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NL-339 (3/77)

DEVELOPMENT AND EVALUATION OF LIGNOSULFONATE-BASED SURFACTANT SYSTEMS FOR EOR OPERATIONS

by

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

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ABSTRACT

This study constituted an extension of the work initiated in this laboratory on the use of lignosulfonates in Enhanced Oil Recovery operations (EOR). The primary objective of this work was two-fold; (i) to find suitable additives and surfactants which, when mixed with lignosulfonates, would considerably reduce the oil-water interfacial tension (IFT), and (ii) to evaluate these formulations in laboratory displacement tests.

Our procedure for developing the desired surfactant systems involved a sequence of strategies wherein conclusions arrived at in the early stages served as the basis for subsequent studies. Firstly, the type and optimum working concentration of the lignosulfonate for a given crude oil was determined. Then, using this optimum concentration, various organic and inorganic reagents were introduced in the search for formulations that have reasonably good interfacial activity. Besides the IFT obtained with the given oil, each formulation was characterized by several physical parameters such as surface tension, pH, density and viscosity.

IFT values lower than 1.0 dyne per centimeter were obtained by the addition of caustic soda into lignosulfonate solutions. However, at soda concentrations less than 1.0%, blank solutions produced lower IFT than in the presence of lignosulfonate. A mechanism has been proposed to explain this trend. Butanol-1, in the concentration range 1-10% by volume, was the most effective of all the various organic reagents tested. Following the procedure outlined, a formulation consisting of 6% C-21, 2% Nacl and 1.0% Butanol-1 achieved an IFT down to 1.44 dyne per centimeter. This system yielded about 78% tertiary oil recovery in the displacement test.

The most important discovery arising from this study was the doubly-beneficial effect of mixing lignosulfonates with petroleum sulfonates. A limiting concentration ratio for the mutual compatibility of the two surfactants has been identified. Within the limit of mutual tolerance, as much as a further 100% IFT reduction over that obtained with Petrostep alone, has been observed. In addition the viscosity of these mixed surfactant systems increased by up to 400% of the viscosities of ordinary Petrostep solutions. However, beyond this critical concentration ratio the two surfactants became incompatible, multiple phases appeared and the system viscosity was drastically reduced. The high oil recoveries obtained in the displacement floods with these mixed surfactant systems confirmed the favorable trends observed in the development studies. As was also noted in the development studies, those unstable mixed surfactant formulations yielded much less tertiary oil. A thorough structural characterisation is needed to gain further insight into these complex mixed surfactant systems. In the meantime, a tentative mechanism has been proposed to explain our observations.

ACKNOWLEDGEMENT

My immense thanks are duly extended to my two supervisors - Drs. G.H. Neale and V. Hornof for their invaluable assistance and guidance. They saw to the prompt procurement of the various materials and equipment and meticulously guided every aspect of the work including the preparation of this report.

Mr. G. Gasperetti and his able technical team fabricated the displacement apparatus and promptly attended to all operational problems. Their assistance as well as the goodwill and encouragement of the professors, administrative personnel and fellow students are duly acknowledged. Finally, the author wishes to thank

(i) the proprietors of the Chatham Oil Field for the generous supply of their crude oil

(ii) Energy Research Laboratories of Energy, Mines and Resources (EMR) for the analysis of the Chatham crude and for providing us with the other crudes used in this study.

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PART I

LITERATURE REVIEW

CHAPTER 1

BRIEF OUTLINE OF LIGNIN CHEMISTRY

Since very little work has been reported in the literature on the physico-chemical properties of lignosulfonates, it was necessary to review what is known about the source material, lignin, itself. Although a lot of work has been performed, a considerable uncertainty exists as to the exact structures and mechanisms of reaction of various lignins. Excellent treatises on lignin chemistry are presented by Brauns(17) and Hagglund.(16)

Lignin has been defined as that incrustating material of a plant which is built up of phenyl-propane building blocks and which carries the major part of the methoxyl content of wood. It constitutes about 30% of the plant's wood with 75% of it associated with the middle lamella and the rest in the outer layers of cell walls. Its main duty is to cement and anchor the cellulose fibres.

Lignin is a polymer with a molecular weight of the order of 3000 to 100,000. The molecular weight varies with wood type, method of lignin isolation and method of measurement. The building block generally has a molecular weight in the range of 840 to 880. A typical elementary analysis is as follows: Carbon- 61 to 65%, Hydrogen- 5 to 6.5%, the remainder being oxygen. It is now generally accepted that the lignin building block consists of a di- or tri-hydroxy benzene molecule partially or completely etherified with a side chain of about three C atoms. Whereas other hydroxy, carbonyl or even double bonds can occur in the side chain, it is generally believed that no such carbonyl or double bonds occur in conjugation with the benzene ring. Lignin and its derivatives can be hydrogenated, oxidised, sulfonated, acylated, and hydrolysed.

1.1 Some physical properties of Lignins

(a) Solubility

Native lignin (protolignin) at ordinary temperatures is insoluble in both organic and inorganic solvents. However, with vigorous treatment, it dissolves accompanied by some structural modifications such as degradation, condensation, hydrolysis or repolymerisation. Depending on the reagent used, various isolated lignins are obtained such as (i) with mineral acids-Klason (acid) lignins, (ii) with alcohols or phenols-alcohol or phenol lignins, (iii) with Cupro-ammonium hydroxide-Cuoxam lignins. Brauns(17) presents an excellent discussion of these isolated lignins.

(b) Viscosity and Density

Lignin solutions in the various solvents mentioned above have low specific viscosities. This indicates a lower degree of polymerisation than in cellulose. The densities of such solutions are equally low.

(c) Colloidal Nature

Lignin dispersions in aqueous or organic solvents are colloidal in nature. This probably explains the Freundlich-type adsorption of dyestuffs, bases and alkalis. The adsorption capacity of Cuoxam spruce lignin for various solvents is in the order benzene < water < ether < methanol < acetone.

(d) X-ray and Ultra Violet (uv) Absorption Spectra

The elucidation of the complex structure of lignin has been facilitated by X-ray and uv absorption studies. By comparing the uv and X-ray spectra of lignins with those of aromatics of known structure, most of what is now known of the structure of lignin has been determined.

1.2 Oxidation of Lignins

Lignins, ordinary and isolated, as well as derivatives such as ligninsulfonates are easily oxidised by many oxidising agents including oxygen, ozone, hydrogen peroxide and nitrobenzene in neutral, acid or alkaline media. Under careful oxidation, characteristic oxidation products are obtained and these have proved useful in the elucidation of the lignin structure. Oxidation in acid media usually results in demethoxylation with the formation of acids such as Carbonic, acetic and formic acids, also oxalic, luvulinic acids as well as various aldehydic substances. Alkaline media oxidation of ligninsulfonates and ordinary lignins with nitrobenzene results in the formation of vanillin as the principal product.

1.3 Sulfonation of Lignin

Ligninsulfonates are obtained when lignin is treated with a solution of calcium bisulfite and sulfur dioxide at elevated pressures and temperatures. A detailed discussion of this process is presented by Brauns,(17) Wenzel(15) and Kirk-Othmer.(13) The sulfonic acid groups are thought to replace hydroxyl groups in the α - position of the benzene nucleus or to enter the side chain through non-isolated double bonds or carbonyl groups. The sulfite spent liquor resulting from this digestion contains 15 to 18% solids analysed as follows:

TABLE 1

ANALYSIS OF SULFITE LIQUOR

COMPONENT	COMPOSITION
Ligninsulfonates	50-65%
Wood sugars (hexose and pentose)	15-22%
Sulfonic acids and residue	12%
Resins and extractives	0-3%
Ash	<10%

The degree of sulfonation depends on the severity of the digestion and varies from a minimum of 3.5% to a maximum of 12.5%.

1.4 Alkaline Hydrolysis of Lignin - Production and Properties of Alkali Lignins

Alkali lignins include sulfate(Kraft) and soda lignins. The former is obtained when wood is digested with a mixture of caustic soda and sodium sulfide, while the latter features caustic soda alone. The primary product of this reaction is sodium lignate (Black liquor). The black liquor is first concentrated to about 25 to 30% solids and then saturated counter-currently with combustion gases (principally Carbon dioxide) to reduce the pH from about 12 to 10. A precipitation of the lignate occurs and after treatment with sulfuric acid, the alkali lignin is obtained. These are marketed under various trade names such as Indulin, Meadol and Tomlinite.

The molecular weight of Kraft lignins is of the order of 1050 to 1600 (12) which is much lower than that of sulfite or native lignins. However the basic unit is the same as in ordinary lignins and the elementary composition is quite similar. Alkali lignins, though insoluble in water and most organic solvents, easily dissolve in alkaline media and can be sulfonated and hydrogenated like other lignins.

Lignins in general are used as fillers, extenders, dispersants and lubricants. The American Can Company (19,20) has listed a number of possible uses of their Marasperse (lignosulfonates) products. However, less than 10% of the millions of tonnes of lignin derivatives produced annually from pulp and paper mills are presently being utilised, the bulk of the material being discharged into nearby streams.

CHAPTER 2

PHYSICO-CHEMICAL PROPERTIES OF LIGNOSULFONATES

2.1 Production and Properties

When sulfite spent liquor is treated with lime, calcium lignosulfonates precipitate out. If calcium lignosulfonate is treated with sulfuric acid, ligninsulfonic acid is obtained. The latter can then be converted into sulfonates of sodium, magnesium or ammonia by appropriate treatment with hydroxides of these metals.

Bansal(1) has tabulated the major physical properties of lignosulfonates. More extensive details can be found in American Can Company bulletins.(19,20) Their very high solubility in water and little or none in organic solvents explains their limited surfactant ability.(1) Gardon and Mason(14) used dialysis and ultrafiltration to fractionate lignosulfonates into various molecular weight fractions. They measured the diffusion coefficient, viscosity, conductivity and also performed methoxyl, sulfur, phenolic hydroxyl analyses. The average molecular weight obtained was in the range of 3500 to 100,000. These authors studied also the polyelectrolytic behaviour of lignosulfonates. They concluded that these substances are highly polydisperse and possess gel-like structure with linear chains cross-linked to give an approximately spherical structure. They also attributed the interfacial activity of lignosulfonates to the orientation of the molecules adsorbed at the interface in a lipophilic-hydrophilic manner.

Keirstead(12) observed that the surface tension of aqueous solutions of lignosulfonates decreases with concentration and also with the lowering of pH (at any given concentration). Gardon and Mason(14) have explained the low specific conductivity and reduced viscosity of lignosulfonate solutions in terms of their polyelectrolytic behaviour.

2.2 Applicability of Lignosulfonates as Enhanced Oil Recovery Surfactants

The two most notable properties of lignosulfonates limiting their use as oil recovery surfactants are: (i) the poor amphiphilicity, and (ii) the very high molecular weights. As a result of these drawbacks micelle formation of lignosulfonate aggregates is almost ruled out. Conversely, the highly favored petroleum sulfonates easily form micellar aggregates. This characteristic coupled with their good amphiphilicity enables them to solubilize both oil and water in various microemulsion formulations. However, in recognition of their surfactant properties and most importantly their relative cheapness and abundance, various patents(22,24) have been issued proposing the use of lignosulfonates in oil recovery operations. Bansal(1) has discussed in depth these patents. Felber and Dauben(35) proposed the use of lignosulfonate gels for sweep improvement of reservoirs containing loose streaks or severe fractures. Also an increasing amount of lignosulfonates is now being used in formulating water and emulsion-based drilling muds. The present work has been undertaken in an effort to increase the scope and effectiveness of lignosulfonates as enhanced oil recovery surfactants.

CHAPTER 3

ENHANCED OIL RECOVERY 1 : SECONDARY RECOVERY OPERATIONS

3.1 Distinction between Primary, Secondary and Tertiary Recovery Processes

Crude oils are thought to be formed by the thermal conversion of organic materials deposited in marine sediments that were subsequently buried in the earth's crust. The resulting organic liquids float upwards through the water-saturated pores and fissures, and when they encounter traps (such as impermeable faults, stratigraphic discontinuities or anticlines) a stagnant pool (crude oil reservoir) results. As the oil moves into the reservoir formation, it displaces the in-place brine and the initial saturation varies from 40 to 80%. The original reservoir brine accounts for most of the non-oil saturation and is usually associated with interstices of rock grains and smaller pores, hence the name interstitial (connate) water. Reservoir rocks consist of two major minerals; a predominance of quartz is associated with sandstone formations, while limestone forms the bulk of carbonate reservoir rock matter. Between these two extremes, varying amounts of clays, gypsum and shaly materials are found in most petroleum reservoirs. It should thus be expected that the mineral composition will affect among other things, the porosity and permeability of the reservoir.

In primary crude oil production, the oil is forced up the well-bore by the internal pressure of the reservoir fluids.

With continued production, this internal fluid pressure declines to the point where it is insufficient to force oil up and out through the well-bore. To restore this flow, water is usually injected into the reservoir in what is referred to as conventional water flooding. A number of reagents including acids, alkalis, polymers and salts are now introduced into the secondary flood water in an effort to improve its performance. However, capillary and viscous forces limit the oil recovery efficiency of secondary floods to the extent that the average cumulative recovery during primary and secondary production is about 30%. Tertiary recovery processes are those initiated after secondary flooding in an attempt to produce the remaining 70% of the oil originally in place. Secondary and tertiary processes together constitute Enhanced Oil Recovery (EOR) operations.

3.2 The Role of Capillary and Viscous Forces in Oil Recovery

It is now widely accepted that capillary forces mainly are responsible for trapping residual oil in pores of reservoir rocks. The capillary pressure, P_c, is the excess pressure at the interface of two immiscible fluids at equilibrium in a capillary. ~~In a non-cir~~cular capillary, the capillary pressure can be related to interfacial tension, (γ), as follows:

$$P_c = \gamma\left(\frac{1}{r_1} + \frac{1}{r_2}\right) \qquad \ldots\ldots (1)$$

where r_1, r_2 are the principal radii of curvature of the oil-water meniscus. The capillary pressure concept can be expressed in various terms including that applicable to a porous medium.(18) However, the strong dependence on interfacial tension is quite obvious, and this explains the importance of low interfacial tension for any significant enhanced oil recovery in practice.

Viscous forces, as expressed in terms of injected and displaced phase mobilities, λ , are equally important. An injected fluid may succeed in releasing oil from the pores, but if the Mobility Ratio (M) defined by

$$M = \frac{\lambda_{\text{displacing phase}}}{\lambda_{\text{displaced phase}}}$$

is unfavorable, the oil recovery suffers.

One way of understanding the significance of capillary and viscous forces is via the sweep, contact factor and displacement efficiencies.(21) Bansal(1) has discussed these efficiencies in depth. There is some disagreement in the literature as to how low the IFT has to be reduced by an injected phase in order to recover additional oil. Mungan(4) reported an increased recovery of up to 6.5% by lowering γ_{ow} from 40 to 0.5 dynes per centimeter. Wagner and Leach(26) contend that the IFT must be down to 0.07 dynes per centimeter to achieve increased oil recovery. Dyes et al(33) have used models of five-spot, direct and staggered line-well patterns to demonstrate the importance of M. As illustrated in Refs. 1 and 21, M should be less than 5 for a good 'sweep' of the pattern.

More recently, the concept of capillary number, N_{ca}, has been introduced to relate both viscous and capillary forces. The capillary number can be quantitatively defined as follows:

$$N_{ca} = \frac{\mu_w \, v_w}{\phi \, \gamma_{ow}}$$

where μ_w = aqueous phase viscosity

v_w = aqueous phase velocity of flow

ϕ = bed porosity

γ_{ow} = oil-water interfacial tension

From Fig. 1, it is seen that 100% displacement efficiency can be attained at a N_{ca} of about 10^{-2} to 10^{-1}. N_{ca} values obtained in water flooding are generally about 10^{-6}, hence the low order of magnitude of oil recovery achievable by such floods.

Considering the capillary configuration shown in Fig. 2, for $r_2 > r_1$, Moore and Slobod (Ref. 63, chapter 7) obtained the following relationship:

$$\bar{V} = \frac{v_1}{v_2} = \frac{\dfrac{4Lq\mu}{\pi r_2^2 \cos\theta \, \gamma_{ow}} + r_2^2 \left(\dfrac{1}{r_1} - \dfrac{1}{r_2} \right)}{\dfrac{4Lq\mu}{\pi r_1^2 \cos\theta \, \gamma_{ow}} - r_1^2 \left(\dfrac{1}{r_1} - \dfrac{1}{r_2} \right)} \quad \ldots\ldots(2)$$

where

$\bar{V}$ = velocity ratio

v_1, v_2 are velocities of the interface in capillaries 1 and 2 of radii r_1, r_2, respectively

q = aqueous phase flow rate

L = length of pore

θ = contact angle

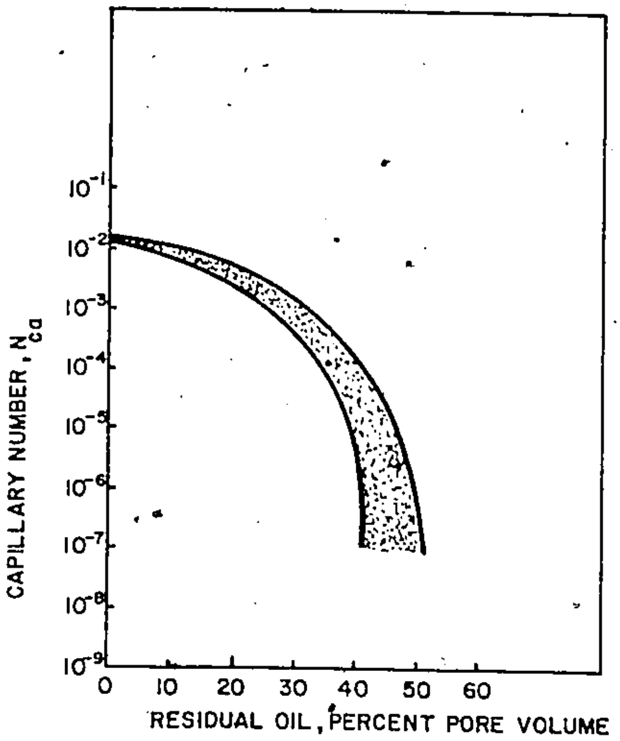


Fig.1 - DEPENDENCE OF RESIDUAL OIL SATURATION ON CAPILLARY NUMBER.

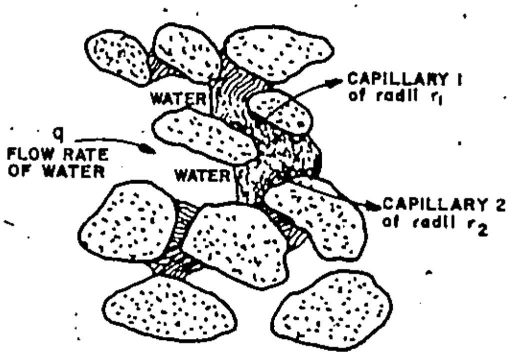


Fig. 2 - MODEL OF CAPILLARIES IN A POROUS MEDIUM

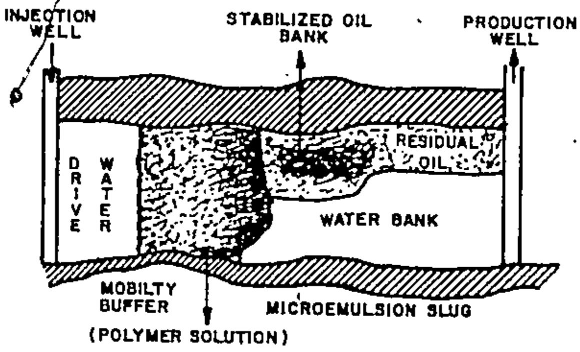


Fig.3 - MICELLAR FLOODING PROCESS

if viscous forces dominate the capillary ones, then Eqn. (2) simplifies to

$$\bar{V} = \frac{r_1^2}{r_2^2} \quad \ldots\ldots (3)$$

and residual oil is left in smaller pores. On the other hand, when capillary forces dominate,

$$\bar{V} = \frac{r_2^2}{r_1^2} \quad \ldots\ldots (4)$$

and flow is faster in smaller pores, residual oil is trapped in larger ones.

3.3 Caustic Water Flooding:

The classical Dupre' equation in the form:

$$W_{os} = \gamma_{ow} \{ 1 + \cos\theta \} , \quad \ldots\ldots (5)$$

where

W_{os} = work of adhesion of oil onto rock surface

highlights the importance of reservoir wettability in oil recovery processes. The actual wettability of a petroleum reservoir is a complex function of the various rock-fluid interactions. In particular, the adsorption of natural surfactants (contained in the crude oil) on to the rock surface imparts varying degrees of oil-wetness to an erstwhile water-wet formation. Bansal(1) has reviewed the current thinking on wettability effects in oil recovery.(2,3,5,6,7,10,11,26) Reversing wettability of the reservoir from an oil-wet to a water-wet condition appears to be the more beneficial path. A variety of reagents including acids, bases, salts and chelating agents have been utilised after elaborate laboratory screening studies to develop suitable secondary recovery fluids for use in a given reservoir situation. The most popular reagent, and that which has been found most effective in several applications, is caustic soda.

Cooke et al^(37)^ have proposed the following mechanisms as being operative in alkaline water flooding:
(i) drastic reduction of oil-water interfacial tension,
(ii) Wetting of matrix grains by oil,
(iii) formation of water drops inside the oil phase,
(iv) drainage of oil from volume between alkaline water drops forming an oil-in-water emulsion. Other authors$^{(10,38,39)}$ have observed this emulsification process and attributed it to soap formation resulting from the reaction between the caustic and carboxylic acids present in the oil. The presence of these acids appears to be necessary for a successful caustic flood. Ehrlich and Waygal$^{(11)}$ assigned a minimum acid number of 0.1 to 0.2 mg KOH per gram of oil (or an interfacial tension of the crude against 0.1% NaOH less than 0.5 dynes per centimeter) as being necessary for additional oil recovery by caustic flooding. Cooke et al$^{(37)}$ however put the minimum acid number at 1.5, while Jennings$^{(38)}$ noted that heavier oils (about 20° API) are more favorable than lighter ones. Jennings' observations on the gravity of crudes favorable to caustic flooding are consistent with the choice of caustic flooding for the heavy Albertan Lloydminster crudes.$^{(10)}$

In addition to the properties of the reservoir crude, several other environmental factors affect the performance of caustic floods:-

(a) Interstitial Water:

The presence of brine (10,39) has been found beneficial in lowering the caustic-oil interfacial tension. However, there exists an optimum salinity and caustic concentration at which this reduced IFT is obtained. Various divalent ions such as Ca^{2+}, and Mg^{2+} also present in connate water adversely affect the performance of caustic floods. These usually form insoluble hydroxides with the caustic resulting in reduced strength and interfacial activity. Cooke et al (37) have found the use of Na_2CO_3 beneficial in containing these divalent ions while Dranchuk et al (10) favor the use of chelating agents.

(b) Mineralogy:

Wilson (65) has amply discussed the effects of various environmental elements in caustic floods. Clays usually exchange their Ca^{2+} for H^+ in the caustic system, thus introducing undesirable divalent ions into the flood water. Gypsum also interacts adversely with the caustic. A preflush of low salinity brine has been recommended for reducing the problems associated with reservoir clays.

(c) Flood rates, Temperature:

Uren and Fahmy (30) have demonstrated the importance of flooding rates in general fluid injection processes. High flood rates prevent the attainment of equilibrium among the various interfacial species and could adversely affect caustic and other flooding processes. On the other hand, too low an injection rate will decrease the productivity and hence the rate of return on investment.

Egbogah(40) has recently reviewed the effects of temperature and pressure on oil-water interfacial tension. He noted that moderately high temperatures and pressures are favorable to IFT reduction. However, as Wilson(65) and Cooke(37) observed, other factors such as increased base consumption may offset the benefits of reduced IFT.

CHAPTER 4

ENHANCED OIL RECOVERY II : TERTIARY RECOVERY OPERATIONS

4.1 General Aspects

Several tertiary oil recovery techniques ranging from light hydrocarbon miscible processes through chemical to thermal processes, have been developed and are currently being tested in pilot schemes. Herbeck et al (21) and Gangoli and Thodos (48) present excellent treatments of these various schemes. Bansal (1) has amply illustrated the several alternatives of tertiary oil recovery. The most popular and that with possibly the greatest oil recovery potential is micellar flooding. Gogarty, in his two recent reviews, (56,62) gives a detailed analysis of the process in its various forms; the breakthroughs, the bottlenecks and the future potentials. He cautions that tertiary oil recovered by this process is and will remain expensive until alternatives for the expensive petroleum sulfonates and polymers can be developed.

A typical micellar flooding process is depicted in Fig. 3. Economic considerations require that a finite slug of the micellar system be followed by a polymer mobility buffer bank for mobility control, both being driven by the drive water. However, before a reservoir is ear-marked for tertiary flooding, the residual oil saturation to water flooding (s_{orw}) should be greater than certain minimum value. Wyman (8) puts this at 25 to 30% and using a cost of error reduction criterion, he has selected the following logging techniques for accurate determination of this parameter:

(i) nuclear magnetism log

(ii) pulsed neutron/ log-inject-log

(iii) resistivity/ log-inject-log

While all micellar formulations involve surfactants (ionic or non-ionic), water (brine) and oil (crude or refined) as basic constituents, and alcohols, polymers and salts as additives, differences in compositions and phase externality have given rise to various forms.(71,49,43) Some controversy exists as to which of the injection schemes -

(i) low surfactant concentration - high pore volume injection, or

(ii) high surfactant concentration - low pore volume, is the better.

Gogarty(56,62) favors the latter, but admits more work is needed to confidently establish the superiority of one over the other.

4.2 Micelles, Micellar Solutions and Microemulsions

If a surfactant is dissolved in water to a concentration above the critical micelle concentration (CMC), the molecules aggregate into spherical structures called micelles. Fig. 4 is a schematic diagram of micelle formation, oil solubilization and polymer-micelle interactions in surfactant solutions. Depending on the concentration of the surfactant various micellar structures can be formed in solution (Fig. 5).

Emulsion chemists(63) are divided as to the difference between micellar systems and microemulsions. Shah(70) defines a micellar solution as one in which the dispersed droplet size is of the order of 10 to 100 A°. However, no basic

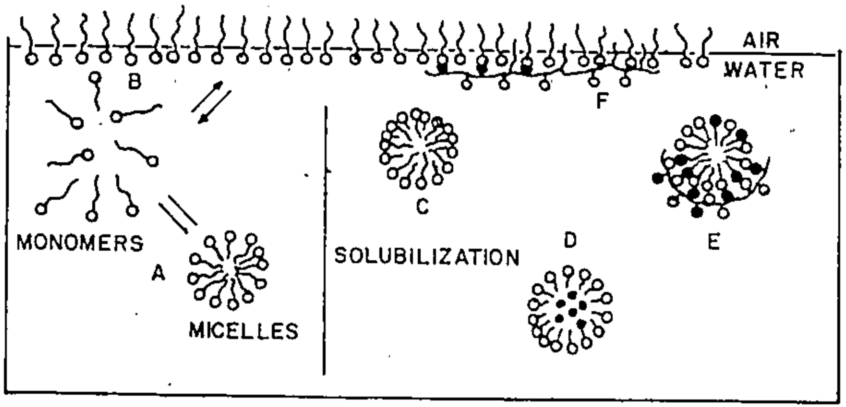


Fig.4- A SCHEMATIC PRESENTATION FOR MICELLE FORMATION (A) ADSORPTION (B), MIXED MICELLE FORMATION (C), SOLUBILIZATION OF OIL IN MICELLES D , POLYMER-MICELLE INTERACTION E , AND SURFACTANT-POLYMER MIXED FILM AT INTERFACES (F) IN SURFACTANT SOLUTIONS.

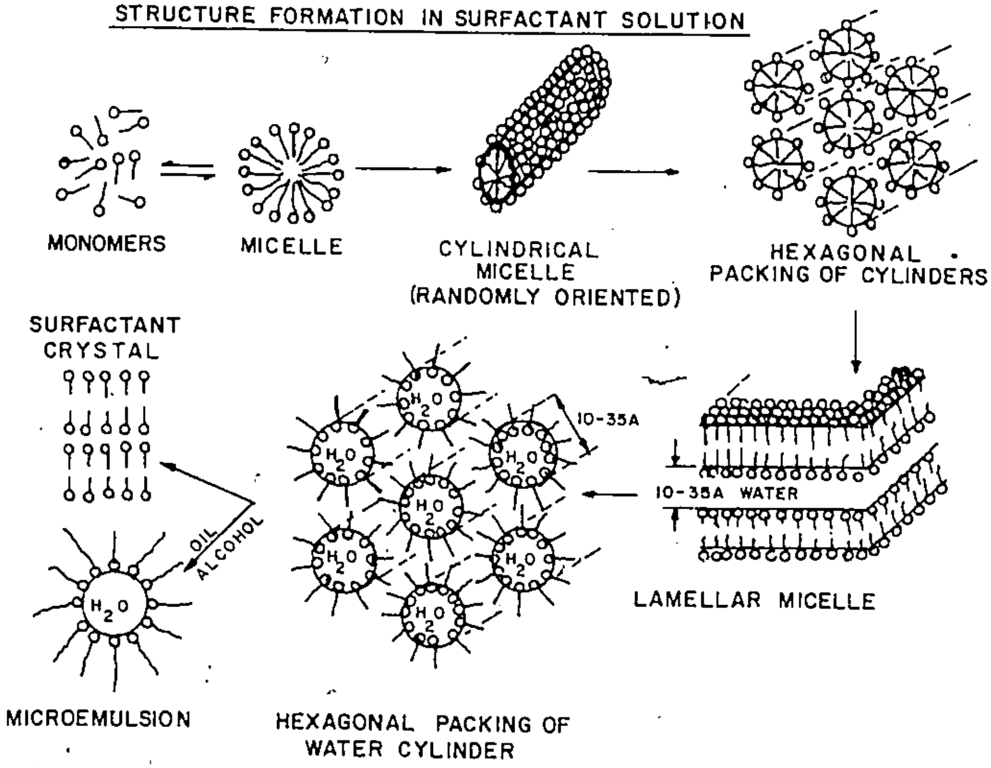


Fig. 5- A SCHEMATIC ILLUSTRATION FOR THE FORMATION OF VARIOUS STRUCTURES IN SURFACTANT SOLUTION UPON INCREASING THE CONCENTRATION OF SURFACTANT

structural difference exists between the two systems and the enhanced oil recovery literature uses both terms interchangeably. Macroemulsions, on the other hand, have dispersed droplets of size of about 2000 to 100,000 A° and are generally opaque and unstable. Microemulsions or micellar solutions possess high stability, are transparent or translucent, and exhibit the peculiar characteristic of phase inversion (through a visco-elastic gel stage) upon increasing the amount of the internal phase relative to the external one (Fig. 6). The viscoelastic gel stage is identified by the appearance of cylindrical micelles and lamellar liquid crystalline structures.

The most important physical properties of microemulsions are as follows:-

(a) Light Scattering:

They exhibit the Tyndal effect, a light scattering phenomenon. Thus, microemulsions appear blue to reflected light and orange-red to transmitted light. Particles less than $1/4\lambda$ (λ = wave length of light) scatter white light in all directions. Also, white light can pass through dispersions of such particles, which thus appear translucent. Light scattering instruments such as the Brice Phoenix Photometer or the Oster Microphotometer can be used to measure accurately the sizes of microemulsion aggregates.

(b) Birefringence:

This is a light scattering phenomenon associated with polarized light. It is a very powerful tool for detecting

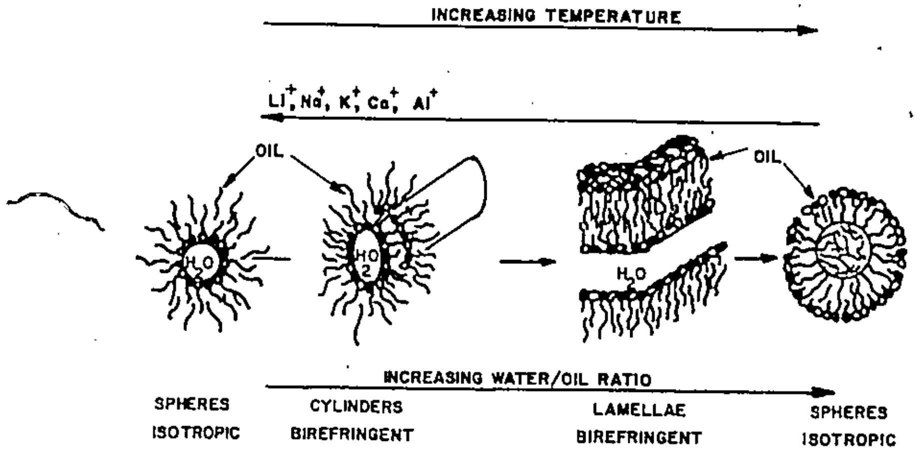
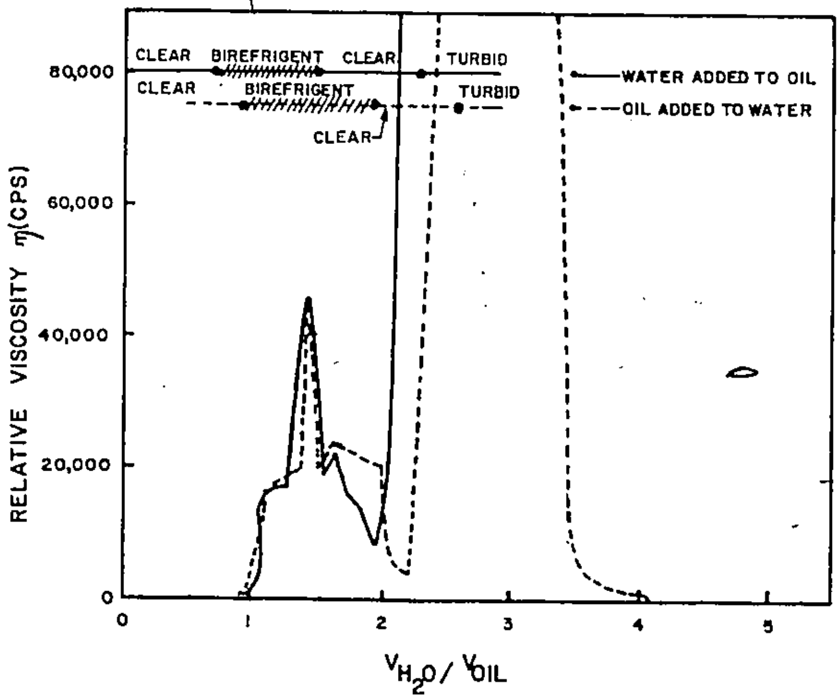


Fig-6: MECHANISM OF PHASE INVERSION IN A MICELLAR SYSTEM



EFFECT OF PHASE VOLUME RATIO ON VISCOSITY

Fig-7: THE EFFECT OF WATER-OIL RATIO ON THE VISCOSITY OF A MICROEMULSION SYSTEM anisotropy in microemulsions. The birefringence instrument consists of a pair of crossed nicols, microscope slides and a source of strong white light. If a drop of a dispersion containing anisotropic aggregates (associated with cylindrical micelles or lamellar structures Fig. 6), is placed on the microscope slides and viewed through the crossed nicols illuminated by the white light, beautifully-colored patterns appear in the field of view. This is referred to as birefringency and is attributed to the scattering and repolarisation of the polarized light by the anisotropic species. For an isotropic micellar structure, the field of view is dark.

(c) Rheology:

The appearance of liquid crystallinity in microemulsions is associated with a sudden increase in viscosity or consistency. Shah et al (50,51,70) have defined and characterized this phase inversion phenomenon by various measurements. The rheological behaviour of a typical micro-emulsion system following phase inversion (from oil external to water external or vice-versa) is plotted in Fig. 7. The maximum in the relative viscosity at a water-oil ratio of 1.4 is attributed to the occurrence of a lamellar structure. A second viscosity peak appears between water-oil ratios of 2.0 and 3.5 following addition of water to oil and oil to water respectively (Fig. 7)

(d) Electric Conductivity:

Conductivity measurements can also be used to detect the appearance of liquid crystalline structures in microemulsions. Fig. 8 is a plot of electrical resistance with water-oil ratio in the neighbourhood of the phase inversion region. The micellar structures (spherical and liquid crystalline) thought to be dominant over various water-oil ratios have been inserted in Fig. 8. A reduction factor of about 100 in the electrical resistance accompanies the phase inversion from oil to water externality.

(e) NMR, X-ray and Electron Microscopy:

Nuclear magnetic resonance (NMR) spectra is another tool used in detecting liquid crystalline structures in a micellar system. Low angle X-ray measurements can furnish information on the sizes of oil and water droplets in a microemulsion. The presence of anisotropic aggregates can equally be detected by X-ray measurements. In electron microscopy (applicable to the study of oil -in-water microemulsions), organic materials containing unsaturated groups are stained with Osmium tetroxide in order that photographs of such materials may be taken without shadow casting.

4.3 Formulation of microemulsions; Theories of Microemulsification:

(a) Formulation of microemulsions:

Microemulsification is a spontaneous process and occurs if and when the chemistry is favorable. The formulation of such systems is still an art despite the elaborate studies by several workers notably Schulman, Prince, Friberg, Shinoda, Kunieda and Shah, aimed at establishing a theoretical basis for the creation of micellar solutions.

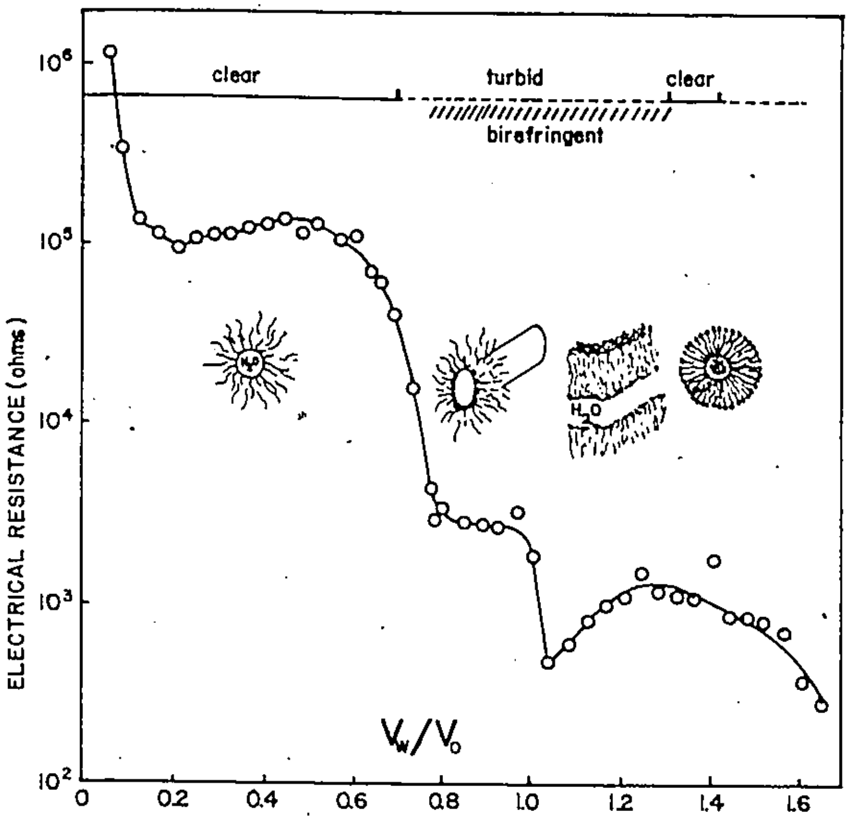


Fig. 8 - THE VARIATION OF ELECTRICAL RESISTANCE WITH WATER-OIL RATIO DURING PHASE INVERSION OF A MICROEMULSION SYSTEM

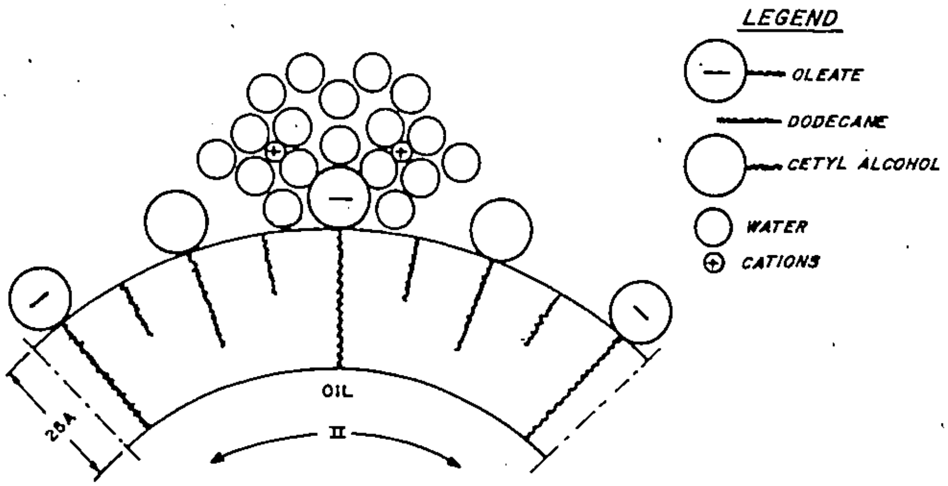


Fig. 9 - POSITIONS AND INTERRELATIONSHIPS AMONG THE INTERFACIAL SPECIES OF A MICROEMULSION SYSTEM

Prince (Ref. 63, chapter 3) discusses the hydrophilic- lipophilic balancesystem (HLB) for emulsifier selection while Shinoda et al (Ref. 63, chapter 4) present the phase inversion temperature(PIT) system and Beerbower and Hill[(63)] the cohesive energy ratio (CER) approach. The latter concept appears to be the most powerful of the three. It has a thermodynamic basis in which the balance of (i) the dispersing tendencies and cohesive energies at the oil side of interface and (ii) the hydrogen bonding cohesive energies and Keemsom dipole interactions at the water side, is quantitatively satisfied. The CER equation provides the desirable ratio of head volume to tail volume for the emulsifier as well as its chemical match with both the oil and water phases. However this is a relatively new approach and has not been extensively tested.

In the HLB system, the HLB of the oil to be microemulsified is determined for both oil and water phase externality. A range of 4 to 7 is often obtained for oil-external, while 9 to 20 is used for water external solutions. With this oil HLB, an emulsifier whose hydrophobic end is similar to the chemical structure of the oil is sought. In most cases, the HLB method furnishes an emulsifier of a desired water solubility but the task of matching its hydrophobic end with the oil involves trial and error.

The PIT system applies mainly to non-ionic surfactants. It is based on the temperature dependency of the HLB of such surfactants. At the temperature of phase inversion (oil/water to water/oil), the hydrophilic-lipophilic tendencies of the surfactant just balance and no emulsion forms. Kunieda and Shinoda (Ref. 63, chapter 4) invented this scheme.

(b) Theories of microemulsification:

The most interfacially active constituents of a microemulsion system are the emulsifier and cosurfactant. These species orientate themselves in a fairly ordered manner, with their hydrophilic heads in the water side and the hydrophobic tails in the oil side of the interface. A Guggenheim-type interface model describes this situation better than the Gibbs model. Fig. 9 shows the positions and interrelationships among the interfacial species of a typical oil/water microemulsion. The zigzag lines represent the aliphatic tails of the surfactant (oleate soap) and cosurfactant (cetyl alcohol) while the circles attached to the tails represent the polar heads or water soluble portions.

Prince (Ref. 63, chapter 5) presents the mixed film theory of microemulsification, popular within the Schulman School of Emulsion Chemists. Shah et al(73) present an up-date of this theory. The main tenet of this theory is the existence of different interactions (tensions) at the oil and water sides of the interphase. The presence of a cosurfactant (alcohol) plays a major role in this theory. It creates the desired asymmetry at the interphase (Fig. 9) which enables the penetration of oil therein. Secondly, the alcohol partitions itself between the interphase and oil phase, thus lowering γ_{ow} to $(\gamma_{ow})_a$.

The difference in the spreading pressures π'_w and π'_o at both sides of the interphase is further accentuated (Fig. 10). In Fig. 10, AB represents the water side π-A profile, while CD denotes that of the oil side of the interphase. Curve EF is the sum of AB and CD. π'_w and π'_o are the film pressures of the flat duplex film at the water and oil sides respectively; while π_w and π_o are the corresponding pressures at the sides of the curved film.

The net spreading pressures on the flat film is given by

$$\pi_{\overline{G}} = \pi'_w + \pi'_o \qquad \ldots\ldots (6)$$

and it decreases from a high initial value (about 40 dynes/cm) as the film expands under the driving force, γ_i, given by,

$$\gamma_i = (\gamma_{ow})_a - \pi \qquad \ldots\ldots (7)$$

where $(\gamma_{ow})_a$ is the oil-water interfacial tension following alcohol (cosurfactant) partitioning. The energy, W, defined by

$$\delta W = - \gamma_i \, dA \qquad \ldots\ldots (8)$$

needed to disperse the internal phase becomes instantly available and emulsification occurs spontaneously. However with continued expansion of the film, π drops to the point where γ_i increases from a negative to an equilibrium value of zero.

Consequently, $\pi_o = \pi_w = 1/2 \, (\gamma_{ow})_a \qquad \ldots\ldots (9)$

The mechanism of curvature of the interphase is illustrated in Fig. 11. The stress of the pressure gradient due to π'_o and π'_w is relieved by bending until a stable condition

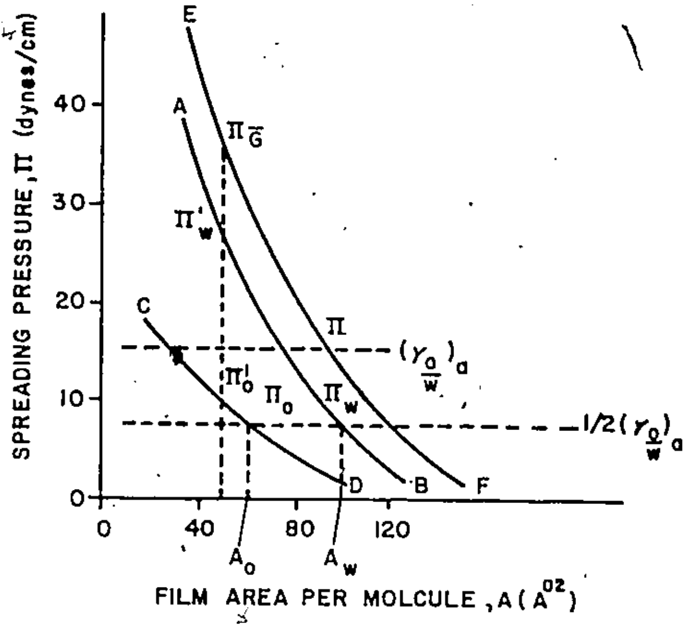


Fig. 10 - Π-A CURVES IN THE MIXED FILM THEORY OF MICROEMULSIONS

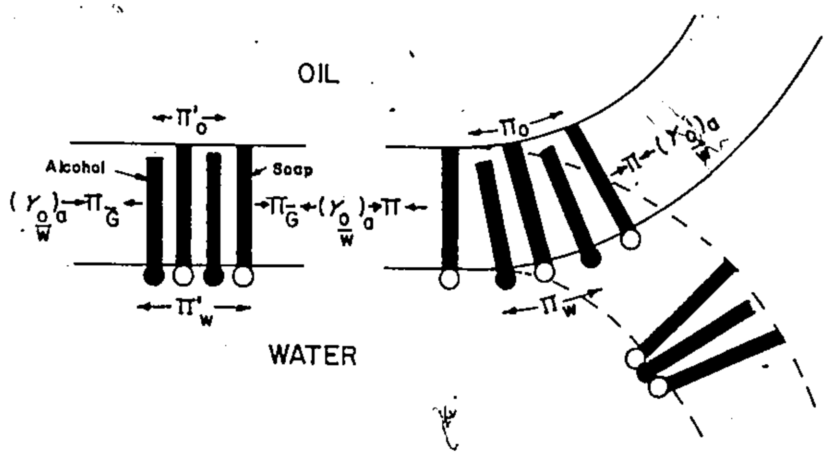


Fig. 11 - MECHANISM OF CURVATURE OF MICROEMULSION FILM

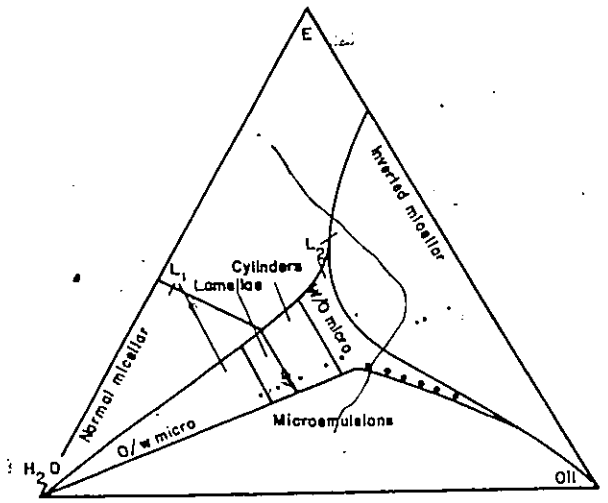


Fig.12- MIXED FILM THEORY HYPOTHETICAL PHASE MAP

is achieved. This corresponds to the situation of Equation (9). The ratio of area per molecule at the two sides of the film changes from 1/1 to A_w/A_o (Fig. 10). Fig, 12 is a hypothetical phase map predictable by the mixed film theory. The three main constituents of a micellar system (oil, water and surfactant, E) are represented by the corners of the triangle in Fig. 12. Also shown are approximate regions of microemulsions, micellar solutions, macroemulsions and liquid crystalline phases.

4.4 Aspects of Microemulsion Flooding:

(a) Phase-volume and solubilization

For a micellar system to give a satisfactory oil recovery,

(i) the right balance among the various constituent phases must be obtained

(ii) the integrity of the slug must not be jeopardised by invasion of the polymer buffer bank or the interstitial water. Extensive studies are therefore necessary before a suitable micellar system (for a particular application) can be developed. At present, tailoring surfactant systems for micellar flooding is basically a trial and error operation. This explains in part the high costs in terms of labour and materials.

The composition and phase behaviour of microemulsions can be adequately described by ternary diagrams.(44,45,46) Fig. 13 is a simple ternary diagram for the 3 main constituents of a micellar system. An injection composition, such as C, should be in the single phase region, in order that the desirable miscible

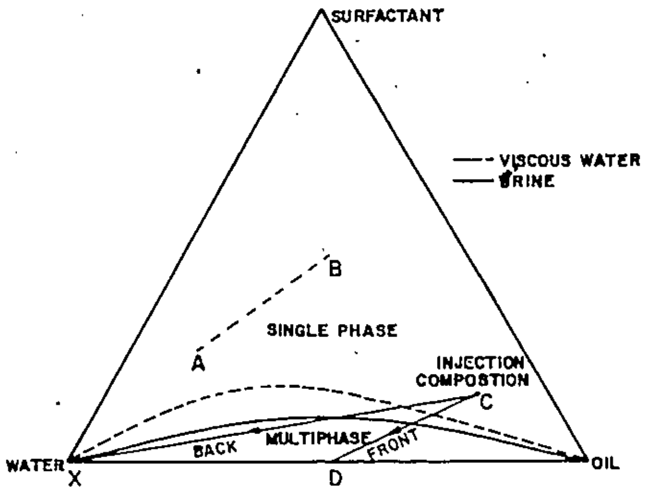


Fig.13 – A TYPICAL TERNARY DIAGRAM REPRESENTATION OF A MICROEMULSION SYSTEM

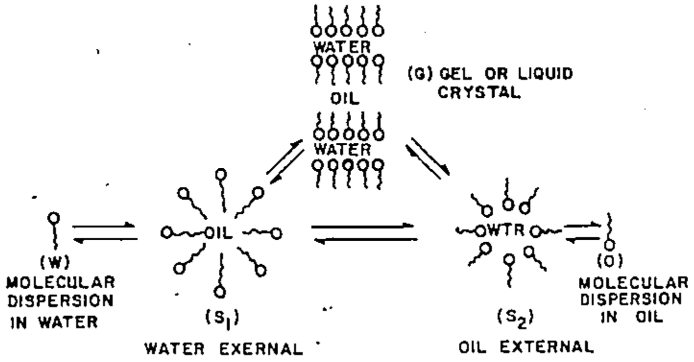


Fig. 14 – WINSOR'S CONCEPT OF INTERMICELLAR EQUILIBRIUM

displacement can be achieved. A displacement process in which the injection composition changes from B to A (single phase region of Fig. 13) is a miscible one. However, Healy and Reed(44 to 46) contend that although a micellar flood might start off miscibly, in the later stages of displacement (when an oil bank has been formed) it could be proceeding immiscibly. This is attributed to dilution effects (1) at the leading edge by the stabilized oil-water bank (path C-D) and (2) at the trailing edge by connate water or polymer buffer invasion (path C-X) as depicted in Fig. 13. In order that oil recovery remains high during this immiscible flooding, the vertical extent of the multiphase region should be minimal and low IFT should be maintained at both the front and back ends of the microemulsion slug.

Fig. 14 is a schematic diagram of Winsor's concept of inter-micellar equilibrium occurring between various phases and micellar structures. The arrows here indicate equililbria between two different structures - eg. (S_2+G) represents two immiscible phases in equilibrium, namely a water/oil microemulsion (S_2), and the other a lamellar structure (G). Intermicellar equilibria in the single phase such as (S_1,G), (S_2,G) can also exist. The system (O+S_1) is Winsor's type I, (S_2+W) is type II, while the situation (S_1+S_2+O) is a type III system. Figs. 15 to 18 are micellar structure maps generated by Healy and Reed(45) using petroleum sulfonate 400 as surfactant and a paraffinic-naphthenic oil mix as the oil ~~component~~, in various salinities

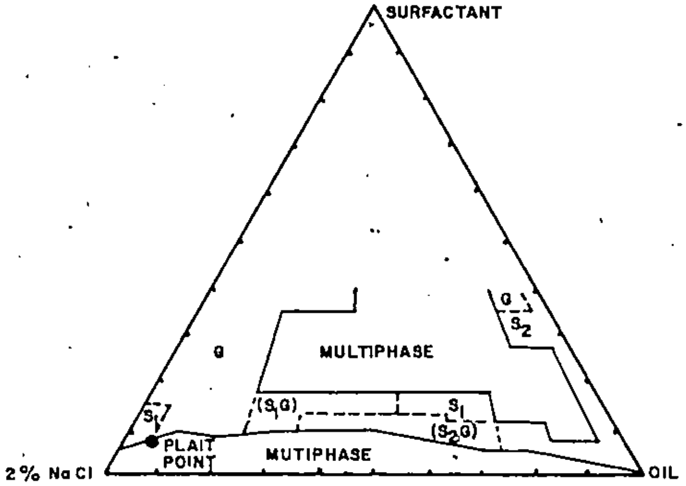


Fig-15: MICELLAR STRUCTURE MAP, 2 PERCENT Na Cl

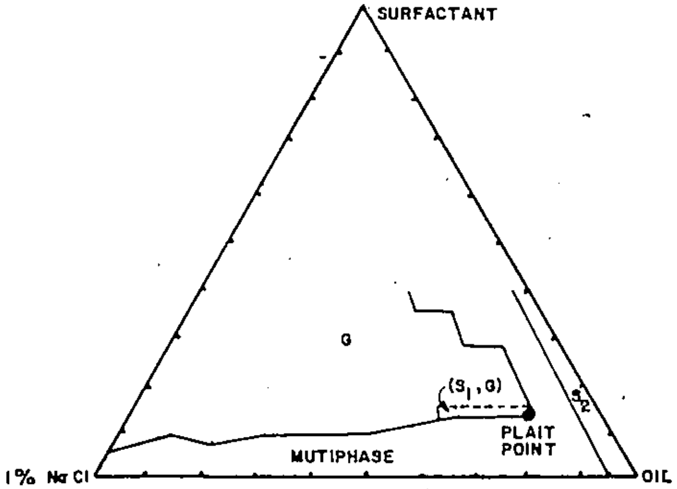


Fig-16: MICELLAR STRUCTURE MAP, 1 PERCENT Na Cl

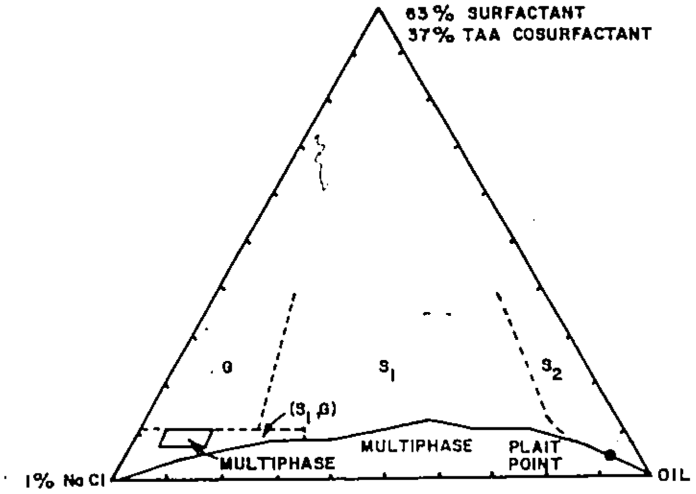


Fig. 17-MICELLAR STRUCTURE MAP, I PERCENT Na Cl, 37 PERCENT TAA

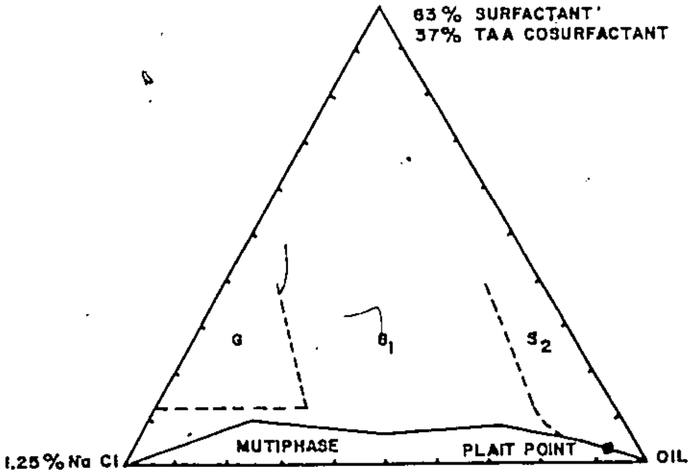


Fig. 18- MICELLAR STRUCTURE MAP AT OPTIMUM SALINITY, 1.25 PERCENT Na Cl, 37 PERCENT TAA

(Figs. 15, 16), and in optimum salinity with the addition of a cosurfactant, (Fig. 18). The predominance of the G-phase at 1% salinity is obvious in Fig. 16, but that is drastically reduced by cosurfactant introduction (Fig. 17). A large central multiphase region appears at 2% salinity (Fig. 15), but that also is replaced by the single S_1 phase at optimum salinity and in presence of cosurfactant (Fig. 18). Hill et al(42) have also observed the drastic IFT reduction with salinity optimisation, while Gogarty and Tosch(43) concluded that viscosity and stability control is aided by brine presence. Cosurfactants moderate system viscosity and increase the oil solubilization potential of the microemulsion. Jones and Dreher(49) discuss these effects in detail.

(b) Influence of Reservoir Environmental Elements in Micellar/ Polymer Flooding:

(i) Crude Oil Properties:

A crude oil gravity of about 20° API and a reservoir viscosity of about 100 cp (65) represents the probable upper limit of micellar flooding. Beyond these limits, thermal recovery is often considered. The chemical nature of the crude determines the IFT achievable with a given micellar system. Wade et al(52,53,64) have introduced the Equivalent Alkane Carbon Number, EACN, concept as a tool in formulating microemulsion slugs for a given crude based on ultra-low IFT. Gale and Sandvik(54) have noted that in order to achieve ultra-low tensions (10^{-2} to 10^{-4} dynes/cm), the presence of high equivalent weight species and a broad-equivalent weight distribution of petroleum sulfonates are desirable.

Wasan et al (67,76) conclude that low interfacial shear viscosity (ISV) is important for rapid coalescence of oil droplets during oil bank formation and for reduction of film rigidity.

(ii) Interstitial Water:

Whether the micellar system is a soluble oil, (71) oil-external, (45,47) or water-external, (44,45,46) high reservoir water salinity is harmful. Surfactant precipitation can occur at high salinity and this is accentuated by the presence of multivalent ions such as Ca^{2+}, Mg^{2+}, Fe^{3+}, B^{3+}. Chang (59) and Gogarty (62,66) also discuss the effects of high salinity on polymer solutions. Chang (59) reports as much as 90% reduction in the viscosity of polyacrylamide solutions even at moderate salinities. Hill et al (42) recommend a low salinity preflush and the addition of sequestering agents such as sodium phosphate ($Na_3P_3O_{10}$) in the micellar system as a way of reducing the adverse effects of high reservoir salinity and multivalent ions. Shah et al (58) have found that adding ethoxylated sulfonates to petroleum sulfonates improves the brine tolerance considerably.

(iii) Mineralogy:

(a) Surfactant Adsorption:

The high adsorption capacities of reservoir clays is mainly responsible for the serious adsorption or retention losses in micellar slugs and polymer solutions. By an ion-exchange mechanism, clays also introduce divalent ions into the slugs. This adsorption phenomenon is currently under active study by several workers. Trogus et al (37) have observed that for non-ionic surfactants, adsorption decreases with molecular weight, while for anionics the reverse is true. Bae and Petrick (28) noted that the adsoprtion of petroleum sulfonates is selective. The higher equivalent weight and most interficially active components (Molecular weight greater than 500) are adsorbed to a greater extent. High surfactant concentration and flow rate, as well as the presence of mineral oil in the microemulsion, reduce adsorption losses. Larson and Hiraski (55) studied separately, and then collectively, the effects of surfactant partitioning, adsorption and swelling of the oleic phase and concluded that at low residual oil saturation to surfactant flooding (S_{orc}) these effects are drastically reduced. Other authors, notably Malmberg and Smith (69) and Hanna and Somasundaran, (68) present theoretical principles as well as experimental investigations of the effects of several variables such as ionic strength, pH, phase continuity and wettability on petroleum sulfonate adsorption.

(b) Polymer Adsorption:

Willhite and Dominguez (73) present a detailed discussion on polymer retention in flow through porous media. They attribute the permeability reduction ability to polymer retention in the matrix. High salinity (59) increases polymer adsorption while some sacrificial agents (65) have been suggested for minimising polymer adsorption losses.

(iv) Geology/ Lithology:

Polymer flooding is feasible in reservoirs of depths greater than 500 ft and permeabilities greater than 50 md. (59) Wilson (65) maintains that at too low a permeability, the polymer resistance factor, (R), becomes very high. The presence of cavities, streaks or fractures in the reservoir can reduce the sweep efficiency drastically. The inaccessible pore volume (IPV) (57) is largely responsible for the invasion and dilution of the micellar slug by the polymer solution. IPV also accounts for the attenuation of the polymer bank and consequent invasion by the drive-water. Gupta and Trushenski(57) observed that shear degradation (more severe in polyacrylamide than biopolymers) causes severe losses in the polymer resistance factor, and that this impairs mobility control.

(v) Temperature:

High reservoir temperatures,(65) especially in adverse salinity situations, can lead to phase separation in the micellar slug. Polymer stability is also temperature sensitive (bio polymers are more temperature sensitive than polyacrylamides). Bacterial degradation of the polymer increases at high temperatures and in the presence of oxygen. The use of oxygen scavengers(65) such as formaldehyde, hydrogen sulfite and glyoxal has been recommended in this context.

PART II

EXPERIMENTAL METHODS

CHAPTER 5

STRATEGIES FOR THE FORMULATION OF SURFACTANT SYSTEMS

5.1 General Outline:

Out of five crude samples received from EMR, two were selected for this particular study. One of them, an Albertan Lloydminster crude (Table 2) was selected because of its high gravity and viscosity. The other, a Gosfield South crude (obtained from Ontario) was chosen because of its moderate gravity and viscosity (Table 3). Two lignosulfonate species, known commercially as Marasperse C-21 and N-22 were also available. Their specifications are presented in Tables 7 and 8 of Ref. 1. In essence, the formulation procedure developed uses a criterion of better interfacial activity (lower IFT) to screen the lignosulfonates for type and concentration optimum for a given crude oil. With this basic information, several additives (organic and inorganic) are then separately tested for compatibility and further IFT reduction (over that obtained with lignosulfonates alone). Finally an optimisation study of the most successful systems is made.

Studies for the Lloydminster crude could not go beyond the preliminary stage before the available supply became exhausted. The Gosfield crude sample lasted nearly up to the conclusion of the lignosulfonate-additives investigations. The second major part of the studies was performed with live Chatham crude, also from Ontario. This crude, according to

TABLE 2

* CHARACTERISTICS OF ALBERTAN LLOYDMINSTER CRUDE

EMR Lab. No. : 70 - 69
Date Sampled : January 29, 1969
Specific gravity at 60°F : 0.914
Sulphur % (by weight) : 3.24
Viscosity at 100°F : 188 SSU
API gravity at 60°F : 23.3
Color : Black

TABLE 3

* CHARACTERISTICS OF GOSFIELD SOUTH; AN ONTARIAN CRUDE

EMR Lab. No. : 611 - 77
Field : Gosfield South
Location : Gosfield South TWP; Section 4.
Interval tested; depth : 2404 - 2418 ft
Producing zone : Trenton
Geological Age : Ordovician
Date Sampled : March 10, 1977
Specific gravity at 60°F : 0.816
API gravity at 60°F : 41.9
Pour point : 30.0°F
Viscosity at 100°F : 38 SSU
Sulfur % (by weight) : 0.25
Nitrogen % (by weight) : 0.03
Color : Greenish - black

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* Source - Report of Crude Petroleum Analysis, Canada Centre for Mineral and Energy Technology, Energy Research Laboratories-Ottawa.

TABLE 4

*+ ANALYSIS OF CHATHAM; AN ONTARIAN CRUDE

Specific gravity, 60/60°F	0.828
Carbon % (by weight)	85.70
Hydrogen % (by weight)	13.39
Nitrogen % (by weight)	0.04
Sulfur % (by weight)	0.18
Ash % (by weight)	0.007
Water % (by volume)	nil

+ Petroleum and Gas Laboratory - Energy Research Laboratories, Canada Centre for Mineral and Energy Technology - Ottawa.

* Analysis performed on special request from our laboratory

EMR is supposed to have same origin as the Gosfield crude. Significant differences were found however as evident from Tables 3, 4, 7 and 8. The first part of the study involving simple inorganic and organic additives produced IFT values down to about 1.0 dynes/cm only. In the search for ultra-low (10^{-2} to 10^{-4} dynes/cm) tensions, mixed surfactant formulations of petroleum sulfonate (Petrostep 420 and 450) and lignosulfonate (Marasperse C-21) were investigated. In the first formulation scheme, the optimum lignosulfonate concentration for a given crude determined from earlier studies was held constant while Petrostep was added in increasing concentrations until phase separation occurred. The degree of IFT reduction, system rheology and stability were the major parameters of interest. This strategy was not very successful, so a new one was developed, in which the Petrostep concentration was fixed at 2%, 3% and 4% in each case, and lignosulfonate added in increasing amounts until phase separation occurred.

In all cases each formulation was characterised by surface tension, pH, density and viscosity measurements. Table 15 gives the specifications of chemicals used in this study.

5.2 Sequence of Formulation Strategies:

Strategy 1 :- Preliminary Screening for lignosulfonate type and optimum concentration

Step (i):- For lignosulfonate (say C-21) concentrations in the range of 0 to 10%, the IFT against a given crude oil is measured in each case.

Step (ii):- Step (i) is repeated for the other lignosulfonate species (N-22).

Step (iii):- Physical characteristics such as surface tension, pH, density and viscosity of each formulation are obtained.

Step (iv):- From (i) and (ii), the lignosulfonate type and optimum concentration for further investigations are selected.

Strategy 2 :- Screening for Effective pH Reagents. (Inorganic Additives), and Their Optimum Concentrations.

Sulfuric acid and caustic soda were the pH reagents used. Since the presence of Ca^{2+} in Marasperse C-21 could interfere with caustic, N-22 was preferred.

Step (i):- At the optimum N-22 concentration from strategy 1, solutions of definite pH, covering the entire pH range, are prepared by adding a few drops of concentrated sulfuric acid or saturated caustic solution.

Step (ii):- IFT measurements against the given oil are performed as in strategy 1.

Step (iii):- Surface tension and density data are similarly obtained.

Step (iv):- From results of Steps (i) and (ii) it is determined whether acidic or alkaline medium is favorable (in most cases alkaline).

Step (v):- Based on the conclusion of step (iv), caustic soda within the concentration range of 0 to 3% is introduced into the optimum N-22 concentration.

Step (vi):- Steps (ii) and (iii) are repeated for these lignosulfonate-caustic systems.

Step (vii):- Using the same caustic concentrations in water (blank solutions), steps (ii) and (iii) are again repeated.

Step (viii):- By comparing results obtained from steps (vi) and (vii) a decision is made as to whether the caustic could perform better on its own.

Strategy 3 :- Screening for Effective Organic Additives and their Optimum Concentrations.

The reagents, and the order in which they were used, are as follows; acetone, methanol, 1-Butanol, tertiary butanol. Solubility problems prevented the testing of higher alcohols.

Step (i):- To the lignosulfonate concentration determined in strategy 1, increasing amounts of a given additive are added to achieve cosurfactant concentrations in the range of 0 to 10% by volume.

Step (ii):- IFT, surface tension, pH, and density measurements are performed as before for the various formulations.

Step (iii):- On the basis of the degree of IFT reduction achieved and the concentration levels needed to achieve such interfacial activity, the most effective additive is then selected.

Strategy 4 :- Brine Introduction and Optimisation Schemes

Step (i):- For aqueous brine solutions of strengths in the range of 0 to 5%, IFT (against a given crude), surface tension, pH and density measurements are performed as before.

Step (ii):- An optimum working brine concentration based on the relative IFT reduction is then selected.

Step (iii):- The salinity obtained from Step ~~(iii)~~ is then imposed on the systems developed from strategy 2. The usual measurements are performed on the resulting formulations.

Step (iv):- From the results of step (iii), a decision is made on the effectiveness of brine addition in either or both the lignosulfonate-caustic and blank caustic systems.

Step (v):- The working salinity of step (ii) is again introduced into the lignosulfonate solution (strategy 1) in the presence of the organic additive selected from strategy 3. The IFT and the other system properties are measured again.

Step (vi):- Based on the results of step (v), the influence of brine on the interfacial activity of the lignosulfonate-organic additive solutions is determined. If a favorable trend is indicated, the cosurfactant concentration is then fixed at a practical level (less than 5%), while the salinity is adjusted. The IFT and the other properties of the resulting solutions are measured.

Step (vii):- From step (vi) measurements, an optimised system containing a practical cosurfactant concentration is finally obtained.

Strategy 5 :- Scheme for Formulation of Petroleum Sulfonate (Petrostep 420 and 450) + lignosulfonate C-21 Mixed Surfactant Systems.

Strategy 5A:- "Lignosulfonate major-Petrostep minor" Systems.

The optimum salinity for these Petrostep products has been specified as 1.5%.(25)

Step (i):- Maintaining the optimum lignosulfonate concentration obtained from strategy 1 and a salinity of 1.5%, increasing amounts of Petrostep 420 are added until phase separation occurs.

Step (ii):- Measurements of IFT, surface tension, pH, density and viscosity of resulting formulations are performed.

Step (iii):- For the compatible systems of step (ii), hexanol is added in increasing amounts until phase separation again occurs. The physical parameters are again measured.

Step (iv):- From the above, a decision is made as to whether the strategy permits the addition of Petrostep (with or without hexanol) in amounts sufficient to yield ultra-low IFT. Otherwise a change of strategy is needed.

Strategy 5B:- "Petrostep major-lignosulfonate minor" Systems.

Step (i):- For Petrostep (say 420) concentrations in the range of 2 to 5%, increasing amounts of Marasperse C-21 are added in each case until phase separation occurs.

Step (ii):- IFT, surface tension, pH, density and viscosity measurements are performed for each formulation

Step (iii):- Steps (i) and (ii) are repeated for Petrostep 450 and possibly 465.

Strategy 6 :- Formulations for Displacement Runs.

For a given crude oil, strategies 1 to 5 are sufficient for developing lignosulfonate based surfactant systems suitable for EOR operations, following evaluation in laboratory displacement tests. Because the crude oil system had to be changed during the later part of the surfactants' development phase of the study, basic characterisation studies as per strategy 1 had to be performed. Earlier conclusions from strategies 2 and 3 were utilised in strategy 4 to develop suitable lignosulfonate-additive systems primarily for the displacement experiments.

TABLE 15

SPECIFICATION OF CHEMICALS

1. Sulfuric Acid (concentrated)

   "Baker Analysed" Reagent - assay (H_2SO_4) - 96.80%

2. Sodium Hydroxide

   Pellets, "Baker Analysed" Reagent, assay (by acid base titration) - 97.0%

3. Sodium Chloride

   Crystal, "Baker Analysed" Reagent, assay (NaCl) 99.9%

4. Acetone

   Certified ACS, Fisher Scientific Company

5. Methanol

   "Baker Instra - Analysed" Reagent

6. 1 - Butanol

   "Baker Analysed" Reagent, assay (by GC) - 99.5%

7. Tertiary Butanol

   Fisher Laboratory Reagent

8. 1 - Hexanol

   "Purified" grade Reagent

9. Characteristics of Petroleum Sulfonates

Equivalent Weight	Sulfonate	Free Oil	Water	Inorganic Salt	Control No.
420	60.0	15.6	19.7	4.7	484
450	62.2	15.2	18.5	4.1	593
465	57.5	14.5	24.9	2.8	558

Compositions are on weight percentage basis

Supplied by Stepan Chemical Company, Northfield, Illinois, USA

10. Barium Hydroxide, 8-hydrate

    "Baker Analysed" Reagent, assay ($Ba(OH)_2 \cdot 8H_2O$) - 100.4%

11. Potassium Hydroxide

    Special pellets, low in Chloride - "Baker Analysed" Reagent, assay (KOH) - 86.2%

12. Potassium Biphthalate

    Crystal, "Baker Analysed" Reagent, assay ($1\text{-}KOCOC_6H_4\text{-}2\text{-}COOH$) - 99.98%

13. P - Naphtholbenzein (Indicator)

    Eastman Reagent

14. Methyl Orange (Indicator)

    Certified ACS, Fisher Scientific Company

15. Iso-propyl Alcohol (2-Propanol)

    Certified ACS, Fisher Scientific Company

16. Toluene

    "Baker Analysed" Reagent, assay (by GC) - 100.0%

17. Hexadecyl Trimethyl Ammonium Bromide (HDTB)

    See Bansal (1) Page 41

pH meter Specifications

Type: Beckman Zeromatic SS-3

Electrode: Fisher Standard Combination Electrode

pH buffer solutions for calibration: pH 4, 7, 9 and 10 buffers, Fisher Scientific Company Reagents

CHAPTER 6

PHYSICAL CHARACTERISATION OF SURFACTANT FORMULATIONS AND CRUDE OILS

6.1 Surface and Interfacial Tensions

(a) Measurements with the Fisher Autotensiometer:

This instrument operates on the principle of the du Nouy ring and Wilhemy plate techniques. Bansal(1) has listed the important operational details of the instrument including the method of cleaning the ring and glass ware. Further details of the operating procedure can be found in the instruction manual (Catalog No.14-811) accompanying the instrument. All measurements were made at 25°C, a circulating bath being used for temperature equilibration. For surface tension measurements, interface ageing of 10 minutes was allowed while, for IFT, the period varied from 15 to 40 minutes depending on the pH of the system. A duplicate pair of readings in each case was obtained on a recorder chart.

(b) Measurements using the Spinning Drop Apparatus:

A schematic diagram of this instrument is given in Fig. 19. More details of the design principles and measurement techniques are given by Cayias et al.(74) In brief, a standard capillary tube is loaded with the denser surfactant system, and an appropriate oil droplet is introduced. The tube is then slotted into a cavity on the shaft of the rotor assembly and spun for 3 to 6 hours at speeds ranging from 1200 to 24,000 rpm. The volume of oil charged and the speed of rotor are

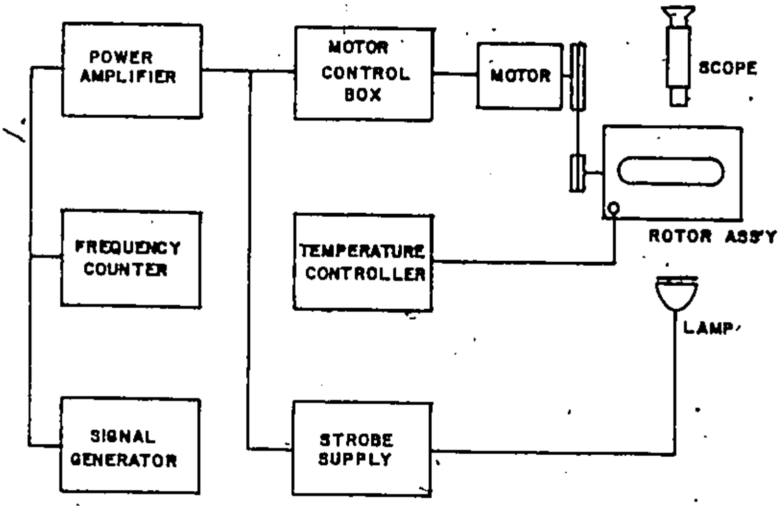


Fig. 19 - SCHEMATIC OF SPINNING - DROP APPARATUS

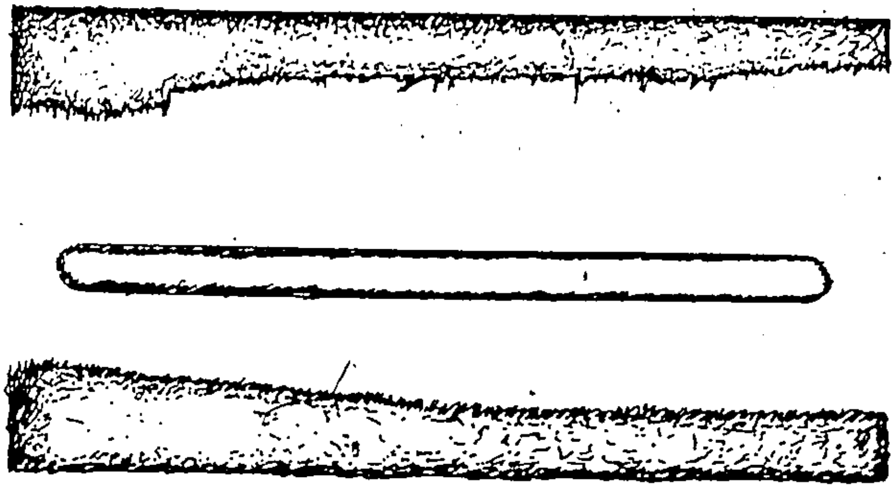


Fig. 20 - A TYPICAL INFINITE LENGTH OIL DROPLET OBTAINED IN THE SPINNING DROP APPARATUS

selected to produce an "infinite length" droplet (Fig. 20). Measurements of the droplet width are performed at hourly intervals (temperature being maintained constant at 25±0.5°C by means of cool air circulation) until three consecutive width readings differ by less than 0.001 cm. Such measurements were made with a precision filiar micrometer mounted on a travelling microscope, with the aid of a stroboscope.

This instrument was used to obtain all the ultralow IFT data of the Petrostep + C-21 mixed surfactant systems.

In each case, approximately equal volumes (40 ml) of the oil and surfactant system were preequilibrated (without any induced mixing) for 12 to 24 hours. The upper oil-rich layer was then carefully separated from the surfactant-rich lower layer. Samples for loading into the capillary tube for tension measurements were taken from these portions. The density of each layer was also measured. The latter data are needed for calculating the IFT from the micrometer readings using equation (15) in Ref. (74).

6.2 pH, Density and Viscosity Measurements:

All pH measurements were made with the Fisher combination electrode attached to Beckman SS-3 pH meter (see Table of specifications). Calibration of the pH meter was carried out using pH 4, 7, 9 and 10 buffers prior to each measurement. Room temperature of 23 to 25°C prevailed during most of the measurements.

Density measurements were made using 25 ml specific gravity bottles after 10 minutes equilibration in a 25°C bath. The reference substance was laboratory distilled water.

Viscosity measurements were also made after 10 minutes equilibration in a 25°C bath using the UL Adapter arrangement of the Brookfield Synchro-lectric viscometer (Ref. 1, page 40).

CHAPTER 7

DISPLACEMENT RUNS - SET-UP AND STRATEGIES

7.1 Experimental Set up:

Unconsolidated Ottawa sand packs were used for all displacement runs. The specifications of the sand, reservoirs and pumps are as given by Bansal.(1) Only minor changes in the Bansal Scheme were made, as follows:

(i) Slight modifications in the piping arrangement, as shown in Fig. 21.

(ii) The core holder's length was reduced to 91.4 cm (3 ft) and only one window, at the down-stream end, was provided. The distance between the two pressure tappings on the core-holder was 30 cm, and the cover-flanges carried stainless steel filters as shown in Fig. 22. Table 5 gives the detailed dimensions of the two core holders used.

(iii) A short piece of tygon tubing was inserted at the down stream end immediately after the covering end flange (Fig. 22). This eliminated the problem of additional oil in the down-stream piping, and thus provided for better monitoring of the oil saturation efficiency.

7.2 Flooding Strategies:

Two strategies were used for the flooding experiments.

(I) Secondary Flooding Mode:

About 3.0 pore volumes (PV) of the surfactant solution was injected in each case. The reference flood was

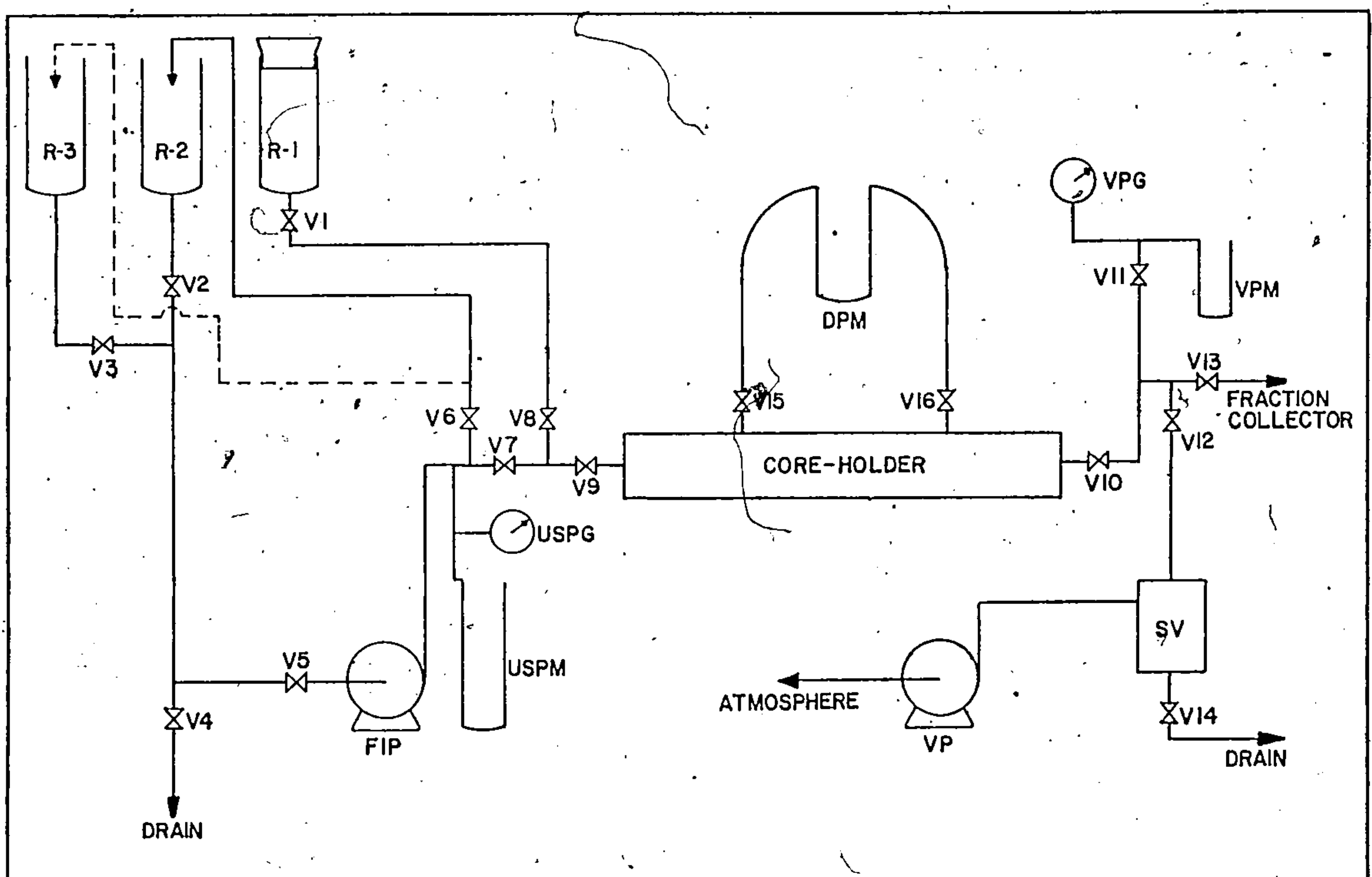
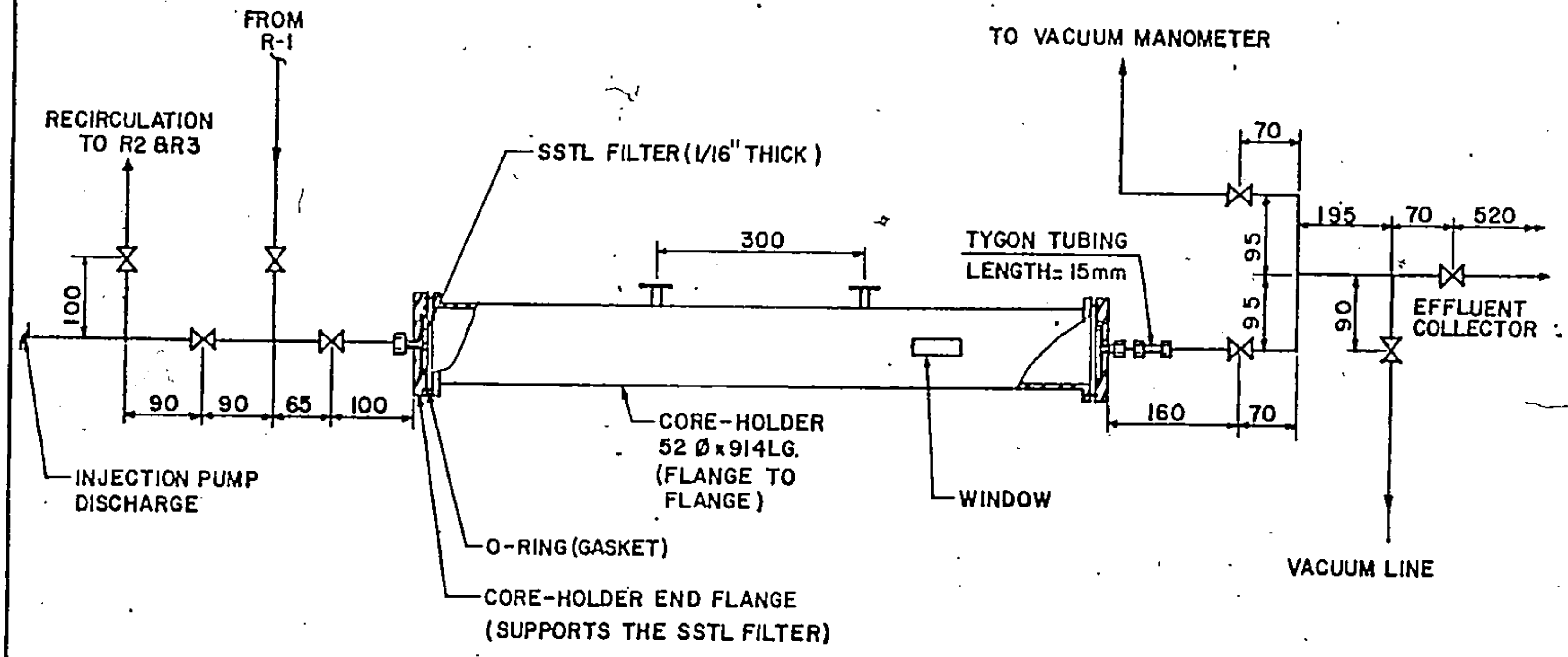


FIG-21: SET UP FOR DISPLACEMENT STUDIES

Legends For Fig. 21

R - 1	Oil Reservoir
R - 2	Water/Secondary Surfactant-system Reservoir
R - 3	Tertiary Surfactant System Reservoir
V1 to V16	Various Isolation and Link-up Valves
FIP	Surfactant Injection Pump
USPM	Upstream Pressure Manometer
USPG	Upstream Pressure Gauge
DPM	In-core Differential Pressure Manometer
VPG	Vacuum Pressure Gauge
VPM	Vacuum Pressure Manometer
SV	Liquid Separation Vessel
VP	Vacuum Pump



ALL PIPING OF DIAMETER 4·5mm
ALL DIMENSIONS ARE IN MILLIMETERS

Fig 22; DETAILS OF CORE-HOLDER FLANGES AND IN-LINE PIPING.

TABLE 5

DETAILS OF CORE-HOLDERS

Dimensions	Core-holders	
	A	B
Average Inside Diameter of pipe, I.D., cm	5.32	5.27
Average Inside Diameter of upstream flange (welded), cm	5.19	5.19
Average Inside Diameter of downstream flange (welded), cm	5.20	5.20
Thickness of upstream flange, cm	0.70	0.70
Thickness of downstream flange, cm	0.80	0.90
Length of core-holder (without end flanges), cm	89.70	89.90
Pipe cross-sectional area, cm^2	22.23	21.20
Total volume of core-holder, cm^3	2025.67	1994.89

that of water (1.5% NaCl) and the following lignosulfonate solutions were used in this scheme: Marasperse N-22 in the concentrations 1, 3 and 6%, Marasperse C-21 in the same concentrations all at a constant salinity of 1.5%.

(II) Tertiary Flooding Mode:

Firstly, 1 PV of water (1.5% NaCl) was injected, followed by about 2 PV of the surfactant solution.

The following formulations were used in the tertiary floods.

(i) 6% C-21 in 1.5% NaCl + 1.0% Butanol-1
(ii) 2% PT 420 in 1.5% NaCl
(iii) 2% PT 420 in 1.5% Nacl + 0.5% C-21
(iv) 2% PT 420 in 1.5% NaCl + 1.0% C-21
(v) 3% PT 420 in 1.5% NaCl
(vi) 3% PT 420 in 1.5% NaCl + 1.0% C-21
(vii) 3% PT 420 in 1.5% NaCl + 2.0% C-21
(viii) 4% PT 450 in 1.5% NaCl
(ix) 4% PT 450 in 1.5% NaCl + 1.0% C-21
(x) 4% PT 450 in 1.5% NaCl + 2.0% C-21

7.3 Flooding Procedure and Effluent Analysis:

Essentially the dearation, saturation and displacement scheme developed by Bansal(1) was used. The cleaned and dried coreholder with associated flanges was packed with sand and weighed to determine the sand content. The porosity and pore-volume of the pack was determined from this data. The in-line piping was also cleaned and dried and the coreholder hooked up. Using appropriate valves (V10, V11, V12, in Fig. 21), the coreholder was put under vacuum for 12 to 18 hours to dearate it completely.

After a leakage test to ensure there was no leakage of air into the system, the oil saturation was commenced by opening valves V8, V1 in Fig. 21. The total saturation time varied from 1200 to 1800 seconds. As soon as the oil appeared in the down-stream tygon tubing all valves were shut off. Meanwhile, the secondary flood solution has been under circulation through the pump and the circulation piping (Fig. 21). After 15 to 30 minutes of circulation, the displacement run was commenced by opening valves V7, V9, V10 and V13 (shown in Fig. 21), all others remaining closed. Observations of the upstream and in-core manometers(UPSM, DPM of Fig. 21) were made at about 15 minute intervals. The times for oil appearance in the effluent collector as well as for water or surfactant breakthrough were noted. After injection of a predetermined quantity of solution (surfactant), the displacement run was discontinued. The set-up was then readjusted for the tertiary run or dismantled for cleaning. The injection pump was kept at the same 25% stroke-length setting, as used by Bansal,(1) for all the runs.

The sequence of effluent collection was as follows:- first a 250 ml, then 200 ml (4 flasks) and the remainder 100 ml flasks in each run. For the higher lignosulfonate concentrations and the mixed surfactant systems, 1 ml(per 35 ml of effluent) of 0.03 Molar hexadecyltrimethyl bromide (HDTB) was used to release any emulsified oil. The effluent (with or without the HDTB emulsion breaker) of about 35 to 36 ml held in each plastic centrifuge tube was centrifuged for 10 minutes and the produced oil and water/surfactant determined volumetrically.

7.4 Live Chatham Crude and Associated Viscosity Variations:

This crude was to be used as received for both surfactant formulations and displacement studies. It was received in closed 5 gallon containers. For the formulation studies, and for most of the secondary flood runs, the oil exhibited constant uniform properties (such as density and viscosity). However, by the time about half of the oil in the container had been used up, abnormal flooding behaviour in the subsequent oil displacement runs was observed. This was characterised by early water breakthroughs and consequent lowering of the final oil recoveries relative to those obtained in the earlier floods. A remeasurement of the oil viscosity indicated a four-fold increase over the initial value. A sample of the oil was carefully taken from the bottom of the tank and examined under a microscope. Fine solid particles were conspicuously present. The oil container was then carefully emptied and a thick (almost oil-free) sediment was observed to remain at the bottom. In order to obtain a stock whose properties were close to those of the oil used in the earlier experiments, the upper half of the oil in the second 5 gallon container was carefully siphoned off. No further investigations as to the composition of the suspended materials, or to their origin, were made.

PART III

EXPERIMENTAL RESULTS AND DATA ANALYSIS

CHAPTER 8

MAIN FEATURES OF THE SURFACTANT FORMULATION STUDIES

8.1 Concentration Units and General Surfactant System Properties:

(a) Units of concentration, phase stability:

The concentration of all solid or semi-solid constituents of the various surfactant systems formulated are in weight per volume of solution (%) Such constituents include lignosulfonates, petroleum sulfonates, salt (NaCl), caustic (NaOH) as well as other additives. The concentration of the liquid additives such as butanol and methanol is expressed in volume per volume of solution (%). In the case of lignosulfonate or lignosulfonate-additive formulations, 10% stock solutions of the lignosulfonate were diluted after the addition of accurately measured amounts of the additive to the required strengths (by the addition of water). In the case of the petroleum sulfonates, 5% stock solutions were prepared by gradual leaching of the weighed material with warm water (40 to 60°C). In order to make up a desired mixed surfactant system, the calculated amounts of salt (NaCl) and Marasperse C-21 were weighed out, dissolved in water and then introduced into an appropriate volume of the stock solution. The mixture was then brought to the required concentration by the addition of water.

The surfactant system thus prepared is said to be (i) stable if no visible sediments, solid precipitates (or phase separation) appear in it, within one month of preparation of the system, (ii) slightly unstable if there is sedimentation or phase separation within the one-month period but the sediment disappears on shaking. (iii) highly unstable if insoluble precipitates and suspended particles appear in the system.

(b) Data Presentation:

Table 6 (Appendix A) lists the surface tension, pH and density of all the surfactant formulations prepared in this study. Those systems denoted by asterisk exhibited varying degrees of instability, all others were stable for the entire duration of the study. The surface tension data are the true (absolute) values obtained after correction of the apparent recorder readings. A typical computer routine for correcting the apparent tension data is shown in Appendix D.

Table 7 gives the interfacial tension data obtained using formulations under different strategies and involving different crude oils. Except in the case of the mixed surfactant systems, all other data were obtained with the du Nouy tensiometer and corrected as per Appendix D.

The viscosity and density of the various crudes are given in Table 8(A) of Appendix A; while Table 8(B) summarises the viscosities of most of the significant (by interfacial activity) formulations made. As indicated, the viscosities of some of the mixed surfactant systems were not exactly reproducible, exhibiting dependency on shearing rate, shearing time and age of solution. This thixotropic trend is demonstrated further in Table 9.

The data given in Tables 6, 7, 8 have been plotted in order to emphasize the important trends in the values obtained. Figs. 23 to 32 are plots of surface tension vs. concentration (of lignosulfonate, brine or additive as appropriate), and concentration vs. pH; for the various formulations. The strategies for which each study was made and the crude system involved are also indicated. Similarly Figs. 33 to 42 are interfacial tension vs. concentration, and concentration-viscosity plots for the various surfactant systems and crude oils. The various curves presented do not represent any correlations or regression models. They merely illustrate trends in the data which are not amenable to intra-or extra-polations.

8.2 Highlights of the Formulation Studies for Lloydminster Crude:

From Fig. 23, acidification of Marasperse N-22 (for the same concentration) produced a reduction in surface tension, however as can be seen from Fig. 33, the IFT against the Lloydminster crude increased over those obtained with the natural solutions. Marasperse N-22 at concentrations above 1% gave lower IFT than C-21 and 6% was optimum for the concentration range investigated. Inavailability of the Lloydminster crude prevented any further work beyond the characterisation (by strategy 1) study.

8.3 Highlights of the Formulation Studies for Gosfield South Crude:

The IFT trends in the strategy 1 preliminary studies are shown in Fig. 34. Marasperse C-21 at 6% concentration was chosen instead of the N-22. For strategy 2 pH screening studies, both 6% and 10% N-22 were used. The IFT trends are also shown in Fig. 34. From these, it was concluded that an alkaline medium was better than an acidic one, and that 6% N-22 was optimum at high pH. Following strategy 2 further, lignosulfonate-caustic systems of definite alkaline strengths were studied for interfacial activity as presented in Fig. 35. The results were compared with the reference blank caustic solutions. It was obvious that at concentrations less than 1% caustic, the blank solutions performed better than the N-22 - caustic systems. The IFT data obtained in the strategy 3 (organic additives screening) studies, are presented in Fig. 36. The lignosulfonate concentration was fixed at 6%, and the concentrations of the various additives ranged from 1 to 20% (by volume). It is thus seen from Fig. 36, why 1-butanol was selected for further studies. The IFT data from strategy 4 studies have been plotted under various coordinates in Fig. 37. From the IFT data values obtained with brine in the concentration range of 0 to 5%, 2% concentration was chosen for incorporation into the N-22 - caustic and C-21 - butanol systems. No significant reduction in the IFT of the caustic systems was obtained by the introduction of the brine; however the reduction in the C-21 - butanol systems was significant especially at lower butanol concentrations. The final plot in Fig. 37 resulted from an optimisation study using live Chatham crude. Here, the concentration of butanol-1 was kept at 1% and the salinity varied between 0 to 10%.

A summary of the low tension formulations involving lignosulfonates and various additives is as follows:-

System	IFT (range) dynes/cm
6% N-22 + NaOH (0.1 to 3%)	1.24 to 0.25
Blank NaOH - 0.1 to 3%	0.25 to 1.28
6% N-22, 2% NaCl + NaOH (0.1 to 3%)	1.28 to 0.42
2% NaCl + NaOH (0.1 to 3%)	0.42 to 1.28
6% C-21 + butanol - 1 (1 to 10%)	7.08 to 1.68
6% C-21, 2% NaCl + butanol - 1 (1 to 10%)	3.75 to 1.72

8.4 Main Features of the Formulation Studies for Live Chatham Crude:

From the results presented above, it became obvious that the incorporation of more active surfactants into the lignosulfonates was necessary for the attainment of ultra-low IFT. As earlier explained, the Chatham crude was supposed to be of the same origin as the Gosfield crude. Thus after a preliminary density and viscosity measurement of the new crude (to ensure reasonable comparison with those of Gosfield crude), the strategy 5 studies were undertaken. Following the conclusions from results obtained in strategies 1 and 2, 6% C-21 was maintained as per strategy 5(A). Petrostep 420 could be added only up to 0.5% before phase separation occurred, even then, the IFT was only about 0.30 dynes/cm. Addition of hexanol-1 did not help much as can be seen from Table 7. The rest of the data of Tables 6, 7, 8 and 9 on the mixed-surfactant systems were obtained by strategy 5(B). In the case of the 2% Petrostep concentration, phase separation occurred at a lignosulfonate concentration of 2% and beyond, while at 3% and 4% Petrostep concentrations, the C-21 tolerance was 3% maximum. The resulting surface tension vs. C-21 concentration plots are presented in Figs. 29 and 30, while the more interesting IFT vs concentration and viscosity-concentration plots are given in Figs. 38, 39 and 40. As is evident from these plots, the IFT dropped from about o.11 dynes/cm to about ($1x10^{-2}$) dynes/cm as the lignosulfonate concentration was gradually increased. An optimum was reached, after which the IFT started to increase again. A similar trend in viscosity increase was noted. The viscosity of these mixed surfactant systems increased as much as four fold over those of Petrostep solutions alone.

In strategy 6 studies, the Chatham crude was characterised as per strategy 1 in order to ensure that it was not very different from the Gosfield crude. The IFT data of Table 7 indicated that a significant difference does infact exist between the two crudes. In particular, the water (1.5% NaCl) tension value was only 4.55 dynes/cm with Chatham but close to 20 dynes/cm for Gosfield crude. However, some important conclusions made earlier were utilised in formulating the strategy 6 surfactant systems reported in Tables 6, 7 and 8. The surface tension and pH data for these systems are plotted in Figs. 31 and 32 while the IFT and viscosity data are presented in Figs. 41 and 42. At 1.5% constant salinity, N-22 appeared better than C-21 (Fig. 41) and an optimum concentration (for IFT reduction) of 3% was also noted. However the reduction in IFT over the water (1.5% NaCl) value obtained with these lignosulfonate solutions was not very significant. As evident from Fig. 42, N-22 solutions containing butanol-1 showed better properties than corresponding C-21 systems, especially at 3% lignosulfonate concentration.

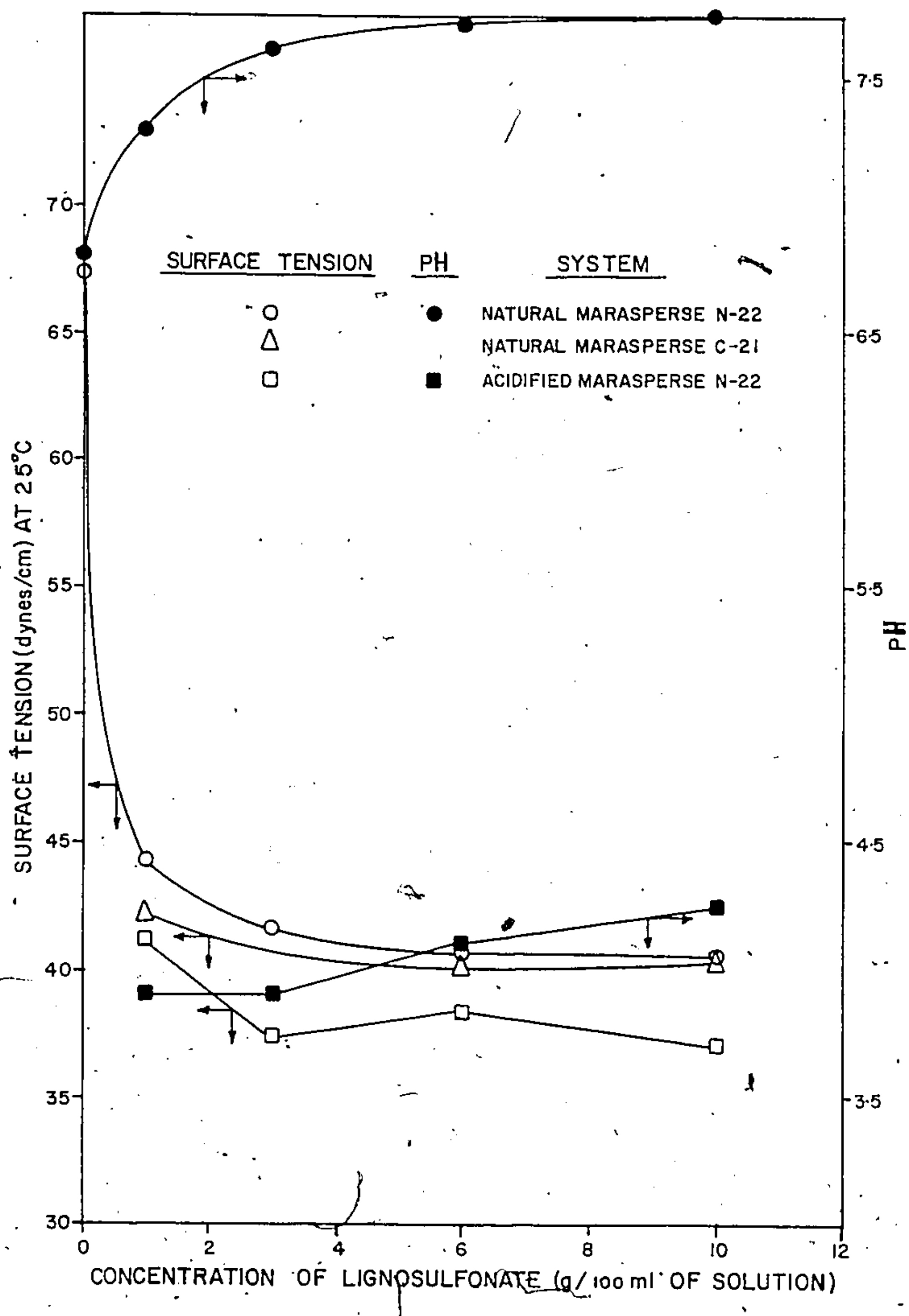


Fig.23-SURFACE TENSION AND PH PLOTS FROM STRATEGY-I STUDIES FOR LLOYDMINSTER CRUDE

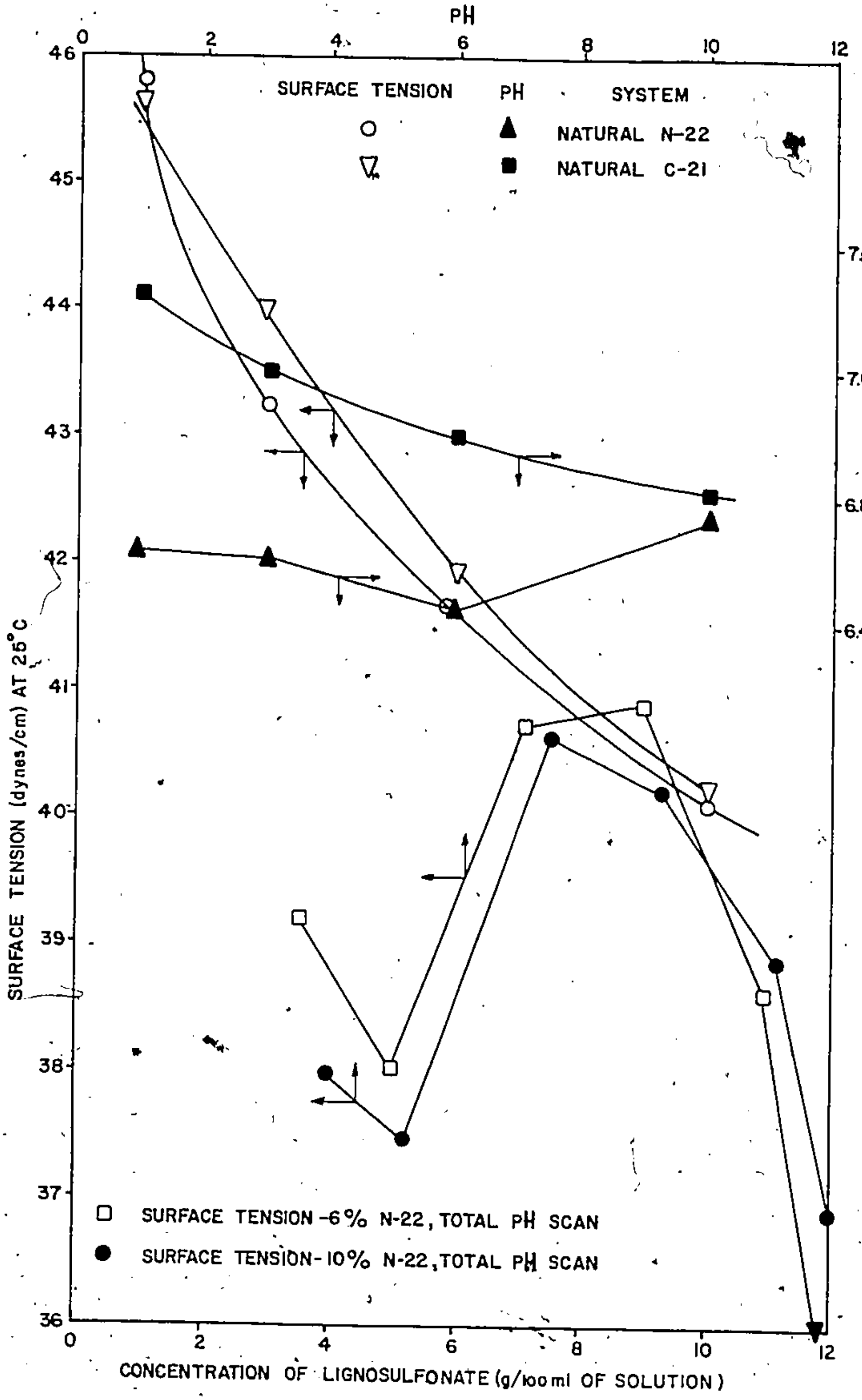


Fig.24- SURFACE TENSION AND PH FROM PRELIMINARY STUDIES (STRATEGIES 1&2) FOR GOSFIELD SOUTH CRUDE

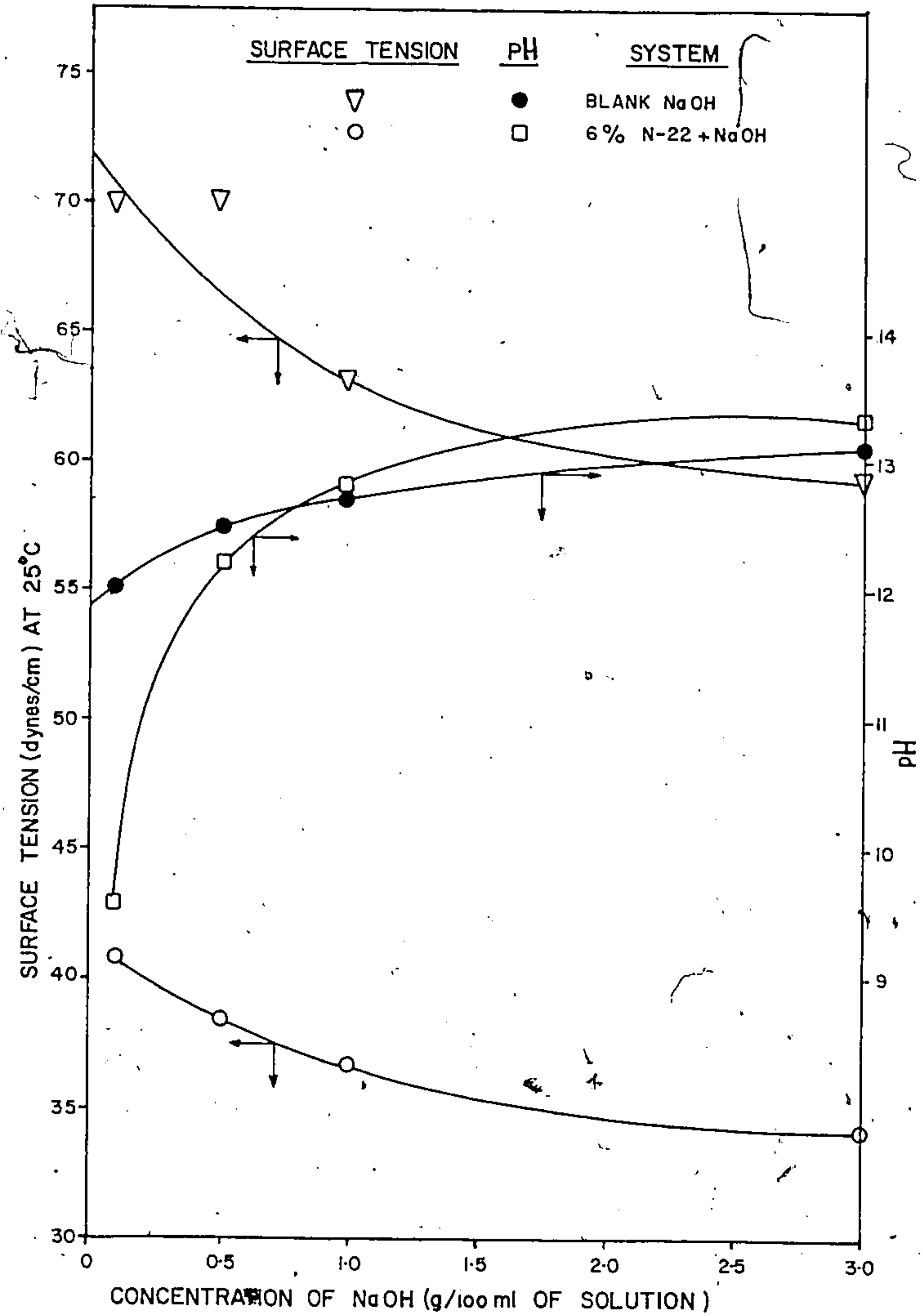


Fig.25- SURFACE TENSION AND PH PLOTS FOR N-22+CAUSTIC SYSTEMS (STRATEGY-2)

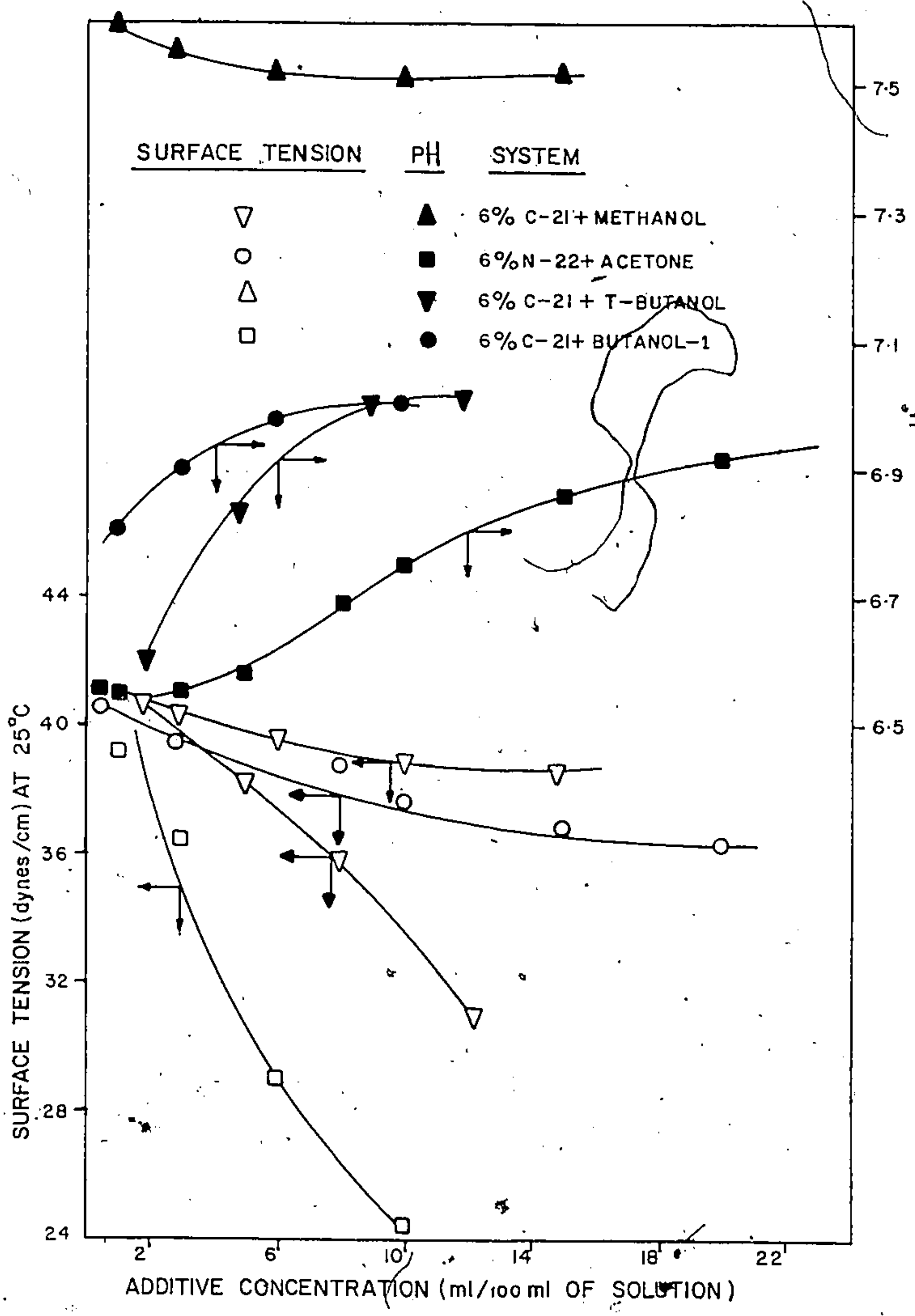


Fig. 26- SURFACE TENSION AND PH PLOTS FOR STRTEGY-3 SURFACTANT SYSTEMS.

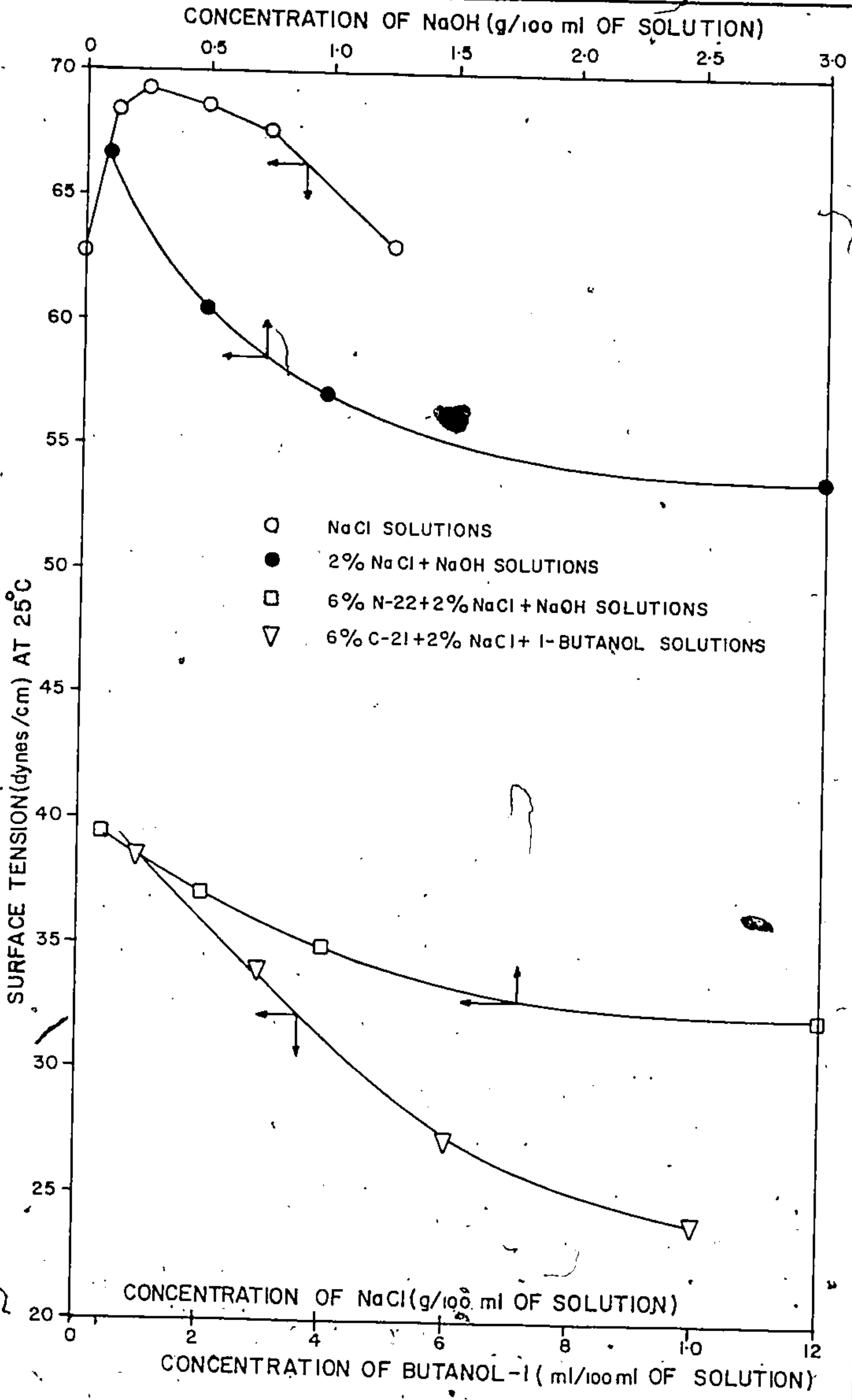


Fig. 27- SURFACE TENSION PLOTS FOR STRATEGY-4 SURFACTANT SYSTEMS

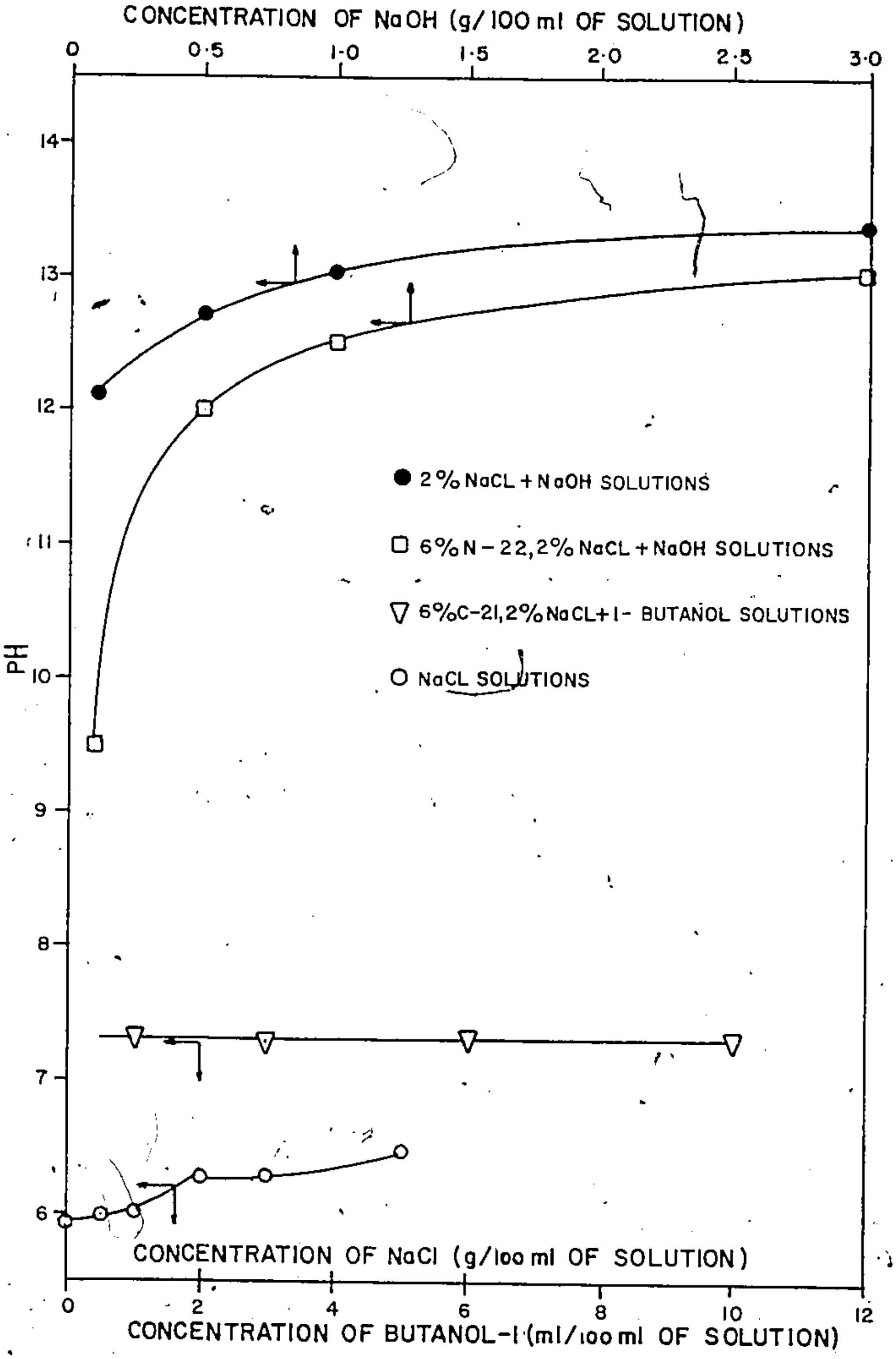


Fig. 28- PH PLOTS FOR STRATEGY-4 SURFACTANT SYSTEMS

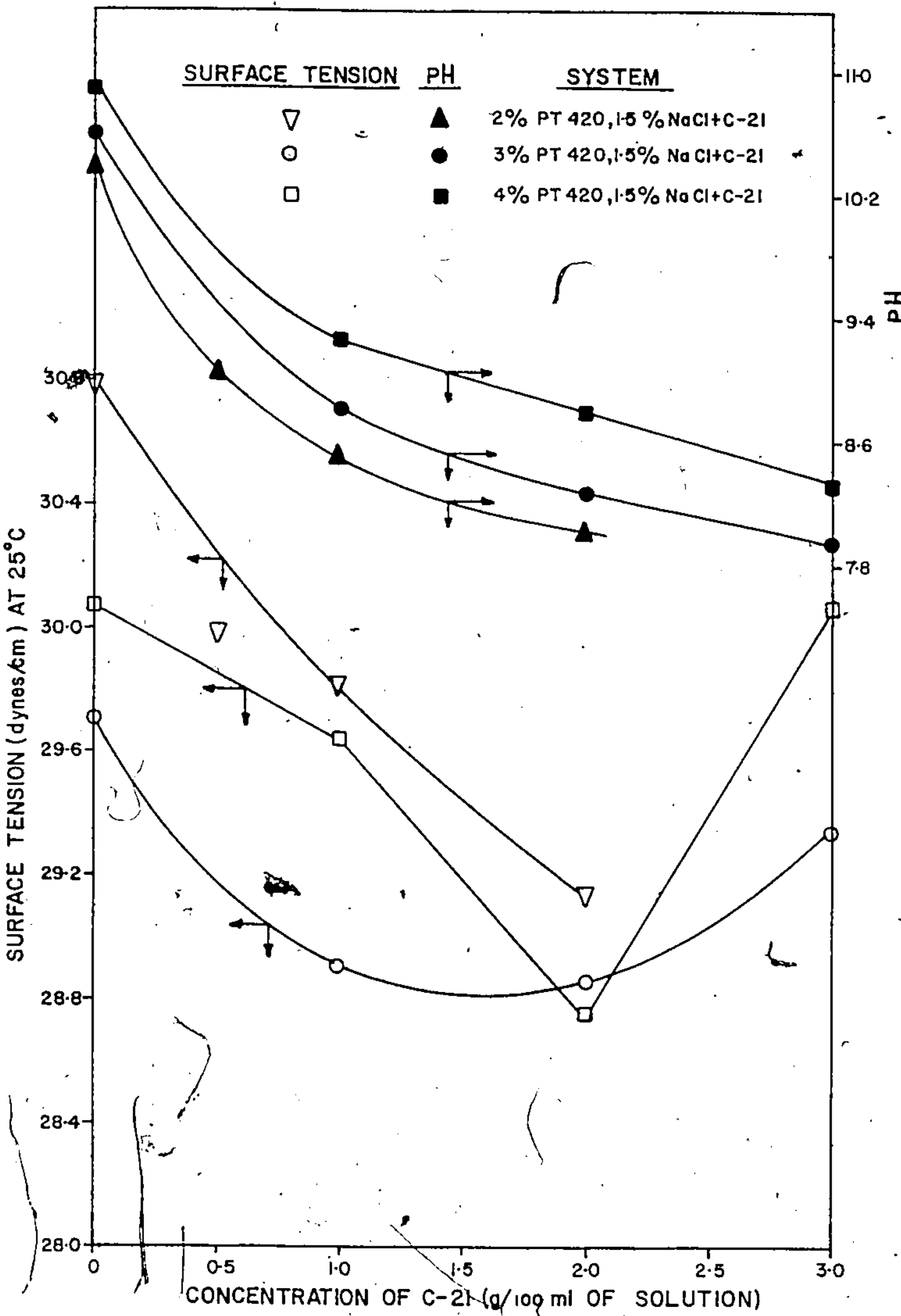


Fig.29-SURFACE TENSION AND PH PLOTS FOR PETROSTEP 420+ C-21 MIXED SURFACTANT SYSTEMS(STRATEGY-5)

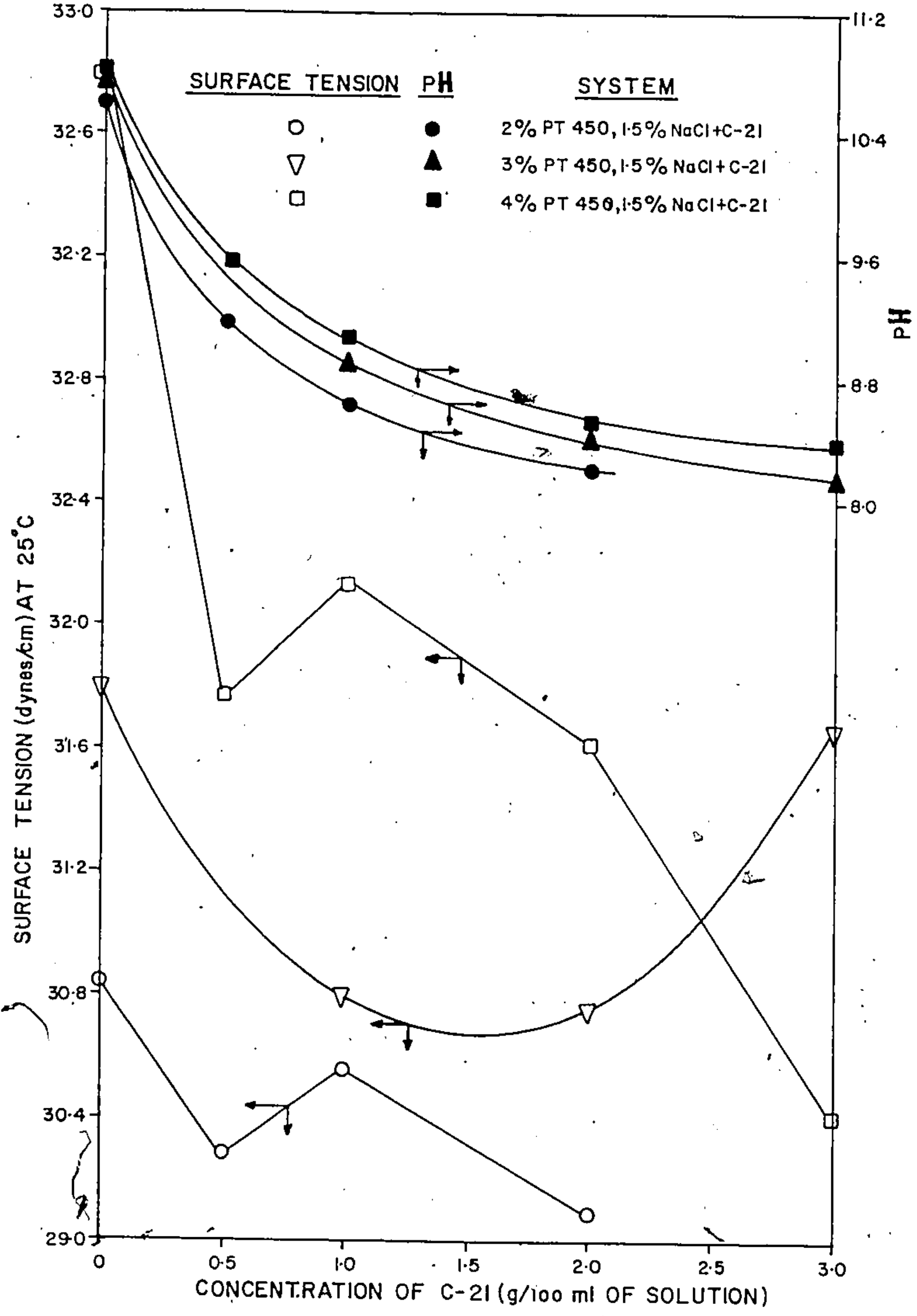


Fig. 30-SURFACE TENSION AND PH PLOTS FOR PETROSTEP 450+ C-21 MIXED SURFACTANT SYSTEMS (STRATEGY-5)

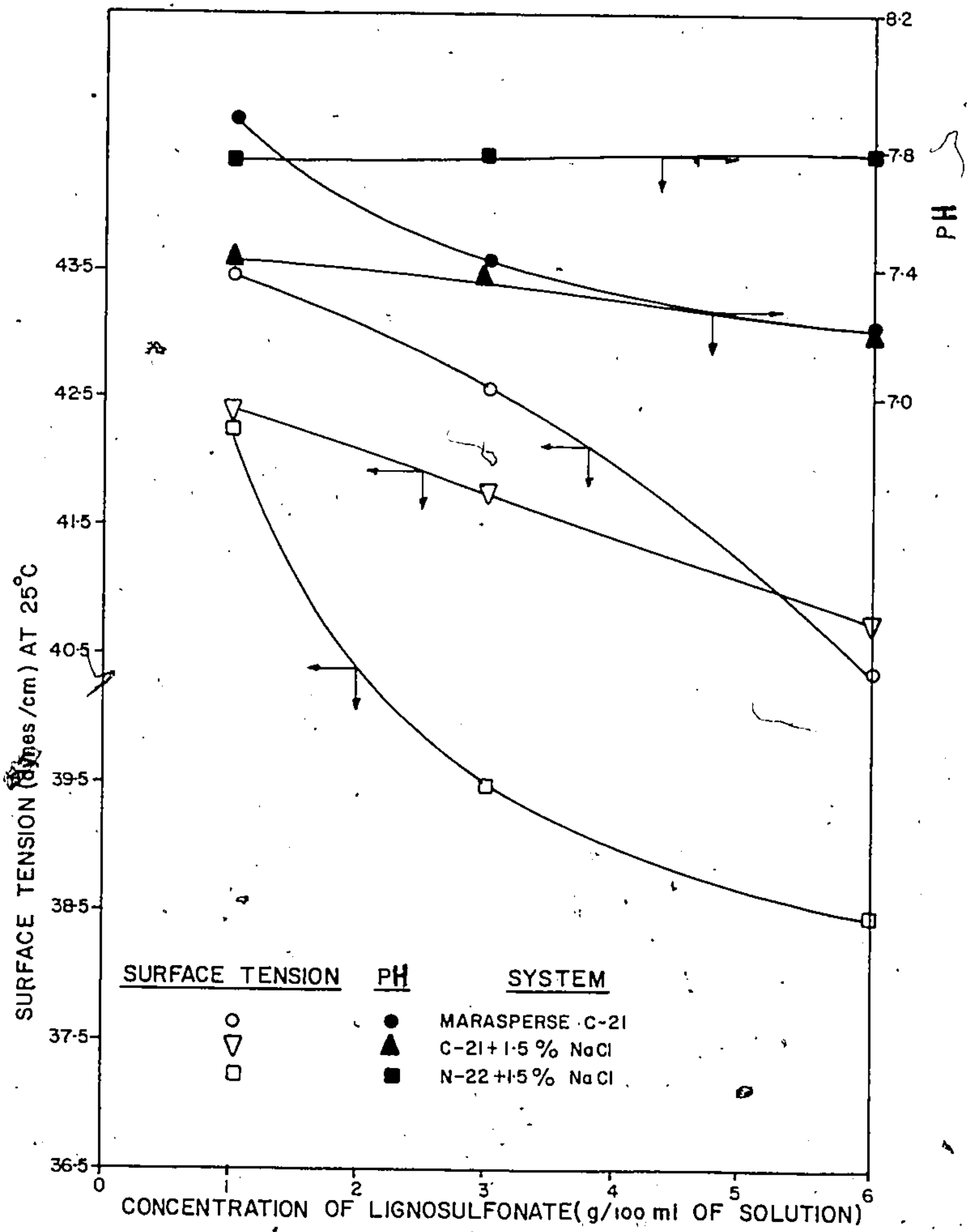


Fig. 31-SURFACE TENSION AND pH PLOTS FOR STRATEGY 6 SURFACTANT SYSTEMS

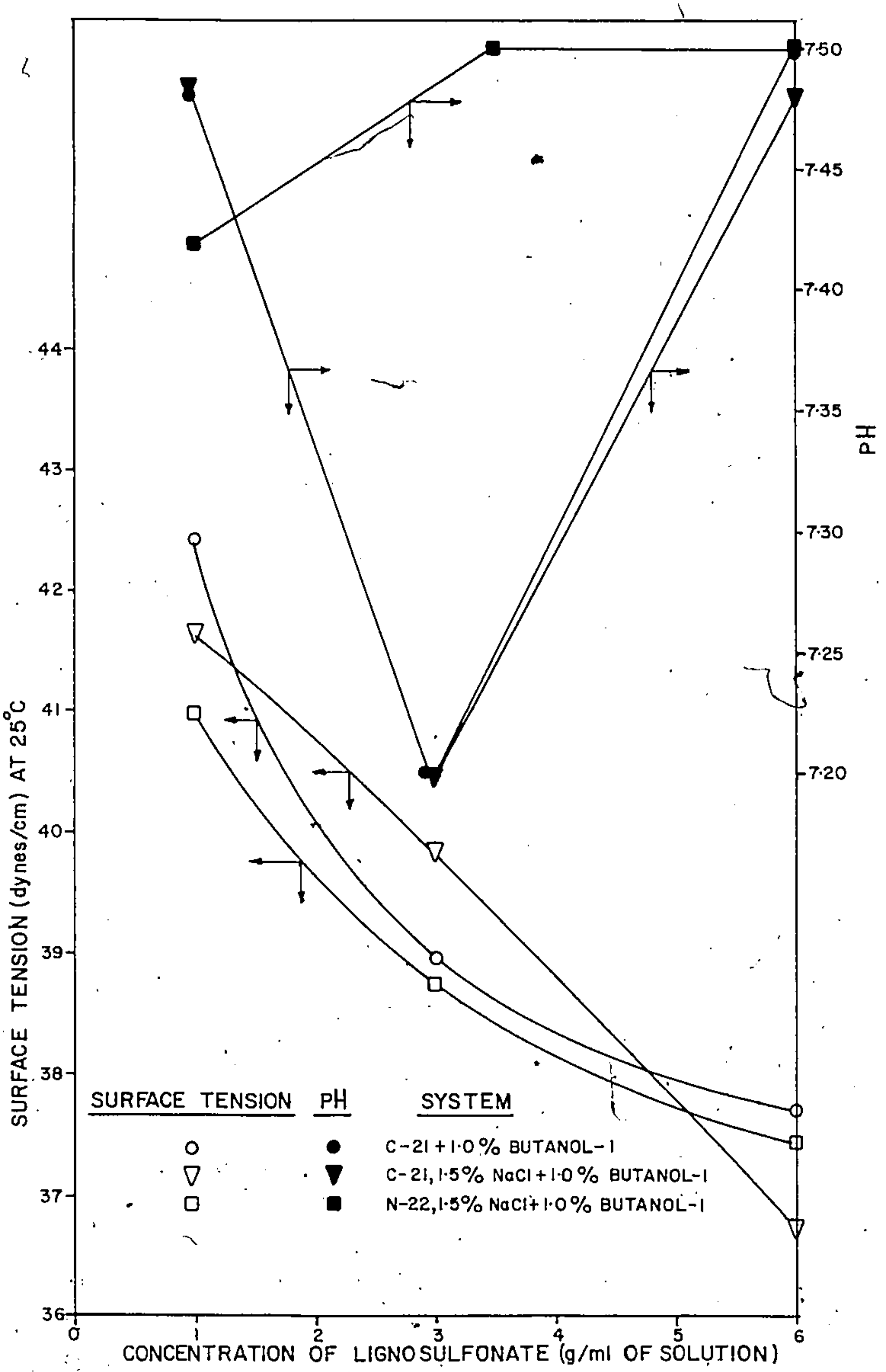


Fig.32- SURFACE TENSION AND PH PLOTS FOR C-21 + BUTANOL-1 SYSTEMS (STRATEGY-6)

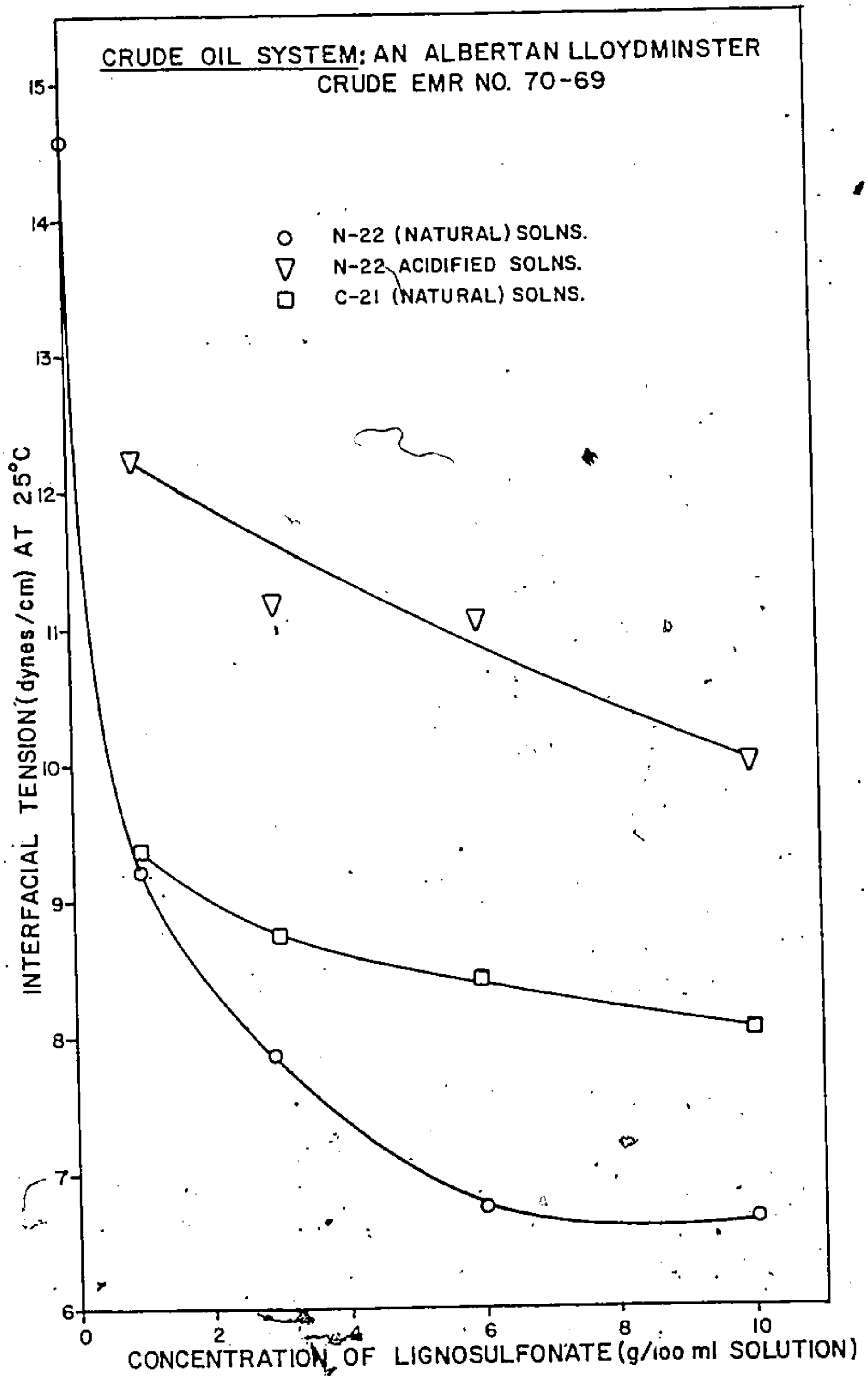


Fig. 33 - IFT PLOTS FROM PRELIMINARY STUDIES (STRATEGY-I) FOR LLOYDMINSTER CRUDE

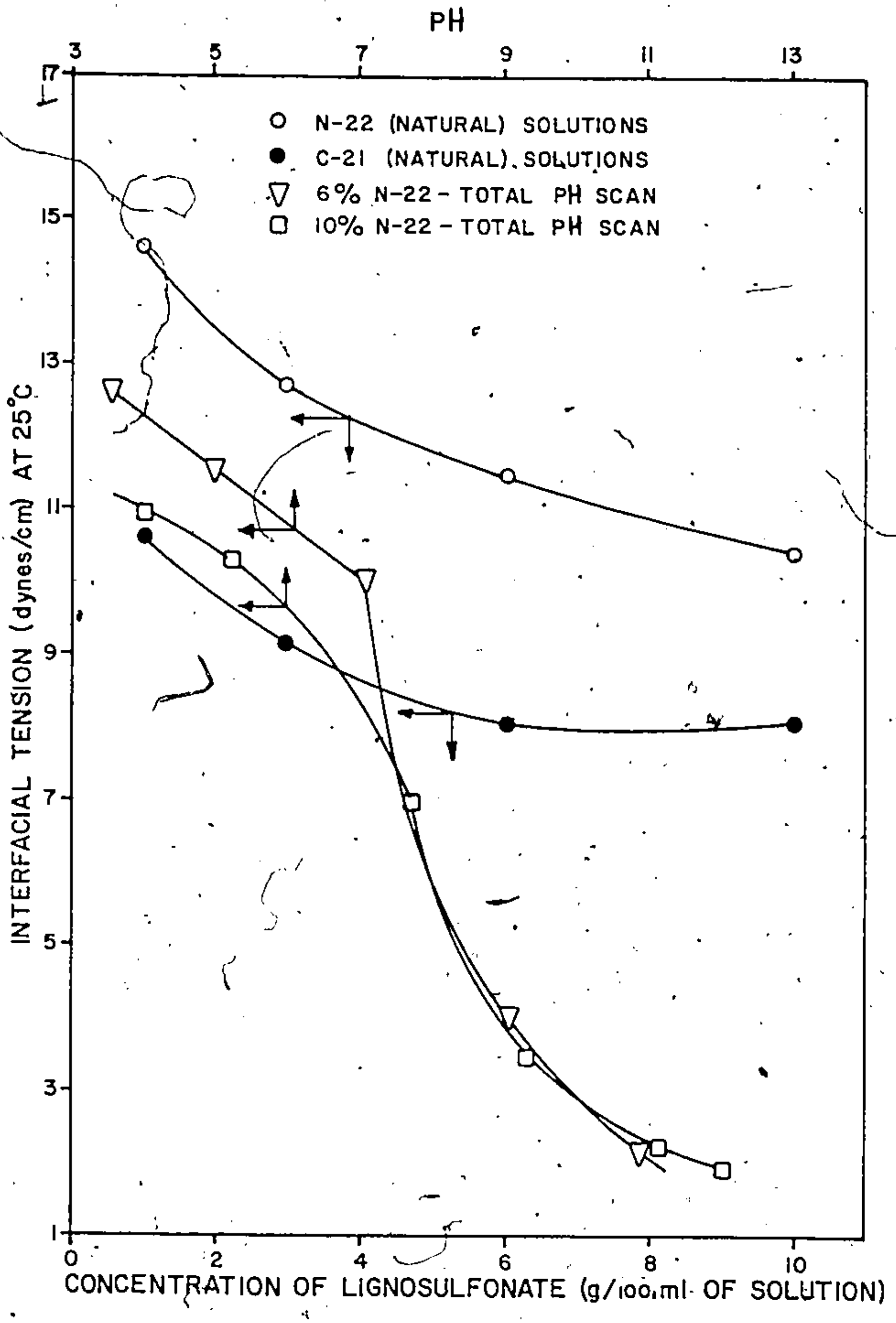


Fig. 34 – IFT PLOTS FROM STRATEGIES 1&2 STUDIES FOR GOSFIELD SOUTH CRUDE

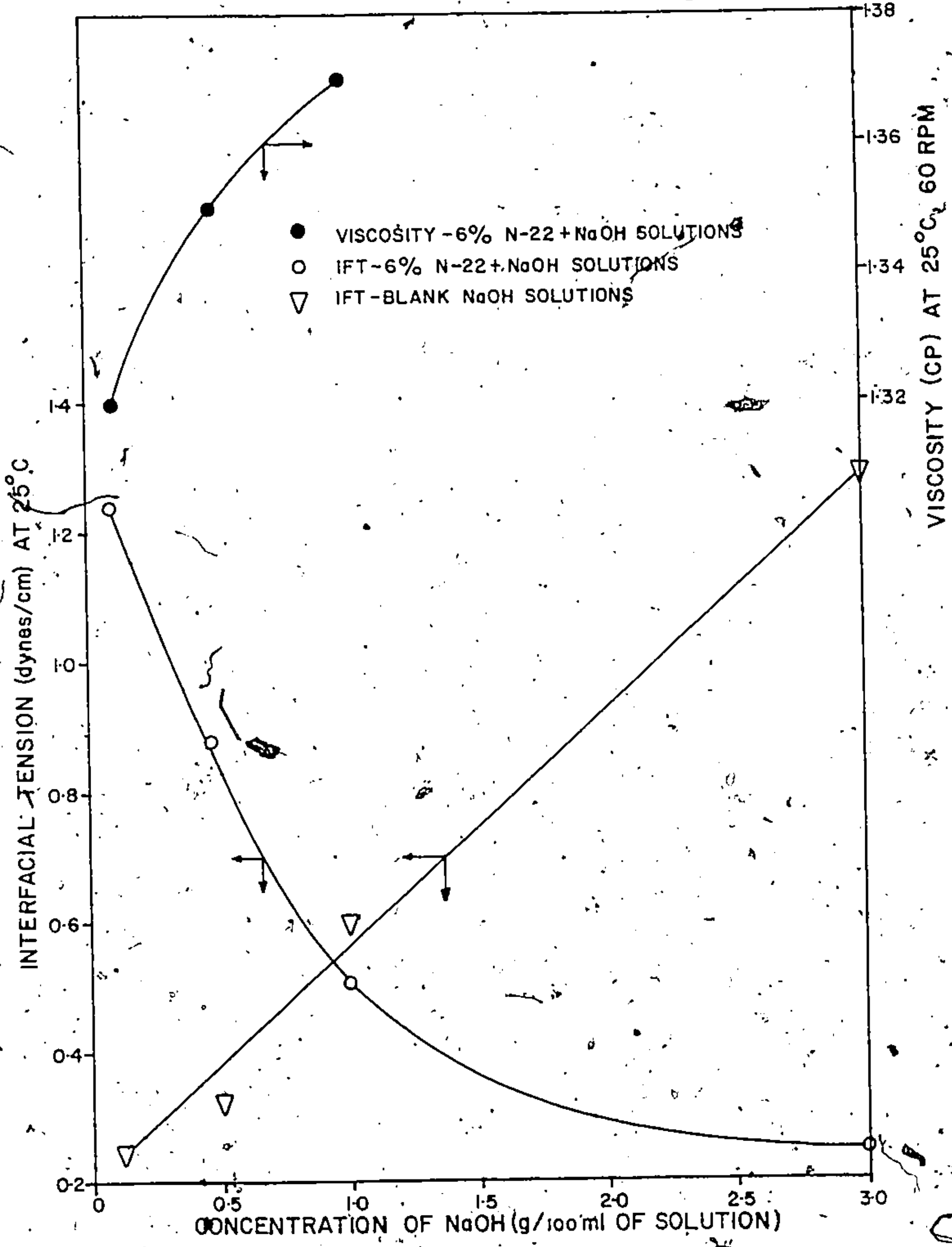


Fig. 35-IFT AND VISCOSITY PLOTS FOR LIGNSULFONATE-CAUSTIC SYSTEMS (STRATEGY-2 STUDIES FOR GOSFIELD SOUTH CRUDE)

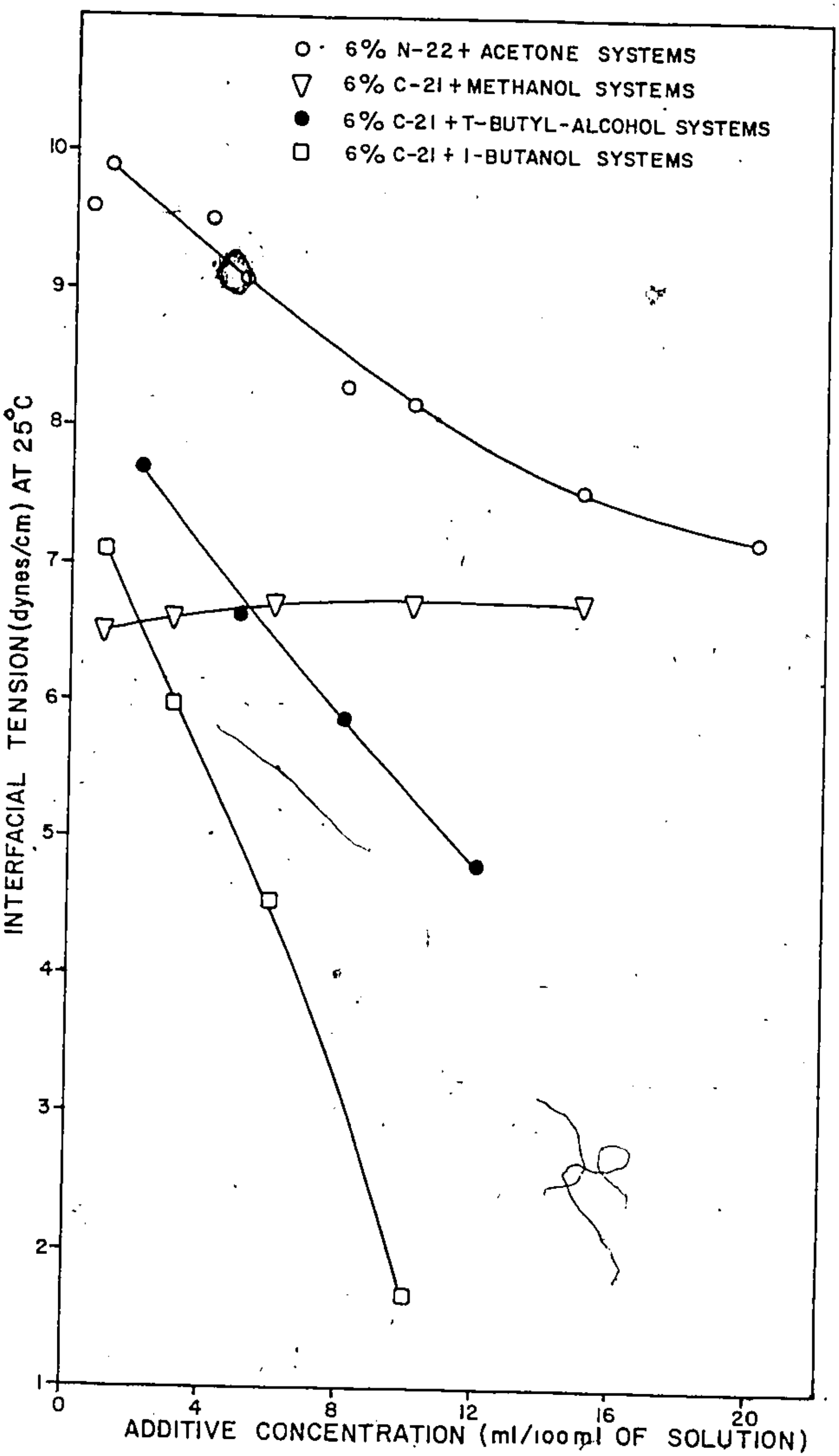


Fig.36- IFT PLOTS FROM STRATEGY-3 STUDIES FOR GOSFIELD SOUTH CRUDE

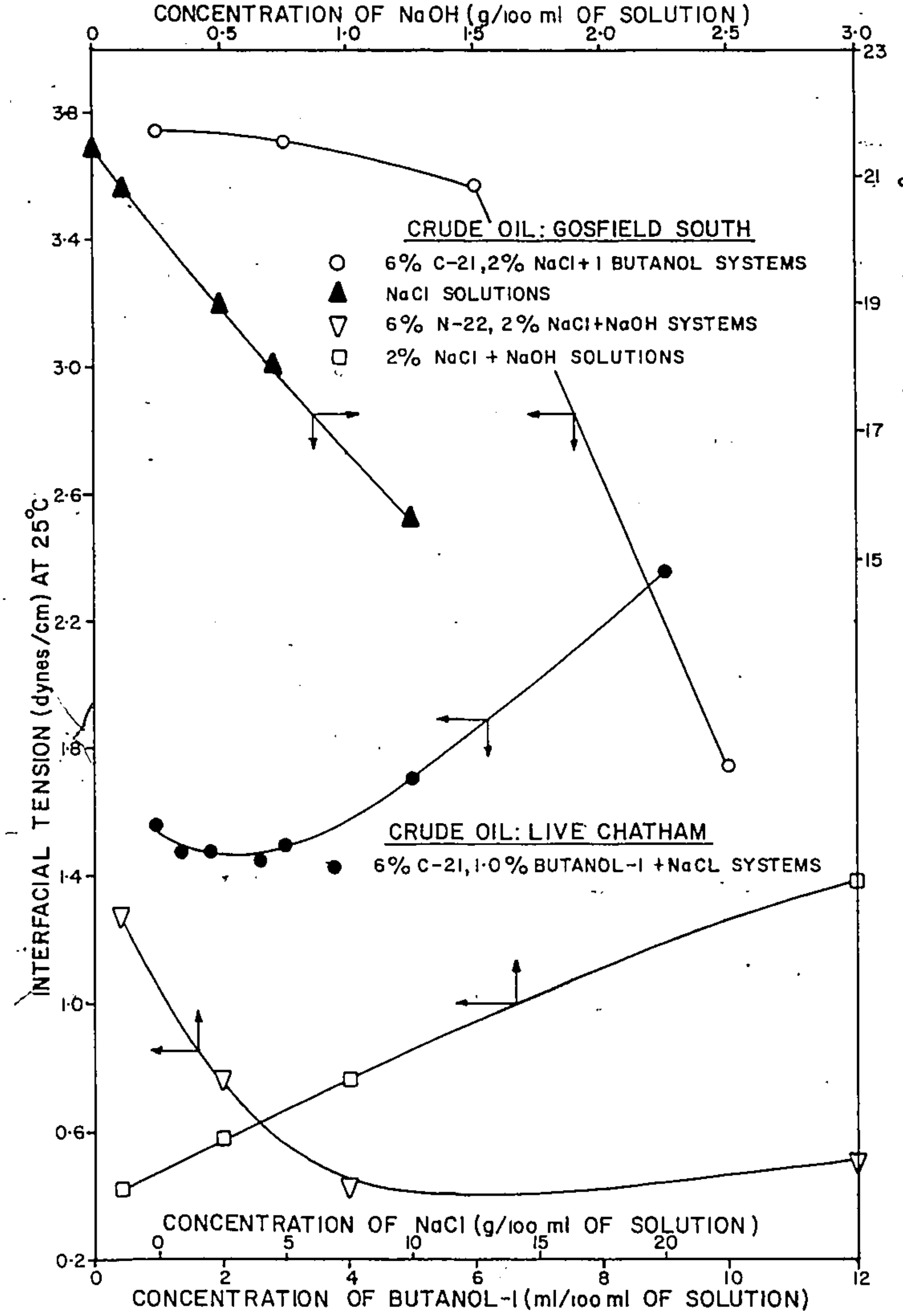


Fig. 37-(i) IFT PLOTS FROM STRATEGY-4 STUDIES FOR GOSFIELD SOUTH CRUDE
(ii) IFT PLOTS FROM BRINE OPTIMISATION STUDIES FOR LIGNOSULFONATE - BUTANOL-1 SYSTEMS AND LIVE CHATHAM CRUDE

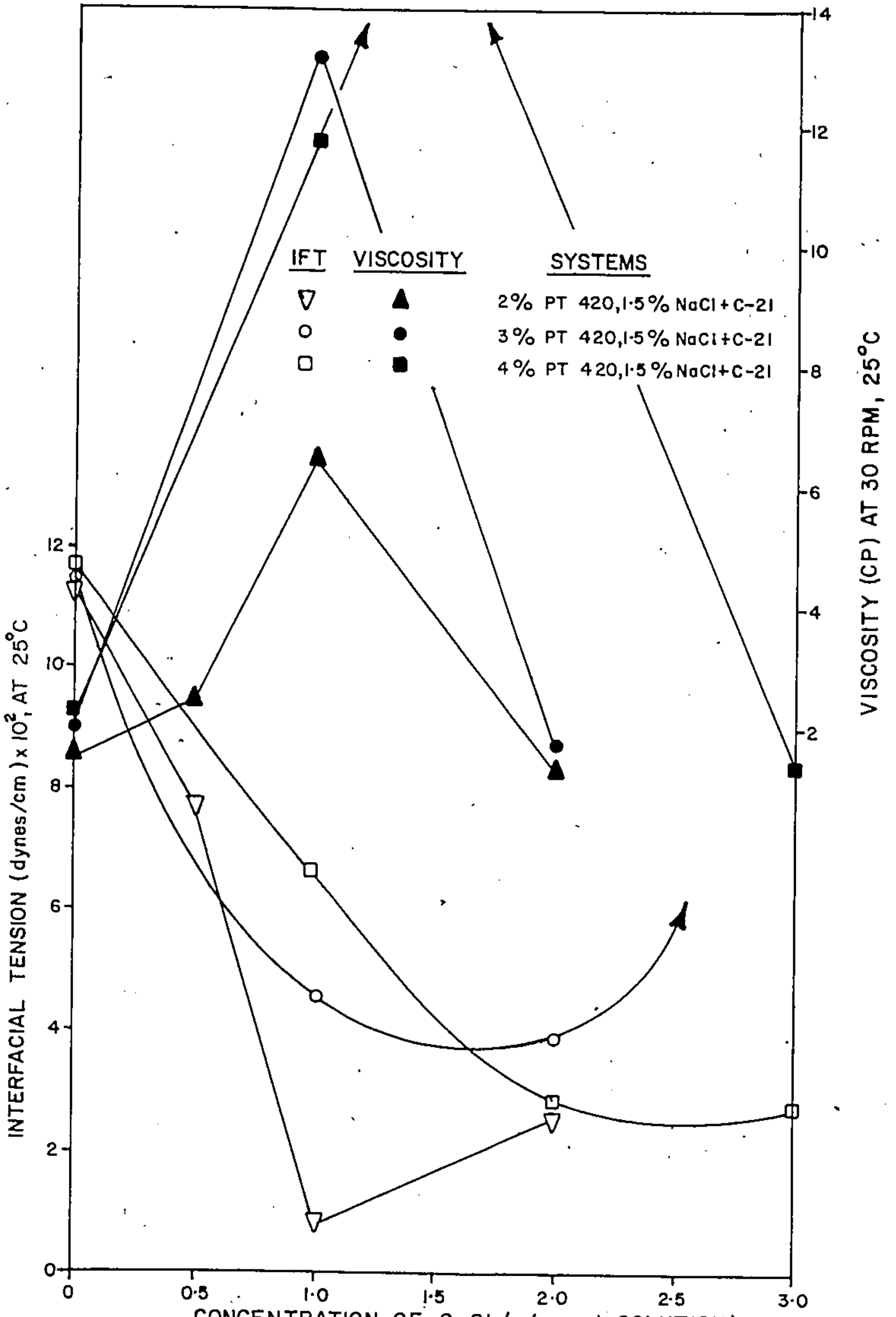


Fig. 38- IFT AND VISCOSITY PLOTS FOR PETROSTEP 420 + C-21 MIXED SURFACTANT SYSTEMS (STRATEGY-5 WITH LIVE CHATHAM CRUDE)

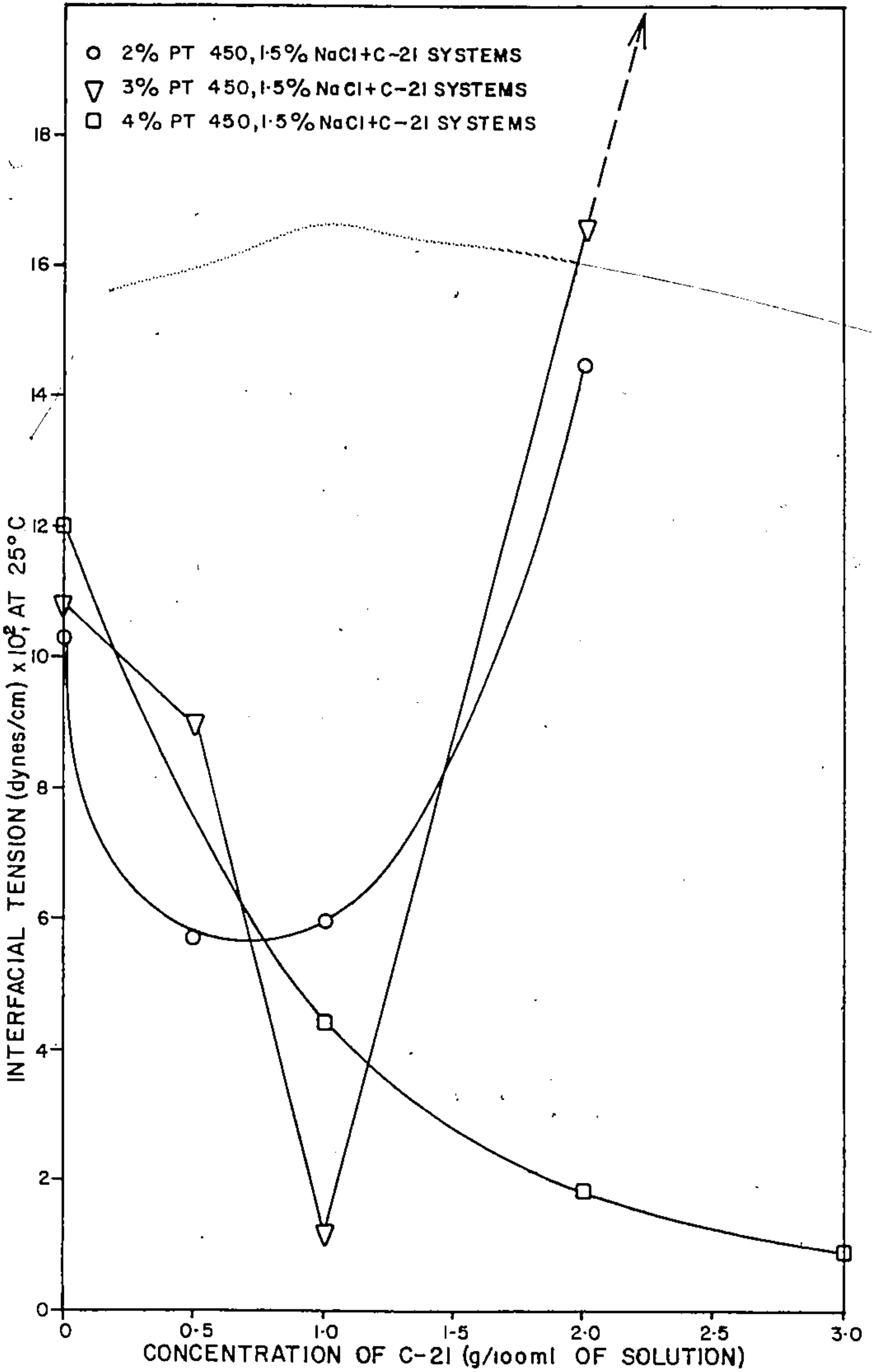


Fig. 39-IFT PLOTS FOR PETROSTEP 450 +C-21 MIXED SURFACTANT SYSTEMS AND LIVE CHATHAM CRUDE

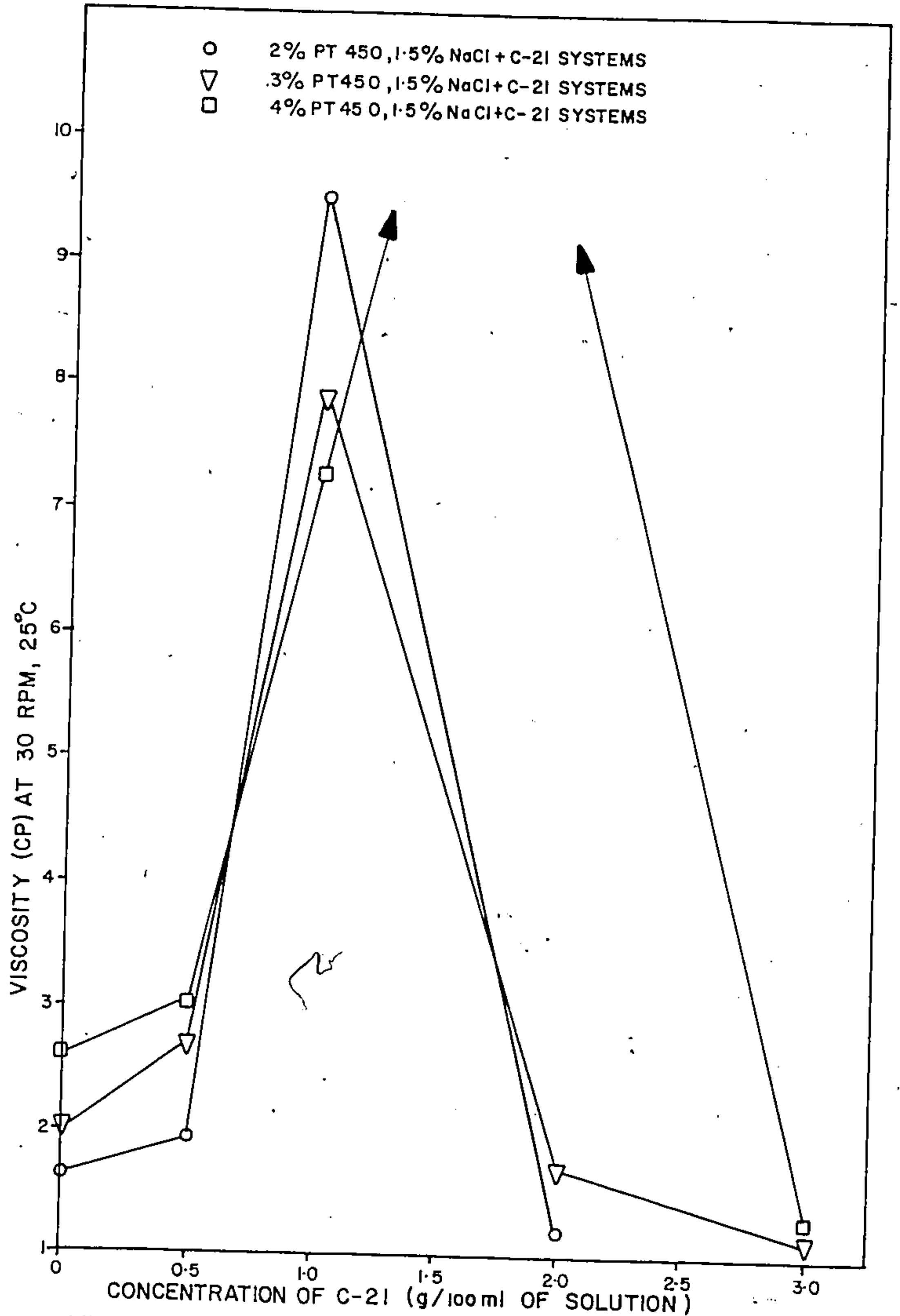


Fig. 40- VISCOSITY PLOTS FOR PETROSTEP 450+C-21 MIXED SURFACTANT SYSTEMS (STRATEGY-5 STUDIES)

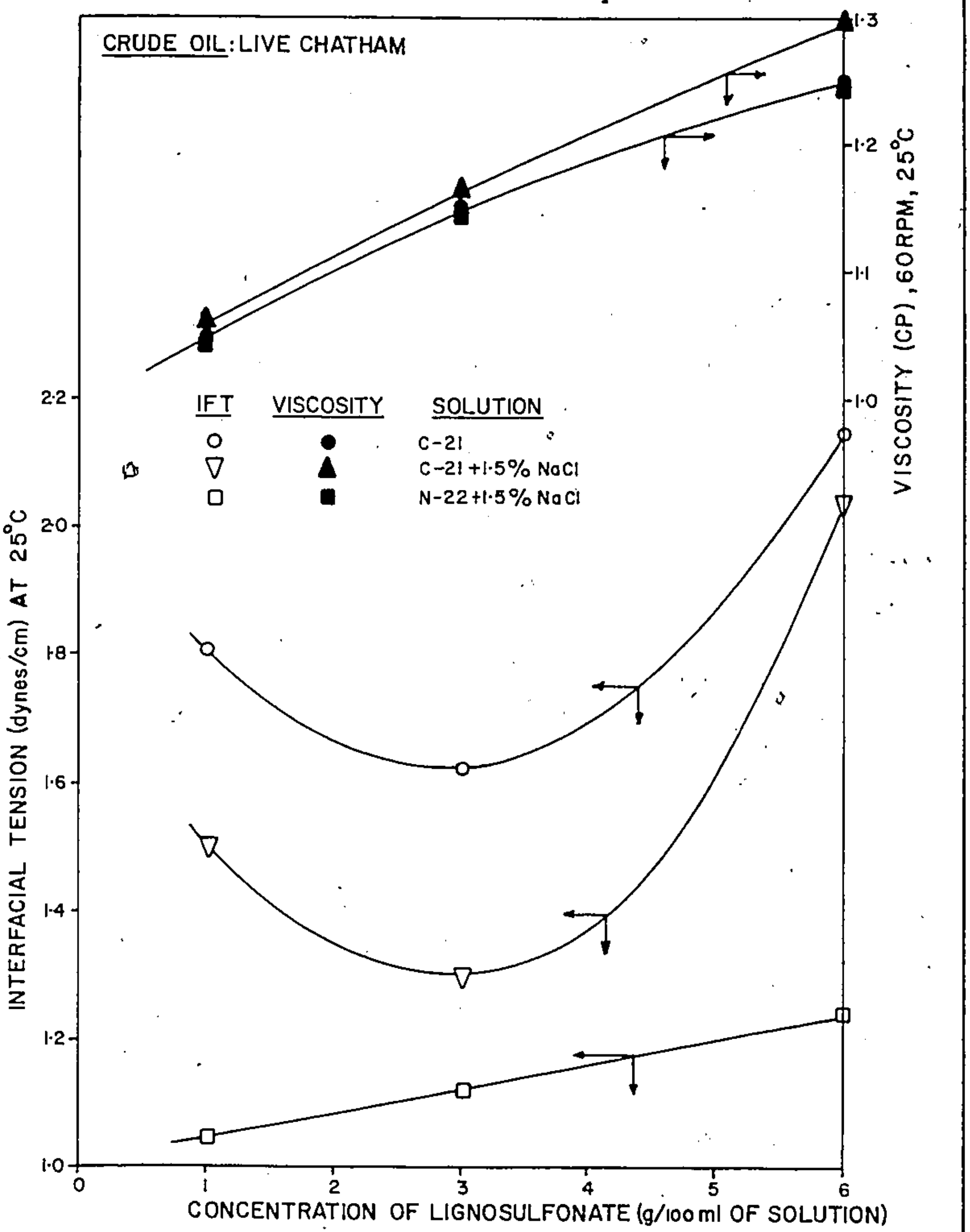


Fig.41- IFT AND VISCOSITY PLOTS FROM STRATEGY-6 STUDIES

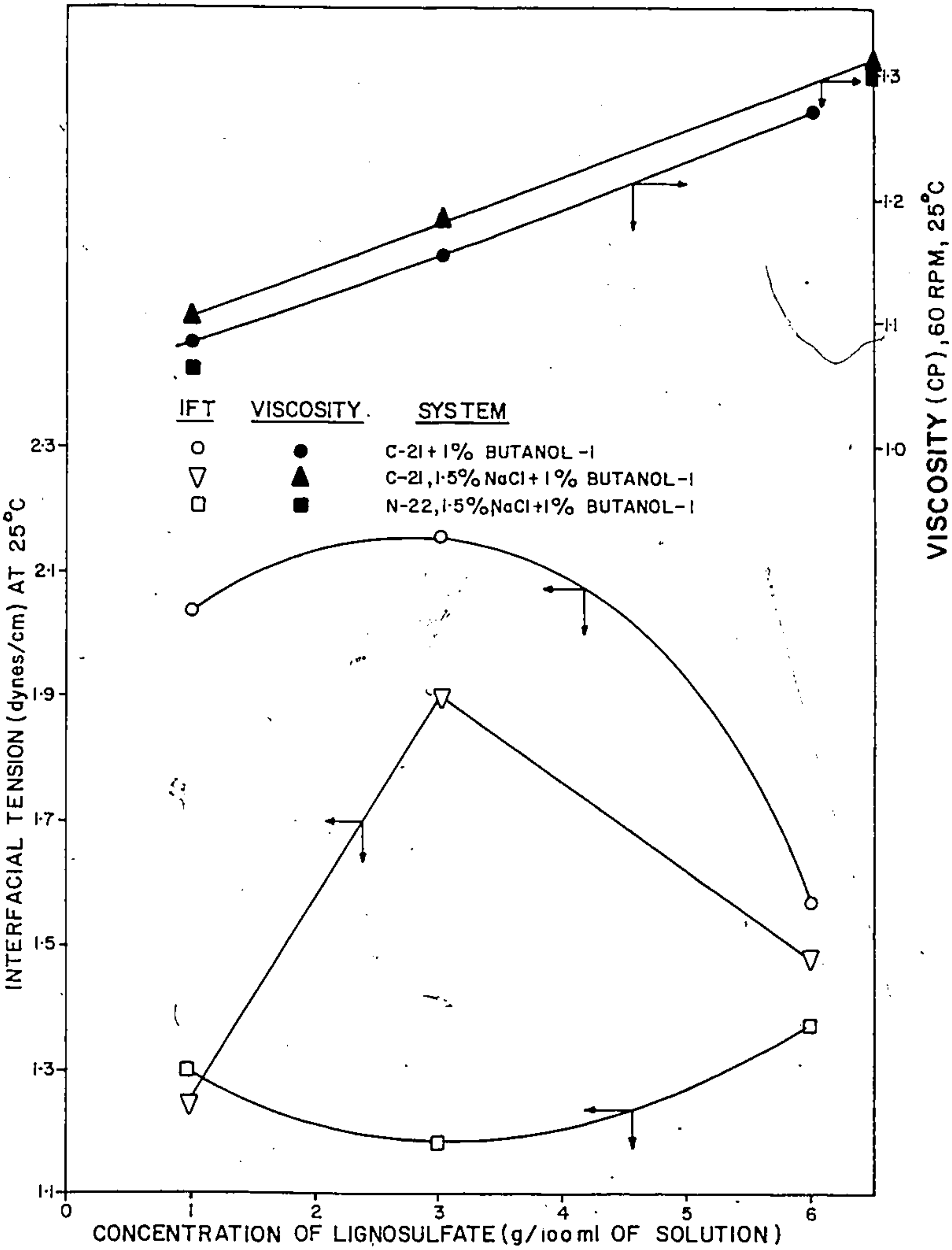


Fig. 42-IFT AND VISCOSITY PLOTS FOR LIGNOSULFONATE + BUTANOL-1 SYSTEMS (STRATEGY-6 STUDIES FOR LIVE CHATHAM CRUDE)

CHAPTER 9

HIGHLIGHTS OF THE DISPLACEMENT RUNS

9.1 General Characteristics:

The flooding conditions pertaining to most of the displacement runs are outlined in Table 11. The injection pump was calibrated first at the beginning and also upon completion of all runs. Fig. 43 shows these calibration plots. The flow rate and pressure drop data for the total brine permeability experiment are plotted in Fig. 44; while the analysis of these data is presented in Appendix B. Appendix C gives the details of the measurements and recovery analysis of a typical run. The concepts of Breakthrough, Breakthrough recovery and final recovery (%) as defined in Ref. 75 apply to each flood. A new concept, the tertiary oil Recovery (%) has been introduced for comparison of the performance of the various tertiary floods. This is also quantitatively defined in Appendix C. In the case of the secondary floods, the concept of Additional Recovery (AR) used by Bansal et al (75) was employed as a basis for comparison.

9.2 Results of Secondary Flood Runs:

A summary of the data obtained with the various floods is presented in Table 12. Approximately 3.0 PV total surfactant injection was achieved in all cases. The average injection rates (Appendix C), varied from run to run; despite the fact that the pump setting was kept constant at 25% stroke length. The production histories by run numbers (Table 12) are given in Figs. 45 to 51. As could be seen (Table 12), the final recovery obtained with water (1.5% NaCl) was as high as 83%.

Additional recoveries with the ordinary lignosulfonate solutions were not expected to be much higher considering the degree of IFT reduction achieved and the unfavorable mobility ratios.

9.3 Results of Tertiary Flood Runs:

The surfactant systems employed in this flooding scheme are listed in Table 13. Also shown is the variation in oil viscosity and surfactant injection rates from run to run. Run No. 8 (Table 13) explored the displacement efficiency attainable with the 6% C-21 + 1% butanol-1 system developed from strategies 1 to 4 studies. Run No. 18, a 3 PV water (1.5% NaCl) flood serves as a reference for the other floods. Figs. 52 to 62 give the production histories of the ten tertiary floods.

Despite the variations in oil viscosity and flooding rates, the high tertiary recoveries obtained confirm the trends observed in the formulation studies. Run No. 14, (Fig. 56) with the incompatible 3% Petrostep 420 + 2% C-21 system (phase separation observed in formulation studies) produced less tertiary oil (58%) than the base water flood (66%). Run No. 17 (Table 13) with the high viscosity (thixotropic) 4% Petrostep + 2% C-21 system yielded only 67% tertiary oil after 3 PV total injection. However from the final WOR of 3.10, some significant additional oil was mobilized towards the end of the flood; thus an ultimate recovery of 100% could be envisaged.

TABLE 11

GENERAL FLOODING CHARACTERISTICS FOR ALL RUNS

(i) Dimensions of core-holder

Internal Diameter (I.D.)	5.32 cm
Length (flange to flange)	91.20 cm
Cross-sectional area, A_c	22.23 cm^2
Volume, V_c	2025.67 cm^3

(ii) Porous Medium

Type: Unconsolidated Ottawa Sand Grade C-190

Total Brine (1.5% NaCl) permeability, K	57.82 darcies
Bed porosity, ϕ	0.342 to 0.345
Sand grain density	2.65 g/cm^3
Mean Average particle diameter	3.51×10^{-2} cm

(iii) Crude Oil System:

Identification:	Live Chatham Crude
Oil Saturation Efficiency:	> 98.00% (for all floods)

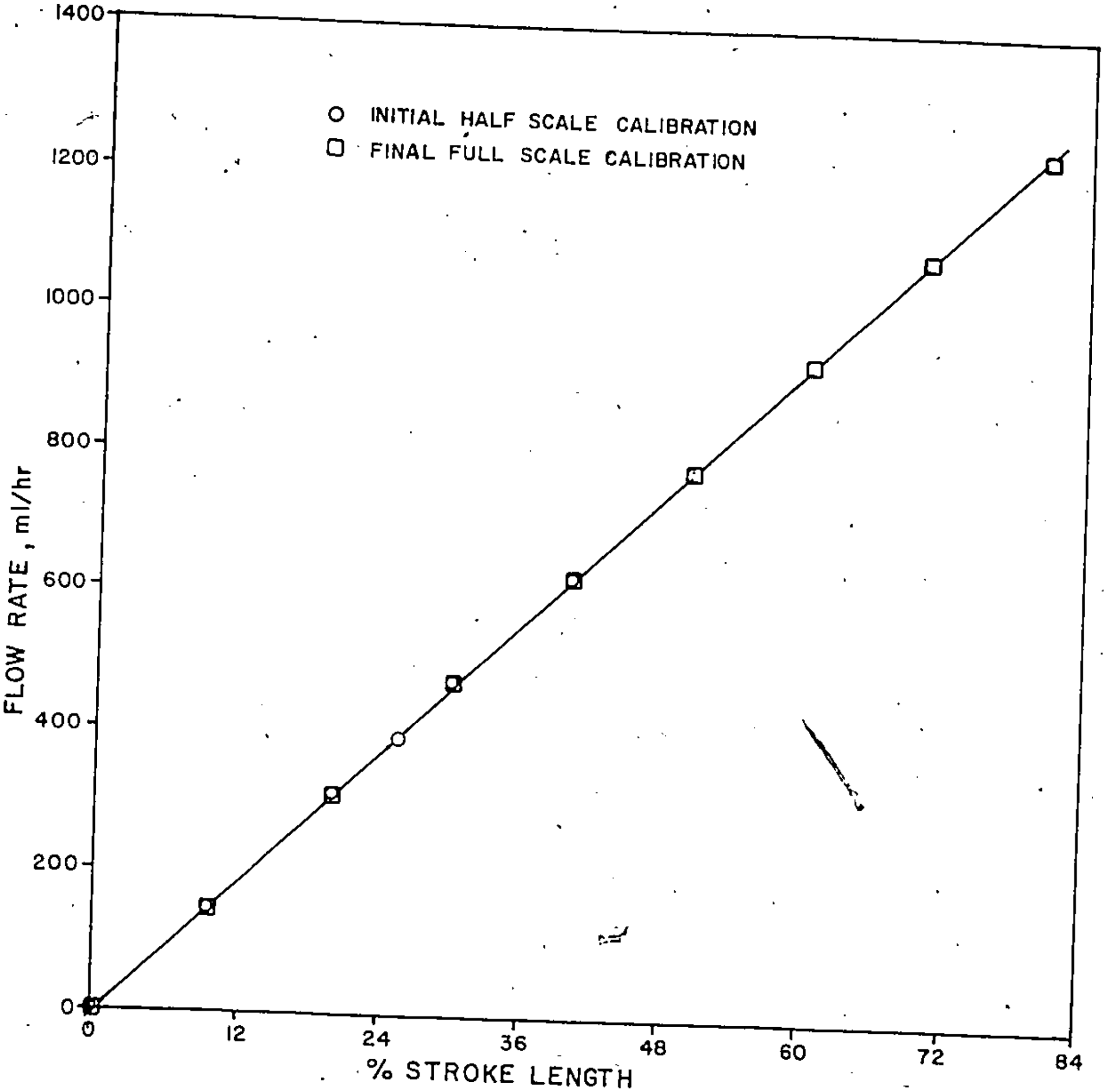


Fig. 43 - INJECTION PUMP - CALIBRATION CURVES

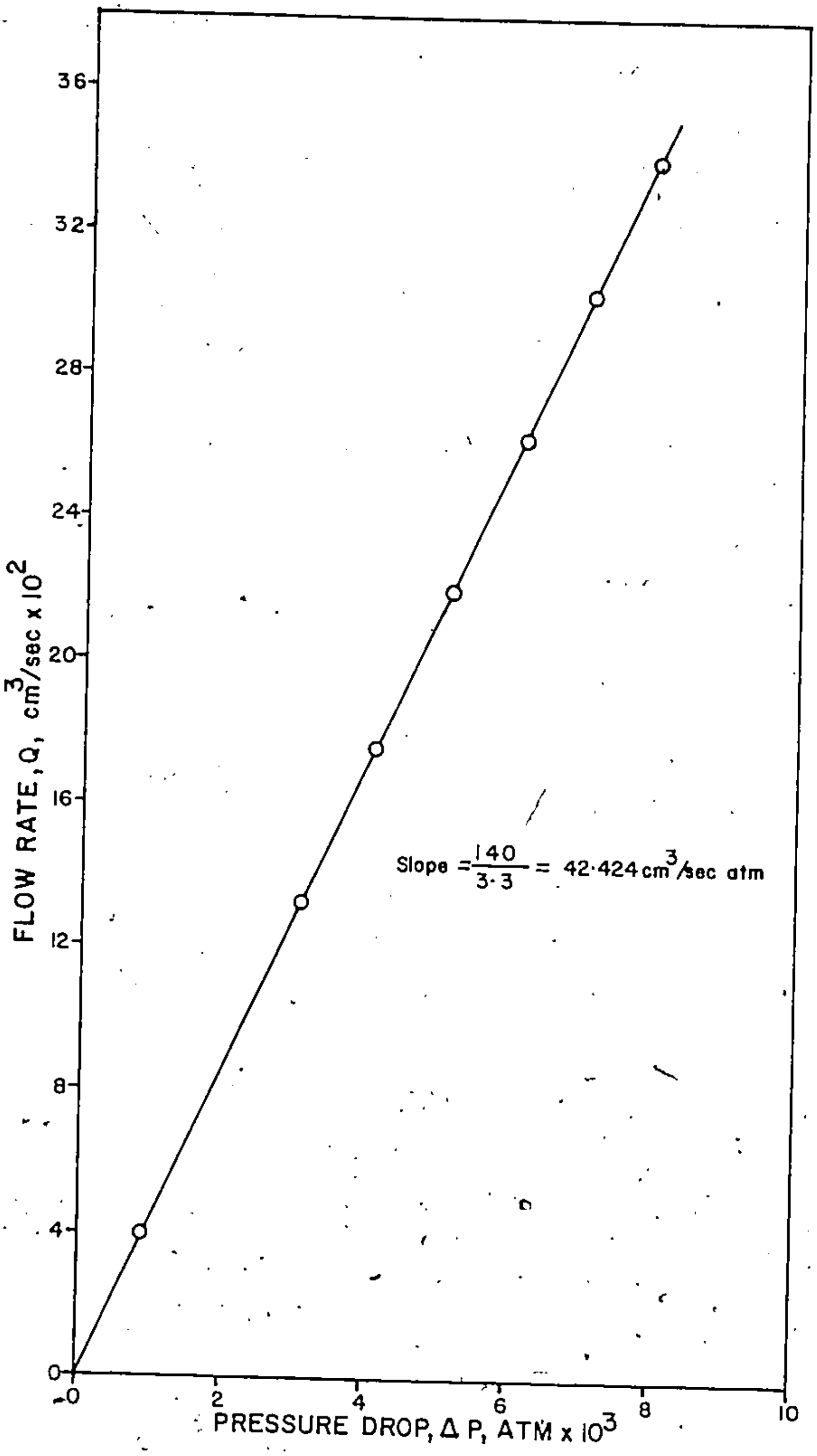


Fig. 44- FLOW RATE VS PRESSURE-DROP PROFILE FOR DETERMINATION OF PERMEABILITY OF POROUS MEDIUM

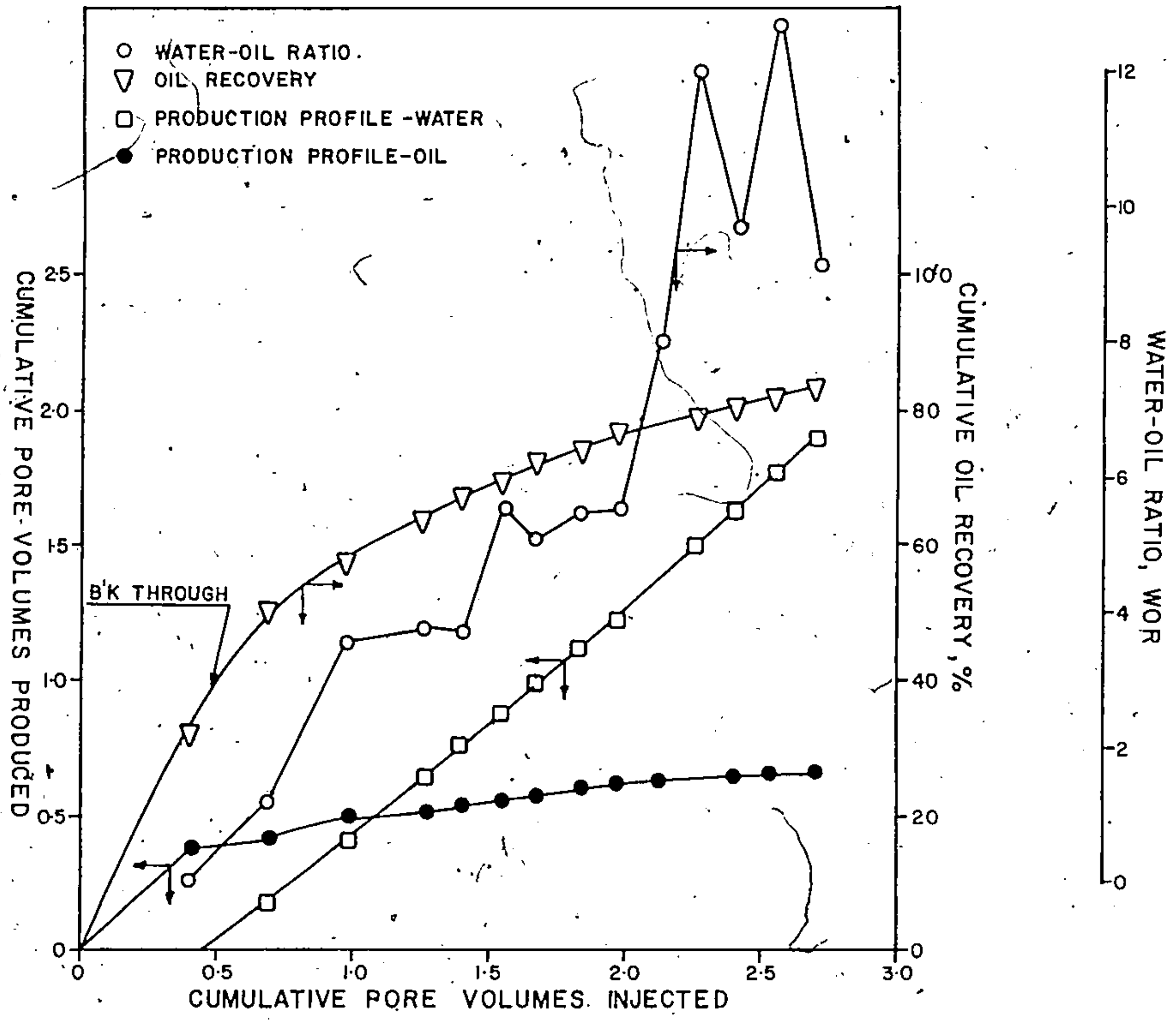


FIG. 45 - PRODUCTION HISTORY FOR RUN NO. 1 - 1·5 % NaCl IN SECONDARY FLOODING

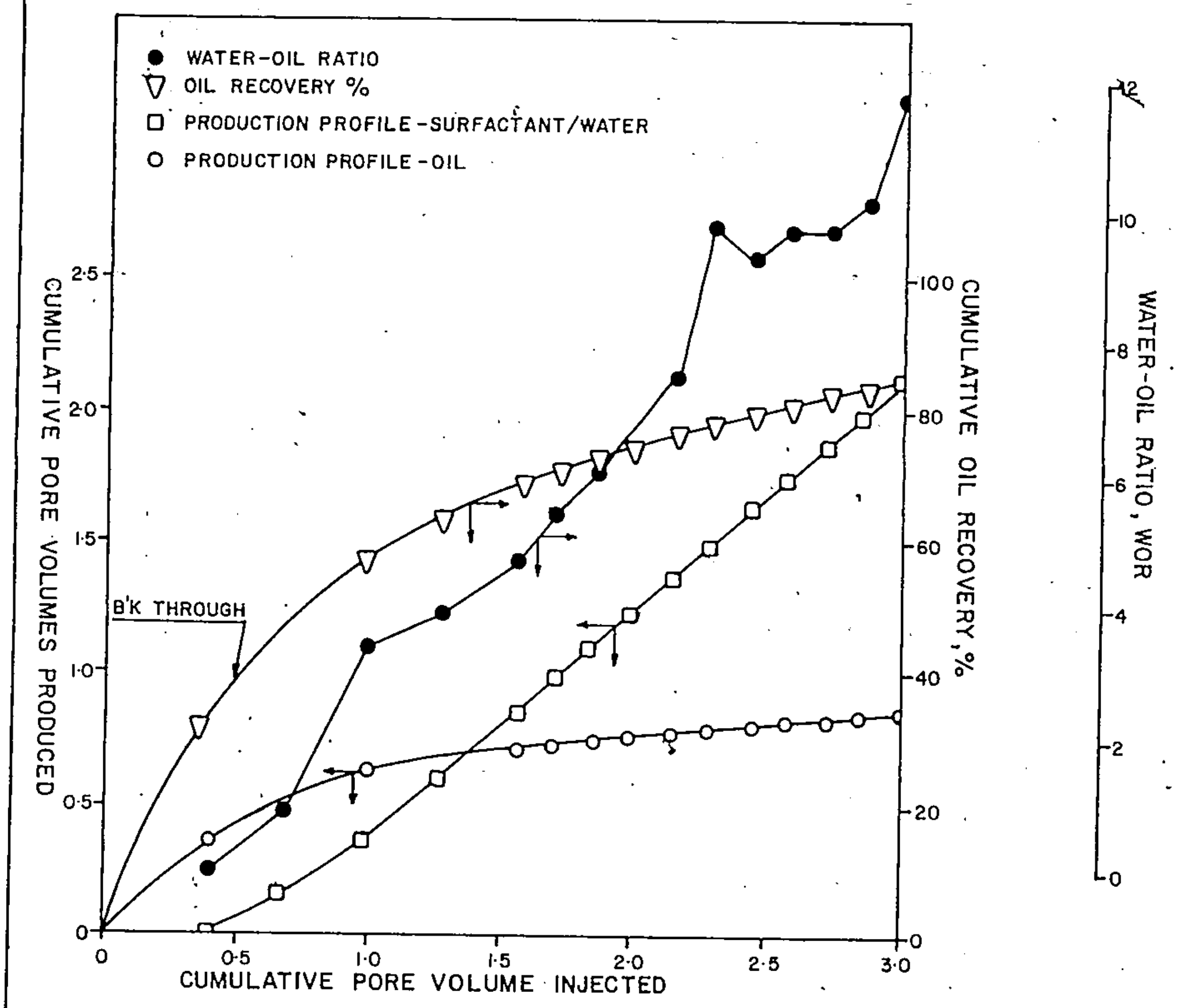


Fig.46- PRODUCTION HISTORY FOR RUN NO. 2-SECONDARY FLOODING WITH 1% N-22 IN 1·5% NaCl

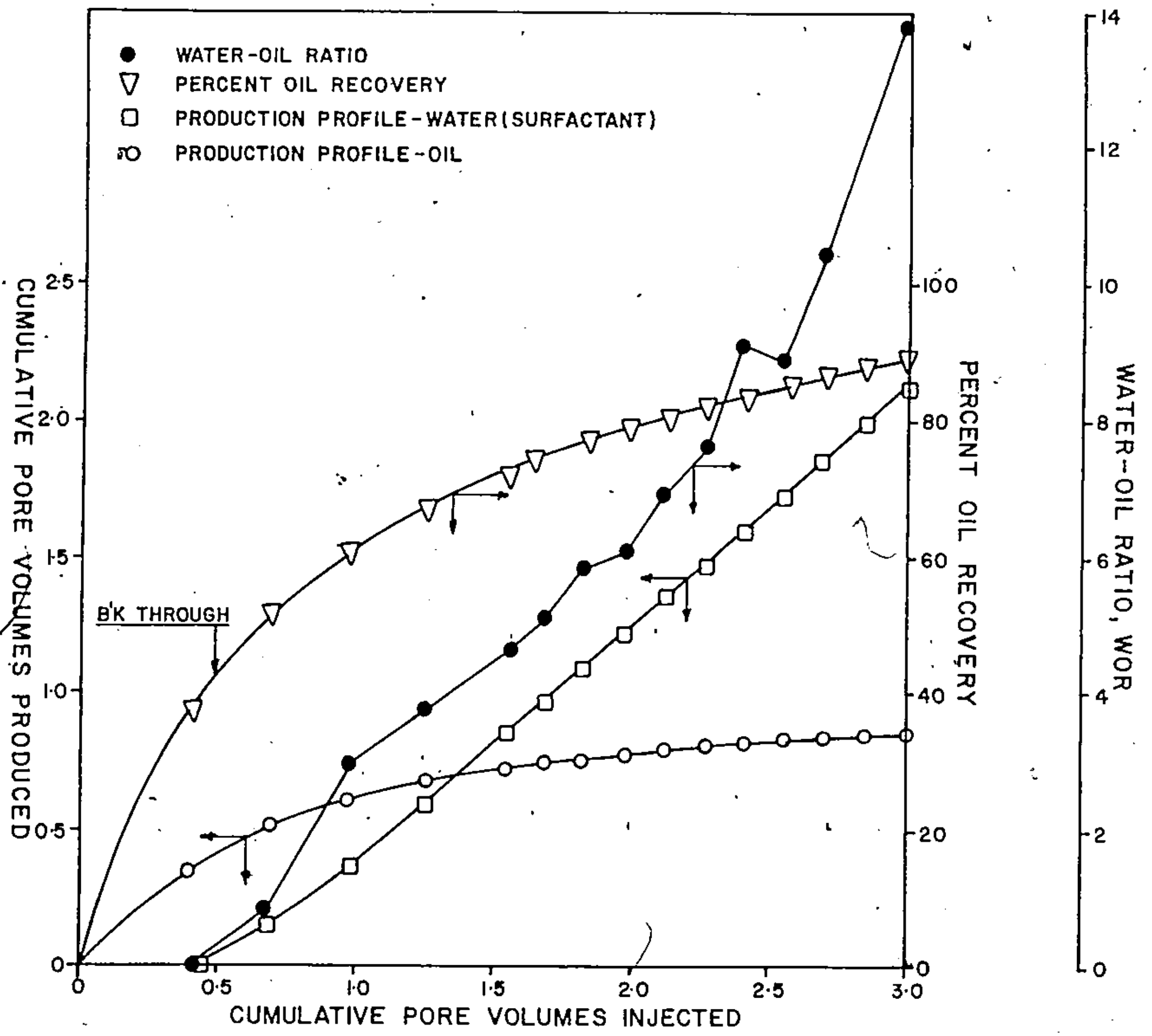


Fig.47–PRODUCTION HISTORY FOR RUN NO.3-SECONDARY FLOODING WITH 3%N-22 IN 1·5%NaCl

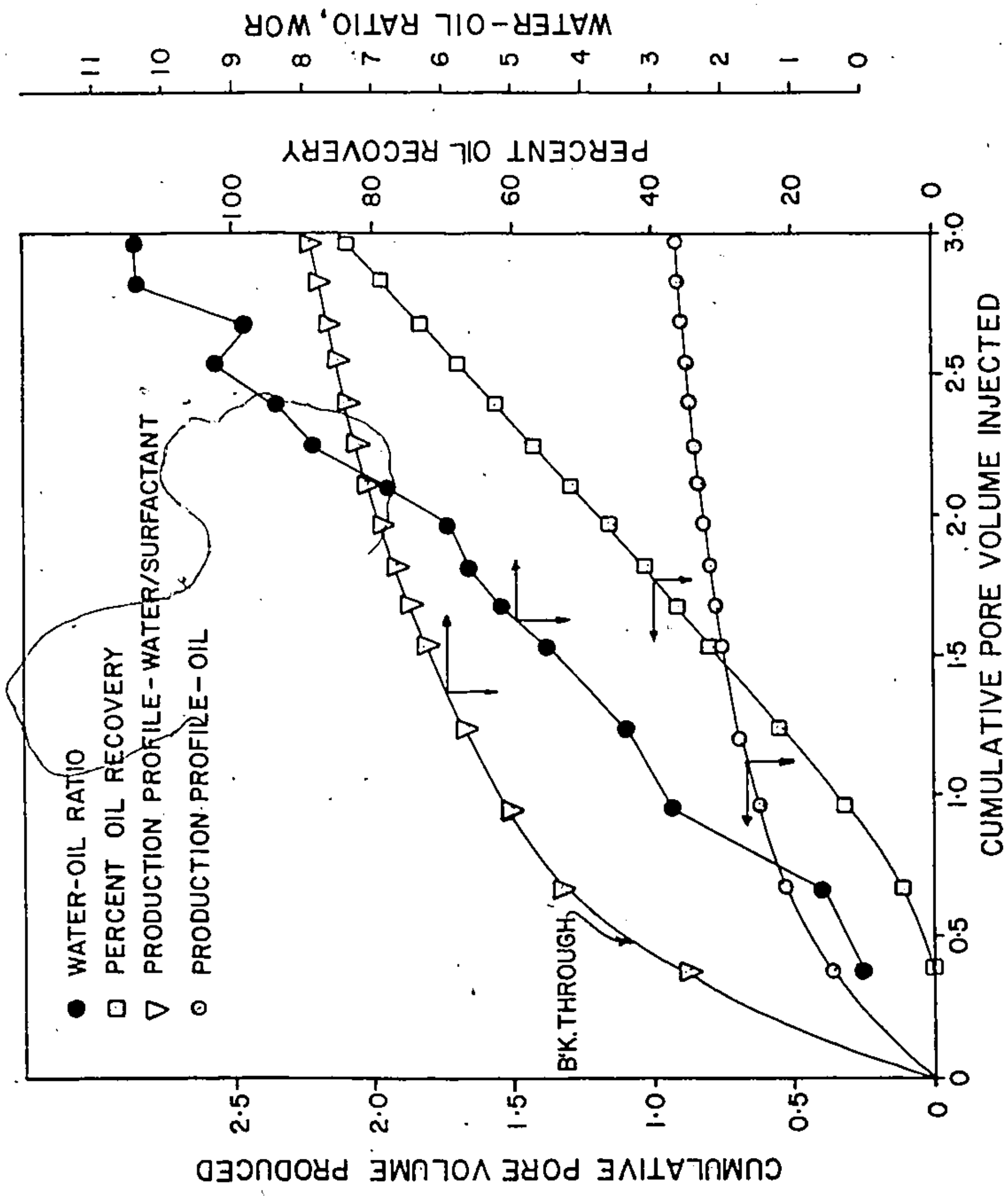


Fig. 48 PRODUCTION HISTORY FOR RUN NO.4 -SECONDARY FLOODING WITH 6% N-22 IN 1·5% NACL

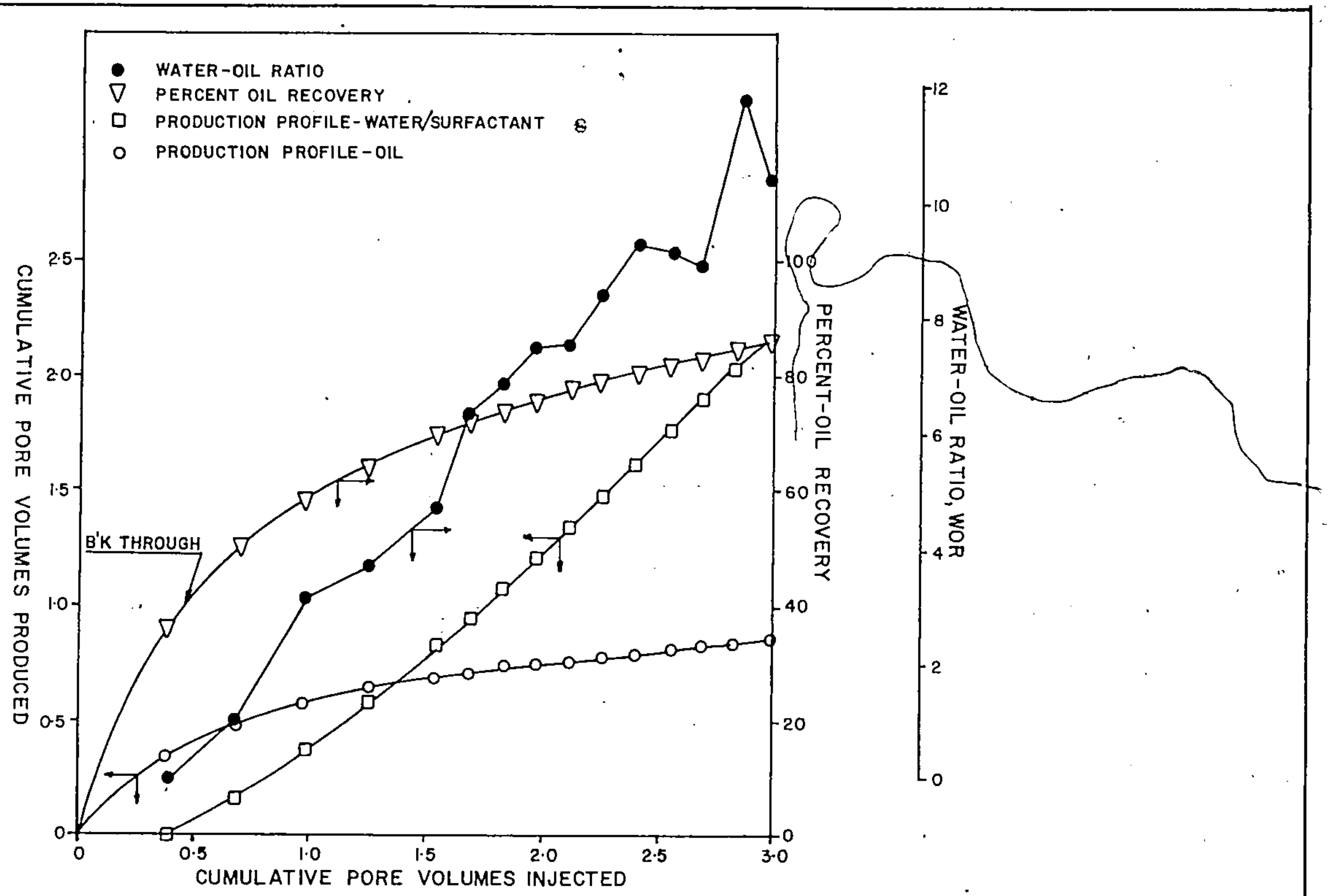


Fig.49- PRODUCTION HISTORY FOR RUN NO.5, SECONDARY FLOODING WITH 1·0% C-21 IN 1·5% NaCl

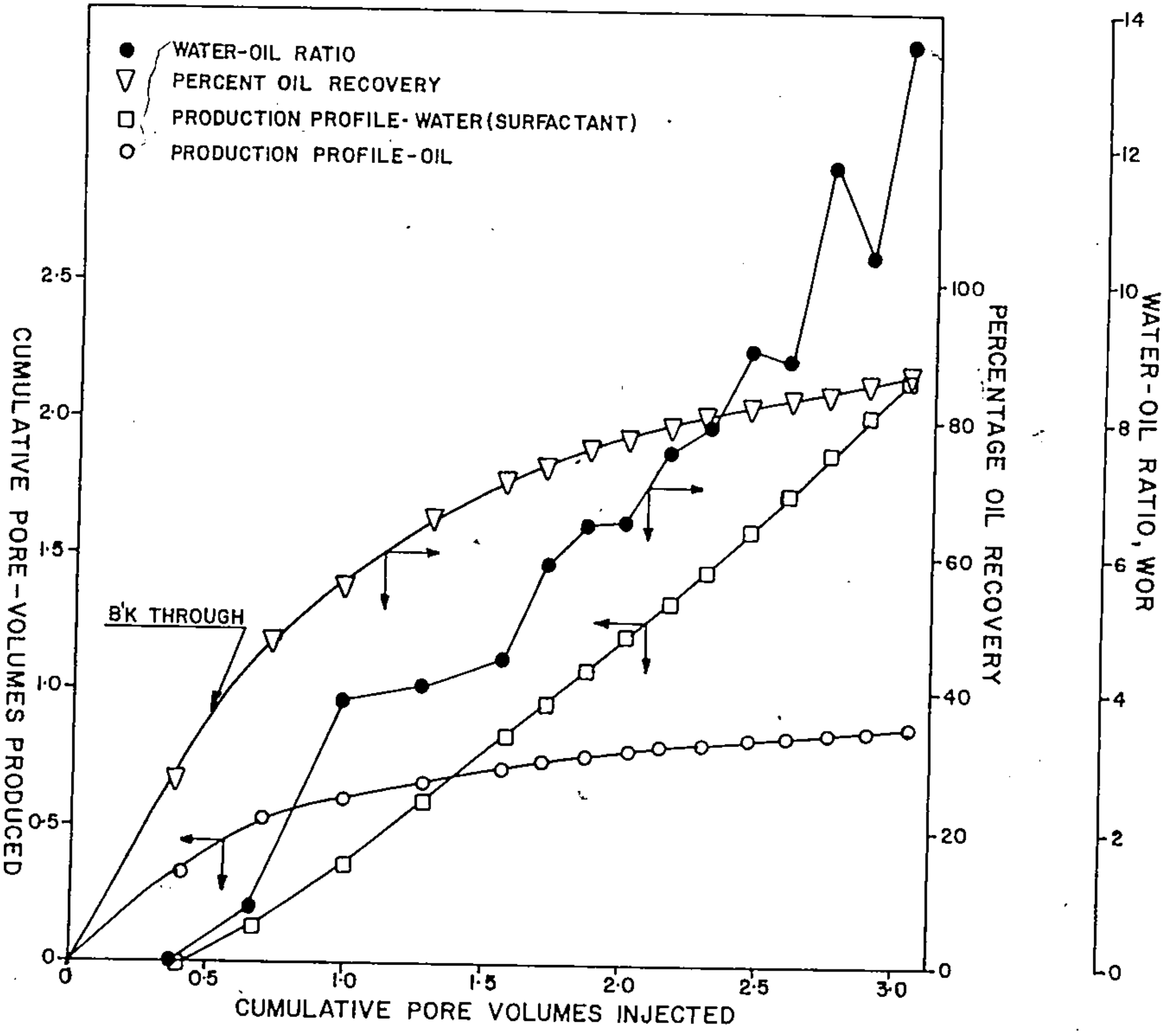


Fig.50-PRODUCTION HISTORY FOR RUN NO.6 - SECONDARY FLOODING WITH 3% C-21 IN 1·5% NaCl

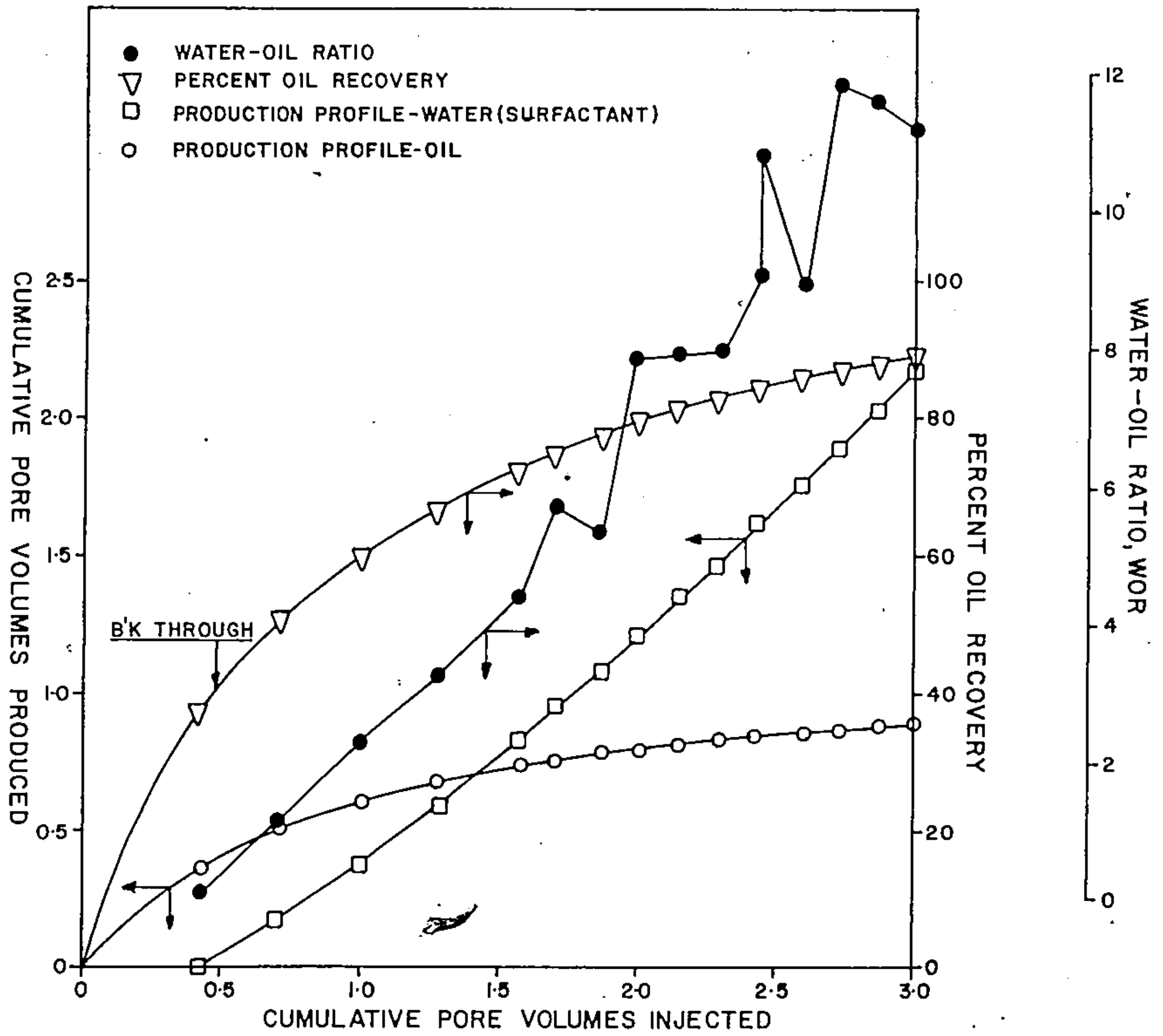


Fig.51- PRODUCTION HISTORY FOR RUN NO.7-SECONDARY FLOODING WITH 6% C-21 IN 1·5% NaCl

TABLE 12

Summary of Results of Secondary Recovery Floods

Run No.	Surfactant Identity	System Viscosity cp, 25°C and 60 rpm	1 FT dynes/cm at 25°C	Average Flood Rate mℓ/hr	PV injected	Oil Recovery (%)					Average Final WOR
						Surfactant BK through	1PV	2PV	2.7PV	Final	
1	1.5% NaCl	1.01	4.55	393.0	2.70	36.0	58.0	75.0	83.0	83.0	10.9
2	1% N-22 + 1.5% NaCℓ	1.05	1.05	391.0	3.01	39.0	57.4	74.5	82.0	84.7	11.0
3	3% N-22 + 1.5% NaCl	1.15	1.11	374.3	2.98	42.0	60.5	78.2	86.0	88.6	12.0
4	6% N-22 + 1.5% NaCl	1.24	1.24	373.4	2.97	43.0	61.2	79.3	87.0	89.2	10.4
5	1% C-21 + 1.5% NaCl	1.06	1.50	373.4	2.97	40.2	59.0	76.0	83.0	85.5	11.0
6	3% C-21 + 1.5% NaCl	1.16	1.30	377.9	3.02	38.0	56.0	77.4	84.0	86.4	11.9
7	6% C-21 + 1.5% NaCl	1.30	2.05	371.9	3.00	40.0	60.0	79.0	86.0	88.1	11.5

Crude oil viscosity range: 5.30-5.50 cp at 25°C, 30 rpm

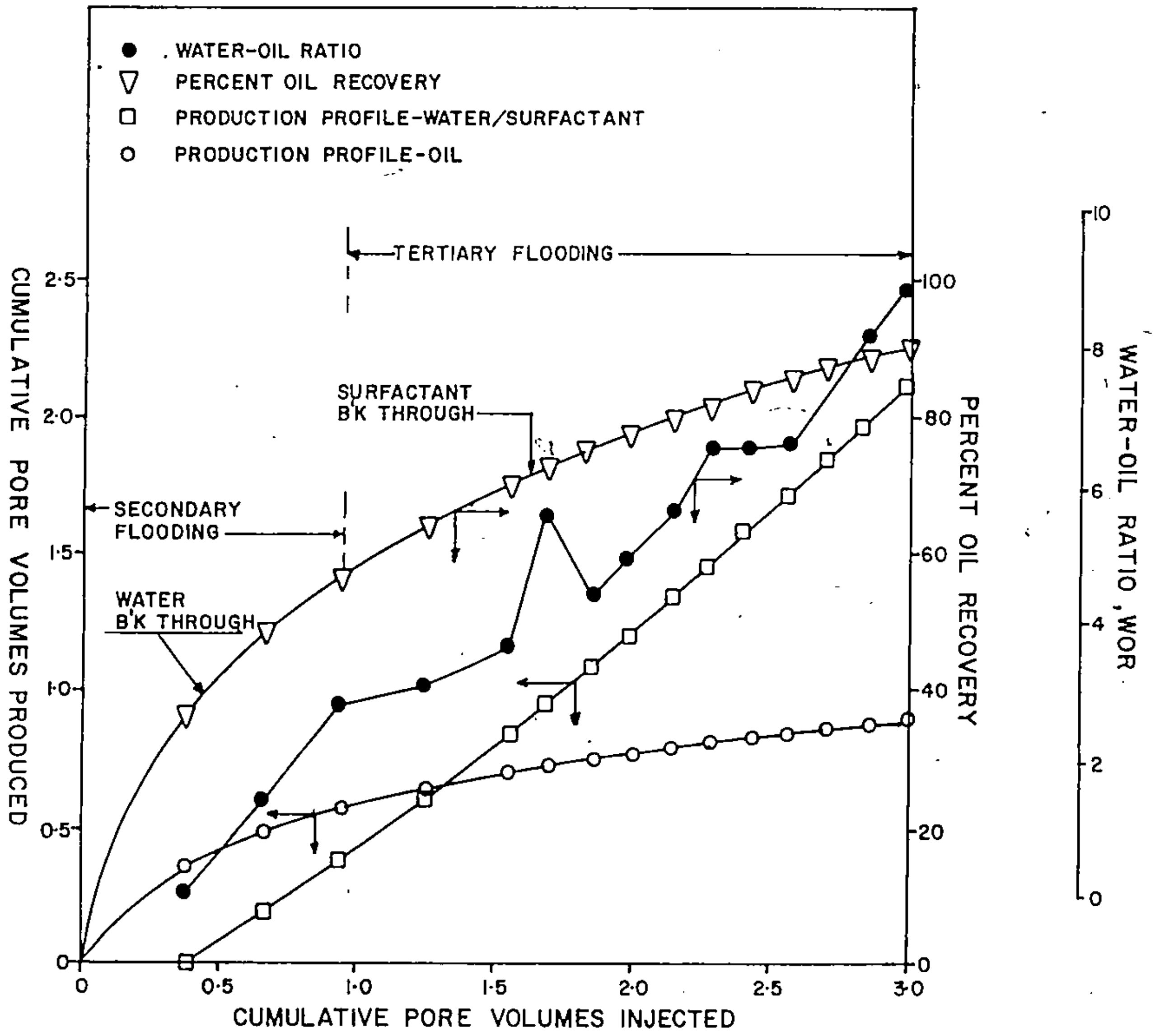


Fig.52- PRODUCTION HISTORY FOR RUN NO.8, TERTIARY FLOODING WITH 6% C-21+1·5% NaCl+1% BUTANOL SYSTEM

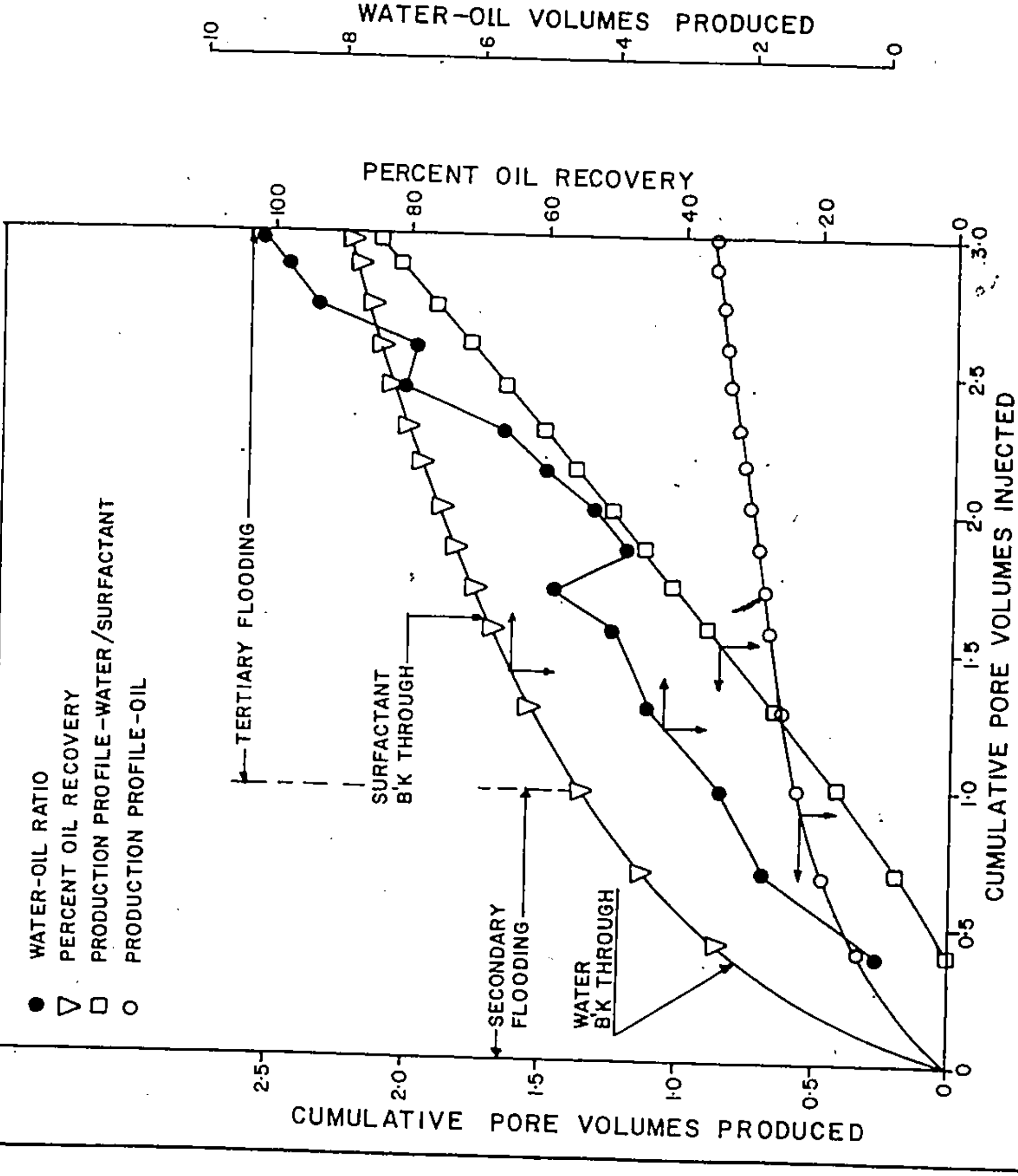


Fig.53- PRODUCTION HISTORY FOR RUN NO.9, TERTIARY FLOODING WITH 2% PT 420 IN 1·5% NaCl SYSTEM

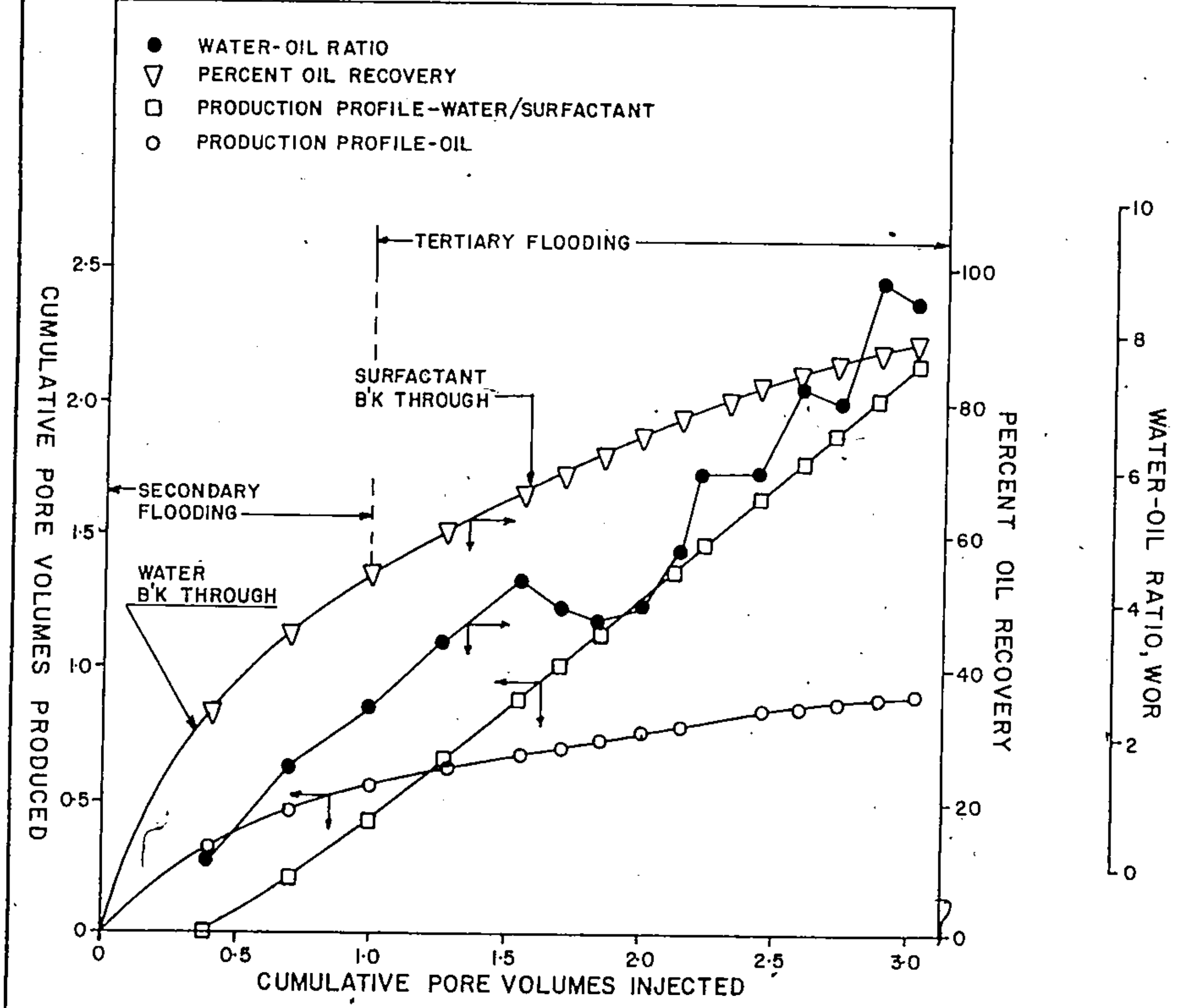


Fig.54-PRODUCTION HISTORY FOR RUN NO.10- TERTIARY FLOODING WITH 2% PT 420+1·5% NaCl+0·5%C-21 SYSTEM

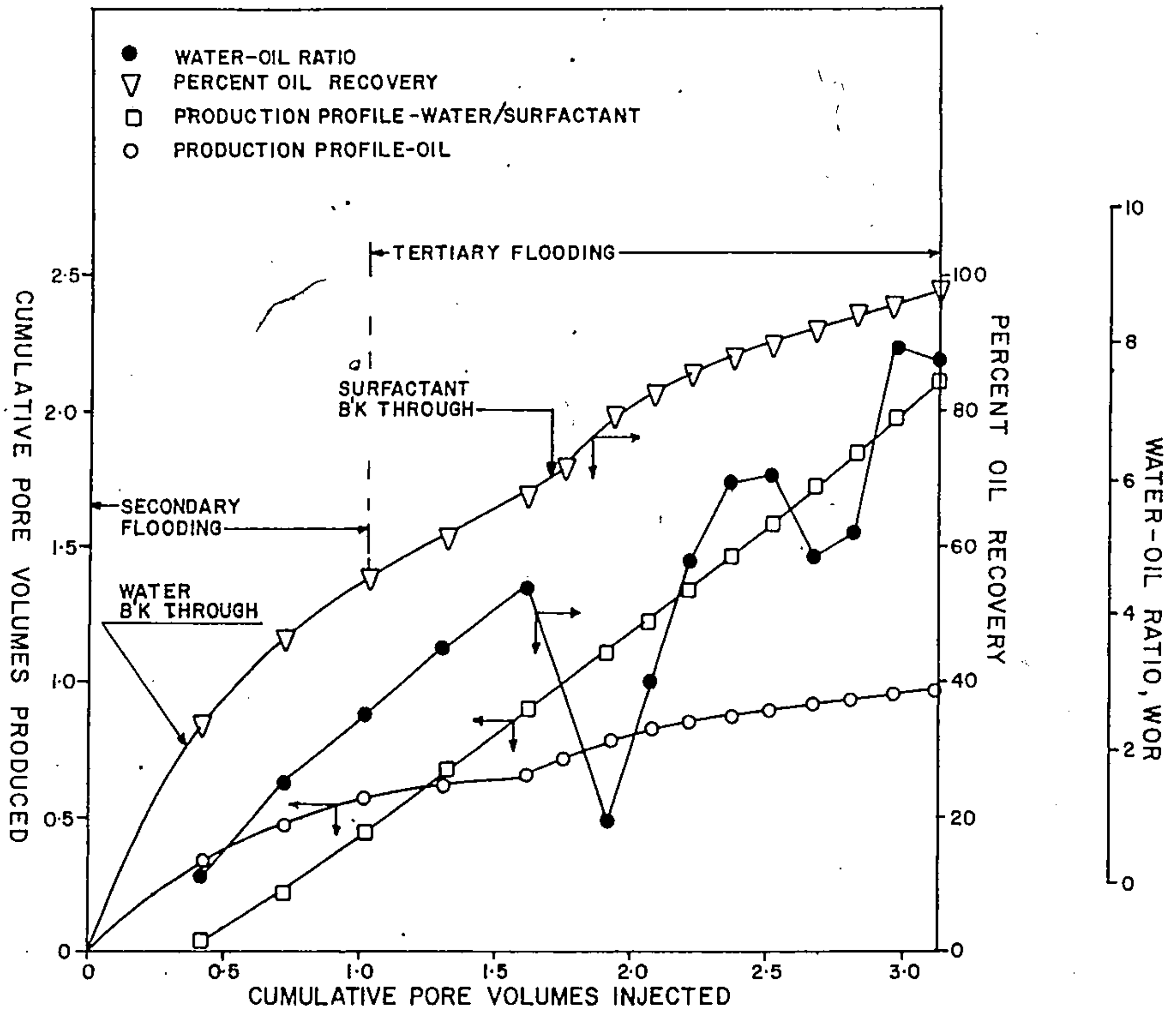


Fig.55- PRODUCTION HISTORY FOR RUN NO.11, TERTIARY FLOODING WITH 2% PT 420+1·5% NaCl+1% C-21 SYSTEM.

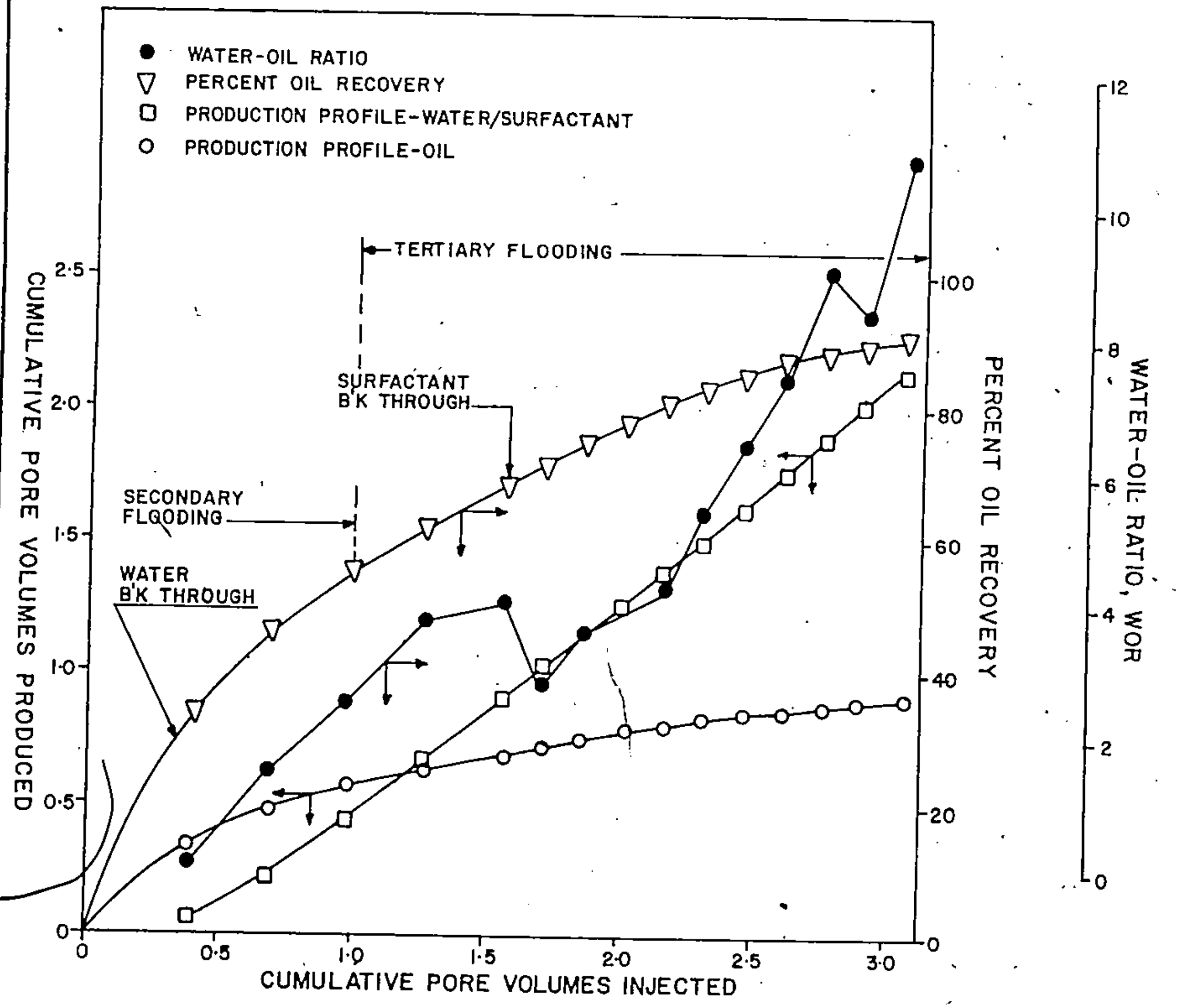


Fig.56- PRODUCTION HISTORY FOR RUN NO.12 , TERTIARY FLOODING WITH 3% PT 420 + 1·5% NaCl SYSTEM

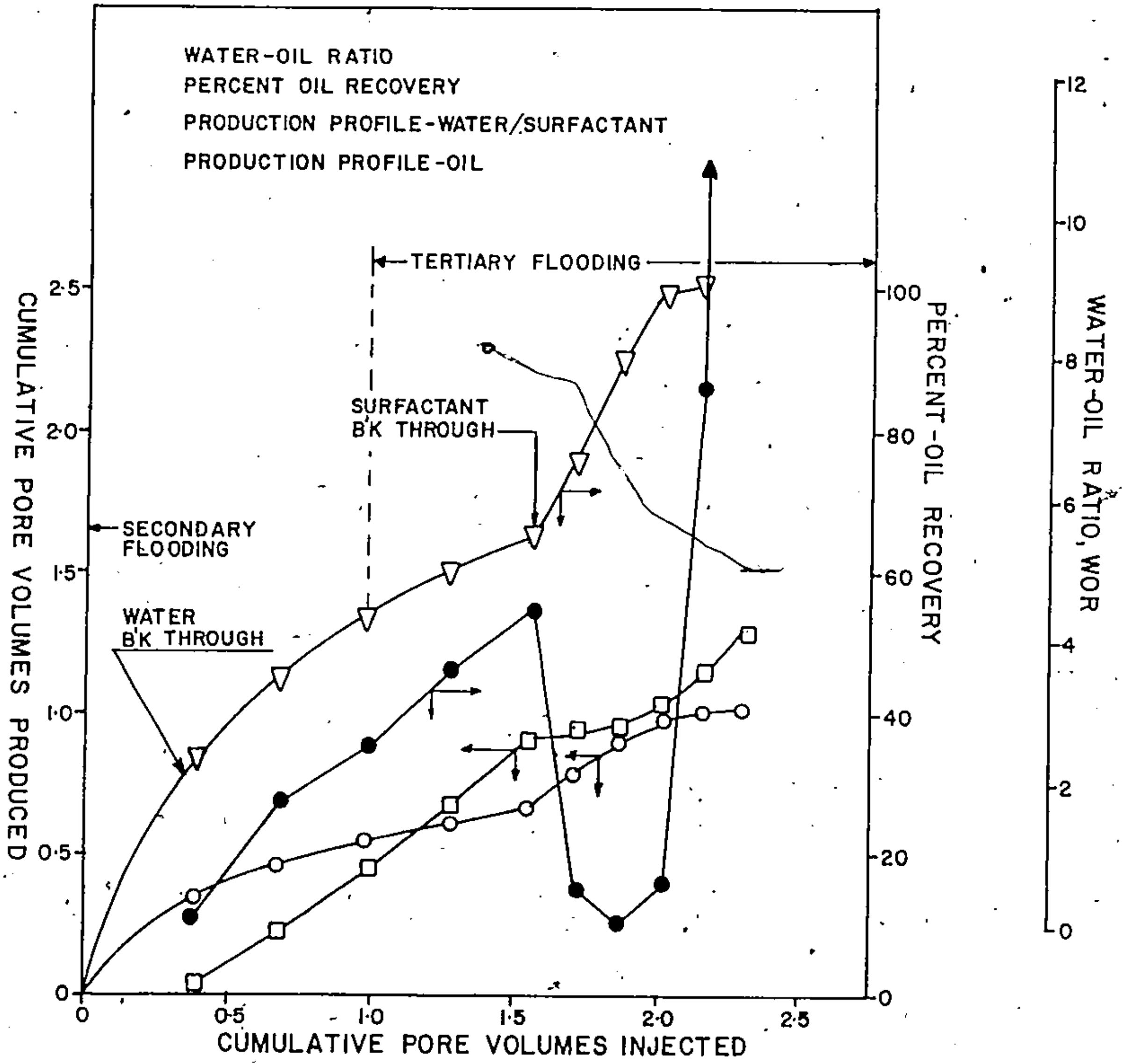


Fig.57-PRODUCTION HISTORY FOR RUN NO.13 TERTIARY FLOODING WITH 3% PT 420, 1·5% NaCl + 1% C-21 SYSTEM

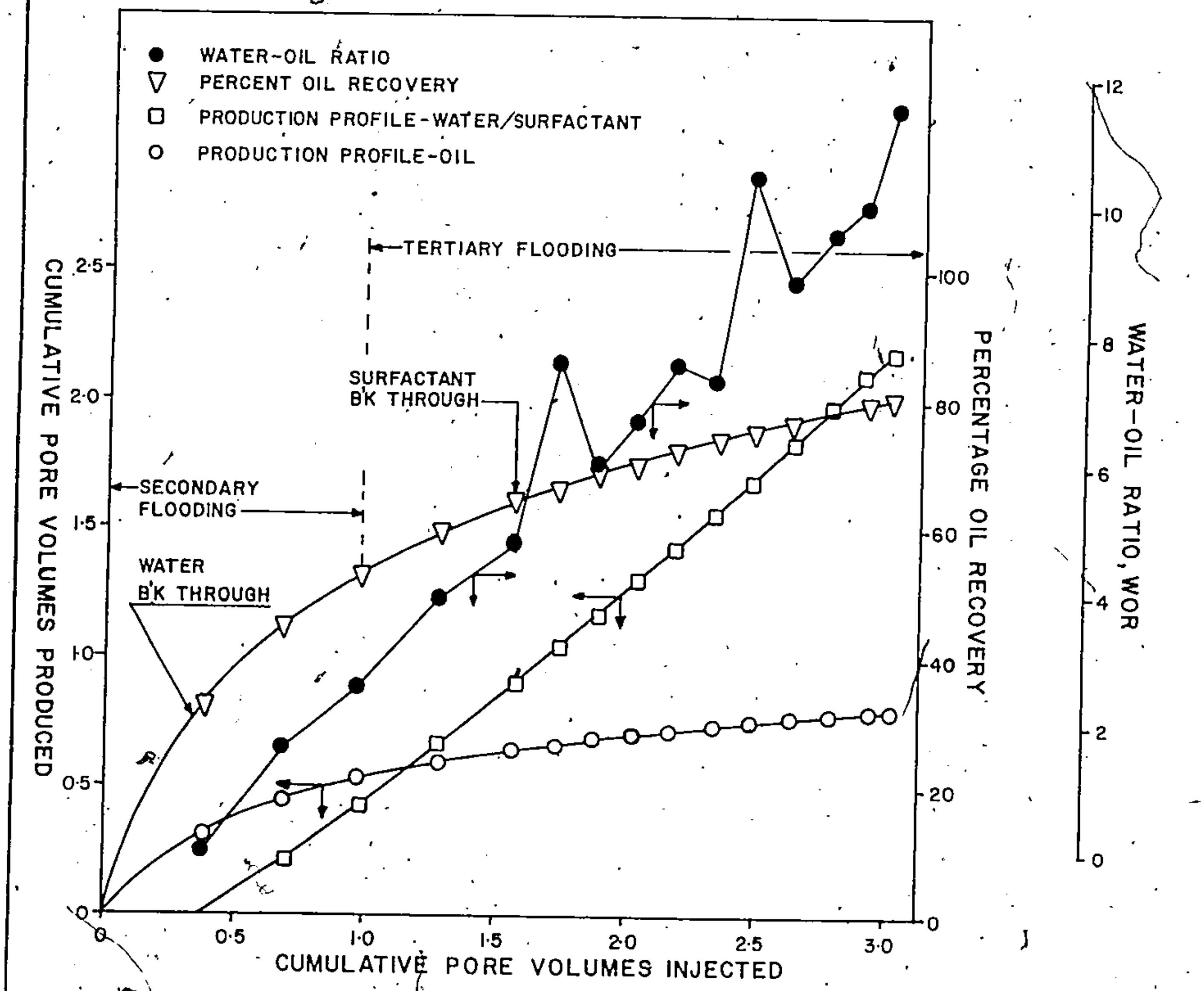


Fig.58 PRODUCTION HISTORY FOR RUN NO.14 TERTIARY FLOODING WITH 3% PT420+1.5%NaCl+2% C-21 SYSTEM

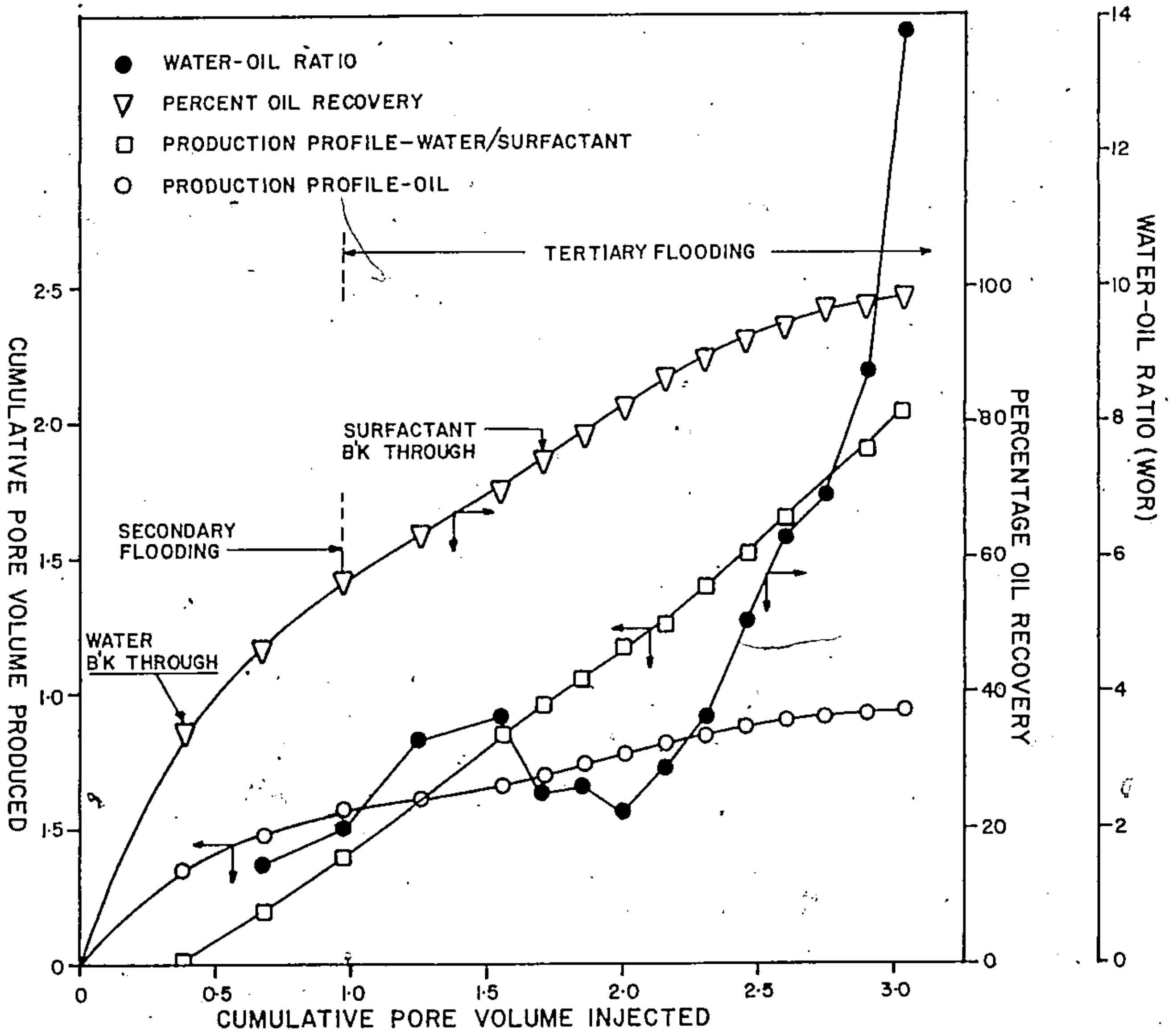


Fig.59- PRODUCTION HISTORY FOR RUN NO.15 TERTIARY FLOODING WITH 4% PT·450+1·5% NaCl SYSTEM

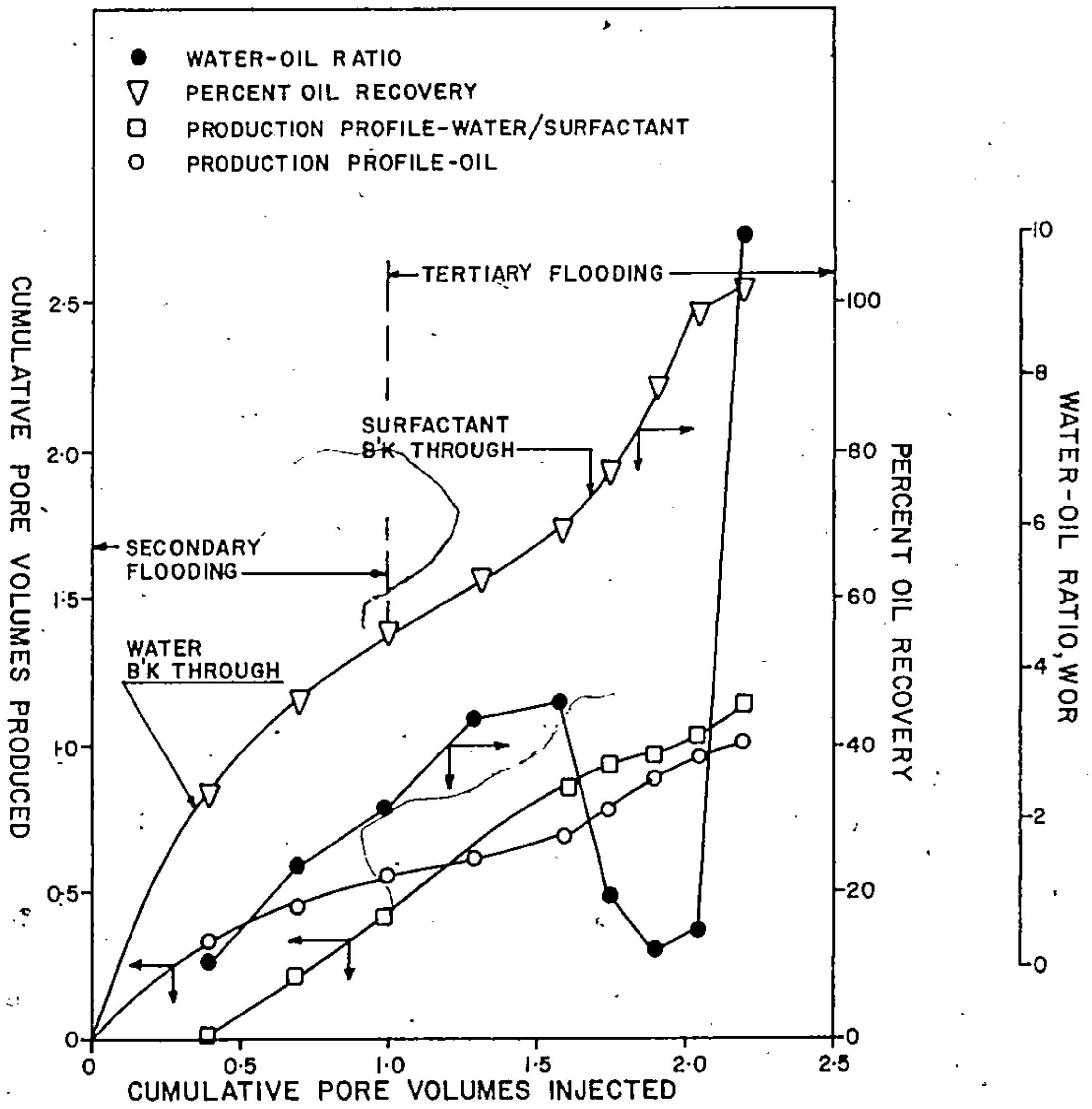


Fig.60- PRODUCTION HISTORY FOR RUN NO.16, TERTIARY FLOODING WITH 4% PT 450, 1·5% NaCl+1%C-21 SYSTEM

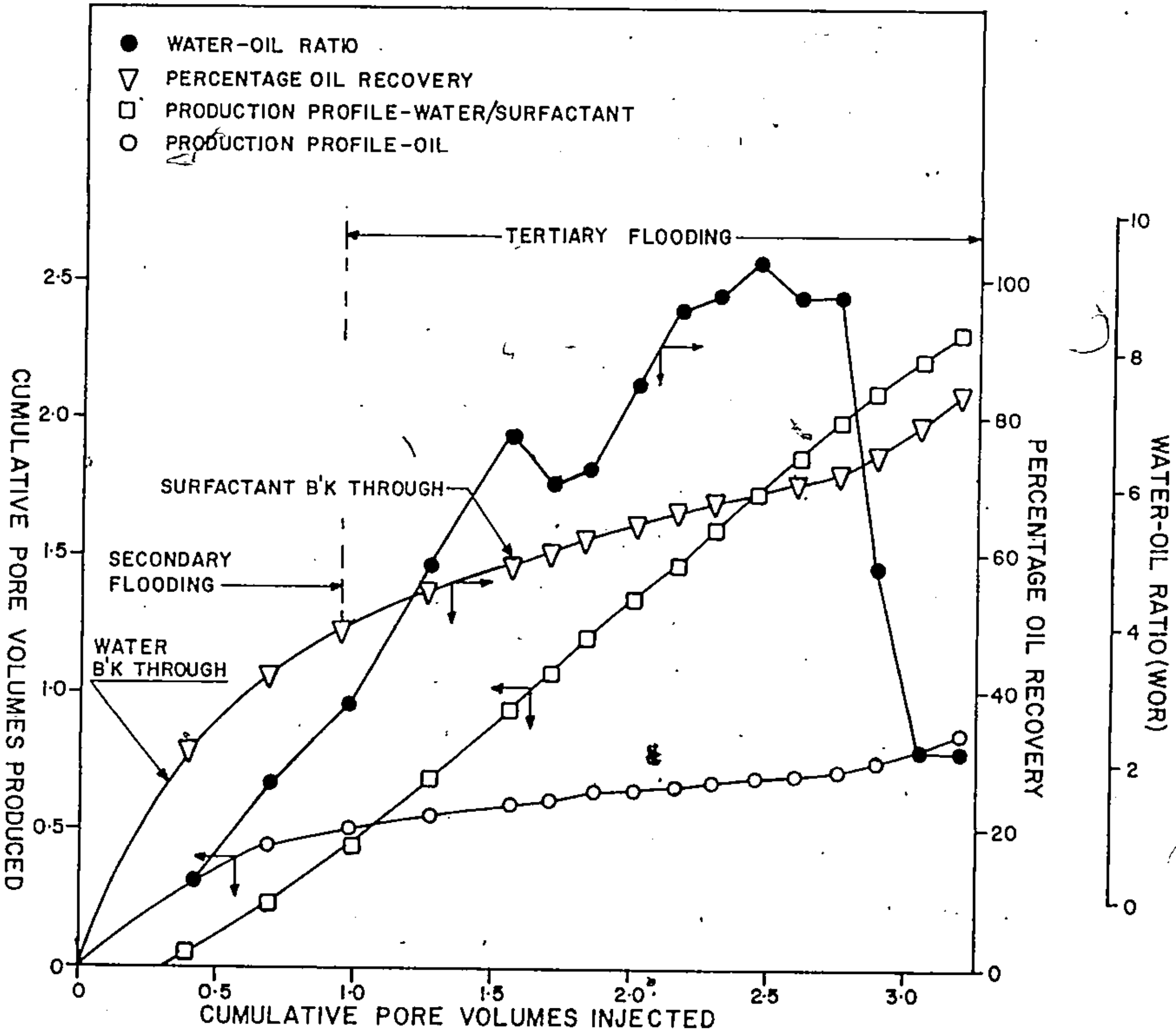


Fig.61-PRODUCTION HISTORY FOR RUN NO.17 TERTIARY FLOODING WITH 4% PT 450 +1·5% NaCl +2% C-21 SYSTEM

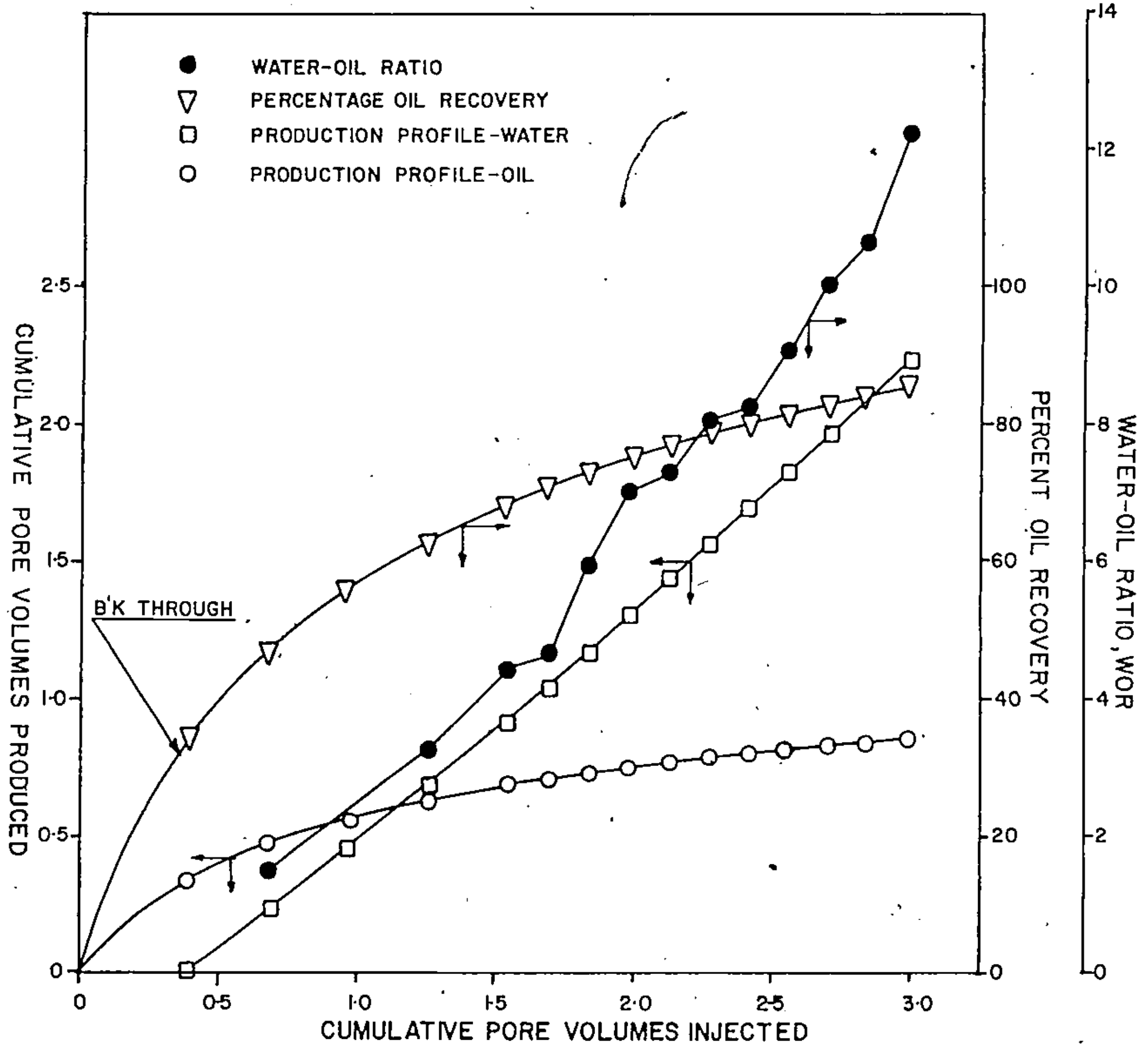


Fig.62-PRODUCTION PROFILE FOR RUN NO. 18-SECONDARY FLOODING WITH 1·5% NaCl (TO 3 PV) SYSTEM

Table 13

Summary of Results of Tertiary Floods

Run No.	Surfactant System		Crude oil Viscosity cp, 30 rpm	IFT dynes/ cm,25°C	Flood Rate (ml/hr)		Injected PV		Percentage Oil Recovery					Tertiary oil Recovery (%)	Average final WOR
	Identity	Viscosity cp, at 30 rpm			Secondary	Tertiary	Secondary	Tertiary	Water B'K through	Secondary flood	Surfactant B'K through	2PV	Final		
8	6% C-21, 1.5%NaCl +1.0% Butanol -1	1.32	5.50	1.48	360.0	373.0	0.93	2.06	39.0	56.0	71.0	77.5	90.3	78.00	8.50
9	2%PT 420 +1.5% NaCl	1.54	5.70	0.114	374.4	377.0	0.98	1.99	31.0	55.0	68.0	75.5	88.2	73.78	8.96
10	2%PT 420, 1.5% NaCl + 0.5%C-21	2.44	5.94	7.72x 10^{-2}	391.0	392.0	0.98	2.03	29.0	53.5	66.0	74.0	88.6	75.48	8.53
11	2%PT 420, 1.5% NaCl+1.0% C-21	6.42	6.10	8.22x 10^{-3}	389.9	376.9	1.00	2.08	30.0	55.0	70.0	82.0	98.8	97.33	7.90
12	3%PT 420 +1.5% NaCl	2.00	6.25	0.115	388.2	399.7	0.98	2.04	29.0	55.0	67.5	77.0	90.9	79.78	9.36
13	3%PT 420, 1.5% NaCl +1.0% C-21	5.50	6.44	4.57x 10^{-2}	401.9	396.7	1.00	1.32	31.0	53.0	65.5	96.0	100.0	100.0	∞
14	3%PT 420, 1.5% NaCl+2.0% C-21	4.30	6.38	3.89x 10^{-2}	394.6	402.3	0.98	2.04	30.0	53.0	64.2	70.0	80.4	58.30	10.70

Table 13 (continued)

Run No.	Surfactant System		Crude oil viscosity cp, 30 rpm	IFT dynes/ cm,25°C	Flood Rate (ml/hr)		Injected PV			Percentage Oil Recovery				Tertiary oil Recovery (%)	Average final WOR
	Identity	Viscosity cp, at 30 rpm			Secondary	Tertiary	Secondary	Tertiary	Water B'K through	Second-ary flood	Surfact-tant B'K through	2PV	Final		
15	4% PT 450 + 1.5% NaCl	2.30	6.40	0.120	362.8	380.5	0.96	2.06	32.5	57.0	74.5	82.0	98.2	95.81	11.30
16	4%PT 450, 1.5% Na-Cl+1.0% C-21	9.65	7.10	4.44×10^{-2}	395.7	402.1	0.99	1.20	31.0	55.0	74.0	95.5	100.2	100	10.0
17	4%PT 450, 1.5% Na-Cl+2% C-21	62.00	7.48	1.88×10^{-2}	394.1	393.0	0.98	2.11	25.0	50.0	58.5	63.5	83.7	67.40	3.10
18	1.5% Na-Cl	1.01	6.20	4.55	387.5	-	3.00		31.5	56.5	-	75.0	85.3	66.21	11.40

PART IV

DISCUSSION OF RESULTS

CHAPTER 10

TRENDS IN THE PHYSICAL PROPERTIES AND THEIR INFLUENCE ON THE INTERFACIAL ACTIVITY OF VARIOUS SURFACTANT FORMULATIONS:

Some important trends observed in surface tension, pH, density and viscosity of the various surfactant systems are outlined. The effects of these parameters on the interfacial activity exhibited by the various surfactant systems are also examined.

10.1 Trends in the Properties of Surfactant Systems Containing Lignosulfonate With or Without Simple Additives:

The additives implied here are the simple pH reagents (acids and bases) as well as the organic reagents employed during the formulation studies. They exclude the petroleum sulfonates which are consequently discussed else where in this chapter.

(a). pH and surface tension of additive free lignosulfonate, and Lignosulfonate-inorganic additive systems:

As mentioned earlier, these data are given in Appendix A and plotted in Figs. 23 to 32. The pH of natural lignosulfonate solutions was in the range of 6.6 to 7.75, and showed no definite concentration dependency. American Can Company quotes a pH range of 7 to 8 for their lignosulfonates at 3% concentration. In some cases, values below 7 were obtained. The slight acidity of the laboratory distilled water (pH 6 to 7) partly accounts for these lower pH values obtained. For these systems too, the surface tension dropped by a maximum of 5 dynes/cm as the concentration of lignosulfonate was raised from 1 to 10%. However for the same concentration, when the pH was reduced to approximately one half of the natural value, the surface tension decreased by about 7 to 10%. This trend of surface tension lowering with pH was also observed by Keirstead.(12) However the decrease in surface tension did not produce a corresponding decrease in IFT. As can be seen from Table 7, the IFT against Lloydminster crude with the acidified lignosulfonates increased by 30 to 50% over those obtained with the natural solutions. It is probable that in an acidic medium, some of the lignosulfonate molecules adsorbed at the oil-water interface are forced back into the solution; consequently, the spreading pressure and the zeta potential drop and the IFT rises.

In the complete pH scan tests, the surface tension first dropped as the pH was raised from 3 to 5, then it increased to a maximum at pH of 7 to 9 before dropping again at a pH above 10 (Fig. 24). The IFT decreased steadily in the direction of the favorable alkaline medium. Brine addition (Fig. 31) reduced the slight concentration dependency of pH even further, while little or no surface tension lowering was observed.

(b) pH and Surface Tension of Lignosulfonate Solutions Containing Organic Additives:

As is evident from Fig. 26, the pH increased only slightly with increasing additive concentration in most cases. Even at additive concentrations up to 20%, the maximum drop in surface tension was of the order of 3.0 dynes/cm except for the butanols (where surface tension values below 30 dynes/cm were obtained at concentrations above 6% (Fig. 26)). The lower IFT values produced by the lignosulfonate-butanol-1 systems could be associated with the comparatively low surface tension values. At butanol-1 concentration of 10%, a slight phase separation occurred. The much lower IFT obtained at this concentration (1.68 dynes/cm, compared to 4.54 dynes/cm at 6%) is attributed to the presence of an alcohol film at the interface. It appears that at lower butanol concentrations the combined effects of

(i) mass transfer (solubility) within the aqueous phase,

(ii) the greater spreading pressures exerted by the much bigger and charged lignosulfonate molecules, prevented any significant butanol presence at the interface. However, as Gardon and Mason(14) suggest, the presence of brine reduces the degree of dissociation of the lignosulfonate, consequently, the charge on the molecule drops and the butanol finds its way into the interface.

(c) Density and Viscosity Trends:

From Tables 6 and 8, the densities and viscosities of these systems were generally low even in the presence of additives. Only slight increases were observed by the addition of the inorganic reagents. Gardon and Mason(14) attribute the low density and viscostiy values to the polyelectrolytic character of lignosulfonates in solution. A moderate pseudoplasticity was also observed in accordance with an earlier observation by Bansal.(1)

10.2 Mechanism of Lignosulfonate-Caustic Interaction:

As indicated in chapter 8, the IFT steadily decreased as more caustic was introduced into the 6% N-22 solution. On the other hand, the IFT of the reference caustic solutions showed an increasing trend. The former trend is in agreement with the predictions of American Can Company.(20) A mechanism of increased zeta potential following caustic addition and consequent enhanced emulsion-stabilising tendency of the lignosulfonate system was proposed to explain this phenomenon.(20,1) How the emulsion comes into being (considering the little or no olei-philicity of lignosulfonate) was not explained.

For the latter trend, various workers(39,10) have observed optimum caustic concentrations around 0.1 and 1.0% for IFT. Erlich et al(11) and Bansal et al(39) all agree that natural surfactants (soaps) are formed by the reaction of the caustic and the natural acids in the oil at the oil-water interface. An electro-capillary phenomenon(39) has been proposed to explain how spontaneous emulsification at the optimum caustic concentration occurs with consequent decrease in IFT and increase in electrophoretic mobility.

The increasing IFT trend obtained with the blank caustic systems indicates that the optimum concentration is about 0.1% in this case. The ionisation of the soap (RCOONa) molecules was probably suppressed at the higher caustic concentration investigated. The interfacial charge density dropped and this resulted in a reduced emulsification tendency and in the breaking of any emulsions that may have been formed.

The IFT thus increased as this effect was accentuated at higher caustic concentrations. In the lignosulfonate-caustic systems; some caustic was probably lost through relatively mild oxidation and hydrolysis reactions with the lignosulfonate. The shift in pH of these solutions to lower values after a few days standing suggests such effects. However, these are expected to be very small at room temperature conditions. Enough free caustic is thus present at the interface to produce the emulsifying soap molecules. Because of the increased zeta potential, the resulting emulsions are prevented from breaking even at the high caustic concentrations, and the IFT decreased steadily.

10.2 Trends in Properties of Lignosulfonate-Petroleum Sulfonate Mixed Surfactant Systems:

(i) pH, Surface and Interfacial Tensions, Concentration and Phase compatibility Effects:

Healy and Reed(44 to 46) have observed that in low surfactant concentration microemulsion systems equilibrated with the oil phase, upper, middle and lower phases occur. The bulk of the surfactant is in the middle layer and this gives rise to the tensions γ_{mo} (middle-upper) and γ_{mw} (middle-lower). These tensions were consequently associated with the optimal salinities for IFT (S_γ) and for phase behaviour (S_ϕ). By our equilibration procedure, γ_{mo} values were measured.

As given in Table 7, the surface tensions of these systems were of the order of 20 to 30 dynes/cm. This is roughly the same order of magnitude as those of crude oils;

and probably accounts for the low IFT obtained. The pH decreased from about 11.0 (at zero lignosulfonate concentration) to 8-9 at the optimum conditions. At lignosulfonate concentrations above the tolerance limit, the pH dropped to a value between 7 and 8. It appears that the effective pH range is from 8 to 10.

In general, mutual compatibility of both surfactants within the Petrostep concentration range covered, was observed at a concentration ratio,

$$C_{cr} = \frac{C_{Petrostep}}{C_{C-21}} \geqslant 1.5$$

In all cases, 1.0% C-21 could be introduced without any significant phase instability. Kalfoglou(24) did recommend using this lignosulfonate concentration in his patent. He was probably not aware of the concentration criticality and the attendant IFT and viscosity trends observed in this work. The critical concentration ratio quoted above is expected to depend on the composition of the petroleum sulfonate and also on lignosulfonate type and composition.

(ii) Viscosity Trends:

As can be seen from Tables 8 and 9, ordinary, Petrostep systems were Newtonian or mildly pseudoplastic. This is in agreement with the known rheology of such systems. Also the viscosities were generally low (less than 3 cp). But as increasing amount of lignosulfonate was added till the optimum, the viscosity increased by as much as 400% close to phase separation. After phase separation, the viscosity dropped to values around 2 cp. The thixotropic trends (Table 9) exhibited by formulations close to the critical concentration ratio are significant. By thixotropy is implied the shear rate, shearing time (at same shear rate) and system age dependencies of the viscosities of these systems. Shah et al (Ref. 63, chapter 7) had observed such thixotropic trends in the rheology of a microemulsion system consisting of hexadecane (as oil), hexanol (as cosurfactant), and potassium oleate (as surfactant).

(iii) Phase and Interfacial Behaviour of the Mixed-Surfactant Systems- A Mechanistic Explanation:

The physical properties of microemulsions as well as phase-composition relationships (by ternary diagrams) have been presented in Part I. The rheology and birefringency properties of the liquid crystalline structures have also been discussed. As is evident from the ternary diagrams, Figs. 12, 15, 16, 17 and 18, increasing ~~the~~ surfactant concentration while the oil content of the microemulsion is held constant, can result in transitions from isotropic micelles (S_1, S_2) to the liquid crystalline structures, G. Also, the Winsor's intermicellar equilibrium concept permits the existence of single phases (S_1, G) and (S_2, G). Bansal and Shah (58) working with ethoxylated sulfonates (EOR - 200) + petroleum sulfonates (Petrostep 465) mixed surfactant systems, observed a phase change pattern, namely, isotropic ——> precipitation ————> birefringent ——> phase separation. They noted that the optimal salinities (S_γ, S_ϕ) increased with the addition of EOR - 200 into the petroleum sulfonate, and consequently the IFT was reduced. They suggested that a synergistic effect was operative.

In this study, the phase pattern for the mixed-surfactant systems appears to be;

isotropic $\rightleftarrows$ birefringent $\longrightarrow$ phase separation.

Although no birefrigency measurements were performed, the rheological trends suggest the presence of liquid crystalline structures. The magnitude of the viscosities obtained at appreciable C-21 concentrations indicate that liquid crystalline structures do not dominate; but are in fact in equilibrium with the isotropic micelles.

The gradual breakdown of the spherical micellar structures could be attributed to the electro-kinetic properties of lignosulfonates. This enables the molecules to establish at the interface exerting spreading pressures which increase with concentration. Because of the wide molecular-weight distribution, the lignosulfonate molecules at the interface have different chain lengths and degrees of sulfonation. This explains why only some of the spherical micelles are broken to form the less interfacially active liquid crystalline structures. A predominance of the latter would necessarily increase the IFT. At lignosulfonate concentrations beyond the mutual tolerance limit, the micellar structure is completely broken down and pushed out of the interphase resulting in precipitation and loss of interfacial-activity.

10.4 Acid Number of Chatham and Gosfield South Crudes:

This measurement was carried out for the following reasons.

(i) To determine the acid content of both crudes in an attempt to explain the differences in water (1.5% NaCl) - oil IFT.

(ii) To determine the suitability of these crudes for caustic water flooding.

The method of determination was as per ASTM D 976-64/IP 139/65. The specifications of chemicals used are given in Table 15 and the results obtained are as follows:-

Crude Oil	Acid Number
Gosfield South	0.2996 mg KOH/g oil
Live Chatham	0.2992 mg KOH/g oil

There is no significant difference in the acid numbers of the two crudes. At the time of measurement, the age of the Gosfield crude sample was 22 months and that of the Chatham crude, 6 months. This probably accounts for the higher value obtained for the former.

On the basis of these results, the differences in oil-water IFT cannot be explained; but the acid number is probably too low for caustic water flooding consideration. The latter conclusion is based on the work of various authors,(38, 11) discussed in part I.

CHAPTER 11

APPRAISAL OF THE DISPLACEMENT EFFICIENCY OF VARIOUS SURFACTANT SYSTEMS

11.1 Secondary Recovery Floods:

The additional recoveries (AR) based on the reference brine (1.5% NaCl) flood (Run No. 1) are given in Table 14. The relevant IFT and viscosity data are included in Table 12.

Despite the fact that the IFT obtained with various lignosulfonate concentrations (Table 12) were all in the range of 1.0 to 2.0 dynes/cm, no additional oil was recovered at 1% lignosulfonate concentration. At 3% and 6% concentrations, the AR's were 3% and 4% respectively for N-22, and 1% and 3% for C-21. Since the viscosities of these solutions were approximately the same, the slightly lower IFT achieved with the N-22 solutions could have contributed to their better performance over the C-21 solutions.

Other variables which might have affected the relative performance of the various floods are as follows:-

(i) Sand Grain Size and Foreign Particle Content:

Uren and Fahmy(30) had observed that finer sand grains resulted in lower oil recoveries in laboratory water flooding experiments. In all displacement runs, although the same C-190 Ottawa sand grade was used, slight differences in grain size and grain size distribution were observed to exist from one bag to another bag. The amount of dark, flaky and

TABLE 14

ADDITIONAL RECOVERIES OF VARIOUS SECONDARY FLOODS

Run. No.	System Identification	Break through	Additional Recoveries At 1 PV	2 PV	Final (2.7 PV)
1	1.5% NaCl	0.0	0.0	0.0	0.0
2	1% N-22 in 1.5% NaCl	3.0	-0.6	-0.5	-1.0
3	3% N-22 in 1.5% NaCl	6.0	2.5	3.2	3.0
4	6% N-22 in 1.5% NaCl	7.0	3.2	4.3	4.0
5	1% C-21 in 1.5% NaCl	4.2	1.0	1.0	0.0
6	3% C-21 in 1.5% NaCl	2.0	-2.0	2.4	1.0
7	6% C-21 in 1.5% NaCl	4.0	2.0	4.0	3.0

non-quartzite particles varied also from bag to bag. These could have affected the oil recoveries to a slight extent.

(ii) Flooding Rates and Length of Core-holder:

As indicated in Table 12, the injection rates varied from 393 ml/hr for the first two runs to about 374 ml/hr for run Nos. 3 to 7. The flood rates correspond to frontal advance velocities in the packed bed of 13.9 and 13.2 ft/day respectively. In practice, reservoir flooding velocities are about 1 ft/day; thus displacement runs were conducted at much higher flooding velocities. The short flood path (3 ft of core length) could have resulted in the non-attainment of interface equilibrium between the oil and the injected phases. It is thus probable that the previously measured IFT values were not realised during the floods. However, according to Bae and Petrick,(28) adsorption losses would be minimal at such high flood rates.

For the higher lignosulfonate concentrations, emulsification could have been responsible in part for the observed decrease in injection rates. On the other hand, the poor performance of the 1% lignosulfonate solutions could be the effect of a significant adsorption loss at such low concentrations.

11.2 Tertiary Recovery Floods:

In these floods, the oil viscosity varied from 5.5 to 7.2 cp, while the injection rate also varied from 360 to 402 ml/hr (Table 13). Some of the variation in flood rates was linked to pump malfunctioning. A quick recalibration test performed after run No. 10 indicated that the pump was operating at a different rate from that of the initial calibration. The wide differences in the viscosities of the various injected surfactant systems could have been responsible in part for the pump malfunctioning. Besides the variations in oil viscosity and flood rates, the quantity of brine (1.5% NaCl) injected in the secondary mode, varied from 0.93 to 1.0 PV. The percent tertiary oil recovery concept appears to be the only meaningful way of comparing the displacement efficiency of these floods. The percent tertiary oil recovery simply means the actual oil recovered beyond the secondary stage expressed as a percentage of maximum oil recoverable (Appendix C).

With the surfactant system consisting of 6% C-21 in 1.5% NaCl and 1.0% butanol-1 (Run No. 8), the tertiary oil recovery was 78% and the additional recovery was 10%. Compared to the 6% C-21 + 1.5% NaCl secondary flood (Run No. 7), this represents a significant 6% improvement as a result of the incorporation of butanol-1.

The mobility ratios, of the 2% Petrostep 420 systems (Run Nos. 9 to 11) decreased from 3.70 (unfavorable) to 0.95 (favorable) with increasing lignosulfonate concentrations. The IFT values (Tables 8 and 13) dropped by approximately 93% as the lignosulfonate concentration was increased from 0 to 1.0%. A significant 23% difference in the tertiary oil recoveries of Run Nos. 9 and 11 systems confirms the superiority of the 2% Petrostep 420 + 1.0% C-21 system over the 2% Petrostep 420 alone.

Similarly, for the 3% Petrostep concentration series (Run Nos. 12 to 14 of Table 13), M varied from about 3.0 for Run No. 12 flood to 1.2 for Run No. 13. The reduction in IFT accomplished by the addition of C-21 was about 60%. Run No. 13 produced 100% tertiary oil at only 1.32 PV tertiary surfactant injection; while Run. No. 12 at 2.04 PV surfactant injection produced only 80% tertiary oil. The surfactant system of Run No. 14 had undergone phase separation upon mixing of the constituents, and consequently the tertiary oil recovery was only 58%. The produced aqueous phase in this Run was much thinner and darker indicating a preferential retention of the active sulfonate material in the packed bed.

At an M value of 2.78, 4% Petrostep 450 recovered 96% tertiary oil, while with the addition of 1.0% C-21 (Run No. 16), M was reduced to 0.73, and consequently 100% tertiary oil was obtained after only 1.2 PV surfactant injection. When 2.0% C-21 was added to the 4% Petrostep 450 (Run No. 17), the surfactant system's measured viscosity of 64.0 cp (thixotropic) meant an M value of 0.12. However, the tertiary oil recovered after 2.1 PV surfactant injection was only 1.0% better than that of the base flood. As noted earlier, after an initial low oil cut, oil production picked up towards the later stages of the flood. This surfactant system could have produced close to 100% tertiary oil had the flood been extended to about 3.0 PV total surfactant injection. From the attenuation of the produced surfactant, it was evident that a considerable retention of the active petroleum sulfonate ingredients occurred soon after the commencement of surfactant injection. This created serious pore-blocking problems and the contact factor(1, 21) dropped drastically. A structural breakdown of the large lamellar structures (probably causing the pore blockage) must have occurred later in the flood. As a result, the contact factor improved and consequently more oil could be contacted and thus produced. Shah et al (Ref. 63, chapter 7) had warned that such low but unfavorable M values obtained with microemulsions containing lamellar structures could adversely affect oil recovery. They recommended the addition of suitable cosurfactants or the alteration of brine, oil or surfactant concentrations for dealing with such problems.

Hill et al(42) working with mixed petroleum sulfonate systems, had observed optimum behaviour near the boundary between the single phase and multiphase regions. This was the case with our mixed surfactant systems. Although a moderate thixotropy trend was observed in these systems, the IFT and M values were generally favorable and the integrity of the surfactant system was not impaired under the continuous injection mode employed. The results of these tertiary floods demonstrate the effectiveness of the mixed Petrostep-lignosulfonate surfactant systems. They also substantiate the inter-micellar equilibrium mechanism proposed earlier. Kalfoglou(24) attributed the additional oil recoveries obtained with such formulations to the preferential adsorption of lignosulfonates on to the reservoir matrix surface. This study clearly demonstrates that a much more complex mechanism is involved and that a limiting concentration ratio of both surfactants is an important parameter. Although adsorption or retention studies were not covered, it is hoped that future work will involve these aspects. In addition, the use of a longer flood path (core-holder length) for future experiments would allow the injection of a finite slug of surfactant to be followed by a polymer buffer bank as is done in practice.

PART V

CONCLUSIONS AND RECOMMENDATIONS

CHAPTER 12

CONCLUSIONS

The following conclusions may be drawn from this study:

(1) A sequential strategy-oriented procedure has been developed for formulating lignosulfonate-based surfactant systems suitable for EOR operations. The effects of the addition of simple organic and inorganic reagents on the interfacial activity of lignosulfonate solutions were systematically investigated.

(2) Caustic soda when added to 6% Marasperse N-22 solutions in various concentrations up to 3% lowered the IFT to values near 1.0 dynes/cm. Blank caustic solutions at concentrations less than 1.0% gave lower IFT values than the lignosulfonate-caustic systems. The low acid numbers of the two crudes extensively studied suggests that caustic flooding might not be an effective enhanced oil recovery scheme.

(3) Out of the several organic additives employed, only butanol-1 produced significant IFT reduction when added in moderate concentrations. By a salinity optimisation study, a formulation consisting of 6% C-21, 2% NaCl and 1.0% butanol-1 was obtained. This system had an IFT against Chatham crude of ~1.44 dynes/cm and produced 78% tertiary oil.

(4) The addition of Marasperse C-21 into solutions of Petrostep 420 and 450 produced significant IFT reduction and viscosity improvement. The amount of C-21 that could be added to give a stable system was limited by a concentration ratio, C_{cr} given by

$$C_{cr} = \frac{C_{Petrostep}}{C_{C-21}} \geqslant 1.5$$

Within this concentration limit, the two surfactants were reasonably compatible. IFT values obtained with these mixed surfactant systems were in the range of 10^{-2} to 10^{-3} dynes/cm. As much as 90% further reduction in IFT (obtained with ordinary Petrostep solutions) and viscosity increases up to 400% were consequently realised. However, beyond the limiting concentration, further addition of C-21 led to phase separation and a subsequent increase in IFT. The viscosity of the resulting mixed surfactant systems dropped to very low values. This critical concentration ratio is expected to depend on the composition and equivalent weight of a given Petrostep, as well as on the type and composition of lignosulfonate.

(5) Secondary mode displacement runs with various lignosulfonate concentrations were conducted. The reference water (1.5% NaCl) flood produced a final oil recovery of 83% at 2.7 PV total injection. No additional recovery was obtained with 1.0% solutions of lignosulfonates C-21 and N-22. AR's of 2% and 4% were obtained with 3% and 6% solutions respectively. The slightly lower IFTs of the N-22 solutions might have been partly responsible for the better displacement efficiencies of 3% and 6% N-22 over those of C-21.

(6) Tertiary mode displacement runs were conducted to evaluate some of the mixed surfactant systems formulated. Final oil recoveries obtained with these systems were generally in the

range of 90 to 100%. These high displacement efficiencies are consistent with the favorable IFT and viscosity trends observed in the surfactants' development phase of this study. About 20 to 25% more tertiary oil was produced (in some cases at much lower total PV injected) with the addition of C-21 than when Petrostep alone was used. Mixed surfactant systems which were observed to be unstable or which had abnormally high viscosities did not recover more oil than the base brine flood. A pore-blocking effect which decreased the contact factor might have been responsible for the low oil recoveries obtained.

(7) A mechanism of intermicellar equilibrium of isotropic micelles and liquid crystalline structures has been tentatively proposed to explain the properties of these mixed surfactant systems.

CHAPTER 13

RECOMMENDATIONS

The following recommendations are made based on the results of this study:

A. Water flooding of the Chatham Crude Reservoir:

The rather high oil recovery obtained with brine (1.5% NaCl) indicates that water flooding of the reservoir will be effective. If not already done, reservoir studies should be commenced in preparation for such a flooding scheme. We recommend the use of properly-tailored lignosulfonate solutions in the proposed water flooding scheme.

B. Further Studies of the Petrostep-Lignosulfonate Mixed Surfactant Systems:

(i) The variation and dependency of the critical concentration ratio, C_{cr}, on the equivalent weight and composition of various Petrosteps should be investigated. Studies should be made using higher concentrations of Petrosteps 420 and 450. Later, the work could be extended to Petrosteps 465 and 500 and possibly to mixtures of various Petrosteps. Other lignosulfonates such as Marasperse N-22, and CE-22 as well as sulfonated Kraft Lignins should be employed. Ultimately, the best combination of Petrosteps and lignosulfonates would be obtained. If necessary, various alcohols would be screened for addition to the Petrostep-lignosulfonate mixture in order to develop surfactant systems of high oil recovery efficacies.

(ii) A proper identification of the various structures present in these mixed surfactant systems is of utmost importance. Electrical conductivity, birefringence, X-ray, electron microscopy and NMR measurements would be needed to identify and characterize these structures. Sizes of dispersed particles could be measured with the Brice Phoenix Photometer.

C. Improvement on the Displacement Set-up:

(i) Future displacement runs should be conducted in an environment with a better temperature control. Additional thermo-regulating facilities should be provided in the laboratory; otherwise a temperature-controlled chamber should be erected over the entire displacement set-up.

(ii) The possibility of conducting displacement runs at reservoir temperatures and pressures should also be explored.

(iii) Longer sand packs or reservoir cores should be used in future experiments.

(iv) A more efficient and reliable injection pump capable of operating well at low flood rates should replace the present Milton-Royal pump.

(v) The analysis of produced fluids should also be done with automatic and more precise instruments such as the spectrophotometer or the high pressure separator.(60)

(vi) Measurements of pressure drop in the core should be done with differential pressure transducers.

CHAPTER 14

NOMENCLATURE

A. (Abbreviations Used in this work)

AR	Additional Recovery (%)
CMC	Critical Micelle Concentration, g/l
C-21	Marasperse C-21 Lignosulfonate
EOR	Enhanced Oil Recovery
HLB	Hydrophilic - Lipophilic Balance
IFT	Interfacial Tension - Surfactant System / Crude Oil, Dynes/cm
N-22	Marasperse N-22 Lignosulfonate
Petrostep, PT	Stepan's Petroleum Sulfonate
PV	Pore Volume, ml
WOR	Water-Oil-Ratio, Dimensionless

B. (Subscripts)

cr	Critical ratio
mo	Microemulsion rich (middle) layer-oil rich (upper) layer interface
mw	Microemulsion rich (middle) layer-water (brine) lower layer interface
o	Oil (Crude or Synthetic)
os	Oil - Sand interface
p	Polymer
s	Sand
w	Water or aqueous surfactant system

C. (Mathematical Expressions)

A	Interfacial area per molecule, cm^2
A_c	Core holder cross-sectional area, cm^2
C	Concentration (wt %)
C_{cr}	Critical concentration ratio, dimensionless
f	Fractional Flow of a given phase in a porous medium, dimensionless
g	Acceleration due to gravity, 980 cm/s^2
h	Difference between the two levels of the lower manometer fluid due to applied differential pressure, cm
K	Permeability in darcies
L	Pore-length, distance between two pressure-tappings on core holder, cm
M	Mobility ratio, dimensionless
N_{ca}	Capillary Number, dimensionless
q, Q	Aqueous phase flow rate, cm^3/s
R	Resistance factor of polymer, dimensionless
S_{orc}	Residual oil saturation to chemical flooding, (% PV)
S_{orw}	Residual oil saturation to water flooding, (% PV)
S_γ, S_ϕ	Optimal salinity for interfacial tension and for phase behaviour respectively, weight %
V_1, V_2	Velocity in pore of radius r_1 and r_2 respectively, cm/s
$\bar{V}$	Velocity ratio, dimensionless
W	Work, ergs

W_s	Weight of sand in core holder, g

D. (Greek Symbols)

λ	Mobility of any phase (oil or aqueous)
λ'	Wave length of white light, 5600 A°
μ	Viscosity, cp
γ, γ_{ow}	Oil-water interfacial tension, dynes/cm
θ	Contact angle, degrees
γ_i	Effective interfacial tension at any stage of microemulsification, dynes/cm
π	Spreading pressure at the sides of a curved interphase, dynes/cm
π'	Spreading pressure, dynes/cm, at any side of the flat film
$(\gamma_{ow})_a$	Reduced oil - water interfacial tension due to alcohol partitioning, dynes/cm
ΔP	Pressure drop across a certain length of porous medium, atm
ρ_1, ρ_2	Density of upper manometer liquid and lower manometer liquid respectively, g/cm^3
γ_{mo}, γ_{mw}	Oil-microemulsion phase and water-microemulsion phase interfacial tensions respectively, dynes/cm

CHAPTER 15

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APPENDICES

APPENDIX A

PROPERTIES OF VARIOUS SURFACTANT SYSTEMS AND CRUDE OILS:

(1) All surface tension data were obtained at 25 ± 0.1°C after 10 minutes interface ageing and consequently corrected to obtain the true values (see Appendix D).

(2) All interfacial tension data (excluding those for the mixed surfactant systems) were measured at 25 ± 0.1°C, after 15 to 40 minutes interface ageing, with the du Nouy tensiometer. The spinning drop tension data (for the mixed surfactant systems) are the average of three consecutive readings over 3 - 5 hour spinning interval at the temperature of 25 ± 0.5°C.

(3) Density measurements were made with the specific gravity bottle after 10 minutes equilibration in a 25°C bath. Distilled water at 25°C was used as reference substance.

(4) Viscosity measurements were performed with the UL Adapter Scheme of the Brookfield Viscometer after 10 minutes equlibration of sample in a 25°C bath. Shearing at various speeds for 5 to 10 minutes (except when reported otherwise) was maintained.

(5) pH measurements were carried out at a temperature range of 23 to 25°C using a Beckman pH meter equipped with a Fisher combination electrode. Calibration with pH 4, 7, 9 or 10 buffers was done before each measurement.

(6) All surfactant systems were considered stable except indicated otherwise (Table 6). Slight separation or sedimentation was associated with slightly unstable systems, while highly unstable ones contained insoluble precipitates.

TABLE 6

SURFACE TENSION, PH AND DENSITY DATA

FORMULATION STRATEGY	SYSTEM IDENTIFICATION	TRUE SURFACE TENSION, dynes/cm	PH	DENSITY g/cm^3
	Lab distilled water	67.26	6.80	0.9971
1A	1% N-22	44.20	7.30	1.0015
	3% N-22	41.50	7.30	1.0105
	6% N-22	40.65	7.70	1.0237
	10% N-22	40.52	7.75	1.0420
1*	1% N-22 acidified	41.18	3.90	1.0015
	3% N-22 acidified	37.36	3.90	0.0106
	6% N-22 acidified	38.47	4.10	1.0237
	10% N-22 acidified	37.06	4.25	1.0421
1	1% C-21	42.09	-	1.0014
	3% C-21	41.35	-	1.0019
	6% C-21	40.04	-	1.0228
	10% C-21	40.53	-	1.0397
1B	1% N-22	45.79	6.43	1.0015
	3% N-22	43.22	6.41	1.0105
	6% N-22	41.75	6.25	1.0237
	10% N-22	40.09	6.53	1.0420
	6% N-22 acidified	39.18	3.52	1.0242
	6% N-22 acidified	38.00	5.00	1.0227
	6% N-22 acidified	40.71	7.10	1.0222
	6% N-22 acidified	40.89	9.00	1.0231
	6% N-22 acidified	38.60	10.90	1.0265
	6% N-22 acidified	34.76	12.20	1.0365
	10% N-22 acidified	37.96	4.02	1.0419
	10% N-22 acidified	37.44	5.23	1.0397
	10% N-22 basified	40.62	7.50	1.0396

A= Beginning of formulation studies for Lloydminster crude.
*= Special strategy 1 studies.
B= Beginning of formulation studies for Gosfield South crude.

/2

2	10% N-22 basified	40.19	9.32	1.0407
	10% N-22 basified	38.85	11.10	1.0439
	10% N-22 basified	36.86	12.00	1.0462
	1% C-21	45.65	7.25	1.0014
1	3% C-21	44.04	7.02	1.0019
	6% C-21	41.90	6.80	1.0228
	10% C-21	40.19	6.62	1.0397
	6% N-22 + 0.1% NaOH	40.75	9.60	1.0246
	6% N-22 + 0.5% "	38.36	12.20	1.0281
	6% N-22 + 1.0% "	36.65	12.80	1.0331
2	6% N-22 + 3.0% "	33.99	13.30	1.0526
	Blank 0.1% "	69.92	12.00	0.9981
	" 0.5% "	70.15	12.51	1.0024
	" 1.0% "	63.12	12.70	1.0076
	" 3.0% "	59.22	13.10	1.0277
	6% N-22 + 0.5% Acetone	40.75	6.55	1.0221
	6% N-22 + 1.0% "	39.33	6.55	1.0217
	6% N-22 + 3.0% "	39.47	6.55	1.0201
	6% N-22 + 5.0% "	38.53	6.58	1.0179
	6% N-22 + 8.0% "	38.82	6.70	1.0146
	6% N-22 +10.0% "	37.49	6.75	1.0125
3	6% N-22 +15.0% "	36.79	6.85	1.0017
	6% N-22 +20.0% "	36.24	6.92	1.0012
	6% C-21 + 1.0% CH_3OH	41.09	7.59	1.0224
	6% C-21 + 3.0% "	40.52	7.55	1.0196
	6% C-21 + 6.0% "	39.62	7.52	1.0154
	6% C-21 +10.0% "	38.97	7.52	1.0100
	6% C-21 +15.0% "	38.56	7.52	1.0033
	6% C-21 + 1.0% Butanol-1	39.19	6.80	1.0202
	6% C-21 + 3.0% " "	36.49	6.90	1.0194
	6% C-21 + 6.0%*+ "	29.00	6.98	1.0156
	6% C-21 +10.0% " "	24.43	7.00	1.0096
	6% C-21 + 2.0% T-Butanol	40.62	6.60	1.0186
	6% C-21 + 5.0% " "	38.34	6.83	1.0163
	6% C-21 + 8.0% " "	35.93	7.00	1.0131
	6% C-21 +12.0% " "	30.96	7.05	1.0086

*+= Limit of solubility of Butanol-1.

3/

	Lab distilled water	62.67	5.92	0.9971
	0.5% Nacl	68.55	6.00	1.0009
	1.0% "	69.23	6.00	1.0043
	2.0% "	68.54	6.28	1.0113
	3.0% "	67.26	6.28	1.0183
	5.0% "	62.86	6.45	1.0317
	6% C-21+2.0%NaCl+1% 1-Butanol	38.49	7.30	1.0354
	6% C-21+2.0%NaCl+3.0% " "	34.20	7.30	1.0331
4	6% C-21+2.0%NaCl+6.0% " "	26.95	7.29	1.0293
	6% C-21+2.0%NaCl+10.0%" "	24.06	7.29	1.0223
	6% N-22+2.0%NaCl+0.1% NaoH	39.48	9.48	1.0375
	6% N-22+2.0%NaCl+0.5% "	36.78	12.00	1.0414
	6% N-22+2.0%NaCl+1.0% "	34.84	12.50	1.0462
	6% N-22+2.0%NaCl+3.0% "	32.24	13.00	1.0661
	2.0% NaCl + 0.1% NaoH	66.73	12.10	1.0123
	2.0% NaCl + 0.5% "	60.30	12.72	1.0165
	2.0% NaCl + 1.0% "	56.98	13.00	1.0216
	2.0% NaCl + 3.0% "	53.77	13.40	1.0418
4C	6% C-21+ 5.0%NaCl+1.0% 1-Butanol	38.64	7.30	1.0557
	6% C-21+10.0% " +1.0% " "	38.13	7.20	1.1019
	6% C-21+*20.0% " +1.0% " "	38.95	6.98	1.1507

4C= Start of formulation studies for Chatham crude.

* = Limiting brine tolerance.

	6% C-21+1.5%NaCl+ 0.1% PT420	31.77	6.58	1.0329
5	6% C-21+1.5%NaCl+ *0.5% PT420	29.81	6.50	1.0332
	6% C-21+1.5%NaCl+ 0.3% PT420	30.53	6.10	1.0222

*= Precipitation and phase separation point.

4/

/4 (Table 6 cont'd)

6% C-21 + 1.5% NaCl +0.1%PT420 +0.2% Hexanol	30.37	7.29	1.0332
6% C-21 + 1.5% NaCl +0.1%PT420 +0.4% Hexanol	28.38	7.31	1.0335
6% C-21 + 1.5% NaCl +0.3%PT420 +0.2% Hexanol	28.38	7.30	1.0336
6% C-21 + 1.5% NaCl +0.3%PT420 +0.4% Hexanol	28.05	7.53	1.0335
3% PT420 + 1.5% NaCl	29.70	10.60	1.0121
3% PT420,1.5%NaCl + 1.0% C-21	28.91	8.80	1.0153
*3% PT420,1.5%NaCl + 2.0% C-21	28.86	8.32	1.0173
**3% PT420,1.5%NaCl + 3.0% C-21	29.36	7.96	1.0237
2% PT420 + 1.5% NaCl	30.77	10.38	1.0107
2% PT420+1.5%NaCl + 0.5% C-21	29.98	9.03	1.0128
*2% PT420+1.5%NaCl + 1.0% C-21	29.84	8.50	1.0148
**2% PT420+1.5%NaCl + 2.0% C-21	29.14	7.99	1.0186
4.0%PT420+ 1.5% NaCl	30.07	10.90	1.0136
4.0%PT420+ 1.5% NaCl+1.0% C-21	29.65	9.22	1.0177
4.0%PT420+ 1.5% NaCl+2.0% C-21	28.76	8.70	1.0218
**4.0%PT420+ 1.5% NaCl+3.0% C-21	30.06	8.30	1.0231
2% PT450+1.5% NaCl	29.84	10.60	1.0105
2% PT450+1.5% NaCl+0.5% C-21	29.24	9.15	1.0127
*2% PT450+1.5% NaCl+1.0% C-21	29.56	8.70	1.0147
**2% PT450+1.5% NaCl+2.0% C-21	29.09	8.20	1.0180
3% PT450+1.5% NaCl	30.82	10.81	1.0123
3% PT450+1.5% NaCl+1.0% C-21	29.79	8.90	1.0164
*3% PT450+1.5% NaCl+2.0% C-21	29.74	8.44	1.0185
**3% PT450+1.5% NaCl+3.0% C-21	30.67	8.14	1.0226
4% PT450+1.5% NaCl	32.83	10.82	1.0137
4% PT450+1.5% NaCl+0.5% C-21	30.77	9.50	1.0158
4% PT450+1.5% NaCl+1.0% C-21	31.14	9.08	1.0179
*4% PT450+1.5% NaCl+2.0% C-21	30.62	8.50	1.0221
**4% PT450+1.5% NaCl+3.0% C-21	29.41	8.38	1.0233

*= Slightly unstable (slight phase separation).

**= Highly unstable (precipitation point).

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	6% C-21+1.0% 1-Butanol	37.71	7.50	1.0217
	6% C-21+1.0% 1-Butanol+1.0% NaCl	36.80	7.48	1.0287
	6% C-21+1.0% 1-Butanol+2.0% NaCl	36.70	7.46	1.0355
	6% C-21+1.0% 1-Butanol+4.0% NaCl	35.92	7.40	1.0490
	1.5% NaCl	68.56	6.10	1.0076
	1.0% C-21	43.53	7.90	1.0017
	1.0% C-21 + 1.5% NaCl	42.45	7.40	1.0120
	6.0% C-21	40.46	7.25	1.0236
6	6.0% C-21 + 1.5% NaCl	40.82	7.25	1.0339
	1% C-21 + 1.0% 1-Butanol	42.43	7.48	1.0003
	1.0% C-21+1.5%NaCl+1.0%1-Butanol	41.64	7.48	1.0107
	3.0% C-21+1.0% 1-Butanol	38.97	7.20	1.0091
	3% C-21+1.5%NaCl+1.0% Butanol-1	39.85	7.20	1.0195
	1.0% N-22 + 1.5% NaCl	42.35	7.76	1.0120
	3.0% N-22 + 1.5% NaCl	39.57	7.78	1.0208
6	6.0% N-22 + 1.5% NaCl	38.54	7.79	1.0340
	1.0% N-22+1.5%NaCl+1.0%1-Butanol	41.02	7.42	1.0107
	3.0% N-22+1.5%NaCl+1.0+1-Butanol	38.96	7.50	1.0196
	6.0% N-22+1.5%NaCl+1.0%1-Butanol	37.46	7.50	1.0328
	3.0% C-21	42.64	7.45	1.0104
	3.0% C-21+1.5% NaCl	41.85	7.40	1.0208

6/

TABLE 7

INTERFACIAL TENSION DATA

FORMULATION STRATEGY	CRUDE OIL SYSTEM	SYSTEM IDENTIFICATION	TRUE INTERFACIAL TENSION dynes/cm
	Alberta Lloydminster EMR No. 70-69	Lab Distilled water	14.57
	Alberta Lloydminster EMR No. 70-69	1% N-22	9.21
	Alberta Lloydminster EMR No. 70-69	3% N-22	7.87
	Alberta Lloydminster EMR No. 70-69	6% N-22	6.73
	Alberta Lloydminster EMR No. 70-69	10% N-22	6.66
	Alberta Lloydminster EMR No. 70-69	7% N-22; pH 3.90	12.24
1	Alberta Lloydminster EMR No. 70-69	3% N-22; pH 3.90	11.19
	Alberta Lloydminster EMR No. 70-69	6% N-22; pH 4.10	11.05
	Alberta Lloydminster EMR No. 70-69	10% N-22; pH 4.25	10.02
	Alberta Lloydminster EMR No. 70-69	1% C-21	9.37
	Alberta Lloydminster EMR No. 70-69	3% C-21	8.71
	Alberta Lloydminster EMR No. 70-69	6% C-21	8.51
	Alberta Lloydminster EMR No. 70-69	10% C-21	8.06
	Gosfield South Crude EMR No. 611-77	1% N-22	14.60
1	Gosfield South Crude EMR No. 611-77	3% N-22	12.64
	Gosfield South Crude EMR No. 611-77	6% N-22	11.50
	Gosfield South Crude EMR No. 611-77	10% N-22	10.42
2	Gosfield South Crude EMR No. 611-77	6% N-22; pH 3.52	12.48

2/

/2 (Table 7 cont'd)

	Gosfield South Crude EMR No. 611-77	6% N-22; pH 5.00	11.60
2	" " "	6% N-22; pH 7.10	9.94
	" " "	6% N-22; pH 9.00	3.94
	" " "	6% N-22; pH 10.90	2.20
	" " "	6% N-22; pH 12.20	1.11
	" " "	10% N-22; pH 4.02	10.85
	" " "	10% N-22; pH 5.23	10.23
	" " "	10% N-22; pH 7.50	6.96
	" " "	10% N-22; pH 9.32	3.48
	" " "	10% N-22; pH 11.10	2.20
	" " "	10% N-22; pH 12.00	1.93
	" " "	1% C-21	10.61
	" " "	3% C-21	9.11
	" " "	6% C-21	8.02
	" " "	10% C-21	8.04
	" " "	6% N-22 + 0.1% NaOH	1.24
	" " "	6% N-22 + 0.5% NaOH	0.89
	" " "	6% N-22 + 1.0% NaOH	0.51
	" " "	6% N-22 + 3.0% NaOH	0.25
	" " "	Blank 0.1% NaOH	0.25
	" " "	" 0.5% "	0.32
	" " "	" 1.0% "	0.60
	" " "	" 3.0% "	1.28
3	" " "	6% N-22 + 0.5% Acetone	9.60
	" " "	6% N-22 + 1.0% "	9.89
	" " "	6% N-22 + 3.0% "	9.51
	" " "	6% N-22 + 5.0% "	9.09
	" " "	6% N-22 + 8.0% "	8.28
	" " "	6% N-22 +10.0% "	8.14
	" " "	6% N-22 +15.0% "	7.58
	" " "	6% N-22 +20.0% "	7.21
	" " "	6% C-21 + 1.0% CH_3OH	6.52
	" " "	6% C-21 + 2.0% "	6.66
	" " "	6% C-21 + 6.0% "	6.72
	" " "	6% C-21 +10.0% "	6.73
	" " "	6% C-21 +15.0% "	6.74

3/

/3 (Table 7 cont'd)

3	Gosfield South Crude EMR No. 611-77	6% C-21 + 1.0% 1-Butanol	7.08
	" " "	6% C-21 + 3.0% " "	5.96
	" " "	6% C-21 + 6.0% " "	4.54
	" " "	6% C-21 +10.0% " "	1.68
	" " "	6% C-21+2.0% T-Butyl Alcohol	7.70
	" " "	6% C-21+5.0% " " "	6.62
	" " "	6% C-21+8.0% " " "	5.88
	" " "	6% C-21+12.0%" " "	4.82
4	" " "	Lab Distilled Water	21.47
	" " "	0.5% NaCl	20.79
	" " "	1.0% "	21.18
	" " "	2.0% "	18.96
	" " "	3.0% "	18.02
	" " "	5.0% "	15.59
	" " "	6%C-21+2.0%NaCl+1.0%1-Butanol	3.75
	" " "	" " + " " +3.0%" "	3.71
	" " "	" " + " " +6.0%" "	3.58
	" " "	" " + " " +10.0%" "	1.72
	" " "	6% N-22+2.0% NaCl +0.1% NaOH	1.28
	" " "	6% N-22+2.0% NaCl +0.5% "	0.77
	" " "	6% N-22+2.0% NaCl +1.0% "	0.42
	" " "	6% N-22+2.0% NaCl +3.0% "	0.51
	" " "	2% NaCl + 0.1% NaOH	0.42
	" " "	2% NaCl + 0.5% "	0.59
	" " "	2% " + 1.0% "	0.77
	" " "	2% " + 3.0% "	1.28
	Live Chatham Crude	6%C-21+5.0%NaCl+1.0%Butanol-1	1.50
	" " "	" " +10.0% " + " " "	1.71
	" " "	" " +20.0% " + " " "	2.36
	" " "	6%C-21+1.5%NaCl+0.1% PT420	0.475
	" " "	" " + " " +0.5% " "	0.230
	" " "	" " + " " +0.3% " "	0.308
	" " "	6%C-21+1.5%NaCl+0.1% PT420 +0.2% Hexanol	0.486

4/

/4 (Table 7 cont'd)

4	Live	Chatham	Crude	6%C-21+1.5%NaCl+0.1% PT420 +0.4% Hexanol	0.585
	"	"	"	6%C-21+1.5%NaCl+0.3% PT420 +0.2% Hexanol	0.544
	"	"	"	6%C-21+1.5%NaCl+0.3% PT420 +0.4% Hexanol	0.519
5	"	"	"	3% PT420 + 1.5% NaCl	0.115
	"	"	"	3%PT420+1.5%NaCl+1.0%C-21	$4.570\mathrm{x}10^{-2}$
	"	"	"	" " " + " " +2.0%" "	$3.890\mathrm{x}10^{-2}$
	"	"	"	" " " + " " +3.0%" "	0.348
	"	"	"	2%PT420 + 1.5% NaCl	0.114
	"	"	"	2%PT420 + 1.5% " +0.5% C-21	$7.720\mathrm{x}10^{-2}$
	"	"	"	" " " + " " +1.0% "	$8.220\mathrm{x}10^{-3}$
	"	"	"	" " " + " " +2.0% "	$2.590\mathrm{x}10^{-2}$
	"	"	"	4% PT420 + 1.5% NaCl	0.116
	"	"	"	4% PT420 + 1.5% " +1.0% C-21	$6.770\mathrm{x}10^{-2}$
	"	"	"	4% PT420 + 1.5% " +2.0% "	$2.820\mathrm{x}10^{-2}$
	"	"	"	4% PT420 + 1.5% " +3.0% "	$2.770\mathrm{x}10^{-2}$
	"	"	"	2% PT450 + 1.5% NaCl	0.103
	"	"	"	" " " + 1.5% " + 0.5%C-21	$5.700\mathrm{x}10^{-2}$
	"	"	"	" " " + " " + 1.0% "	$5.900\mathrm{x}10^{-2}$
	"	"	"	" " " + " " + 2.0% "	0.145
	"	"	"	3% PT450 + 1.5% NaCl	0.108
	"	"	"	" " " + " " + 0.5%C-21	$9.020\mathrm{x}10^{-2}$
	"	"	"	" " " + " " + 1.0% "	$1.180\mathrm{x}10^{-2}$
	"	"	"	" " " + " " + 2.0% "	0.166
	"	"	"	" " " + " " + 3.0% "	0.21
	"	"	"	4% PT450 + 1.5% NaCl	0.120
	"	"	"	" " " + " " + 0.5% C-21	$9.740\mathrm{x}10^{-2}$
	"	"	"	" " " + " " + 1.0% C-21	$4.440\mathrm{x}10^{-2}$
	"	"	"	" " " + " " + 2.0% "	$1.880\mathrm{x}10^{-2}$
	"	"	"	" " " + " " + 3.0% "	$9.130\mathrm{x}10^{-2}$
6	"	"	"	6% C-21 + 1.0% Butanol-1	1.57
	"	"	"	" " " + " " "+1.0%NaCl	1.48
	"	"	"	" " " + " " "+2.0% "	1.48

5/

/5 (Table 7 cont'd)

6	Live Chatham Crude	6% C-21 + 1.0%Butanol-1 +4.0%NaCl	1.44
	" " "	1.5% NaCl	4.55
	" " "	1.0% C-21	1.81
	" " "	3.0% C-21	1.62
	" " "	6.0% C-21s	2.16
	" " "	1.0% C-21 + 1.5% NaCl	1.50
	" " "	3.0% " + " "	1.30
	" " "	6.0% C-21 + 1.5% NaCl	2.05
	" " "	1.0% C-21 + 1.0% Butanol-1	2.03
	" " "	3.0% C-21 + 1.0% Butanol-1	2.15
	" " "	1.0% C-21+1.5%NaCl +1.0%Butanol-1	1.24
	" " "	3.0% C-21+1.5%NaCl +1.0%Butanol-1	1.90
	" " "	1.0% N-22 + 1.5% NaCl	1.05
	" " "	3.0% N-22 + 1.5% NaCl	1.11
	" " "	6.0% N-22 + 1.5% NaCl	1.24
	" " "	1.0% N-22 +1.5%NaCl+1.0%Butanol-1	1.29
	" " "	3.0% N-22 +1.5%NaCl+1.0%Butanol-1	1.18
	" " "	6.0% N-22 +1.5%NaCl+1.0%Butanol-1	1.37

TABLE 8-A

VISCOSITY DATA

CRUDE OIL SYSTEMS

SYSTEM NAME	DENSITY (g/cm^3)	VISCOSITY (cp)	AT VISCOMETER SPEED, rpm
Albertan Lloydminster EMR No. 70-69	0.9176	∿102	6
Ontarian-Gosfield South EMR No. 611-77	0.8121	4.22	60
		4.31	30
Ontarian-Chatham (Top cut)	0.8192	5.28	60
		5.30	30
Ontarian-Chatham (Middle cut)		5.81	60
		5.94	30

TABLE 8-B

VISCOSITY OF SURFACTANT SYSTEMS

SYSTEM NAME	VISCOSITY, cp, at VISCOMETER SPEED, rpm 60	30	12	6
6% N-22 + 0.1% NaOH	1.32	1.48	1.90	2.50
6% N-22 + 0.5% NaOH	1.35	1.38	1.63	1.70
6% N-22 + 1.0% NaOH	1.37	1.48	1.75	2.20
1.0% C-21 + 1.0% 1-Butanol	1.08	1.13	1.35	--
1.0% C-21 + 1.0% 1-Butanol + 1.5% NaCl	1.10	1.16	1.35	--
3.0% C-21 + 1.0% 1-Butanol	1.15	1.22	1.50	--
3.0% C-21 + 1.0% 1-Butanol + 1.5% NaCl	1.18	1.26	1.62	--
1.0% N-22 + 1.5% NaCl	1.05	1.10	1.38	--
3.0% N-22 + 1.5% NaCl	1.15	1.26	1.48	--
6.0% N-22 + 1.5% NaCl	1.24	1.35	1.60	--
1.0% N-22 + 1.5% NaCl + 1.0% 1-Butanol	1.06	1.18	1.42	--
3.0% N-22 + 1.5% NaCl + 1.0% 1-Butanol	1.18	1.28	1.65	--
6.0% N-22 + 1.5% NaCl + 1.0% 1-Butanol	1.30	1.46	1.72	--

2/

/2 (Table 8-B cont'd)

6% C-21 + 1.0% 1-Butanol	1.27	1.38	1.65	--
6% C-21 + 1.0% 1-Butanol + 1.0% NaCl	1.30	1.37	1.78	--
6% C-21 + 1.0% 1-Butanol + 2.0% NaCl	1.33	1.39	1.70	--
" " + " " " + 4.0% "	1.36	1.45	1.75	--
6% C-21	1.25	1.32	1.70	--
6% C-21 + 1.5% NaCl	1.30	1.38	1.68	--
1.5% NaCl	1.01	1.13	1.25	--
1.0% C-21	1.05	1.16	1.35	--
3.0% C-21	1.15	1.28	1.58	--
1.0% C-21 + 1.5% NaCl	1.06	1.21	1.40	--
3.0% C-21 + 1.5% NaCl	1.16	1.21	1.50	--
+2% PT420 + 1.5% NaCl	1.45	1.54	1.82	--
2% PT420 + 1.5% NaCl + 0.5% C-21	2.34	2.44	2.75	--
*2% PT420 + 1.5% NaCl + 1.0% C-21	4.43	6.42	8.30	--
2% PT420 + 1.5% NaCl + 2.0% C-21	1.14	1.30	1.55	--

+= For all mixed surfactant Systems - Measurements made within 1 week of system preparation.

*= Mildly thixotropic - data taken after 10 mins. of shearing.

3% PT420 + 1.5% NaCl	1.96	2.00	2.32	--
*3% PT420 + 1.5% NaCl + 1.0% C-21	--	13.08	19.72	--
3% PT420 + 1.5% NaCl + 2.0% C-21	1.68	1.73	2.48	--
4% PT420 + 1.5% NaCl	2.18	2.28	2.50	--
*4% PT420 + 1.5% NaCl + 1.0% C-21	--	11.76	12.62	--
**4% PT420 + 1.5% NaCl + 2.0% C-21	--	--	30.20	34.0
4% PT420 + 1.5% NaCl + 3.0% C-21	1.19	1.26	1.50	--
2% PT420 + 1.5% NaCl	1.52	1.63	1.85	--
2% PT420 + 1.5% NaCl + 0.5% C-21	1.79	1.91	2.20	--
*2% PT420 + 1.5% NaCl + 1.0% C-21	6.50	9.48	9.30	--
2% PT420 + 1.5% NaCl + 2.0% C-21	1.11	1.18	1.45	--
3% PT450 + 1.5% NaCl	1.94	1.98	2.25	--
3% PT450 + 1.5% NaCl + 0.5% C-21	2.62	2.65	3.10	--

*= Moderately thixotropic - measurements made after 10 mins. shearing

**= Strongly thixotropic - measurements made after 10-20 mins. shearing

Systems (already indicated in Table 6) containing precipitates were allowed to settle and clarified solutions used for viscosity measurements.

3/

(Table 8-B cont'd)

*3% PT450 + 1.5% NaCl + 1.0% C-21	7.12	7.86	8.70	--
*3% PT450 + 1.5% NaCl + 2.0% C-21	1.55	1.67	2.10	--
3% PT450 + 1.5% NaCl + 3.0% C-21	1.13	1.28	1.50	--
4% PT450 + 1.5% NaCl	2.54	2.58	3.10	--
4% PT450 + 1.5% NaCl + 0.5% C-21	2.95	2.97	3.34	--
*4% PT450 + 1.5% NaCl + 1.0% C-21	6.63	7.26	7.88	--
**4% PT450 + 1.5% NaCl + 2.0% C-21	--	--	42.00	41.95
4% PT450 + 1.5% NaCl + 3.0% C-21	1.20	1.28	1.50	--

*= Moderately thixotropic - measurements made after 10 mins. shearing

**= Strongly thixotropic - measurements made after 10-20 mins. shearing

Systems (already indicated in Table 6) containing precipitates were allowed to settle and clarified solutions used for viscosity measurements.

TABLE 9

THIXOTROPIC BEHAVIOUR OF SOME MIXED SURFACTANT SYSTEMS

(a) System Identification: 2% Petrostep 420 + 1.5% NaCl + 1.0% C-21

Age of solution: 3 days

Total shearing time (minutes) / Viscometer Speed (rpm)	Viscosity, cp at Total Shearing Time 2	10	20	30
60	4.91	4.40	-	-
30	-	-	9.50	8.20

(b) System Identification: 2% Petrostep 450 + 1.5% NaCl + 1.0% C-21

Age of solution: 5 days

Total Shearing time (minutes) / Viscometer Speed (rpm)	Viscosity, cp at Total Shearing Time 5	10	12	15	20
60	-	-	7.41	7.51	-
30	5.40	7.98	-	-	9.74 (increasing)

(c) System Identification: 3% Petrostep 420 + 1.5% NaCl + 1.0% C-21

		Viscosity, cp at Total Shearing Time					
	Total Shearing time (minutes)	2	5	7	10	20	30
Age (days)	Viscometer speed (rpm)						
1	30	-	-	5.50	5.48	-	-
4	30	7.56	8.28	-	8.26	-	-
7	30	11.22	-	-	11.34	-	-
10	30	-	11.82	-	12.04	-	-
20	30	-	12.14	-	12.18	11.80	-
27	30	-	5.18	-	5.50	9.04	9.50 (increasing)
(d)	System Identification: 4% Petrostep 450 + 1.5% NaCl + 1.0% C-21						
1	30	9.62	9.68	-	-	-	-
2	30	-	11.82	-	12.04	-	-
13	30	-	15.04	-	14.80	-	-
22	30		9.04	-	9.50	9.94	10.30 (increasing)

APPENDIX B

TOTAL BRINE PERMEABILITY OF THE UNCONSOLIDATED OTTAWA SAND (C-190) PACK:

Theory:

Darcy's law applied to the flow of a fluid in a porous medium can be expressed in the form

$$Q = \frac{K\,A\,\Delta P}{\mu\,L} \qquad \text{.....} \quad (1)$$

where Q = Liquid flow rate, cm^3/s

K = Total permeability, darcy

A = Crosssectional area, cm^2

ΔP = Pressure drop across two fixed points, atm

μ = Liquid viscosity, cp

L = Distance between two fixed points, cm

Equation (1) is subject to the following assumptions:

(i) Steady state flow

(ii) Laminar flow (Re <1)

(iii) 100% saturation with a single fluid

(iv) Fluid does not react with rock

(v) Homogeneous and isotropic conditions

Experimental:

Bansal(1) had ascertained that for the Milton Royal injection pump, laminar flow conditions exist over all settings (0 to 90%) of stroke-length. The conditions were maintained in order to ensure the above assumptions to be reasonably valid. The core was packed, dearated and saturated with 1.5% NaCl as in normal displacement runs.

Data and Analysis:

Injected fluid: 1.5% NaCl

Fluid Density at 25°, ρ = 1.0076 g/cm^3

2 - liquid system manometer:

Lower liquid (1.75 specific gravity Merian Blue) density at 25°, ρ_2 = 1.745 g/cm^3

Upper manometer liquid - 1.5% NaCl, ρ_1 = 1.0076 g/cm^3

Bed porosity, ϕ, = 0.344

Crosssectional area of core holder, A_c = 22.23 cm^2

Mean room temperature = 25.2°C

Distance between pressure tappings on core holder, L, = 30.0 cm

TABLE 10

FLOW RATE AND PRESSURE DROP DATA

Pump Setting % stroke lth.	Flow rate ml/hr	Q ml/s x10^2	Manometer Reading h cm	ΔP atmx10^3
10	141.0	3.92	1.24	0.885
30	473.8	13.20	4.29	3.06
40	630.5	17.50	5.72	4.08
50	787.4	21.90	7.17	5.12
60	942.4	26.20	8.58	6.12
70	1086.3	30.20	9.93	7.08
80	1229.5	34.10	11.23	8.01

Analysis of Data:

From the plot of Q (ml/s) versus ΔP (atm), Fig. 41, the slope is obtained:

$$\text{Slope} = 42.24 \quad \text{cm}^3/\text{ s atm} = \frac{K\,A}{\mu L} \qquad \ldots\ldots (2)$$

and

$$K = \frac{42.24 \times 1.01 \times 30}{22.23} ; \quad \text{darcies}$$

$$= 57.82 \text{ d.}$$

From the theory of manometry, for a U-tube of uniform cross-section,

$$\Delta P = \frac{h(\rho_2 - \rho_1)\, g}{1.0133 \times 10^6} \text{ atm} = 0.7131 \text{ h} \times 10^{-3} \text{ atm}$$

APPENDIX C

EXPERIMENTAL DATA AND RECOVERY CALCULATIONS FOR A TYPICAL DISPLACEMENT RUN:

The experimental data and recovery analysis for Run. No. 11 (Table 13) are presented as follows:

The temperature range for duration of run = 23 to 25°C.

Temperature prevailing during most of the run = 24°C.

Step 1 : **Pore-volume and Porosity**

Weight of coreholder + flanges, bolts = 20 lb, 251 g

Weight of coreholder + Sand pack = 20 lb, 3.7737 Kg

Weight of Sand, W_s, = 3522.7 g

$$\text{Porosity, } \phi, = 1 - \frac{W_s}{V_c \times \rho_s}$$

where V_c = volume of coreholder, cm^3

ρ_s = density of sand, g/cm^3

$$= 1 - \frac{3522.7}{2025.67 \times 2.65} = 0.3438$$

$$\text{Pore volume, PV, } = \phi \times V_c = 0.3438 \times 2025.67$$
$$= 696.35 \text{ cm}^3$$

Step 2 **Dearation, Leakage Test and Oil Saturation**

(a) In-line piping was cleaned and dried with air, then the coreholder was mounted .

(b) The coreholder was opened to the vacuum pump for 15 hours after a preliminary check to eusure no air leakage in the system.

(c) Before saturation with oil, a leakage test was conducted as follows:

The vacuum pump was isolated and the drop in vacuum manometer readings monitored every minute for 27 minutes

TABLE 17

TYPICAL LEAKAGE TEST DATA

Barometric Pressure: 75.5 cm Hg, temperature = 23.5°C

Time	Vacuum Manometer Reading (cm) Hg.		
(seconds)	Right Limb	Left Limb	ΔP
0	37.4	37.80	75.20
60	37.4	37.80	75.20
⋮	⋮	⋮	⋮
480	37.4	37.80	75.20
540	37.3	37.75	75.05
600	37.3	37.75	75.05
660	37.3	37.73	75.03
720	37.3	37.70	75.00
⋮	⋮	⋮	⋮
840	37.3	37.70	75.00
900	37.3	37.65	74.95
⋮	⋮	⋮	⋮
1020	37.3	37.65	74.95
1080	37.2	37.65	74.85
⋮	⋮	⋮	⋮
1260	37.2	37.65	74.85
1380	37.2	37.60	74.80
⋮	⋮	⋮	⋮
1620	37.2	37.60	74.80

(d) Oil Saturation:

Oil viscosity = 6.44 cp at 30 rpm; 24.4°C

The oil reservoir was first filled to the zero mark.

The expected drop in oil level for 1 PV=36.10 cm

Actual drop (at the time oil appeared from the tygon tubing), h = 36.20 cm

Oil saturation time = 1460 seconds

Oil in place = h x reservoir cross-sectional area

$= 36.20 \times 19.3 = 698.7 \text{ cm}^3$

Step 3 Secondary mode flooding with 1.5% NaCl after recirculation through the injection pump for 30 minutes.

Initial flow rate (from recirculation line)

= 390.5 ml/hr

Initial water tank level = 4.70 cm

Expected final water tank level for 1 PV = 2.24 cm

Actual final water tank level at termination of water injection = 2.25 cm

Total water injected = drop in liquid level x reservoir cross-sectional area = 283.5 x 2.24

$= 694.57 \text{ cm}^3$

PV water injected $= \dfrac{694.57}{696.35} = 0.994$

Total run time for water flooding = 6221 s

Average water injection rate $= \dfrac{694.57 \times 3600}{6221}$

= 401.94 ml/hr

Oil appeared first in effluent collector after 145 seconds.

Time for water breakthrough (from effluent collector) = 2146 seconds.

TABLE 16

TYPICAL UPSTREAM PRESSURE - TIME DATA

Time (from start of water run) seconds	Upstream manometer, (cm) Hg		
	Left limb	Right limb	ΔP
180	3.10	2.80	5.90
800	2.80	2.40	5.20
1368	2.50	2.20	4.70
1930	2.30	2.00	4.30
2600	2.10	1.80	3.90
4400	2.10	1.80	3.90
6330	2.00	1.70	3.70
8200	2.10	1.90	4.00
10000	2.50	2.30	4.80
11964	2.80	2.50	5.30
13980	2.80	2.60	5.40

Step 4 Surfactant tertiary flooding:

System : 3% Petrostep 420; 1.5% NaCl + 1.0% C-21

Total volume prepared : 1800 ml

Viscosity at 30 rpm, 24.2°C = 5.50 cp

Initial surfactant tank level = 43.35 cm

Expected final level for 2 PV injection = 48.26 cm

Actual final level at flood termination = 46.60 cm

Total surfactant injected = 283.5 x 3.25 = 921.37 ml

Injected PV = $\frac{921.37}{696.35}$ = 1.319

Time at commencement of tertiary flood = 6221 s

Time at termination of tertiary flood = 14583 s

Total surfactant injection time

$$= \frac{(14583 - 6221)}{3600} = 2.323 \text{ hr}$$

Average injection rate, ml/hr = 396.67

Breakthrough of surfactant occurred at 10,040 s

Step 5

TABLE 18

TYPICAL RECOVERY DATA

Time (from commencement of water flood (seconds)	Sample flask (ml)	Sample Number	Total volume recovered	
			oil (ml)	water/surfactant (ml)
2493	250	1	230.0	20.0
4344	200	2	77.5	126.5
6221	200	3	61.7	150.3
8040	200	4	45.2	161.3
9910	200	5	38.0	167.0
10849	100	6	70.4	31.6
11781	100	7	100.0	0.0
12717	100	8	65.2	37.3
13651	100	9	12.0	90.0
14583	100	10	0.0	101.0

Total oil recovered = 700 ml

Total water + surfactant recovered = 8850 ml

Step 6 **Model recovery calculations:**

(a) **Injected PV**

(i) Water flood:

Average injection rate (water) = 401.94 ml/hr

after 2493 s, total water injected

$= \frac{401.94 \times 2493}{3600}$ = 278.34 ml

Injected PV = $\frac{278.34}{696.35}$ = 0.40

(ii) Surfactant flood:

Average injection rate (surfactant) = 396.67 ml/hr

At time from start of secondary flooding =8040 seconds

Time from start of tertiary flooding =8040-6221

=1819 seconds

Total surfactant solution injected $= \frac{1819 \times 396.67}{3600}$

= 200.43 ml

PV Surfactant injected = $\frac{200.43}{696.35}$ = 0.288

Total injected PV (water + surfactant) at

8040 seconds total injection time = 0.994 + 0.288

= 1.28

(b) **Cumulative produced pore volume (PV):**

At time from start of secondary flooding = 2493 s

Total oil recovered = 230.0 ml

PV oil produced = $\frac{230.0}{696.35}$ = 0.33

Total water produced = 20.0 ml

PV water produced $= \frac{20.0}{696.35} = 0.029$

At time from start of secondary flooding = 4334 s

Additional PV oil produced $= \frac{77.50}{696.35} = 0.11$

Cumulative oil produced up to 4334 s

$= 0.11 + 0.33 = 0.44$ PV

Additional PV water produced

$= \frac{126.5}{696.35} = 0.182$

Cumulative water produced $= 0.029 + 0.182$

$= 0.21$ PV

(c) <u>Cumulative Percentage oil recovery</u>:

Total oil in place = 698.7 ml

After 2493 s injection time, total

oil produced = 230.0 ml

Percentage oil recovery $= \frac{230.0}{698.7} \times 100 = 32.92$

After 4334 s injection time, cumulative

oil produced = 230.0 + 77.5 = 307.50 ml

Cumulative percentage oil recovery

$= \frac{307.50}{698.7} \times 100 = 44.01$

(d) <u>Water - Oil ratio (WOR)</u>:

After 2493 s injection time, oil cut in 250 ml

effluent collected = 230.0 ml

Water cut in ~~efflu~~ent sample = 20.0 ml

WOR = 20/230 = 0.087

Oil cut in effluent collected from 2493 to

4334 s of injection time = 77.5 ml

Water cut in effluent stream = 126.50 ml

WOR (tabulated against 0.69 PV injected at time 4334 s in Table 19)

$$= \frac{126.50}{77.50} = 1.63$$

(e) Breakthrough and Final recoveries:

(i) Water Breakthrough recovery

Total PV injected at water breakthrough

$$= \frac{401.94 \times 2146}{3600 \times 696.35} = 0.344$$

From Fig. 57 on the percentage oil recovery vs. cumulative PV injected plot, at an abscissa value of 0.344, the water breakthrough is read, and its value = 31.0%

(ii) Surfactant breakthrough recovery

PV of surfactant solution injected at breakthrough

$$= \frac{(10040 - 6221) \times 396.67}{3600 \times 696.35}$$

$$= 0.60$$

Cumulative PV injected at surfactant breakthrough = 1.00 + 0.60 = 1.60

Similarly from Fig. 57, at an abscissa value of 1.60, the surfactant breakthrough recovery

= 65.5%

(iii) Secondary flood, 1 PV, 2 PV and 3 PV recoveries

These are read from the percentage oil recovery vs. cumulative injected PV profile of Fig. 57 at the appropriate abscissa values (Table 13).

(iv) Final oil recovery, tertiary oil recovery

Total oil produced at termination of run = 700.0 ml

$$\text{Final oil recovery} = \frac{700}{698.7} \times 100 = 100.18\%$$

Maximum oil recoverable = 100 - secondary

flood recovery = 100 - 53.0 = 47.0%

$$\text{Tertiary oil recovery} = \frac{100.18 - 53.0}{47.0} = 100\%$$

(f) TABLE 19

A TYPICAL DATA TABLE FOR THE PRODUCTION HISTORY PLOTS

Effluent Sample No.	PV injected cumulative	WOR	Cumulative oil	PV produced water/surfactant	% oil recovery
1	0.40	0.087	0.33	0.03	33.92
2	0.69	1.63	0.44	0.21	44.01
3	1.00	2.43	0.53	0.43	52.84
4	1.29	3.57	0.59	0.66	59.31
5	1.58	4.39	0.65	0.90	64.75
6	1.73	0.45	0.75	0.94	74.82
7	1.88	0.00	0.89	0.94	89.14
8	2.03	0.57	0.98	1.00	98.47
9	2.17	7.50	1.00	1.12	100.19
10	2.32	∞	0.00	1.27	100.19

(g) Average WOR at flood termination:

Average WOR at flood termination is the average of the WOR of the last two effluent samples

$$= \frac{\infty + 7.50}{2} = \infty$$

APPENDIX D

A TYPICAL COMPUTER ROUTINE FOR CORRECTING APPARENT TENSION DATA OBTAINED WITH THE DU NOUY TENSIOMETER

1. Calculation of the Correction Factor:

The relationship between the apparent tension (surface or interfacial) and the true or absolute value is given by:

$$S = P \times F \qquad \text{.....} \quad (1)$$

where

S = absolute (true) tension, dynes/cm

P = apparent (measured) tension, dynes/cm

F = correction factor, dimensionless

The correction factor, F, is dependent on the size of ring and the size of wire used in the ring, the apparent tension and the densities of the two phases in contact. These relationships can be expressed by the equation:

$$F = 0.7250 + \sqrt{\frac{0.01452\ P}{C^2\,(D-d)} + 0.04534 - \frac{1.679\ r}{R}} \qquad \text{.....} \quad (2)$$

where

R = radius of ring, cm

r = radius of the wire of the ring, cm

D = density of the lower aqueous phase, g/cm^3

d = density of the upper phase, g/cm^3

C = circumference of the ring, cm

For the ring, serial No. 447, used for most of the tension measurements, the specifications are as follows:-

$C = 6.020$ cm

$R/r = 53.9280802$

Plugging these values, together with the apparent tensions, (P), and the densities, into equation (2), the correction factor, F, for the given value of P is obtained. The absolute tension value corresponding to each measured (apparent) value is then obtained from equation (1).

2. Nomenclature for the Computer Program:

ST	Apparent surface tension, dynes/cm
TI	Apparent interfacial tension, dynes/cm
DS	Density of surfactant solution, g/cm^3
DELDST	= ((D-d), see equation (2)), difference of the density of air from that of the surfacant solution, g/cm^3
DOIL	Density of oil phase, g/cm^3
DELDIT	= (DS-DOIL) Difference of the density of oil from that of the surfactant solution, g/cm^3
XST	Term under the square root sign in equation (2), when apparent surface tesion value is involved
XIT	Term under the square root sign in equation (2), when apparent interfacial tension is involved.
FST	Correction factor for apparent surface tension
FTI	Correction factor for apparent interfacial tension
TST	True (absolute) surface tension, dynes/cm
TIT	True (absolute) interfacial tension, dynes/cm

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C     DEVELOPMENT AND EVALUATION OF LIGNOSULFONATE-BASED
C      SURFACTANT SYSTEMS FOR E.C.R. OPERATIONS
C      PART A,LIGNOSULFONATES ALONE OR WITH SIMPLE PH REAGENTS
C      SURFACE AND INTER FACIAL TENSION DATA
C      CORRECTION OF APPARENT VALUES OBTAINED WITH THE FISHER
C      DU-NOUY AUTO-TENSIOMETER
C      ALL DATA WERE OBTAINED AT TEMPS.OF 25+-0.1DEG-C
C      10 MINS EQUILIBRATION TIME WERE ALLOWED FOR SURFACE TENSION
C      WHILE 15 TO 40 MINS WERE ALLOWED FOR INTER-FACIAL TENSION
C     MEASUREMENTS;TENSION DATA ARE IN DYNES/CM;ALL DENSITIES
C      WERE MEASURED WITH THE SP. GRAVITY BOTTLE AFTER 10 MINS IN
C      25 DEG-CBATH.VALUES ARE IN GM/CC
       DIMENSION ST(30),TI(30),DELDST(30),DELDIT(30),XST(30)
       DIMENSION XTI(30),FST(30),FTI(30),TST(30),TIT(30),DS(30)
        READ 2,N
   2   FORMAT(I2)
        READ 3,(ST(I),I=1,N)
   3   FORMAT(14F5.2)
       READ 3,(TI(I),I=1,N)
       READ  4,(DS(I),I=1,N)
   4   FORMAT(10F6.4)
       READ 5,DOIL,C,RR
   5   FORMAT(2F6.4,F10.7)
C      CALCULATION OF CORR.FACTORS FST-FORSURFACE TENSIONS,FTIFOR
C       INTERFACIAL TENSIONS,AIR DENSITY AT 25DEG-C IS0.0012 GM/CC
       DO  6 I=1,N
        DELDST(I)=DS(I)-0.0012
       DELDIT(I)=DS(I)-DOIL
       XST(I)=(0.01452*ST(I)/(C**2*DELDST(I)))+0.04534-(1.679/RR)
       XTI(I)=(0.01452*TI(I)/(C**2*DELDIT(I)))+0.04534-(1.679/RR)
       FST(I)=0.7250+SQRT(XST(I))
       FTI(I)=0.7250+ SQRT(XTI(I))
       TST(I)=FST(I)*ST(I)
       TIT(I)=FTI(I)*TI(I)
   6   CONTINUE
       PRINT 7
   7   FORMAT(1H1,20X,'SYSTEM-IDENTIFICATION',///)
       PRINT 8
   8   FORMAT(/,12X,'OIL IS EMR CODE NO. 70-69,AN ALBERTAN
      1LLOYD MINSTER CRUDE',/)
       PRINT 24,DOIL
  24   FORMAT(/,20X,'DENSITY OF CRUDE OIL IS ',F6.4,'GM/CC',/)
       PRINT 9
   9   FORMAT(/,12X,'NUMBER',7X,'SYSTEM-NAME',/)
       PRINT 10
  10   FORMAT(/,14X,'1',6X,'LAB-DISTILLED WATER',/)
       PRINT  11
  11   FORMAT(/,14X,'2',6X,'1%-MARASP-N-22;PH 7.30',/)
       PRINT 12
  12   FORMAT(/,14X,'3',6X,'3%-MARASP-N-22;PH 7.60',/)
       PRINT 13
  13   FORMAT(/,14X,'4',6X,'6%-MARASP-N-22;PH 7.70',/)
       PRINT 14
  14   FORMAT(/,14X,'5',6X,'10%-MARASP-N-22;PH 7.75',/)
       PRINT 15
  15   FORMAT(/,14X,'6',6X,'1%-MARASP-N-22;PH 3.90',/)
       PRINT 16
  16   FORMAT(/,14X,'7',6X,'3%-MARASP-N-22;PH 3.90',/)
```

```
      PRINT 17
 17   FORMAT(/,14X,'8',6X,'6%-MARASP-N-22;PH 4.1C',/)
      PRINT 18
 18   FORMAT(/,14X,'9',6X,'10%-MARASP-N-22;PH 4.25',/)
      PRINT 19
 19   FORMAT(/,14X,'10',6X,'1%-MARASP-C-21;PH-NATURAL',/)
      PRINT 20
 20   FORMAT(/,14X,'11',6X,'3%-MARASP-C-21;PH-NATURAL',/)
      PRINT 21
 21   FORMAT(/,14X,'12',6X,'6%-MARASP-C-21;PH-NATURAL',/)
      PRINT  22
 22   FORMAT(/,14X,'13',6X,'10%-MARASP-C-21;PH-NATURAL',/)
       PRINT 25
 25   FORMAT(1H1,10X,'NUMBER',4X,'APP.SURF-TENSICN',4X,
     1'APP.INTER-FAC.-TENSICN',4X,'DENSITY',/)
      PRINT  26,(I,ST(I),TI(I),DS(I),I=1,N)
 26   FORMAT(/,13X,I2,10X,F5.2,15X,F5.2,16X,F6.4,/)
      PRINT 27
 27   FORMAT(1H1,10X,'NC.',3X,'CCR-FACTOR(ST)',3X,'CCR-FACTCR(IT)',
     13X,'TRUE  S.TENS.',3X,'TRUE I-TENSS.',//)
      PRINT 28,(I,FST(I),FTI(I),TST(I),TIT(I),I=1,N)
 28   FORMAT(/,10X,I2,5X,F6.4,13X,F6.4,12X,F5.2,10X,F5.2,/)
      STOP
      END
```

SYSTEM-IDENTIFICATION

OIL IS EMR CODE NO. 70-69,AN ALBERTAN LLOYDMINSTER CRUDE

DENSITY OF CRUDE OIL IS 0.9176GM/CC

NUMBER	SYSTEM-NAME
1	LAB-DISTILLED WATER
2	1%-MARASP-N-22;PH 7.30
3	3%-MARASP-N-22;PH 7.60
4	6%-MARASP-N-22;PH 7.70
5	10%-MARASP-N-22;PH 7.75
6	1%-MARASP-N-22;PH 3.90
7	3%-MARASP-N-22;PH 3.90
8	6%-MARASP-N-22;PH 4.10
9	10%-MARASP-N-22;PH 4.25
10	1%-MARASP-C-21;PH-NATURAL
11	3%-MARASP-C-21;PH-NATURAL
12	6%-MARASP-C-21;PH-NATURAL
13	10%-MARASP-C-21;PH-NATURAL

NUMBER	APP.SURF-TENSION	APP.INTER-FAC.-TENSION	DENSITY
1	72.10	14.30	0.9971
2	48.65	9.50	1.0015
3	45.85	8.50	1.0105
4	45.00	7.25	1.0237
5	44.90	7.25	1.0420
6	45.50	12.30	1.0015
7	41.50	11.45	1.0105
8	42.70	11.45	1.0237
9	41.25	10.60	1.0420
10	46.45	9.65	1.0014
11	45.70	9.10	1.0099
12	44.35	9.00	1.0228
13	44.90	8.65	1.0397

NO.	COR-FACTOR(ST)	COR-FACTOR(IT)	TRUE S.TENS.	TRUE I-TENS .
1	0.9329	1.0187	67.26	14.57
2	0.9086	0.9691	44.20	9.21
3	0.9050	0.9486	41.50	7.87
4	0.9034	0.9289	40.65	6.73
5	0.9025	0.9188	40.52	6.66
6	0.9051	0.9951	41.18	12.24
7	0.9002	0.9772	37.36	11.19
8	0.9009	0.9647	38.47	11.05
9	0.8985	0.9449	37.06	10.02
10	0.9061	0.9706	42.09	9.37
11	0.9049	0.9567	41.35	8.71
12	0.9028	0.9452	40.04	8.51
13	0.9026	0.9314	40.53	8.06