscosity of these lignosulfonates with NaCl shows no change, agreeing with the results reported by Bansal et al[25] and Chiwetelu [8]. They attributed this behaviour to the polyelectrolyte character of lignosulfonate.

From Figures 4-13 and 4-14, it is observed that the only other lignosulfonate exhibiting the same behaviour as Marasperse C-21 is Lignosol SF. As could be seen from Table 3-2, the Marasperse C-21 and Lignosol SF are calcium lignosulfonates, Marasperse C-21 being calcium-sodium based and Lignosol SF calcium based. It is also observed that Lignosol SF shows the same phase behaviour as noticed with Marasperse C-21, but with the sudden increase in viscosity observed at lower concentration of Lignosol SF than of Marasperse C-21. This may be attributed to the calcium content of both lignosulfonates. Lignosol SF contains 6.1% calcium, while Marasperse C-21 contains 4.0% calcium.

Therefore, we could conclude that only those lignosulfonates which are either calcium based or calcium-sodium based lignosulfonates show viscosity increase with Petrostep-420, which may be extended to Petrostep-465.

Also, a pure surfactant was tried with Marasperse C-21, namely, sodium alkyl aryl sulfonate which did not show any increase in viscosity, but in the contrary, it decreases at

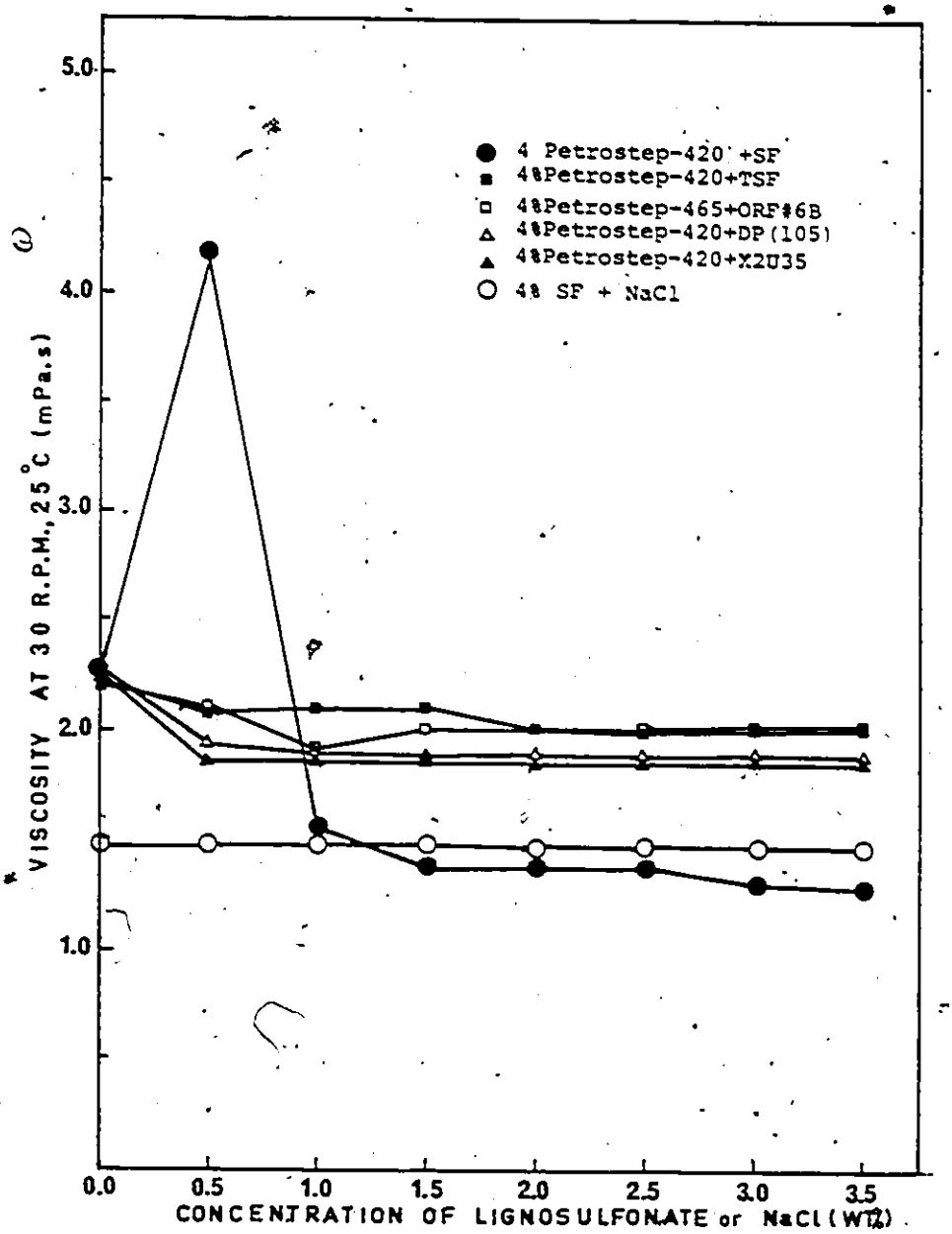


Figure 4-13: Viscosity Plots for Various Systems of Petroleum Sulfonates and Lignosulfonates

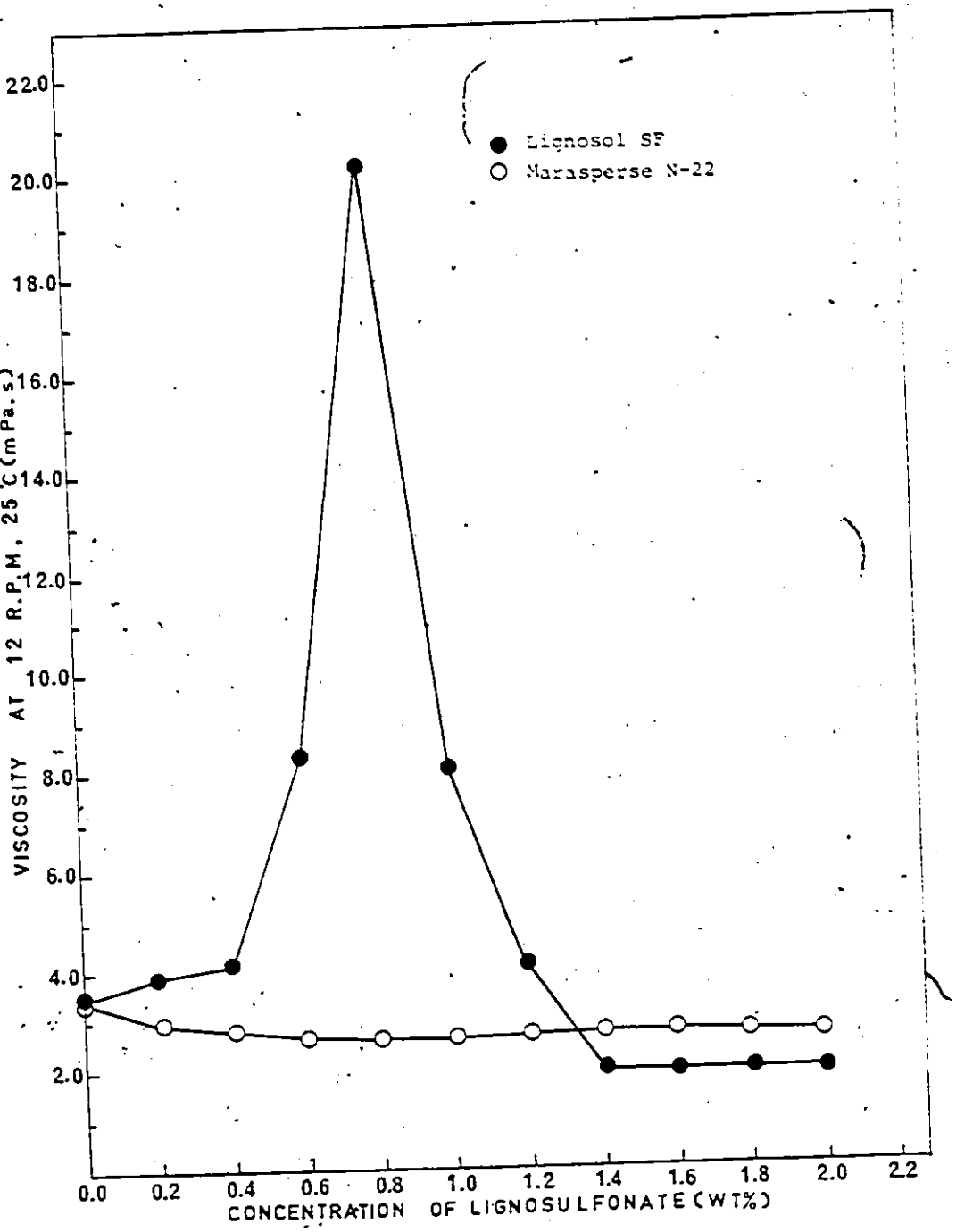


Figure 4-14: Effect of Lignosol SF or Marasperse N-22 on Viscosity of Systems (4% Petrostep-420-1.5% NaCl + SF or N-22)

low concentration of Marasperse C-21 and stabilize after that.

4.9 EFFECT OF TEMPERATURE ON THE VISCOSITY OF MIXED SURFACTANTS

Elevated temperatures in oil reservoirs place some constraints on surfactant systems design for tertiary oil recovery. According to Wilson[24] phase separations can occur for systems which are stable at room temperature, depending on salt concentration, if the temperature is increased.

To examine the effect of temperature on the viscosity of Petrostep-420 and Marasperse C-21 solutions, viscosity measurements for 4% petrostep-420, 1.5% NaCl, and varying concentrations of Marasperse C-21 were taken at increasing temperature up to 85°C, starting at 25°C. At each temperature, the solution was left for 5 minutes to equilibrate, then viscosity readings were recorded.

The results of this experiment are illustrated in Figure 4-15. Phase behaviour could not be observed because of the non-transparent nature of the container used with the Brookfield U.L. Adaptor.

As shown in Figure 4-15, the viscosity decreases with the increase in temperature up to a certain temperature, depending on the concentration of Marasperse C-21, where the viscosity shows an increase, though the reason for this sudden increase is not clear. Falco et al[40] recorded an increase in viscosity with shearing time and attributed it to the disordering and entanglement of the molecules. This may be the

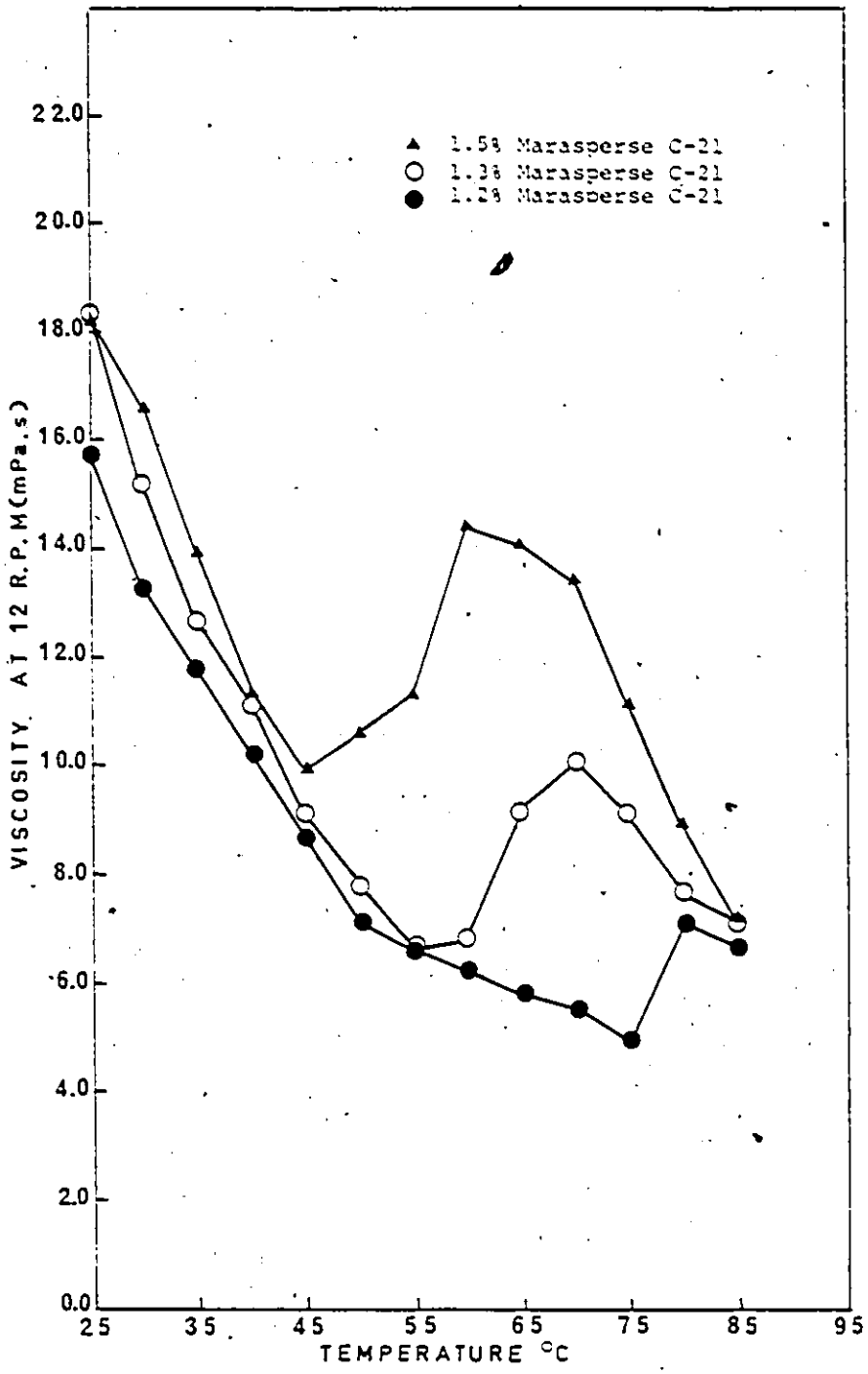


Figure 4-15: Effect of Temperature on Viscosity of

(4% Petrostep-420-1.5% NaCl + C-21)

reason for the sudden increase in viscosity at this temperature.

The results of the viscosity measurements of one system, with increasing and decreasing then increasing the temperature, are shown in Figure 4-16. This Figure indicates that the same behaviour is exhibited upon increasing, decreasing, and again, increasing the temperature. However, at temperatures below 30°C, a sharp increase in viscosity occurs when the solution is cooled. This increase stabilizes after approximately 15 minutes and the viscosity then reaches the value of the original viscosity at which temperature increasing started. From these results it may be concluded that the structural changes are physical in nature rather than chemical.

It is reported in the literature, that the use of some chemicals stabilizes the viscosity upon heating the surfactant solution. For example, Wier[41] patented the use of thiourea as a stabilizer for aqueous solutions' viscosity containing anionic surfactant up to a temperature of 70°C.

4.10 AGING EFFECT

For this experiment, systems of 4% and 3% Petrostep-420, 1.5% NaCl and Marasperse C-21 were prepared, and the viscosity was measured over a period of 10 days. The results of this experiment are depicted in Table 4-6.

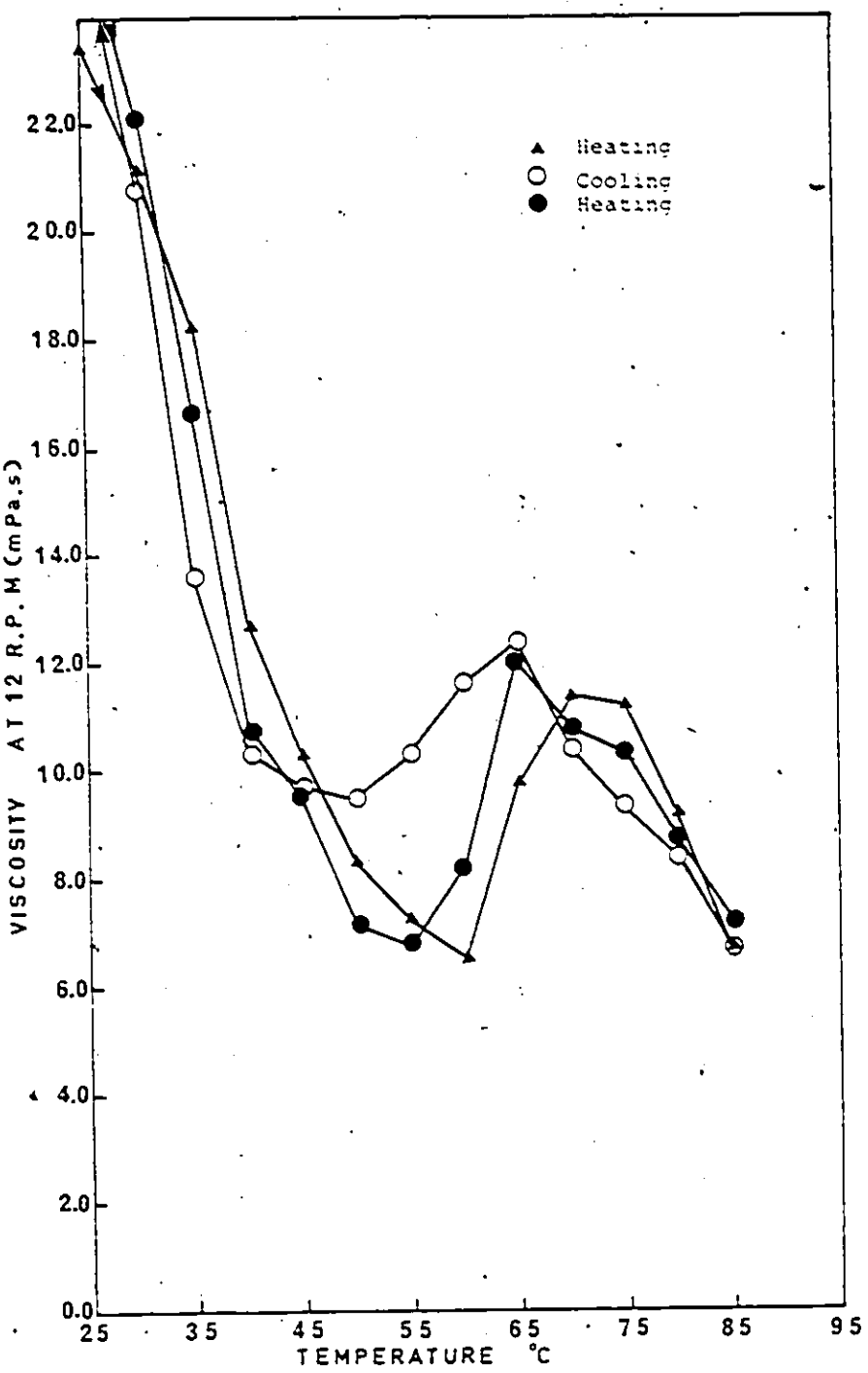


Figure 4-16: Effect of Temperature on Viscosity of System

(4% Protrostep-420-1.5%NaCl+1.4% C-21)

Table 4-6

Aging Effect on the Viscosity of Petroleum Sulfonate-Lignosulfonate Solutions using Brookfield Viscometer at 12 R.P.M.

Sample \ Day	0	1	2	3	4	10
4% Petrostep-420, 1.5% NaCl, 1% C-21	3.50	5.65	9.85	11.80	14.05	17.85
4% Petrostep-420, 1.5% NaCl, 1.4% C-21	13.30	22.05	24.75	22.20	26.15	29.05
4% Petrostep-420, 1.5% NaCl, 1.5% C-21	14.55	19.70	21.60	24.05	25.35	32.80
3% Petrostep-420, 1.5% NaCl, 1% C-21	7.75	13.35	15.05	16.55	16.85	19.40

From this table, it may seem that the viscosity of all of these solutions shows an increase over the 10 day period. It may be concluded that aging the samples of Petroleum sulfonate-lignosulfonate solutions initiate further increase in viscosity.

4.11 SUGGESTED EXPLANATION TO PHASE BEHAVIOUR AND VISCOSITY CHANGES OF MIXED SURFACTANTS

From the results discussed in the preceding sections, the mixed solutions containing Marasperse C-21 with or without sodium chloride (NaCl) and surfactant (Petroleum sulfonate) seem to exhibit a behaviour pattern which may be described in the following.

Isotropic → birefringent → phase separation → precipitation which has also been proposed by Chiwetelu et al[9].

This behaviour is a function of the concentration of Marasperse C-21 being added to the petroleum sulfonate. Those lignosulfonates which contains calcium shows this kind of effect.

At low concentration of Marasperse C-21, the phase behaviour is isotropic with little change in viscosity. Increasing the concentration of Marasperse C-21 cause the solution to become birefringent. Although no measurements for birefringence were conducted, birefringence with the same behaviour in viscosity were documented by Bansal et al[2] and Falco et al[40].

It is in this region that the increase in viscosity and also the decrease in specific conductivity were recorded. With further increases in Marasperse C-21 concentration, a two-phase region appears just below the maximum viscosity recorded. The appearance of the two-phase region is followed by a decrease in lower phase volume as the Marasperse C-21 concentration increases and a small decrease in viscosity.

The volume of the lower region continues to decrease until only a precipitate at bottom of the solution remains as shown in Figure 4-9(a).

The solutions of mixed surfactants are termed micellar solutions for the sake of convenience, since the size distribution of the particles were not measured. Remembering that petroleum sulfonates contain free oil as illustrated in Tabel 3-1, one may speculate that these solutions may be of a microemulsion type. Vijayan et al[42] have stated that those surfactants which contain oil exhibit similar behaviour in the presence or absence of the added oil.

The birefringent region is that region in which lamellar crystalline-liquid is formed [36]. The liquid crystals forming in this region are revealed by the build up of viscosity and the decrease in specific conductivity. Phase separation itself suggests that the region before phase separation is the region of liquid crystals as suggested by Qutubuddin et al[43]. Shah et al [44] proposed that appearance of liquid crystalline structure is accompanied by a sudden increase in viscosity which shows to be true for the solutions studied here. This increase in viscosity was found by Chiwetelu[9,10] to be also accompanied by a corresponding decrease in interfacial tension which according to Frances et al[45] constituted the region of dispersed crystalline liquid.

As mentioned earlier the birefringent region which is liquid crystalline in nature is followed by a phase separation. This produces two phases, a clear upper region, and the lower

more viscous phase which contains most of the surfactant. The same behaviour was found to occur with the addition of oil to the surfactant system [12]. Desai and Shah[46] and Trushenski[47] recorded similar phase behaviour which they attributed to surfactant-polymer incompatibility.

The mechanism for this kind of phase behaviour may be understood if it is taken into consideration that lignosulfonates are polyelectrolytes. In other words, it is a substance consisting a flexible chain molecules with ionizable groups attached [28]. With the increase in the concentration of Marasperse C-21, the lamellar crystalline liquid coagulates which separates due to the size and gravity forming the two phase region.

The higher viscosity readings encountered in the crystalline liquid region are due to the highly packed structure. Even in the two-phase region, the readings are still high. This may be accounted for by the highly packed colloidal structure of the lower phase. In contrast to this the upper layer is more loosely packed resulting in lower viscosity readings. Chou and Shah[36] described the two-phases as a colloid rich liquid phase in the bottom region and colloid-lean liquid phase in the upper region.

Qutubuddin et al[43] propose that the phase separation occurs when micelles are separated from polymer molecules. This and the fact that the upper-phase region contains extra lignosulfonate explain the low viscosity of the upper layer and the increase in specific conductivity. They attribute this

segregation to the decrease in the possible number of conformations in the immediate vicinity of the micellar surface.

Marasperse C-21 is a calcium-sodium based polyelectrolyte, which when added to the surfactant induces an interaction with the electric double layers surrounding the particles. Darby and Mallet[48] proposed that ionization of the polyelectrolyte accompanied by an interaction in the electric-double layers, the charges on the particles being responsible for the increase in viscosity. But with the increase in the concentration of the counter ions, neutralization of the particle charges occurs and hence the viscosity is reduced.

This interaction causes the surfactant anion (RSO_3^-) to equilibrate with Ca^{++} forming $(RSO_3Ca)^+$ [36]. The charged lignosulfonate will be packed in the free space in the lamellar crystals of the surfactant. With the increase in the Marasperse C-21 concentration, the surfactant becomes tightly packed which will break up due to gravity and form the lower layer leaving the extra lignosulfonate in the upper layer.

With more increase in Marasperse C-21 concentration, the micelles become more tightly packed to a point where the structural formation of the surfactant is broken down to form a precipitate. This precipitate is due to limited Ca^{++} tolerance of the petroleum sulfonates[37]. Margeson [12] deduced that at a certain concentration of Marasperse C-21, the formation of a precipitate is due to Ca^{++} tolerance for the petroleum sulfonates.

CHAPTER 5

CONCLUSIONS

The following conclusions may be drawn from this study;

1) The order-of-mixing of the chemicals has no measurable effect on the viscosity of the mixed surfactant solution.
2) Adding sodium chloride to solutions of Petrostep-420 and Petrostep-465 increases the viscosity. This increase rises with increasing NaCl concentration up to a maximum. The viscosity decreases sharply at higher NaCl concentration and is accompanied by the formation of a precipitate.
3) The maximum viscosity of adding NaCl to solutions of Petrostep-420 and Petrostep-465 was found to be ≈ 3.5 times greater for Petrostep-465 than for Petrostep-420.
4) Adding a divalent salt ($CaCl_2$) causes the formation of a precipitate at very low concentrations.
5) Marasperse C-21 alone increases viscosity of Petrostep-420 and Petrostep-465, and initiates a change in phase behaviour. The concentration of Marasperse C-21 at which maximum viscosity is

recorded depends on the type of petroleum sulfonate used.

6) The addition of NaCl or $CaCl_2$ to lignosulfonates does not affect the viscosity or produce any phase change.

7) As the concentration of petroleum sulfonate is increased, increasing concentrations of Marasperse C-21 are required to obtain the maximum viscosity. This **increase in the concentration of petroleum sulfonate and Marasperse C-21 induces higher readings for maximum viscosity.**

8) In the 4% Petrostep-420 system with varying concentration of Marasperse C-21 or NaCl, the increase in viscosity is dependent on the concentration of C-21. As the concentration of C-21 is increased, the maximum viscosity is obtained at decreasing concentrations of NaCl. The formation of precipitate occurs at very low NaCl concentration for solutions of 4% Petrostep-420 and 2.5% Marasperse C-21.

9) The measurements of viscosity and specific conductivity uphold an already proposed mechanism for phase behaviour. This mechanism proposed is stated as follows;

Isotropic → Birefringent → Phase separation → Precipitate

10) Those lignosulfonates which are either calcium or calcium-sodium based, produce a definite

increase in viscosity of petroleum sulfonate solutions.

11) Viscosity decreases with increasing temperature, up to a certain temperature, where a sudden increase in viscosity occurs followed by a decrease.

12) Petroleum sulfonate-lignosulfonate solutions are pseudoplastic.

13) Aging the solutions of petroleum sulfonate-lignosulfonate Marasperse C-21 induces further increase in viscosity from the initial increase induced by the addition of Marasperse C-21 to petroleum sulfonates.

CHAPTER 6

RECOMMENDATIONS

1) A mechanism has been proposed for the phase behaviour of mixed surfactant solutions, but further experimentation on the structural changes accompanying phase behaviour is required. These experiments include birefringcy tests, x-ray diffraction, NMR spectra and microscopic studies at greater magnification.

2) The effect of mixed NaCl and $CaCl_2$ on the viscosity of mixed surfactants could be examined. The effects of other salts such as KCl and $MgCl_2$ would make a revealing study as well.

3) Though it has been concluded in this study that calcium or calcium-sodium based lignosulfonates affect viscosity of petroleum sulfonates, further investigation of lignosulfonates is required.

4) The surfactants used in this study contain free oil and salts. The effect on viscosity of this oil and salt could be studied in a more revealing manner if these surfactants are deoiled and desalted.

5) The effects of adding lignosulfonates to petroleum sulfonates on viscosity have been studied. It has been found that adding some of these lignosulfonates produce an increase in viscosity. In previously conducted

studies, it has been recorded that ultra low interfacial tension accompanies this increase. The efficiency of the surfactant formulations proposed in the region of high viscosity and low interfacial tension, may be best studied in actual field studies.

6) It should be noted that adsoption effect is an important factor in determining the efficiency of surfactant solutions in enhanced oil recovery. In actual field use, adsoption can significantly alter the viscosity of the solutions. Therefore, this effect should be taken into account before injecting the surfactant solutions into an oil reservoir.

NOMENCLATURE

A	cross section area
E	electric Field
F	force
F_R	resistance factor
I	current
K_o	permeability of displaced fluid
k_w	permeability of displacing fluid
k_{ro}	relative permeability of displaced fluid
k_{rw}	relative permeability of displacing fluid
K	cell constant
L	length of pore model
M	mobility ratio
N_c	capillary number
P_1, P_2	pressure at ends of oil capillary
Δp	pressure difference
Q, q	fluid flow rate
R_1, R_2	radii of curvature of ends of oil capillary
S.C.	specific conductivity
V	velocity
γ	interfacial tension
$\dot{\gamma}$	rate of shear
ϕ	porosity
τ	shear stress
λ_o	mobility of displaced fluid
λ_w	mobility of displacing fluid

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Appendix A

Tables of Data

Table A-1

Viscosity Data for 4% Petrostep-420, NaCl at 25°C using Brookfield Viscometer

WT% NaCl	Viscosity (mPa·s) at R.P.M.			
	6	12	30	60
0.0	3.10	2.85	2.04	1.92
0.5	3.20	2.65	2.22	2.08
1.0	3.60	3.20	2.68	2.51
1.2	3.90	3.35	2.88	2.66
1.4	4.40	3.75	3.20	3.00
1.5	4.20	3.55	3.12	3.02
1.6	4.40	3.85	3.48	3.31
1.8	5.1	4.05	3.66	3.44
2.0	5.00	4.30	3.86	3.67
2.2	6.00	4.90	4.52	4.24
2.4	6.10	4.95	4.72	4.28
2.5	6.10	5.00	4.62	4.41
2.6	6.30	5.35	4.86	4.47
2.8	6.60	5.55	5.04	4.78
3.0	3.10	2.55	1.96	1.82
3.50	3.10	2.55	1.88	1.80

Table A-2

Viscosity Data for 4% Petrostep-420, NaCl at 25°C using Brookfield Viscometer

WT% NaCl	Viscosity (mPa s) at R.P.M.			
	6	12	30	60
0.0	3.30	2.70	2.38	2.28
0.5	3.50	2.85	2.48	2.32
1.0	3.60	2.95	2.68	2.51
1.2	3.90	3.25	2.96	2.73
1.5	4.20	3.45	3.10	2.94
1.6	4.60	3.80	3.24	3.07
1.8	5.80	4.80	4.32	3.98
2.0	5.70	4.95	4.46	4.16
2.20	8.50	7.15	6.26	5.88
2.50	10.80	9.35	8.28	7.72
2.6	13.60	12.10	11.34	——
2.8	22.70	20.65	18.26	——
3.0	20.50	18.70	15.98	——
3.2	3.1	2.60	2,24	1.96
3.50	2.90	2.55	2.28	1.94

Table A-3

Viscosity Data for 4% Petrostep-420, NaCl at 25°C
using Brookfield and Cannon-Fenske Viscometers

WT%	Viscosity (mPa·s) using Brookfield Viscometer				Viscosity mPa·s using Cannon-Fenske	
NaCl	6 R.P.M.	12 R.P.M.	30 R.P.M.	60 R.P.M.	1st Trial	2nd Trial
0	2.70	2.20	1.96	1.82	1.5422	1.5370
0.5	3.00	2.60	2.30	2.14	1.7888	1.7876
1.0	3.40	2.95	2.52	2.33	2.1334	2.1020
1.5	3.70	3.10	2.80	2.64	2.7438	2.7063
2.0	4.80	3.90	3.50	3.34	3.4673	3.2896
2.5	5.10	4.30	3.94	3.74	4.7190	4.7220
3.0	2.30	1.75	1.38	1.24	1.1761	1.1609
3.5	2.10	1.60	1.34	1.21		

Table A-4

Viscosity and Specific Conductivity Data for 4% Petrostep-420, Marasperse C-21 at 25°C using Cannon-Fenske Viscometer

WT% C-21	Viscosity (mPa s) at (R.P.M.) 6	12	30	60	SC Micromhos/cm
0.0	2.80	2.15	1.96	1.82	2580
0.5	3.20	2.85	2.46	2.23	2910
0.8	3.70	3.25	2.98	2.72	2920
1.0	3.80	3.30	3.06	2.88	3000
1.2	6.20	5.50	4.98	4.68	2320
1.4	13.20	11.65	10.30	9.94	1800
1.50*	13.60	12.10	11.02	——	1780
1.60	14.90	12.95	11.64	——	2520
1.80	16.40	14.85	13.22	——	3500
2.0	6.80	5.15	4.08	3.84	5700
2.20**	3.30	2.55	2.26	1.96	6000
2.50	2.1	1.85	1.42	1.31	6200
3.0	2.1	1.85	1.44	1.32	6350
3.5	2.30	1.95	1.52	1.36	6380

* Two phase region

** Precipitate

Table A-5

Viscosity and Specific Conductivity for
4% Petrostep-465, Marasperse C-21

WT%	Viscosity (mPa·s) at (R.P.M.)				SC
C-21	6	12	30	60	(mPa·s)
0.0		3.40	2.98		2050
0.5		3.80	3.38		24000
0.8		4.45	3.72		
1.0		4.90	4.22		2000
1.2*		6.95	5.74		2040
1.4		18.80	16.32		2300
1.5		14.65	12.28		2400
1.6		2.70	2.20		5100
1.8		2.20	1.84		5400
2.0		1.95	1.58		5500
2.5		1.85	1.46		5570
3.0		1.75	1.38		5620
3.5		1.80	1.48		———

Table A-6

Viscosity Data for Different Systems of Petrostep-420, 1.5% NaCl, Marasperse C-21 at 25°C

Wt % C-21	4% PETROSTEP-420 Viscosity (mPa·s) at (R.P.M.)				3% PETROSTEP-420 Viscosity (mPa·s) at (R.P.M.)				2% PETROSTEP-420 Viscosity (mPa·s) at (R.P.M.)				1% PETROSTEP-420 Viscosity (mPa·s) at (R.P.M.)			
	6	12	30	60	6	12	30	60	6	12	30	60	6	12	30	60
0.0	3.30	2.70	2.32	2.17	2.90	2.55	2.26	2.09	2.70	2.25	1.82	1.64	2.10	1.70	1.42	1.31
0.2	3.25	2.60	2.24	2.12	3.10	2.65	2.34	2.17	2.90	2.55	2.24	2.01	2.40	1.95	1.52	1.47
0.3	–	–	–	–	–	–	–	–	–	–	–	–	2.50	2.05	1.62	1.41
0.4	3.60	2.95	2.54	2.37	3.40	2.80	2.48	2.27	2.60	2.25	1.96	1.82	3.10	2.60	2.28	2.04
0.5	–	–	–	–	–	–	–	–	–	–	–	–	3.80	3.20	2.76	2.58
0.6	3.95	3.45	2.88	2.62	3.50	2.95	2.58	2.34	2.80	2.50	2.14	1.98	3.70	3.10	2.44	2.30
0.7	–	–	–	–	–	–	–	–	–	–	–	–	2.10	1.70	1.42	1.32
0.8	4.80	4.10	3.56	3.41	4.50	3.95	3.52	3.32	5.90	4.90	4.72	4.56	2.20	1.70	1.40	1.31
0.9	–	–	–	–	10.90	9.25	8.52	8.32	7.70	6.55	5.42	5.18	–	–	–	–
1.0†	5.75	5.15	4.62	4.48	15.10	13.65	12.44	–	8.00	6.70	5.90	5.72	2.10	1.65	1.32	1.20
1.1	–	–	–	–	14.20	12.75	12.08	–	3.30	2.75	2.22	2.08	–	–	–	–
1.2	16.70	14.20	12.96	11.70	11.90	10.60	9.92	–	2.40ƒ	1.95	1.62	1.52	2.00	1.60	1.30	1.18
1.3	–	–	–	–	10.50	9.05	7.76	7.48	–	–	–	–	–	–	–	–
1.4	24.80	21.75	20.02	18.98	5.80	4.25	3.12	2.98	2.20ƒ	1.65	1.40	1.25	2.00	1.60	1.30	1.18
1.5	–	–	–	–	4.30	3.70	3.08	2.84	–	–	–	–	–	–	–	–
1.6	22.90	19.50	17.42	16.81	3.40*	2.85	2.22	2.06	2.20ƒ	1.65	1.38	1.24	2.00	1.55	1.28	1.18
1.7	–	–	–	–	2.30ƒ	1.80	1.46	1.32	–	–	–	–	–	–	–	–
1.8	16.00	14.50	12.94	11.82	3.20	2.55	2.04	1.86	1.90ƒ	1.50	1.34	1.21	1.90	1.55	1.30	1.18
1.9	–	–	–	–	1.90	1.55	1.34	1.21	–	–	–	–	–	–	–	–
2.0	3.10*	2.76	2.44	2.30	2.90	2.35	1.88	1.72	1.90ƒ	1.50	1.34	1.21	2.00	1.60	1.30	1.18
2.1	2.30*	1.95	1.68	1.54	1.90	1.60	1.36	1.24								
2.2	2.10	1.75	1.54	1.42												
2.4	1.95	1.60	1.32	1.22												
2.6	1.90	1.55	1.26	1.18												
2.8	1.90	1.55	1.30	1.24												
3.0	2.05	1.75	1.44	1.34												

* Readings for the shaken solution

ƒ Readings for the upper clear region

† At this concentration and above (for 1% Petrostep-420) a precipitate was formed and viscosity measurements were done for the clear solution

Table A-7

Viscosity Data for 4% Petrostep-420, 1.5% NaCl, Marasperse C-21 at 25 °C using Cannon-Fenske Viscometer

	Density g/cm^3	Kinematic Viscosity	Viscosity mPa·s	Viscometer Reading	Size of Viscometer
0	1.0154	2.9533	2.908	741.3	50
		2.8812*	2.837	723.2	50
0.4	1.0154	3.0199	2.974	215.4	100
		2.9904	2.945	213.3	100
0.8	1.0156	3.4360	3.383	245.1	100
		3.4320	3.379	244.8	100
1	1.0159	4.4462	4.377	317.1	100
		4.3987	4.330	313.7	100
1.2	1.0167	17.233	16.950	469.5	150
		15.159	14.910	413.0	150
		14.892	14.647	405.7	150
1.4	1.0174	12.601	12.385	343.3	150
		11.698	11.498	318.7	150
		10.799	10.614	294.2	150
1.6	1.0177	20.053	19.074	546.3	150
		28.759*	28.259	783.5	150
		32.257	31.696	878.8	150
1.8	1.0181	24.523	24.087	668.1	150
		22.930	22.522	624.7	150
2.0	1.0178	1.0305	1.0124	73.5	100
		1.0305	1.0125	73.4	100

* Left in the oil path for one hour after the first measurement was taken.

Table A-8

Viscosity Data for Different Systems of
Petrostep-465, 1.5% NaCl, Marasperse C-21 at 25°C
Using Brookfield Viscometer

	4% PETROSTEP-420				3% PETROSTEP-420				2% PETROSTEP-420				1% PETROSTEP-420			
Wt % C-21	Viscosity (mPa·s) at (R.P.M.)				Viscosity (mPa·s) at (R.P.M.)				Viscosity (mPa·s) at (R.P.M.)				Viscosity (mPa·s) at (R.P.M.)			
	6	12	30	60	6	12	30	60	6	12	30	60	6	12	30	60
0.0	4.00	3.55	3.18	2.97	3.30	2.70	2.32	2.24	3.10	2.65	2.14	2.01	2.00	1.70	1.52	1.39
0.2	3.90	3.35	3.08	2.89	3.30	2.70	2.38	2.25	2.60	2.40	2.06	1.89	3.40	2.75	2.54	2.41
0.4	4.40	3.75	3.40	3.21	3.40	2.75	2.46	2.31	5.70	4.90	4.10	4.31	1.90	1.55	1.32	1.18
0.6	5.60	4.95	4.12	3.92	7.80	6.70	6.18	5.62	3.80	3.60	3.02	2.61	1.90	1.55	1.32	1.19
0.8	15.70	16.60	14.48	-	6.50	5.85	5.48	5.23	2.70	2.25	1.84	1.62	1.90	1.55	1.32	1.18
1.0	16.40	15.95	14.24	-	4.10	3.45	2.80	2.62	2.10	1.60	1.38	1.21	1.90	1.55	1.32	1.18
1.2	7.10	6.05	5.84	5.61	2.50	2.15	1.68	1.44	2.00	1.55	1.32	1.19	1.90	1.50	1.30	1.15
1.4	5.40	4.75	3.36	3.21	2.50	2.10	1.66	1.45	2.10	1.65	1.34	1.21	1.90	1.50	1.30	1.16
1.6	2.90	2.35	1.84	1.64	3.60	3.05	2.62	2.51	2.00	1.55	1.32	1.20	1.90	1.55	1.32	1.18
1.8	2.80	2.10	1.74	1.48	2.10	1.60	1.34	1.22	2.00	1.60	1.32	1.21	1.90	1.55	1.32	1.18
2.0	3.30	2.35	2.22	2.16	2.10	1.60	1.34	1.21	2.10	1.65	1.34	1.22	1.90	1.55	1.32	1.18
2.2	3.60	2.85	2.66	2.26	2.20	1.75	1.38	1.27	2.00	1.60	1.30	1.21	1.80	1.50	1.30	1.16

Table A-9

Viscosity and Specific Conductivity of Petrostep-420, 1.0% NaCl, Marasperse C-21

2% Petrostep-420 + 1.0% Nacl + C-21			1% Petrostep-420 + 1.0% NaCl + C-21	
C-21 %	Viscosity (mPa.s) at 30 R.P.M.	S.C. Micromhos/cm	Viscosity (mPa.s) at 30 R.P.M.	S.C. Micromhos/cm
0	1.68	15400	1.76	17400
0.2	1.88	15500	1.88	16400
0.4	2.08	15400	2.88	14200
0.6	2.48	14200	1.84	15200
0.8	2.60	13000	1.46	18300
1.0	5.30	12000	1.72	18600
1.2	1.92	18100	1.64	18900
1.4	1.76	19000	1.48	19000
1.6	1.48	19400	1.38	19400
1.8	1.46	19700	1.38	19700
2.0	1.46	19800	1.36	19900

TABLE A-10

Viscosity Data for 4% Petrostep -420, Marasperse C-21, NaCl at 25° C

	4% Petrostep -420 0.0% C-21 + NaCl				4% Petrostep -420 0.5% C-21 + NaCl				4% Petrostep -420 1% C-21 + NaCl			
X WT%	Viscosity mPa.s at				Viscosity mPa.s at				Viscosity mPa.s at			
NaCl	6RPM	12RPM	30RPM	60RPM	6RPM	12RPM	30RPM	60RPM	6RPM	12RPM	30RPM	60RPM
0.0	2.60	2.10	1.86	1.72	3.10	2.50	2.12	2.01	3.70	3.05	2.72	2.56
0.5	2.90	2.50	2.20	2.04	3.20	2.65	2.32	2.18	3.90	3.30	2.98	2.82
1.0	3.30	2.85	2.42	2.23	3.4	2.65	2.30	2.22	3.90	3.35	3.08	2.89
1.5	3.60	3.00	2.70	2.54	3.90	3.35	3.02	2.92	5.30	4.45	4.04	3.86
2.0	4.70	3.80	3.40	3.24	3.80	3.25	2.86	2.65	5.70	5.05	4.76	4.48
2.5	5.10	4.30	3.90	3.74	2.90	3.45	3.08	2.94	2.90	2.45	2.28	2.08
3.0	2.30	1.75	1.38	1.24	2.20	1.85	1.58	1.43	2.0	1.65	1.32	1.22
3.5	2.20	1.70	1.34	1.21	2.10	1.70	1.54	1.40	2.0	1.65	1.32	1.20

TABLE A-10 (Continued)

Viscosity Data for 4% Petrostep -420, Marasperse C-21, NaCl at 25°C

	4% Petrostep -420 0.0% C-21+NaCl				4% Petrostep -420 0.5% C-21+NaCl				4% Petrostep -420 1% C-21+NaCl			
X WT% NaCl	Viscosity mPa.s at				Viscosity mPa.s at				Viscosity mPa.s at			
	6RPM	12RPM	30RPM	60RPM	6RPM	12RPM	30RPM	60RPM	6RPM	12RPM	30RPM	60RPM
0.0	13.4	11.65	10.12	9.96	4.6	3.90	3.44	3.28	2.50	2.05	1.68	1.46
0.5	14.2	12.3	10.62	--	4.2	3.75	3.28	3.16	2.10	1.75	1.42	1.30
1.0	13.40	10.65	9.52	--	5.7	4.5	3.84	3.64	2.40	2.00	1.62	1.46
1.5	17.6	15.5	14.2	--	4.3	3.65	2.98	2.84	2.10	1.85	1.56	1.44
2.0	9.90	9.75	8.10	9.58	2.50	2.15	1.78	1.48	2.20	1.90	1.52	1.34
2.5	2.60	2.20	1.98	1.82	2.40	2.05	1.42	1.26	2.30	1.85	1.40	1.21
3.0	2.10	1.60	1.30	1.18	2.10	1.65	1.32	1.16	2.20	1.70	1.38	1.15
3.5	2.10	1.60	1.28	1.16	2.10	1.65	1.32	1.18	2.10	1.75	1.38	1.14

Table A-11

Viscosity Data for Various Systems of Petroleum Sulfonates and Lignosulfonates

X Wt%	4% PETROSTEP-420 + LIGNOSOL X2 U35		4% PETROSTEP-420 + LIGNOSOL DP(105)		4% PETROSTEP-420+ LIGNOSOL TSF		4% LIGNOSOL SF+ NaCl		4% PETROSTEP-420+ LIGNOSOL ORF #6B		4% PETROSTEP-420+ LIGNOSOL SF	
	VISCOSITY (mPa·s) at (R.P.M.)											
	12	30	12	30	12	30	12	30	12	30	12	30
0.0	2.75	2.14	2.65	2.18	2.70	2.12	1.95	1.48	2.75	2.32	2.75	2.28
0.5	2.55	1.86	2.60	1.98	2.60	2.08	1.95	1.48	2.60	2.20	4.85	4.18
1.0	2.55	1.84	2.55	1.94	2.60	2.08	1.95	1.48	2.50	2.10	1.95	1.56
1.5	2.55	1.84	2.50	1.88	2.60	2.10	1.95	1.48	2.40	1.90	1.65	1.38
2.0	2.55	1.86	2.55	1.88	2.50	2.00	1.95	1.48	2.45	2.02	1.65	1.40
2.5	2.55	1.84	2.60	1.90	2.50	2.00	1.95	1.50	2.45	2.02	1.65	1.38
3.0	2.55	1.84	2.60	1.92	2.50	2.00	1.95	1.48	2.45	2.00	1.60	1.32
3.5	2.55	1.86	2.55	1.90	2.50	2.06	1.95	1.46	2.45	2.04	1.55	1.26

Table A-12

Viscosity Data for 4% Petrostep-420, 1.5% NaCl, Lignosol SF or Marasperse N-22

X WT% SF	4% Petrostep-420 + 1.5% NaCl + SF	
	Viscosity mPa·s at	
	12	30
0	3.50	3.02
0.2	3.90	3.48
0.4	4.10	3.62
0.6	8.30	6.22
0.8	20.20	——
1.0	8.05	6.64
1.2	4.10	3.24
1.4	1.95	1.45
1.6	1.90	1.42
1.8	1.90	1.40
2.0	1.90	1.40

X WT% N-22	4% Petrostep-420 + 1.5% NaCl + N-22	
	Viscosity mPa·s at	
	12	30
0.0	3.35	2.96
0.2	2.95	2.68
0.4	2.80	2.46
0.6	2.60	2.34
0.8	2.60	2.32
1.0	2.60	2.30
1.2	2.65	2.30
1.4	2.70	2.34
1.6	2.65	2.32
1.8	2.65	2.32
2.0	2.65	2.32

Table A-13

Data for the Effect of Temperature on Viscosity of System 4% Petrostep-420 + 1.5% NaCl + Marasperse C-21

Temp. (C°)	Viscosity (mPa·s) at 12 R.P.M.		
	1.2% C-21	1.3% C-21	1.5% C-21
25	15.75	18.35	20.40
30	13.25	15.20	16.60
35	11.75	12.65	13.90
40	10.25	11.10	11.30
45	8.65	9.10	9.95
50	7.10	7.8	10.60
55	6.60	6.60	11.30
60	6.20	6.80	14.40
65	5.80	9.15	14.05
70	5.55	10.10	13.40
75	4.95	9.10	11.10
80	7.1	7.65	8.85
85	6.70	7.15	7.10

Table A-14

Data for the Effect of Heating Cooling then Heating on Viscosity of the System 4% Petrostep-420 + 1.5% NaCl + 1.4% Marasperse C-21 Viscosity (mPa·s) at 12 R.P.M.

Temp. °C	Heating	Cooling	Heating
25	23.65	26.7	26.7
30	21.15	20.80	22.15
35	18.20	13.60	15.70
40	12.70	10.35	10.80
45	10.30	9.70	8.60
50	8.30	9.50	7.15
55	7.25	10.30	6.80
60	6.5	11.6	8.20
65	9.8	12.40	12.10
70	11.40	10.40	10.80
75	11.2	9.35	10.40
80	9.2	8.4	8.80
85	6.7	6.70	7.28