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INTERFACIAL PROPERTIES OF HEAVY CRUDES IN THE PRESENCE OF CHEMICALLY TREATED WATERS

by

EMMANUEL ONU EGBOGAH (C)

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH
IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE
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FACULTY OF GRADUATE STUDIES AND RESEARCH

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research, for acceptance, a thesis entitled "INTERFACIAL PROPERTIES OF HEAVY CRUDES IN THE PRESENCE OF CHEMICALLY TREATED WATERS" submitted by EMMANUEL ONU EGBOGAH in partial fulfilment of the requirements for the degree of Master of Science in Petroleum Engineering.

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ABSTRACT

Interfacial properties of heavy crudes in the presence of chemically treated waters were investigated. The physical characteristics of crude-oil-chemical-solution interfacial films may be described on a quantitative basis in terms of interfacial tension. The investigation was carried out on several crude-oil-chemical-solution systems under laboratory conditions.

Results of the study show that certain nonionic surfactant solutions efficiently reduce interfacial tension to zero at very low surfactant concentrations.

As the interfacial properties of crude oils are a function of the crude oil composition, and particularly of the surface-active constituents of the crudes, a new method--a nitrogen foaming technique--was used to precipitate some surface active agents contained in the heavy (viscous) crude oils. The dependence of interfacial properties on the crude oil content of the surface active constituents was studied.

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LIST OF SYMBOLS

A	-	Area of Surface
API	-	American Petroleum Institute
ASTM	-	American Society for Testing Materials
cm	-	centimeter
cp	-	centipoise
F	-	Free energy
°F	-	Fahrenheit degrees
gm	-	gram
k	-	constant of Eotvos
ml	-	milliliter
M	-	molecular weight
n	-	number of moles of a component
V	-	volume
P_c	-	capillary pressure
P_o	-	pressure in oil phase
P_w	-	pressure in water phase
r	-	radius
T	-	temperature, °F
X	-	degree of association of liquid
μ	-	surface chemical potential
ρ	-	density
θ	-	contact angle
σ	-	surface tension
γ	-	interfacial tension
$W_{S/A}$	-	work of adhesion

INTRODUCTION

There is a general consensus of opinion that the presence of interfacial films between crude oils and water influences the efficiency of oil recovery in water drive and water flood operations. Several investigators have shown that significant reductions in interfacial tension increases recovery. The reduction in interfacial tension has been attributed by these authors to the presence of surface active agents in both the crude oil phase and the water phase used in their study.

The addition of very small quantities of surface active agents may change the course of physicochemical processes and the conditions of interaction between phases. The purpose of the present work, therefore, is to contribute data that would help to determine the ability of different chemicals to reduce interfacial tension. Such data on the interfacial properties of crudes in the presence of chemically treated waters (in the absence of rock chemistry) are presented, and it is hoped that these will provide a background to the understanding of the mechanism and magnitude of the interfacial tension reduction during displacement tests.

A new nitrogen foaming technique which reduces the concentration of surface active agents in the heavy (viscous) crude oils has been devised.

LITERATURE REVIEW

It is probable that many types of surface-active materials are indigenous to crude oils (1). The first evidence that such components must be present in crude oil was the ease with which many crudes form emulsions in the presence of water. In an early study, Lottermoser and Calantar (2) reported that asphaltic materials lead to the formation of stable water-in-oil emulsions. Morrell and Egloff (3) and Uren (4) also name the asphaltic components as the emulsifying agents responsible for the formation of water-in-oil emulsions.

Bartell and Niederhauser (5) were probably the first to attempt to isolate the surface active materials from a number of crude oils. They were successful in isolating such materials from one California crude oil, but could not reproduce their results when they studied a group of other oils in the absence of air. Therefore, they concluded that the isolated substances were formed by an oxidation process during sampling and are not present in the normal fluids of an oil reservoir. Others (6,7,8,9,10,11,12) have demonstrated, however, that surface active materials do indeed exist in petroleum, especially in the more asphaltic crude oils.

Ultracentrifuge studies have shown that the asphaltic components can exist as colloidal particles in petroleum as

well as in a variety of other solvents (13,14,15,16). Such particles are intimately involved with the many other petroleum constituents, and by the very nature of colloidal systems, the physical and chemical properties of crude oils are influenced very significantly (17). The more complex and polar compounds contained in the colloidal systems tend to concentrate at interfaces, thereby affecting the wettability of the solid phase as well as the interfacial phenomena between the oil and water phases. Because of the very large internal surface area of sedimentary rocks, interfacial forces are magnified in their effect and may therefore play an important part in the multiphase flow of oil and water through porous media.

Considerable work has been devoted to isolating surface active components from petroleum. In a series of papers from the U.S. Bureau of Mines, Denekas et al. (8); Dodd et al. (9); Dunning (11), and Dunning et al. (10,12,18) showed that surface active materials could be isolated from crude oils of Oklahoma and California. They found that the surface-active constituents had a high metal content, and they also established that vanadium and nickel porphyrin complexes were the major contributors to the interfacial activity and film-forming tendencies exhibited by their samples. Corwin (19) has also shown that the two major metals bound by the porphyrins in petroleum are nickel and vanadium. He also notes that the combination of these metals with porphyrins renders them oil-soluble while the presence of the metals

in the porphyrins gives these organic compounds extra stability to permit their survival through geologic time. Other researchers (20,21,22,23,83,84) investigating the constitution of petroleum have conclusively shown the presence of metalloporphyric compounds, especially those of nickel, iron and vanadium.

These polar type trace compounds in petroleum seem to be important in the capillary and surface phenomena in petroleum production (24,25). In studying the displacement of crude oil by water in saturated cores, Reisberg and Dorscher (26) have reported that oil recovery was dependent on overcoming the rigid interfacial films that developed at oil-water interfaces and caused the oil to adhere to a water-wetted, hydrophilic surface. The interfacially active materials were found to be asphaltic. Dodd (27) has been able to demonstrate the high viscosity and non-Newtonian behavior of a film formed at a crude oil-water interface.

Greenlee (28), however, has reported that the content of the asphaltic components in an oil does not correlate with the observed surface activity. No simple group of compounds, including the porphyrins, showed sufficient surface activity that it might be said to control the observed phenomena. Greenlee proposed that the greatest film forming power is present when the asphaltenes are in a state of incipient flocculation. Water droplets induce the flocculation and are thus encased in a film of precipitated asphaltenes and resins. Greenlee noted that asphaltenes which had been pre-

cipitated from an oil and then added back to the oil do not show this surface activity; incipient precipitation that can be induced by water droplets is required. Van der Waarden (29) has demonstrated the stability of water-in-oil emulsions and the film forming role played by asphaltenes that are near a condition of incipient flocculation.

The effect of interfacial tension on oil recovery has been studied by many workers. Some investigators (30,31) have found that oil recovery by water flooding was increased if interfacial tension were increased in the water-wet systems and decreased in the oil-wet systems. Mungan (32,33) observed that oil recovery by water flooding could be increased in both oil-wet and water-wet systems by reducing interfacial tension; however, the effect was not as pronounced in water-wet systems. Warren and Calhoun (34) noted that break-through and ultimate recovery increased as interfacial tension decreased in oil-wet cores. Wagner and Leach (35) found that water flooding at very low interfacial tensions resulted in large increases in oil recovery. A few authors (36,37) found that in the face of adsorption, lowering of interfacial tension had a tendency toward reducing the recovery of oil.

The use of surface-active agents to increase oil recovery in water flooding has been considered by several investigators (38,39,40,41,42,43,44,45). Bartell and Miller (46) reported that neither surface tension values of the liquid nor the interfacial tension values of the liquid-liquid system

were dominant factors in the displacement of oil. Effective displacing agents appeared to be those that altered the aqueous solution silica interface either through a high degree of adsorption or through chemical reaction of the interface.

Many chemicals have been tested to determine their ability to alter wettability or reduce interfacial tension. The use of sodium hydroxide has been reported extensively in the literature (26,35,41,46,47,48,49,50,51,52,53,54,55). The use of surfactants is becoming increasingly important (43,44,45,56,57,58).

The presence of an electrolyte, such as sodium chloride, in the aqueous phase, can greatly influence interfacial properties (27,59,60,61) between oil and the aqueous phase. At a given concentration of sodium hydroxide, the addition of sodium chloride to the aqueous phase lowered the interfacial tension (60). Burcik (59) pointed out that surface active compounds in solution, such as sodium hydroxide, are charged. As they diffuse into an interface, and electrical charge is built up, this tends to repel incoming ions. The addition of electrolyte reduces the potential of the interface and permits more unhindered diffusion at the interface, thus lowering interfacial tension.

INTERFACIAL PHENOMENA

Conditions at the Phase Boundary:

For any system of two phases, there is a region of separation between the two phases. The boundary between two homogeneous phases is therefore not a simple geometrical surface upon either side of which extend the homogeneous phases, but rather a lamina or film of a characteristic thickness. The material in this "surface phase" shows properties differing from those of the materials in the contiguous homogeneous phases (62). It is with the properties of matter in this surface layer that this investigation is concerned. Just as in the bulk phase, the matter of the "surface phase" may exist in the solid, liquid and gaseous states; that is, there are various types of interfacial phases. The present investigation is especially conerned with the boundary between two immiscible liquids.

It is commonly observed that a liquid behaves as if it were surrounded by a contracting elastic skin. Drops of liquid, uninfluenced by external forces such as gravity, adopt a truly spherical shape. Young (63) was the first to attempt an explanation of this "surface tension" in terms of the attractive and repulsive forces between the molecules of the liquid. The cohesion between the molecules of a liquid

must surpass their tendency to separate under the influence of thermal motion. This net attraction between neighbouring atoms is fulfilled most completely in the interior of the phase, while those atoms or molecules at the surface are attracted less completely than they would have been in the bulk system. Consequently, the energy of the latter is greater, and, since the free energy of a system tends to a minimum, the surface of such a pure phase will always tend to contract fairly spontaneously.

The total free energy F of a system comprising two bulk phases and an interface is (64):

$$F = F^{\alpha} + F^{\beta} + F^{s} \qquad (2.1)$$

where superscripts α and β refer to the bulk phases, and s to the surface phase. The free energies of the bulk phases are calculated on the assumption that they both remain homogeneous right up to a hypothetical geometric surface.

If a small, reversible change occurs in the system, the free energy change dF is expressed by

$$dF = dF^{\alpha} + dF^{\beta} + dF^{s} \qquad (2.2)$$

For the homogeneous bulk phases, the free energy changes are given by

$$dF^{\alpha} = -S^{\alpha}dT + V^{\alpha}dP^{\alpha} + \mu_1^{\alpha}dn_1^{\alpha} + \mu_2^{\alpha}dn_2^{\alpha} + \ldots \qquad (2.3)$$

$$dF' = -S' dT + V' dP' + \mu_1' dn_1' + \mu_2' dn_2' + \ldots \qquad (2.4)$$

where S, T, V and P refer to entropy, temperature, volume and pressure, respectively. The subscripts refer to components 1, 2,... and n refers to the number of moles of a component whose chemical potential is μ.

The surface free-energy change must include a term for the work required to increase the area of the surface by an infinitesimal amount dA, at constant temperature, pressure and composition. The work of surface expansion is done against a tension σ, referred to as the surface tension. This reversible work is equal to σdA. Since the surface contribution to the volume is negligible, the quantity VdP can be omitted. Then

$$dF^S = -S^S dT + \sigma dA + \mu_1^S dn_1^S + \mu_2^S dn_2^2 + \ldots \qquad (2.5)$$

where μ_1^S, μ_2^S,... are the surface chemical potentials of the various components of the system.

The total free energy change for the system, is given by

$$dF = -SdT + V^\alpha dP^\alpha + V^\beta dP^\beta + \sigma dA + \sum \mu_i^\alpha dn_i^\alpha + \sum \mu_i^\beta dn_i^\beta + \sum \mu_i^S dn_i^S \qquad (2.6)$$

where $S = S^\alpha + S^\beta + S^S$ is the total entropy of the system.

At constant temperature, pressure and composition,

$$dF = \sigma dA \tag{2.7}$$

or

$$\sigma = \left(\frac{\partial F}{\partial A}\right)_{T,P,n} = F_s \tag{2.8}$$

The surface tension σ has the units of dynes/cm. It is a measure of the work required to increase the surface by a unit area, at constant temperature, pressure, and composition. The term F_s is the surface free energy per unit area, expressed in ergs/cm^2. Since it is numerically equal to the surface tension for a pure liquid, σ is commonly used to express either surface tension or surface free energy per unit area.

The relation given by equation (2.8) applies to Newtonian fluids only (64). It has not been used specifically to interpret the results of the present study, but has, however, been included to complete the background theory on surface free energy.

If water is placed in contact with oil the interface between the two liquids has a tendency to contract. This is is represented as γ_i, and is expressed in dynes/cm as is σ. Low values of γ_i are characteristic of oils containing polar groups where the molecules of the hydrocarbon phase must concentrate at the oil-water interface, and where the repulsion between the packed and oriented molecules offsets some-

what the usual contractile tendency of an interface. Interfacial packing occurs because the hydroxyl "heads" of the hydrocarbon molecules can escape from the oil into the water, while the chains remain in the oil, this process resulting in a state of low standard free energy. The introduction of a third component into the system may help to reduce the interfacial tension. The works of Davies, Rideal and others (62) have shown that the greater the miscibility of oil and water, in the presence of the third component, the lower the interfacial tension. Thus, surface-active materials added in increasing amounts to a mixture of water and oil, reduces the interfacial tension progressively to zero. The system then becomes miscible and forms a single phase. With less of the third component than will produce complete miscibility of the phases, spontaneous emulsification may often occur by the "diffusion and stranding" mechanism, even though γ is still quite high. Although complete miscibility of the phases necessarily results in zero interfacial tension, the converse is not true: a monolayer of organic cations concentrated at the mercury-water interface by an electrical field will reduce γ through zero (with consequent spontaneous emulsification) without inducing any apparent miscibility of the phases.

Relations between Surface Tension and Interfacial Tension:

Short-range van der Waals forces of attraction exist between molecules, and are responsible for the existence of the

liquid state (65). The phenomena of surface and interfacial tension are readily explained in terms of these forces. The molecules which are located within the bulk of a liquid are, on average, subjected to equal forces of attraction in all directions, whereas those located, for example, at a liquid-air interface experience unbalanced attractive forces resulting in a net inward pull. As many molecules as possible will leave the liquid surface for the interior of the liquid; the surface will, therefore, tend to contract spontaneously. For this reason droplets of liquid and bubbles of gas tend to attain a spherical shape.

The surface tension σ of a liquid is defined as the force in dynes acting at right-angles to any line of 1 cm length in the liquid surface, and has the units dyne/cm. The surface free energy of a liquid is defined as the work in ergs required to increase the area of the liquid surface, by 1 cm^2, and has the dimensionally equivalent units ergs/cm^2. Surface tension and surface free energy are numerically equal provided that the viscosity of the liquid is not too high.

The same considerations apply to the interface between two immiscible liquids. Again there is an imbalance of intermolecular forces but of a less magnitude. Interfacial tensions usually lie between the individual surface tensions of the two liquids in question.

Treatment of Gibbs:

Gibbs considered the interfacial tension of mercury in equilibrium with water, in relation to the surface tensions of the separate components of the system in equilibrium with each other. He deduced (66) that if $\gamma_{Hg/W}$ represents the interfacial tension between mercury and water, then it is given by

$$\gamma_{Hg/W} = \gamma_{Hg(H_2O\ sat.)/A} - \gamma_{W(Hg\ sat.)/A} \qquad (2.9)$$

and subscripts sat. and A in the terms denote that the surface tensions of the mutually saturated liquids are measured with respect to air. His reasoning in deriving this equation was as follows. On a clean mercury surface (of high surface tension) water will be adsorbed (lowering the surface tension); this film of water corresponds at equilibrium to adsorption from saturated water vapour, and may reach such a thickness that its interior behaves as if it were bulk liquid water. If this is true, the total surface tension (or energy) should thus be the sum of the surface tension of water and the interfacial tension between mercury and water; that is,

$$\gamma_{Hg(H_2O\ sat.)/A} = \gamma_{W(Hg\ sat.)/A} + \gamma_{Hg/W} \qquad (2.9a)$$

Relation (2.9a) is identical with (2.9).

Antonoff's Relationship:

Antonoff's Relationship states that the interfacial tension of two mutually saturated liquids is equal to the difference between their surface tensions, the latter being measured when each liquid has become saturated with the other (67,68). It is thus a generalization of Gibbs' treatment of the mercury-water interface. For water and organic liquids the mutual saturation often occurs slowly; as long as 10 days is sometimes required to reach true equilibrium.

If B(W) and W(B) refer to two typical mutually saturated phases (e.g., benzene and water each saturated with the other), and if the surface tension against air of W is higher than that of B, Antonoff's relation may be written in general terms as:

$$\gamma_{B/W} = \gamma_{W(B)/A} - \gamma_{B(W)/A} \qquad (2.10)$$

where $\gamma_{B/W}$ is the interfacial tension when equilibrium has been attained.

Dupre (69) defined the work of cohesion $W_{B/W}$ as

$$W_{B/W} = \gamma_{B(W)/A} + \gamma_{W(B)/A} - \gamma_{B/W} \qquad (2.11)$$

Combining Antonoff's relation with Dupre's equation gives

$$W_{B/W} = 2\gamma_{B(W)/A} \qquad (2.12)$$

However, it is necessary to point out that Antonoff's relation does not hold quite generally, especially for very polar oils and initially non-spreading oils.

Capillary Pressure

A general expression for capillary pressure as a function of interfacial tension and curvature of the interface is due to Plateau (70) and is given by the following equation:

$$P_c = \gamma\left(\frac{1}{R_1} + \frac{1}{R_2}\right) \qquad (2.13)$$

where R_1 and R_2 are the principal radii of curvature of the interface and γ is the interfacial tension between the two fluids.

The capillary pressure in terms of surface forces across an oil-water interface in a capillary tube is defined by the following equation:

$$P_c = \frac{2\gamma_{WO}\cos\theta}{r} = P_o - P_w \qquad (2.14)$$

where P_c = capillary pressure (dynes/cm^2)

P_o = pressure in the oil phase adjacent to the interface (dynes/cm^2)

P_w = pressure in the water phase adjacent to the interface (dynes/cm^2)

γ_{WO} = interfacial tension between oil and water (dynes/cm^2)

θ = contact angle measured through the water phase

r = radius of the capillary (cm).

From Equation (2.13) it is apparent that capillary pressure varies directly with interfacial tension. Capillary forces can therefore be reduced or eliminated by the same chemicals that will reduce the interfacial tension between crude oil and water.

On a microscopic scale, the entry of water into an oil-filled pore in a water-wet porous medium is assisted by capillary pressure. Consequently, for efficient displacement of oil, in addition to a favourable wettability and geometry, the interfacial tension should be high. The entry of water into an oil-filled pore in an oil-wet porous medium, on the other hand, is resisted by capillary pressure. Therefore, for efficient displacement of oil, the interfacial tension should be low; this will minimize the energy required to displace the oil.

Contact Angles:

When a drop of liquid is placed on a flat solid surface it may spread completely over the surface or, more likely, it may remain as a drop having a definite angle of contact with the solid surface (Fig. 1 on the following page).

Assuming that the various surface forces can be represented by surface tensions acting in the direction of the surfaces, then equating the horizontal components of these tensions, gives:

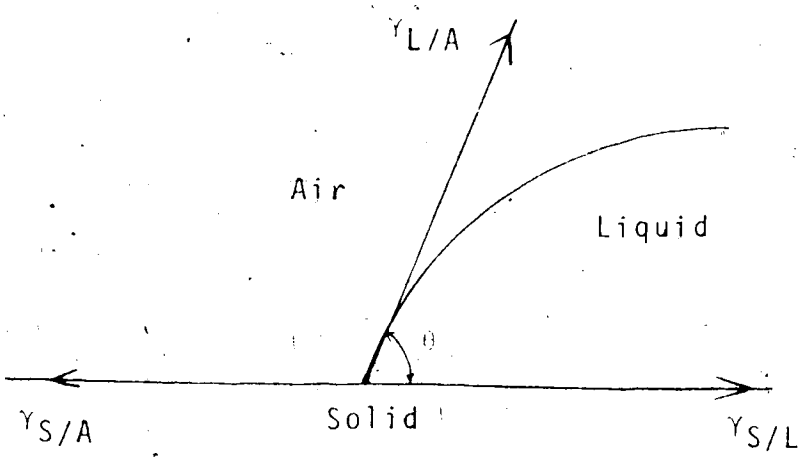

Fig. 1. Contact Angle

$$\gamma_{S/A} = \gamma_{S/L} + \gamma_{L/A} \cos \theta \qquad (2.15)$$

Combining this expression with the appropriate form of the Dupre equation ($W_{S/L} = \gamma_{S/A} + \gamma_{L/A} - \gamma_{S/L}$) will give Young's equation:

$$W_{S/A} = \gamma_{L/A}(1 + \cos \theta) \qquad (2.16)$$

Therefore, zero contact angle results when the forces of attraction between liquid and solid are equal to, or greater than those between liquid and liquid, and a finite contact angle results when the liquid adheres to the solid less than it coheres to itself.

The solid is completely wetted by the liquid if the contact angle is zero and only partially wetted if the con-

tact angle is finite. Complete non-wetting implies a contact angle of 180°, which is an unrealistic situation since it requires that either $W_{S/L} = 0$ or $\gamma_{L/A} = \infty$. Some writers correlate $\theta < 90°$ with wetting and $\theta > 90°$ with non-wetting in order to be in approximate keeping with visual appearances. This correlation is not entirely satisfactory.

Surface (Interfacial) Tension and Adsorption:

The surface tension of a pure liquid is constant at constant temperature, but it may be changed by the addition of some other substance to the liquid (71). Most dissolved non-electrolytes lower the surface tension of water, some do not change it appreciably, and a few raise it slightly. In general, the surface tension of a solution lies between the surface tensions of the two constituents. Since the surface tension of water is higher than that of most other liquids, the addition of such liquids to water gives a solution with a lower surface tension.

The addition of inorganic electrolytes to water invariably results in an increase in surface tension (72). Surface-active agents lower the surface tension of water considerably, even in very dilute solutions. The effect of ions on increasing the surface tension of water is in the same order as the lyoptropic or Hofmeister series: Li > Na > K and F > Cl > Br > I.

The Phenomenon of "Surface Ageing":

When a fresh surface of a solution is produced or when an existing surface is extended, time is required for the readjustment of concentrations between the body of the liquid and the surface layer. Accordingly, different values of the surface tension would be expected, depending on whether rapid measurements are made on a fresh surface (dynamic methods) or on an old surface after equilibrium is established (static methods) (71). The rate of change of surface tension, "surface ageing", depends upon a number of factors. These include the rate of diffusion of the solute to or from the surface, agitation, and other external perturbations (72).

Mention may be made briefly of another type of surface-ageing phenomenon, in this case from an oil phase to an oil-water interface. Many oil-soluble amphipathic compounds (i.e., those containing polar and non-polar portions) show the effect, an excellent example being, say 1 per cent palmitic acid in benzene or hexane. Such a solution in contact with water takes several hours to attain equilibrium, instead of a few seconds, at most, expected from diffusion theory. In such cases the rate appears to be determined by the concentration of monometric long-chain molecules (62,82).

Effect of Temperature on Surface and Interfacial Tensions:

The surface tension of most liquids as well as the interfacial tension between them decreases with increasing temperature in a nearly linear fashion (74,75,76,108) and becomes

very small in the region of the critical temperature when the intermolecular cohesive forces approach zero. A number of empirical equations which relate surface tension and temperature have been suggested, one of the most satisfactory being that of Ramsay and Shields (73):

$$\sigma\left(\frac{MX}{\rho}\right)^{2/3} = k(T_c - T - 6) \qquad (2.17)$$

where M = molecular weight of the liquid

ρ = density of the liquid

X = degree of association of liquid

T_c = critical temperature of liquid.

The quantity $\sigma\left(\frac{MX}{\rho}\right)^{2/3}$ is called the molecular free surface energy, and the constant k which has a value of about 2.1 ergs/degree for hydrocarbon liquids is called the "constant of Eotvos".

Adsorption of Liquid by Liquid; Spreading of Liquid on Liquid; Molecular Orientation:

If a drop of organic liquid (e.g., oil) is placed on the surface of water, the edge of the drop at the air-water interface is subjected to three pulls (77) as indicated in Fig. 2A. These are: (1) γ_3, the surface tension of water, (2) γ_2, the surface tension of organic liquid, and (3) γ_{23}, the interfacial tension of water-organic liquid. The effect of (1) is to pull out the edge and flatten out the drop; the effect of (2) and (3) is to pull in the edge and make the

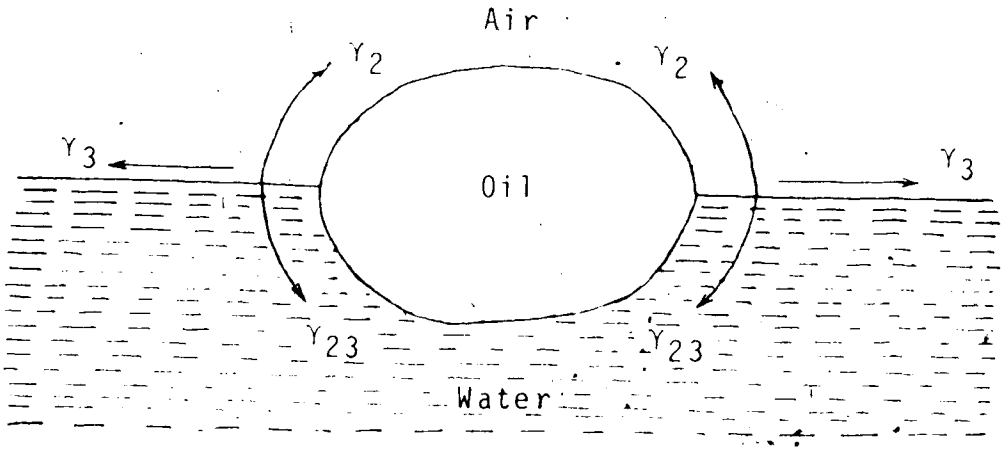

Fig. 2A. Drop of Oil on Water

drop more nearly spherical. Hence if $\gamma_3 \geq \gamma_2 + \gamma_{23}$, the organic liquid will tend to spread over the surface of the water; whereas, if $\gamma_3 < \gamma_2 + \gamma_{23}$, the organic liquid will tend to draw up into a globule.

Although the above formulation is correct, it is so general that it is limited in its usefulness. The theories of spreading based on the facts of molecular orientation at interfaces and on the work of adhesion and cohesion of liquids are more specific and generally helpful in explaining the adsorption phenomena.

Molecular Orientation and the Spreading Process:

The systematic study of oil films on the surface of water was made possible by Pockels (78) who showed that a film on water could be removed completely, or concentrated at any desired portion of the surface, by raking the surface

with a suitable paper or metal strip. Using barriers working on the surface of a trough filled to the brim with water, it was possible to vary the surface available for a given amount of oil. It was observed that there was no decrease in surface tension when the available area exceeded a certain value, but a rapid drop in surface tension set in when the area was decreased below this critical value. This observation was confirmed by Rayleigh (79), who suggested that the first drop in surface tension marked the point where the molecules were crowded as closely as possible to give a film one molecule thick. Hardy (80), has postulated that certain molecules are oriented in the films. These studies enabled Langmuir (81) and Harkins (82) to develop comprehensive theories on the spreading of polar compounds.

Po[redacted]ds and Spreading:

[redacted]s may be classified as: (1) symmetrical (e.g., pent[redacted]$_3CH_2CH_2CH_2CH_3$), in which the two ends of the molec[redacted]are alike; and (2) unsymmetrical (e.g., oleic acid, $C_{17}H_{3}$[redacted]H), in which the two ends of the molecule are dissimil[redacted] The -COOH portion of an organic acid is called a polar [redacted]roup or radical, to distinguish it from the hydrocarbon portion of the molecule. The term polar group is applied to such radicals as -OH, -COOH, -CHO, -CN, -$CONH_2$, -NH_2, -$NHCN_3$, -SH, -NCS, -COR, -COOM, - COOR, -NO_2, -CH, =CH_2, -C=CH, and to other groups containing oxygen, nitrogen, sulphur, the halogens, and double or triple bonds. Compounds

containing such groups are termed polar compounds.

Orientation of Polar Compounds in Films:

When a drop of stearic acid is placed on water, it spreads over the surface to give a film one molecule deep. Since the carboxyl groups of the acid dissolve in water, the molecules of acid orient themselves with the carboxyl groups in the water and the hydrocarbon tails packed in side by side vertically above the carboxyl layer.

Stearic acid is practically insoluble in water because the affinity of the long hydrocarbon chains for water is less than their affinity for each other. If such long hydrocarbon chains happen to get inside the water, they effect a separation of the water molecules; but, since the attraction of water molecules for each other is higher than for the hydrocarbon chains, when the water molecules get together by kinetic motion, they tend to stay together and thus to force out the hydrocarbon chains. Such long chains are carried into aqueous solution only when they are combined with very powerful polar groups.

The principle governing the solubility of one liquid in another is that like attracts like. In accord with this, highly polar liquids are in general mutually soluble, and slightly polar liquids, such as hexane and ottane, are soluble in other slightly polar liquids but are insoluble in highly polar liquids. Hydrocarbons are generally rendered soluble in water by the introduction of polar groups provided that

the hydrocarbon chains are short, but the solubility decreases with increasing length of the hydrocarbon chains. The solution of polar liquids in water lowers the surface (and interfacial) tension, and the concentration of the molecules is higher in the surface film than in the body of the solution.

COMPOSITION AND PROPERTIES OF OILFIELD WATERS

Most oil-field water analyses are given in the ionic form (85,86,87). The "Palmer System", whose interpretation is based on the ionic statement (88) groups together radicals that are either chemically similar or geologically associated. Thus, the common metallic bases sodium (Na^+) and potassium (K^+), and the alkaline earths calcium (Ca^{++}) and magnesium (Mg^{++}), are grouped as alkalis, and are all positive radicals. The acids or negative radicals consist of two groups-- the strong acids, sulphates ($SO_4^=$), and chlorides (Cl^-) and the weak acids, carbonates ($CO_3^=$) and bicarbonates (HCO_3^-).

The character of any brine may be described in terms of its reaction value, given below as:

$$\text{Reaction Value} = \text{Amount by weight (mg/liter)} \times \text{reaction coefficient*}$$

$$= \text{Amount by weight (mg/liter)} \times \frac{\text{valence}}{\text{atomic weight}}$$

*The reaction coefficients for the ions usually determined in water analysis are:

Sodium	(Na^+)	0.0434	Sulphate	($SO_4^=$)	0.0208
Potassium	(K^+)	0.0256	Chloride	(Cl^-)	0.0282
Calcium	(Ca^{++})	0.0499	Nitrate	(NO_3^-)	0.1061
Magnesium	(Mg^{++})	0.8210	Carbonate	($CO_3^=$)	0.0333
Hydrogen	(H^+)	0.9920	Bicarbonate	(HCO_3^-)	0.0164

Salinity and alkalinity are the most important properties of oil-field waters. Salinity is the combination of strong acids ($SO_4^=$, NO_3^-, Cl^-) with bases Na^+, K^+, Ca^{++}, Ba^{++}, Mg^{++}). Alkalinity is the combination of weak acids ($CO_3^=$, HCO_3^-, S_2) with bases.

Russian authors (89) have published extensive data on the chemical composition of the waters of oil formations, or more precisely, the salts dissolved therein. Based on their work, oil-field waters can be said to be of two types: the alkaline sodium bicarbonate type and the hard calcium chloride type. The latter includes the magnesium chloride variety. The two types differ sharply in pH. For alkaline waters the pH is over 8, while for calcium chloride waters the pH lies between 4 and 6. This low pH in calcium chloride waters is explained by Kazmina (1938) on the basis of great amount of CO_2 present in the form of dissolved gas. At the same time, Ovchinnikov et al. (1947) believe that the acidity of calcium chloride waters is the result of the hydrolysis of $CaCl_2$ and $MgCl_2$.

The accumulation of the majority of components in formation waters is not genetically related to petroleum, but

rather to such characteristic phenomenon as the formation of calcium chloride. Salin (1946) proved that the latter is the final stage of metamorphism of the salt content of the waters of the earth's crust. The process consists mainly of the displacement of calcium ion by one of sodium, and the absorption of the calcium by the rocks.

Soda in formation waters for the most part, in any case, is the result of the reaction of crude oils with the surrounding medium.

SURFACE ACTIVE AGENTS

Substances that lower the surface tension of a liquid, or the interfacial tension between two liquids, are known as "surface-active agents" or "surfactants". All such agents possess the common feature of a water-soluble (hydrophilic) group attached to a long hydrocarbon (hydrophobic) chain.

The various surface-active agents used in industry, as well as those without present commercial importance, but reported in technical literature and patents, have been thoroughly reviewed by Schwartz and his associates (90,91) and will not be treated here.

Surfactants include both nonionic and ionic types. Not ionizing in solution, the nonionics are stable in acidic, neutral or alkaline media and can be used in combination with either anionic or cationic surfactants. The anionics are primarily fast-wetting compounds with good spreading action. In solution, they yield negatively charged surface-

active ions.

Surface effectiveness is a function of solubility. Becher (92) believes his data indicate that high interfacial tensions occur when surfactants are not ideally oriented because of perturbing effects of either the surfactant hydrophobe or hydrophile. Fig. 2B shows the possible orientations of a surfactant at the oil-water interface.

In Fig. 2B, A and C correspond to high interfacial tension. In $2B_A$ this arises from the perturbing effect of the hydrophobe on the water structure. As for Fig. $2B_C$ the high interfacial tension arises from the perturbing effect due to presence of hydrophile in the oil phase. This occurs when a surfactant is quite soluble in the oil. Fig. $2B_B$ represents the ideal position - showing perturbation at a minimum.

One effective means of increasing petroleum recovery

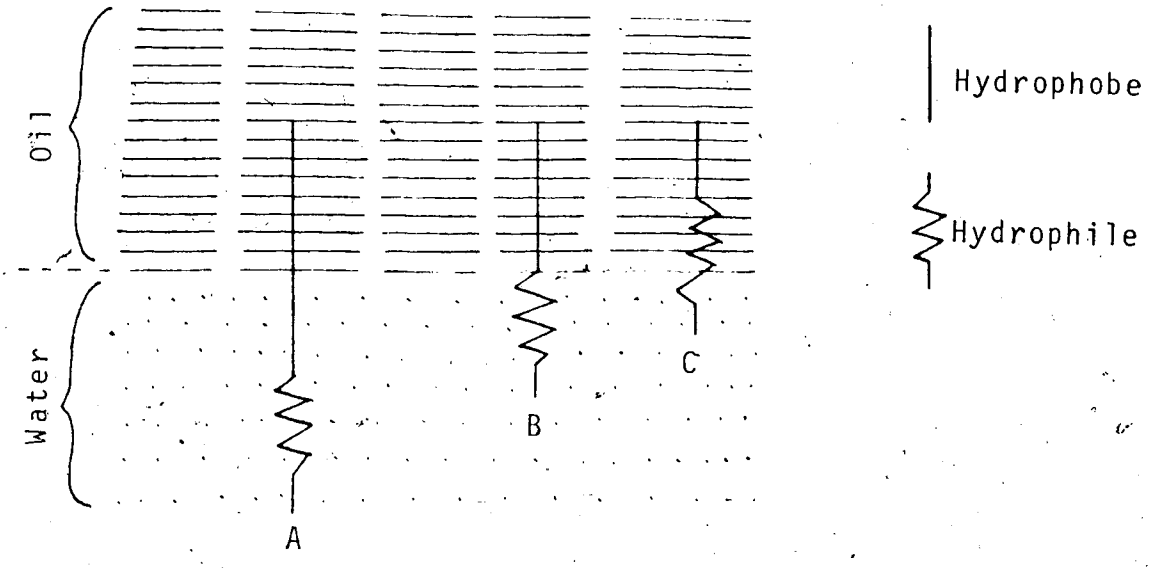

Fig. 2B. Possible Orientations of a Surface Active Agent at an Oil-Water Interface

is by the addition of surfactants to the flood water. The economics of the use of surfactants, however, is determined not only by the method of application but also by the degree of adsorption. Thus, certain workers (93) have pointed out that the use of surfactants is economically advantageous only when the adsorption does not exceed 10^{-4} g/g.

EXPERIMENTAL EQUIPMENT

Viscosity measurements on the crude oils were taken with Cannon-Fenske Viscometers and a Bendix Lab-Vis meter with a calibrated probe. The probe was calibrated with standard oils and Corning glycerine. The temperature was controlled by suspending the crude oil container in a constant temperature water bath during viscosity measurements.

A Cenco du Nuoy tensiometer model 70545 with a platinum ring six centimeters in circumference was used for surface and interfacial tension measurements. Readings were corrected using the correction factor tables of Zuidema and Waters (95).

The interfacial tension measurements between crude oils and distilled water at various temperature intervals were made in a temperature-controlled air bath.

A Beckman Model N pH meter with a glass reference electrode and a Beckman E2 glass electrode was used for pH measurements. The Beckman E2 glass electrode was used because it exhibits linear behaviour throughout the entire pH range and shows minimum deviation in highly alkaline solutions with high sodium ion concentrations. A "Radiometer Copenhagen" pH meter - type TTT1a was used for certain pH measurements and also as a check for the measurements obtained by the Beckman Model N.

A special frothing apparatus (plates 1, 2, 3) was

designed for the removal of porphyric constituents of the crude oils. This apparatus consisted of pressure gauge (Matheson type), manifold, Poly-Flo Tubing 44-P-1/4 (Imperial Eastman), lucite bubblers, regulated rotators and beakers.

The removal of the porphyric constituents was achieved by a foaming technique in which nitrogen was bubbled through the crude in containers rotating at the rate of 1 rpm.

EXPERIMENTAL PROCEDURE

SOURCE AND HANDLING OF MATERIALS

Four crude oils--Lloydminster, Ethyl Lake-Clearwater Formation, Imperial Judy Creek-Beaverhill Lake, and Leduc-Woodbend--all treated only for the removal of water, were used for all testing. These crude oils are identified as crudes LLOYD, ETHYL LAKE, JUDY CREEK and LEDUC in Table A-1. The crude oil gravity ranges from 38° API to 41° API for the "light" crudes and from 13° API to 15° API for the heavy (viscous) crude oils. The bottom sediment and water content was 1.40% by volume for LLOYD crude, 0.18% for ETHYL LAKE and less than 0.05% for the others. The crude oil gravities were determined by the hydrometer method using ASTM (96) test D287-55 and the bottom sediment and water contents were determined using ASTM test D96-58T.

The properties and chemical analysis of various field waters are presented in Tables A-2 and A-3. The chemicals used in the preparation of various solutions (0.002% - 0.1% conc.) were reagent grade and surface active, and are identified in Table A-4. All aqueous solutions were kept in a temperature-controlled chamber.

TEMPERATURE-VISCOSITY MEASUREMENTS

The Cannon-Fenske (Routine and Opaque) Viscometers were

used to measure the viscosities of the crude oils. The standard method of testing for kinematic viscosity ASTM test D445-53T was used. Bendix Lab-Vis meter was also used for some viscosity measurements to confirm the Cannon-Fenske results. The temperature range for the complete series of measurements was 70°F to 210°F. The Cannon-Fenske Viscometer constants were corrected using the calibration data (Viscosity Correction Factor) plot prepared by the Standards Laboratory of the Chemical Engineering Department of the University of Alberta. The opaque viscometers constants were supplied by the Fuels Section of the Research Council of Alberta.

SURFACE AND INTERFACIAL TENSION TEST PROCEDURE

The du Nuoy tensiometer was used to measure the surface and interfacial tensions of solutions and between surfactant solutions and crude oils. The standard method of testing for surface and interfacial tensions of oil against water by the ring method ASTM D971-50 was utilized. The temperature of the fluids during the routine surface and interfacial tension tests was maintained within 2°F for each set of tests. The temperature range for the complete set of tests was 72°F to 78°F except for the special case of investigating the effect of temperature on interfacial tensions where the temperature range was 75°F to 164°F.

The measured surface and interfacial tension readings were corrected using the density corrections of Zuidema and

Waters (95) in graphical form. Due to difficulty in determining the breaking point of the water film at low interfacial tension values, readings less than 0.35 dynes per centimeter were not considered reliable. Such readings were simply recorded as less than 0.35 dynes per centimeter.

ATOMIC ABSORPTION TEST PROCEDURE

Metal complexes of porphyrins are present in petroleum. The concentration levels of such complexes are usually low, generally falling in the range of 10-1,000 ppm, with some reported less than 1 ppm. It is now known that the principal metalloporphyric complexes are those of vanadium, nickel and iron (10,83,84,97,98,99,100,101,102,103).

One hundred milliliters of distilled water was shaken periodically for 48 hours with 25 ml of Lloydminster and Ethyl Lake crude oils respectively. These mixtures were allowed to settle out in a separation funnel. The aqueous portion was drained off and the small amount of the suspended oil was filtered from it. The aqueous portion was then analyzed on the atomic absorption apparatus. The above procedure was repeated with 0.01% solution of surfactant Tergitol NPX.

FOAMING TECHNIQUE

This technique is based on the principle of adsorption. When nitrogen is bubbled through the crude oils a greatly increased surface area is created by the bubbles. The sur-

face active compounds will tend to orient themselves at these surfaces. There is no chemical reaction between the bubbled nitrogen and the nitrogenous polar constituents. The bubbling process produces a froth which is believed to contain some of the metalloporphyric constituents. This froth is skimmed off and the resultant crude oil tested for changes in the interfacial tension against distilled water and some surfactant solutions.

The bubbling period varied between 24 and 72 hours. The froth was skimmed off at six-hour intervals.

MASS SPECTOMETRY TEST PROCEDURE

Although metal complexes occur primarily in the asphaltic fraction of crude oil, nevertheless, there is a considerable porphyrin content in some of the middle fractions (105). The asphaltenes were obtained by dissolving 5 grams of the viscous crude in 25 ml of benzene and precipitating with ten volumes of n-pentane at room temperature. The porphyrins were extracted following the method of Baker et al. (106). The analyses for porphyrin complexes were done by the Mass Spectometry Laboratory, Chemistry Department of the University of Alberta.

DATA ANALYSIS

A statistical analysis of data was not made; however, each data point represents a mean of five measurements.

EXPERIMENTAL RESULTS

FLUID PROPERTIES

The properties of the four crude oil samples used in this work are shown in Table A-1. Lloydminster crude which contained 0.04% of water was dewatered prior to use for the surface and interfacial tension tests.

Variations of the viscosities of the Lloydminster, Ethyl Lake, Imperial Judy Creek and Leduc-Woodbend crude oils with temperature are shown in Fig. 3 and Table B-1. The viscosities of the crude oils decrease with increasing temperature. It is observed that the rate of decrease in viscosities of the heavy crude oils with increasing temperature is greater than that of the conventional (light) crudes. Fig. 4 and Table A-1 show the variation with temperature of specific gravity of the crudes.

SURFACE TENSION MEASUREMENTS

The results of the surface tension measurements for water and oil samples used in this work are given in Table C-1. Fig. 5 (Table C-2) shows the surface tension measurements of distilled water solutions of sodium hydroxide, Tergitol NP-35 and Triton X-100 at various surface aging times. The results obtained with solutions of sodium hydroxide shows that the surface tension of its fresh solution differs from that at equilibrium.

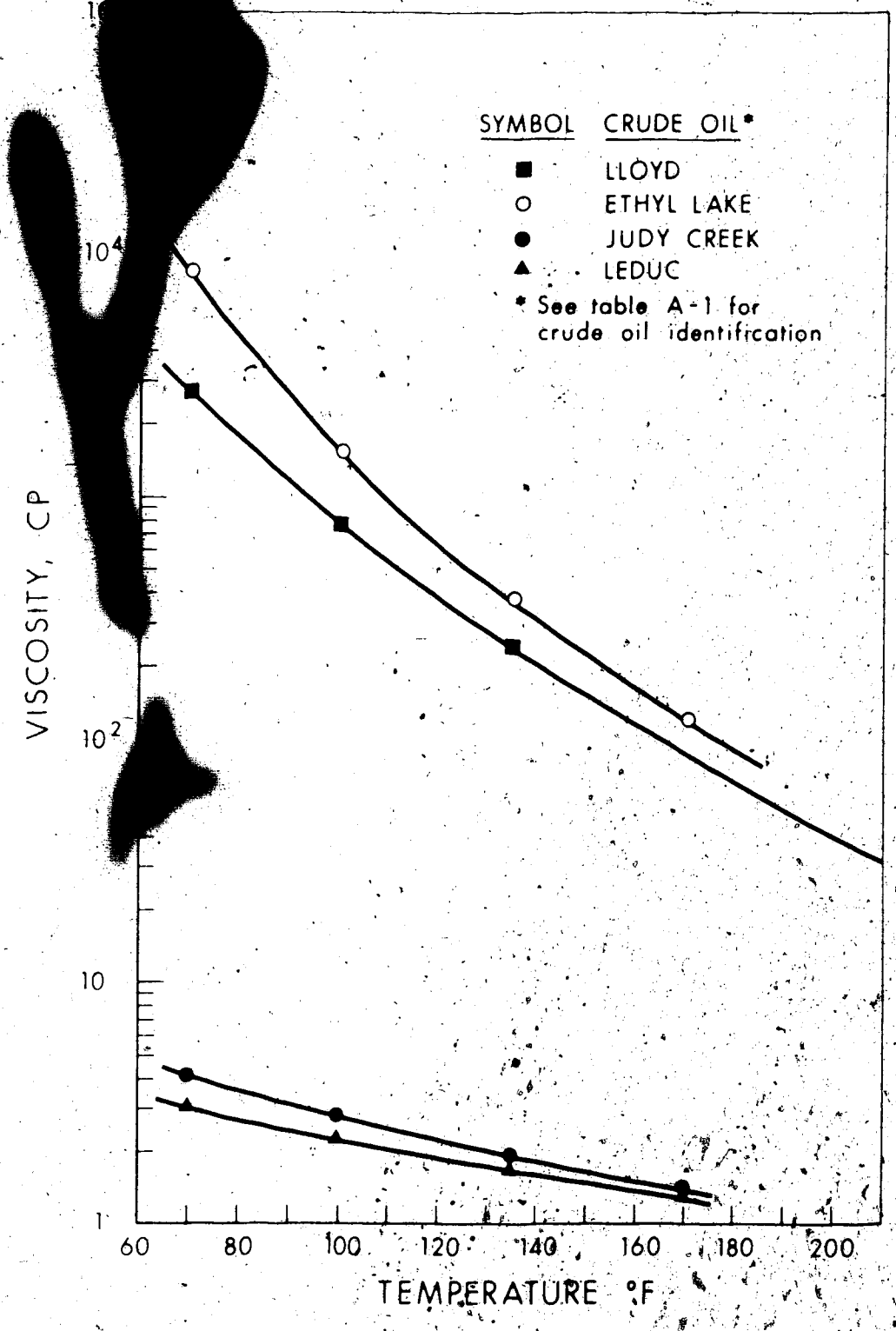

FIGURE 3 - Viscosity of Crude Oils as a Function of Temperature

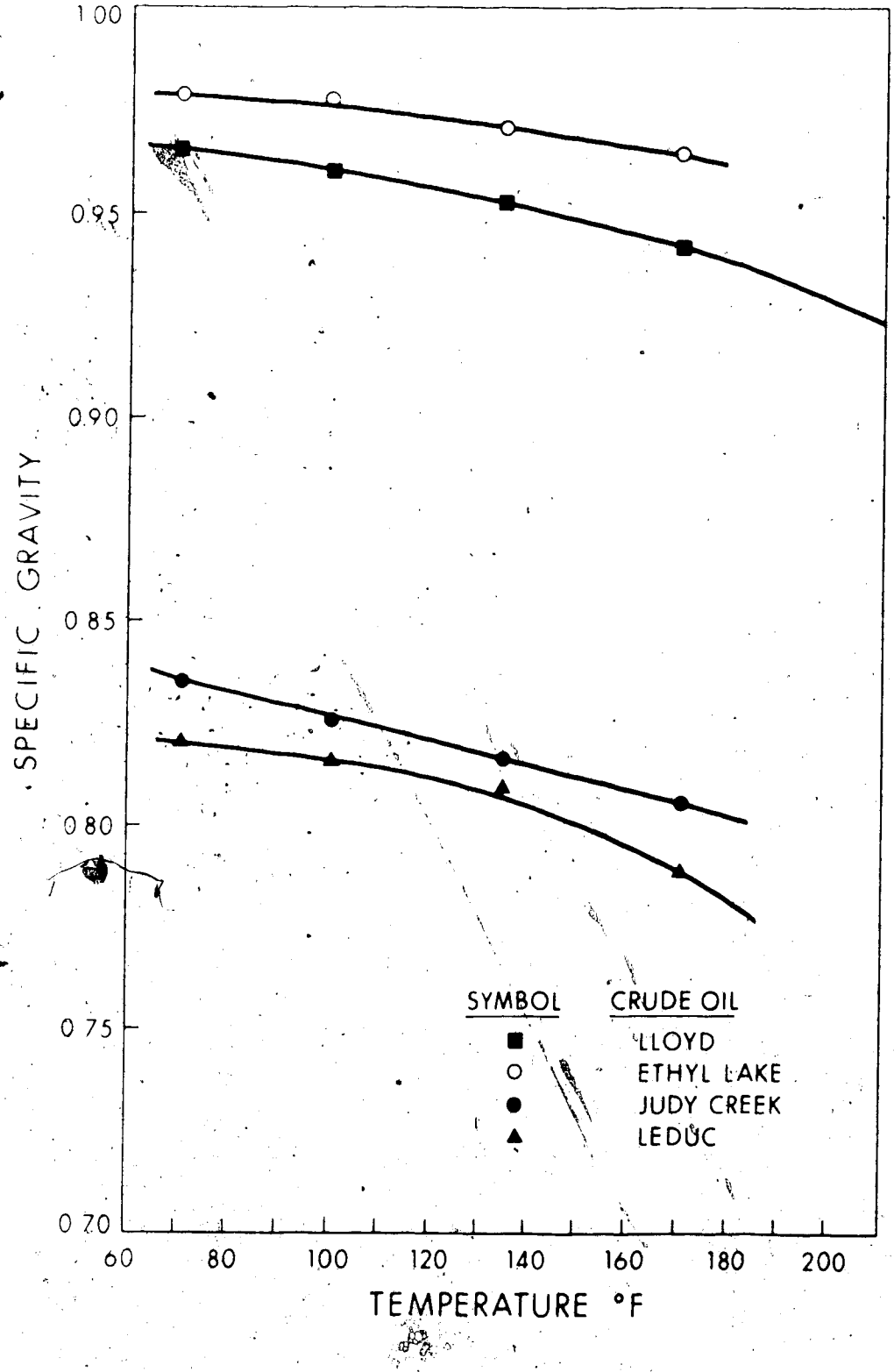

FIGURE 4 - Specific Gravity of Crude Oils as a Function of Temperature

Five to ten minutes may be required for surface stabilization prior to static tension measurements. The data for both Tergitol NP-35 and Triton X-100 show that when surface active agents are in solution, the time for surface equilibrium attainment is considerably reduced.

INTERFACIAL TENSION AND pH MEASUREMENTS

The results of the interfacial tension measurements for the crude oil-distilled water system against temperature at constant pressure are given in Fig. 6 and Tables D-1 and D-2.

The interfacial tension results for the four crude-oil-water systems show a linear relationship with temperature. It may be seen that the slope of this relationship is a function of crude oil viscosity, the absolute value increasing with increasing viscosity. The scatter shown by the interfacial tension results may be attributed to the surface entropy for water and the complexity of the crude oil composition. Continuous loss of volatile fractions from the crude oils with increasing temperature may have influenced the interfacial film behaviour. The apparent temperature-dependent behaviour of crude oils is probably a function of composition.

The effect of various chemicals on interfacial tension was measured for a number of aqueous solutions and crude oils. The results of the tests are presented in Tables D-1 to D-46. The results of the interfacial tension measurements between the various crude oils and field waters are presented

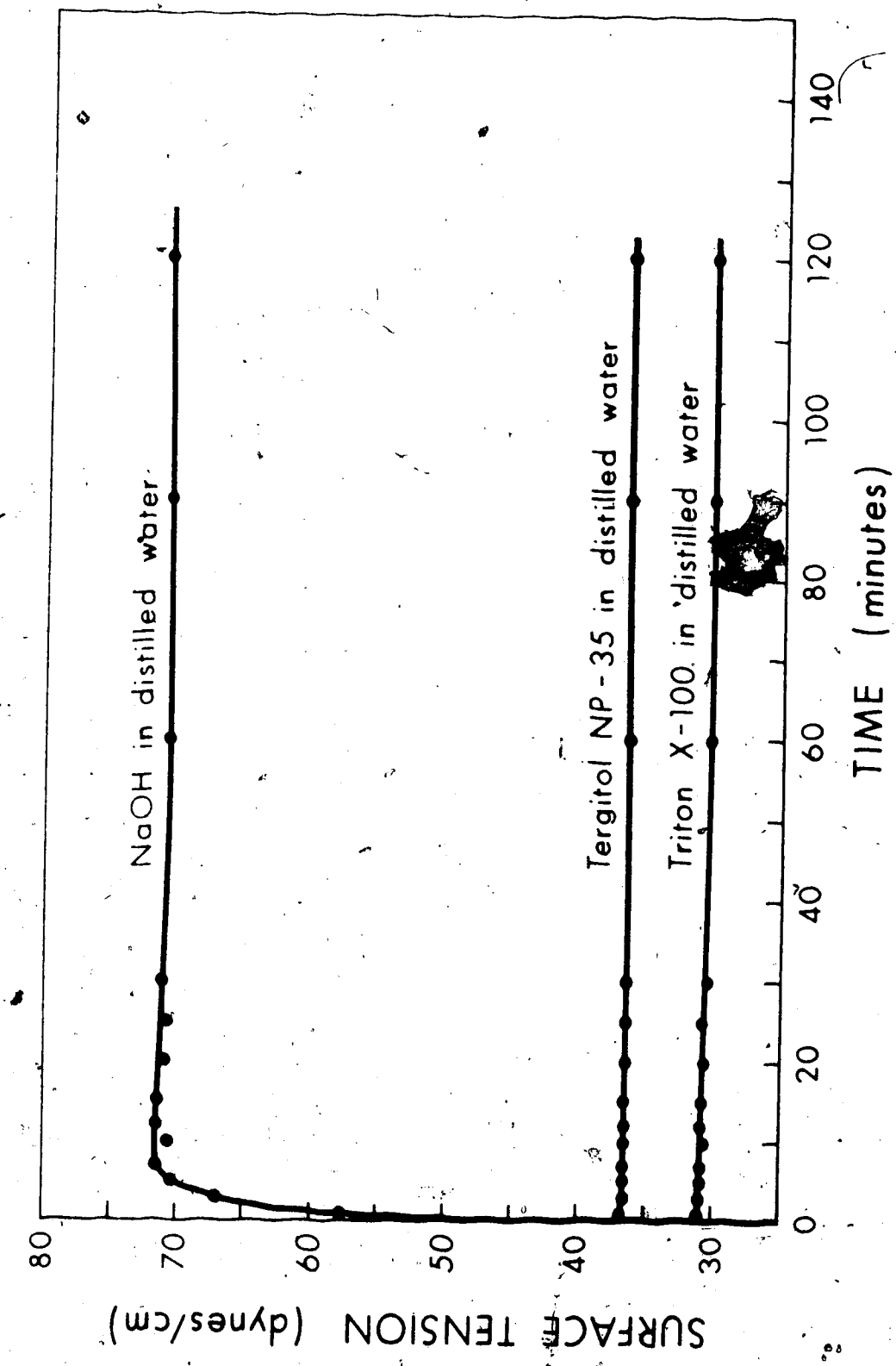

FIGURE 5 - The Effect of Simple Surface-Active Agents Upon the Surface-Ageing Phenomenon

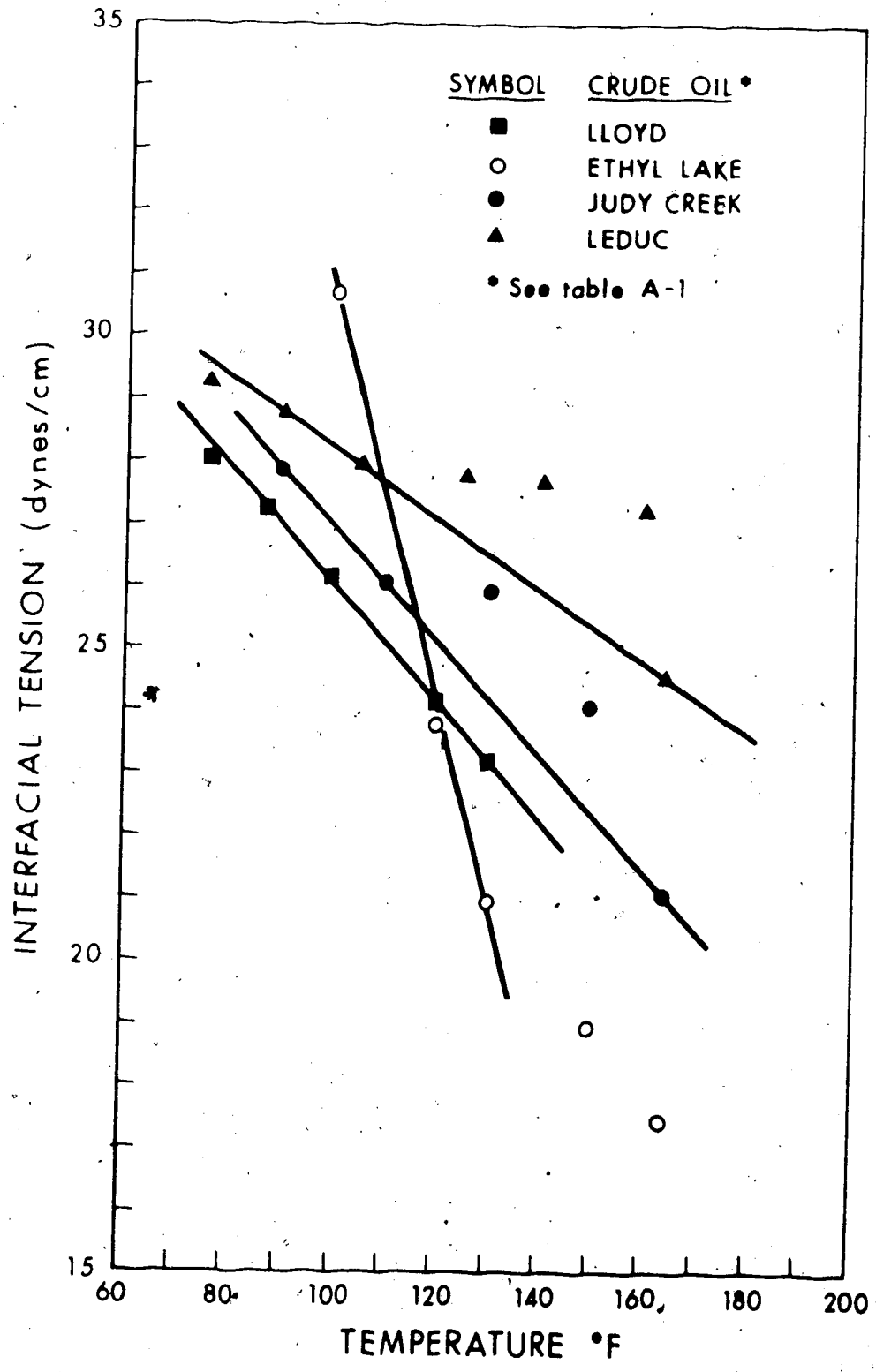

FIGURE 6 - Effect of Temperature on the Interfacial Tension Between Distilled Water and Crude Oils

in Tables D-47 to D-50. The interfacial tension readings have been corrected for ring size and fluid density differences. Visual observation of precipitate in the aqueous solution was recorded. Since the economics of waterflooding requires that as low a concentration as possible be used in any field project, low concentrations of aqueous solutions have been used throughout this investigation.

The effect of sodium hydroxide concentration in distilled water on interfacial tension is shown in Fig. 7. The interfacial tension between viscous Lloydminster crude oil, and distilled water decreased rapidly to an immeasurably low value, less than 0.35 dynes per centimeter, at a sodium hydroxide concentration of 0.06 per cent by weight. The same low value of interfacial tension between the Ethyl Lake crude oil and distilled water was attained at a sodium hydroxide concentration of 0.08 per cent by weight in distilled water. At sodium hydroxide concentration of 0.1 per cent by weight in distilled water the interfacial tension between Imperial Judy Creek crude oil and the solution was 7.64 dynes/cm, and between Leduc crude and the solution a still high value of 17.10 dynes/cm.

The difference in interfacial tension between the viscous crude oils and sodium hydroxide solution and between light crude oils and sodium hydroxide is significant at all concentrations of the solution, and especially at concentrations higher than 0.01 per cent by weight in distilled water.

Figs. 8 and 9 show the comparison of interfacial tensions measurements for sodium hydroxide solutions and viscous

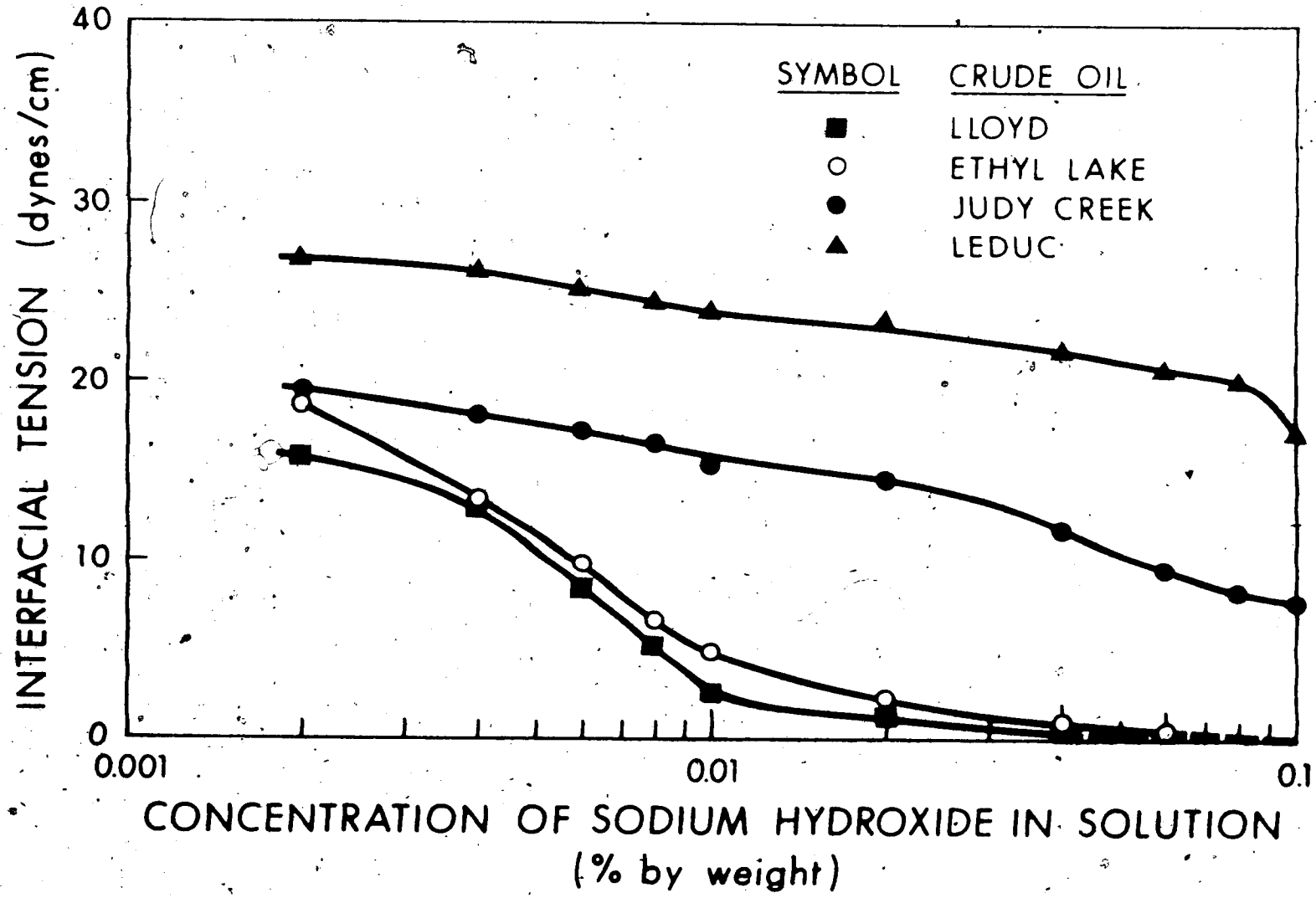

FIGURE 7 - Influence of NaOH Concentration on Interfacial Tension

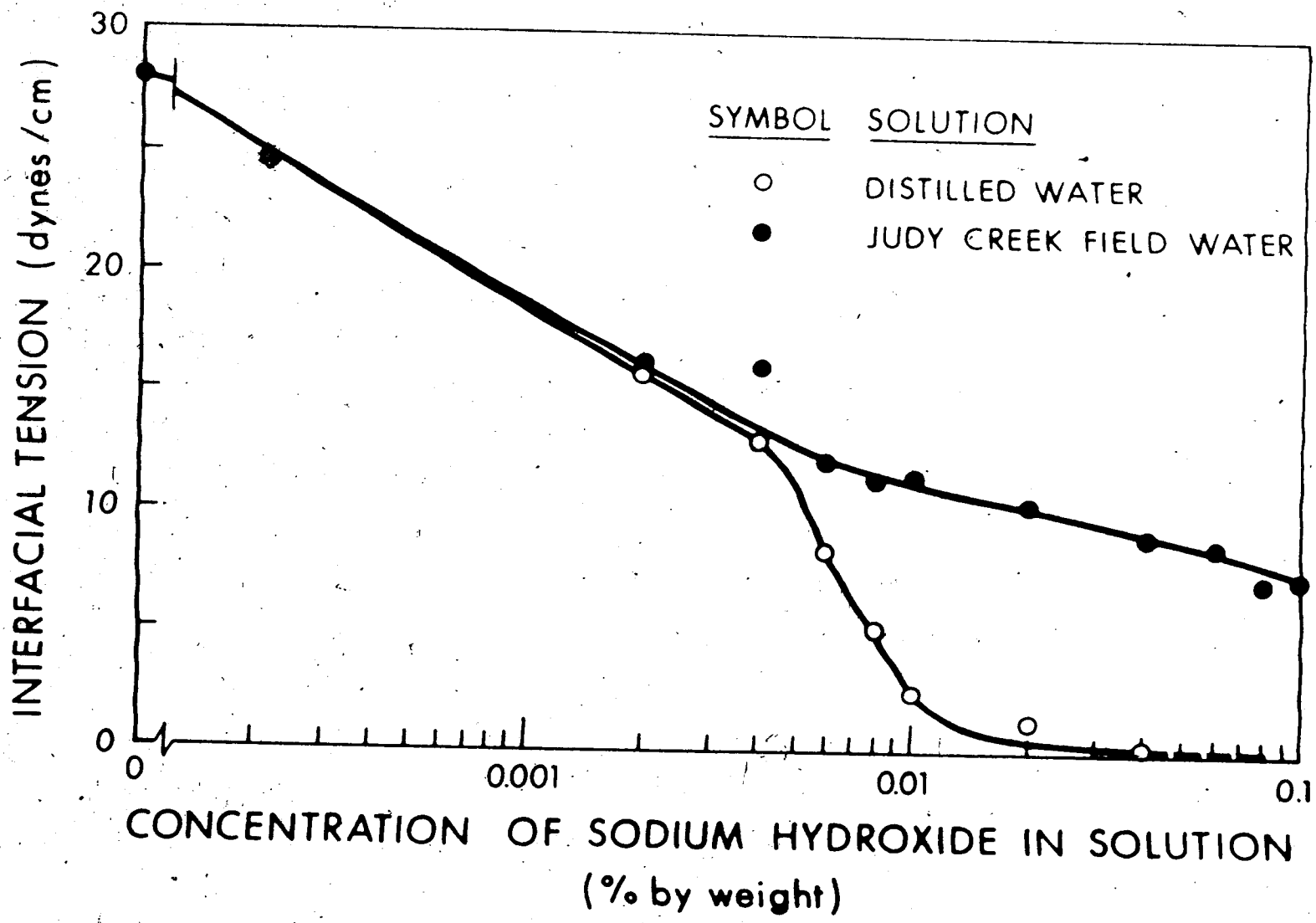

FIGURE 8 - Comparison of Interfacial Tension Measurements for Sodium Hydroxide Solutions and Lloydminster Crude Oil

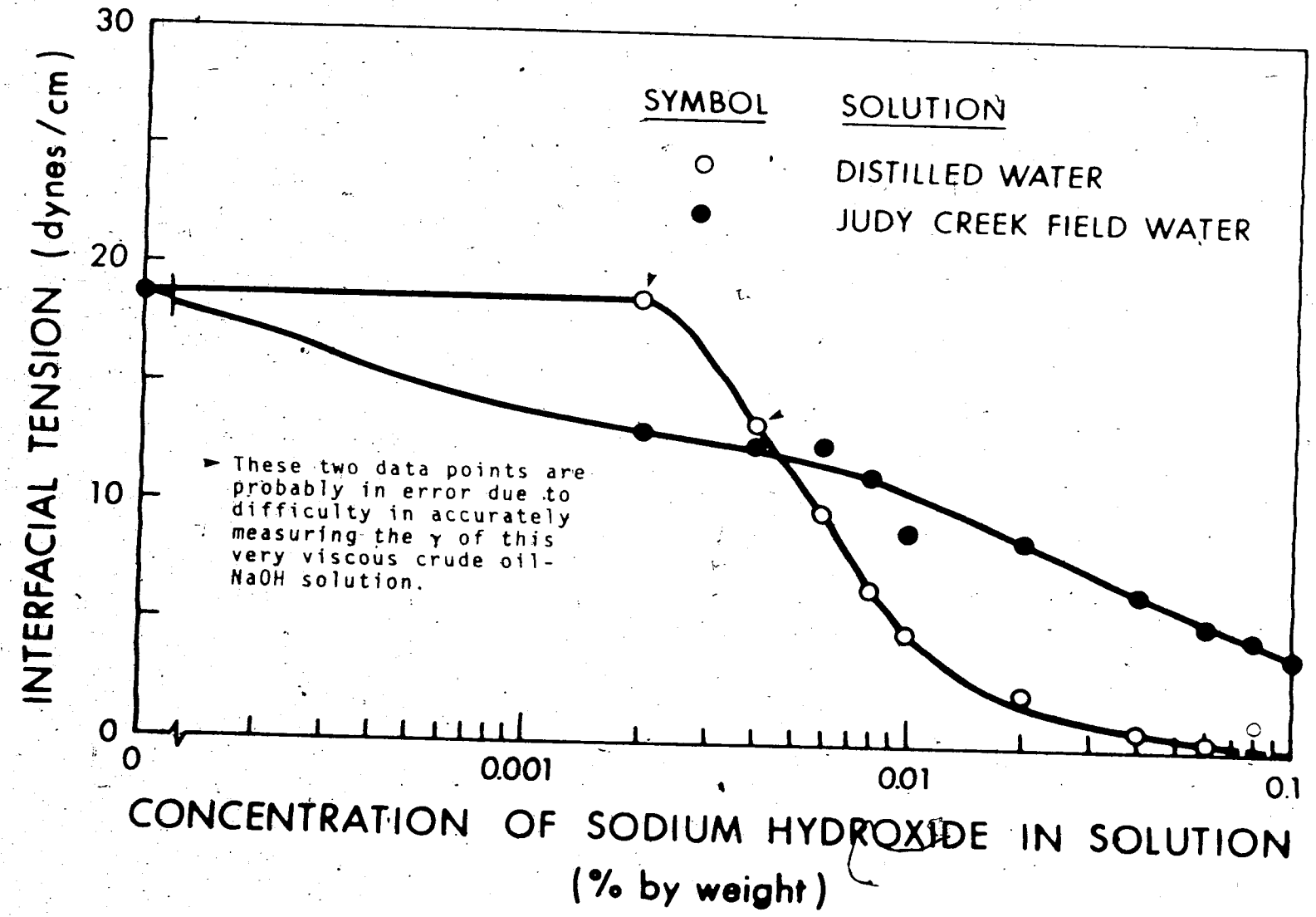

FIGURE 9 - Comparison of Interfacial Tension Measurements for Sodium Hydroxide Solutions and Ethyl Lake Crude Oil

crude oils. Fig. 10 and Fig. 11 show the comparison of interfacial tension measurement for the same solutions and light crude oils. Generally, lower interfacial tension values were obtained for measurements between the crude oils and sodium hydroxide concentrations in distilled water than the same measurements with sodium hydroxide concentrations in field water. The significant difference in sodium hydroxide concentrations required to reach the same interfacial tension can only be attributed to the hardness of the field water due to calcium and magnesium chloride concentration. The interfacial tension between the viscous crude oils and sodium hydroxide solutions are generally significantly lower than the interfacial tension between the light crude oils and the sodium hydroxide solutions.

Visual observation of the aqueous phase during these tests indicated a milky white precipitate formed even at very low concentrations of sodium hydroxide in field water. Subsequent testing indicated that the precipitate was a combination of calcium hydroxide and magnesium hydroxide. The interfacial tension between crude oils and field water was not reduced to a very low value until sodium hydroxide had been added sufficient to precipitate the high calcium and magnesium content of the field water. The precipitation of calcium and magnesium results in increased concentration of sodium chloride in the system as follows:

$$CaCl_2 + 2NaOH \rightarrow Ca(OH)_2 + 2NaCl$$

$$MgCl_2 + 2NaOH \rightarrow Mg(OH)_2 + 2NaCl$$

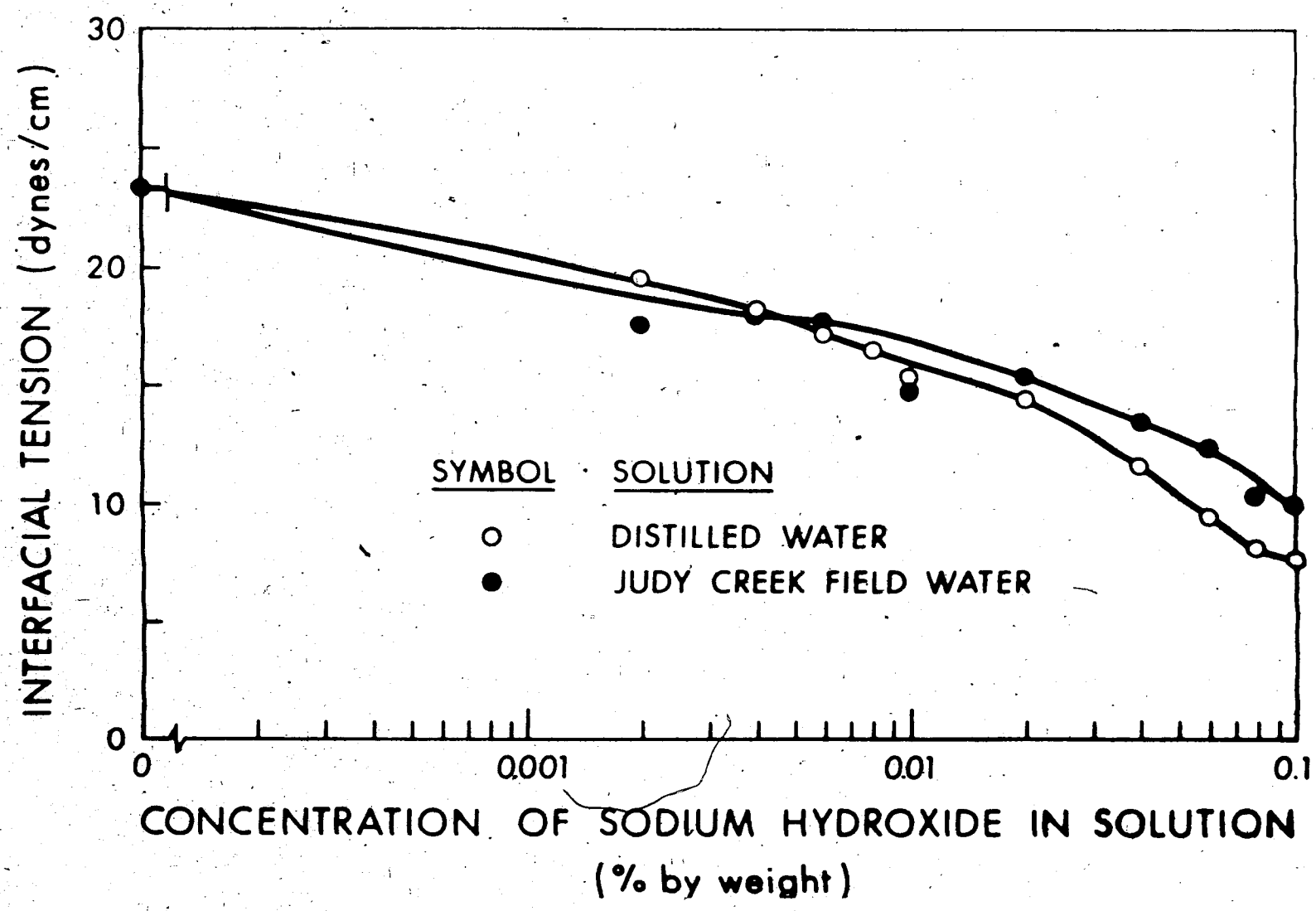

FIGURE 10 - Comparison of Interfacial Tension Measurements for Sodium Hydroxide Solutions and Imperial Judy Creek Crude Oil

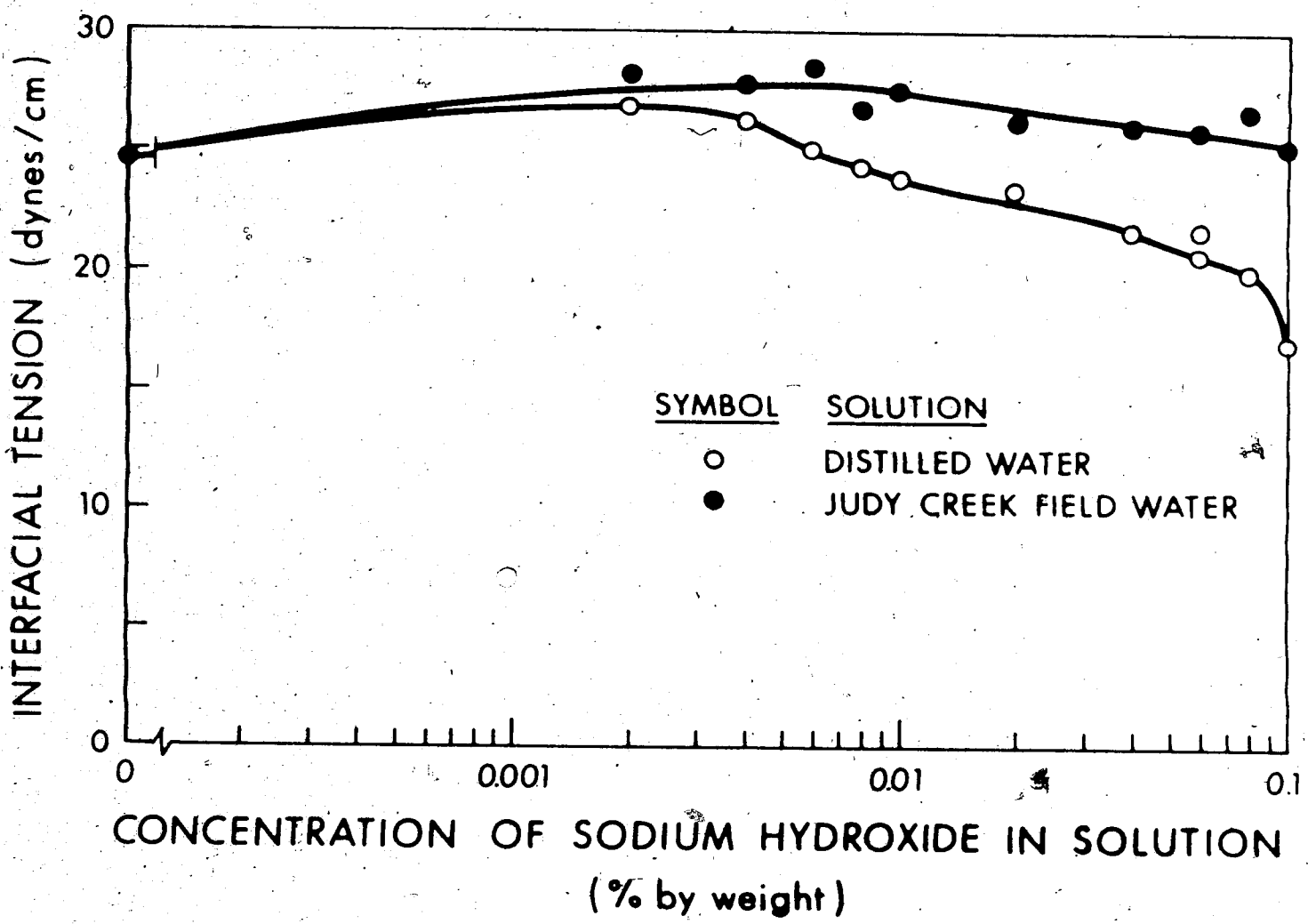

FIGURE 11 - Comparison of Interfacial Tension Measurements for Sodium Hydroxide Solutions and Leduc-Woodbend Crude Oil

Usually, the addition of inorganic electrolytes to water invariably results in an increase in surface or interfacial tension. Thus, the appearance of sodium chloride in the system could raise the interfacial tensions even if only by a small amount. Gibbs' surface concentration theory could be used to explain the sodium chloride behaviour in the system. The surface concentration of sodium chloride in the system is relatively small because of negative adsorption. Consequently the change in interfacial tension between the crude oils and the field water is therefore correspondingly small.

The interfacial tension test results shown in Fig. 12 for solutions containing a non-ionic surfactant--Tergitol NPX--were considerably lower than those of solutions containing sodium hydroxide. The interfacial tension between the two viscous crude oils (Lloydminster and Ethyl Lake) and distilled water decreased very rapidly to an immeasurably low value less than 0.35 dynes/cm at a surfactant concentration of 0.02 per cent by volume. At a surfactant concentration of 0.1 per cent by weight in distilled water, the interfacial tension between the two light crude oils (Imperial Judy Creek and Leduc-Woodbend) and the solution were 2.18 dynes/cm and 4.16 dynes/cm, respectively. These interfacial tension values are four times less than those obtained with sodium hydroxide solutions. The test results for the other non-ionic surfactants are shown in Fig. D-1 to Fig. D-5 inclusive. The test results for the anionic surfactants shown in Figs. D-6 and D-7 are considerably poorer than those of

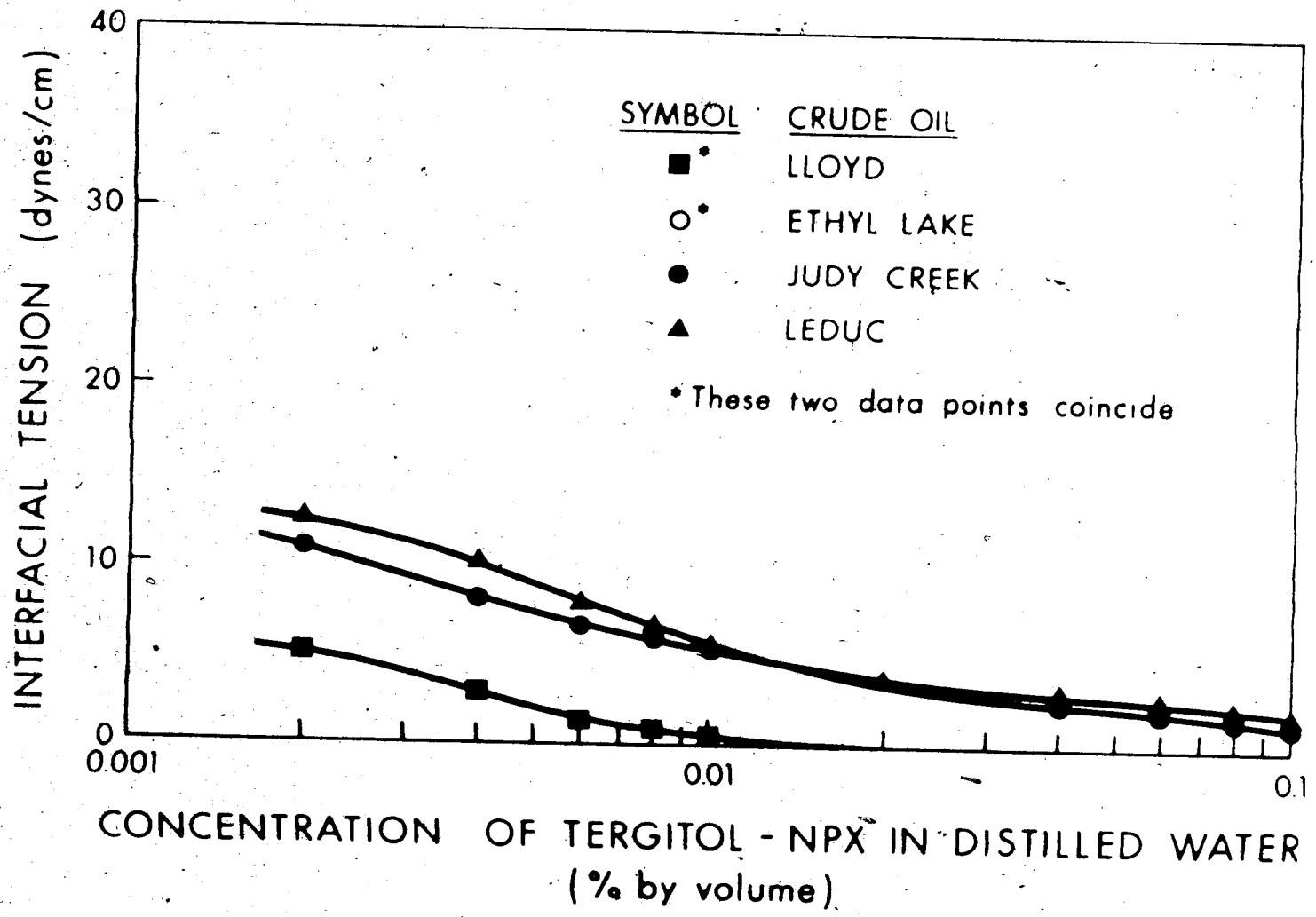

FIGURE 12 - Influence of Tergitol NPX Concentration on Interfacial Tension

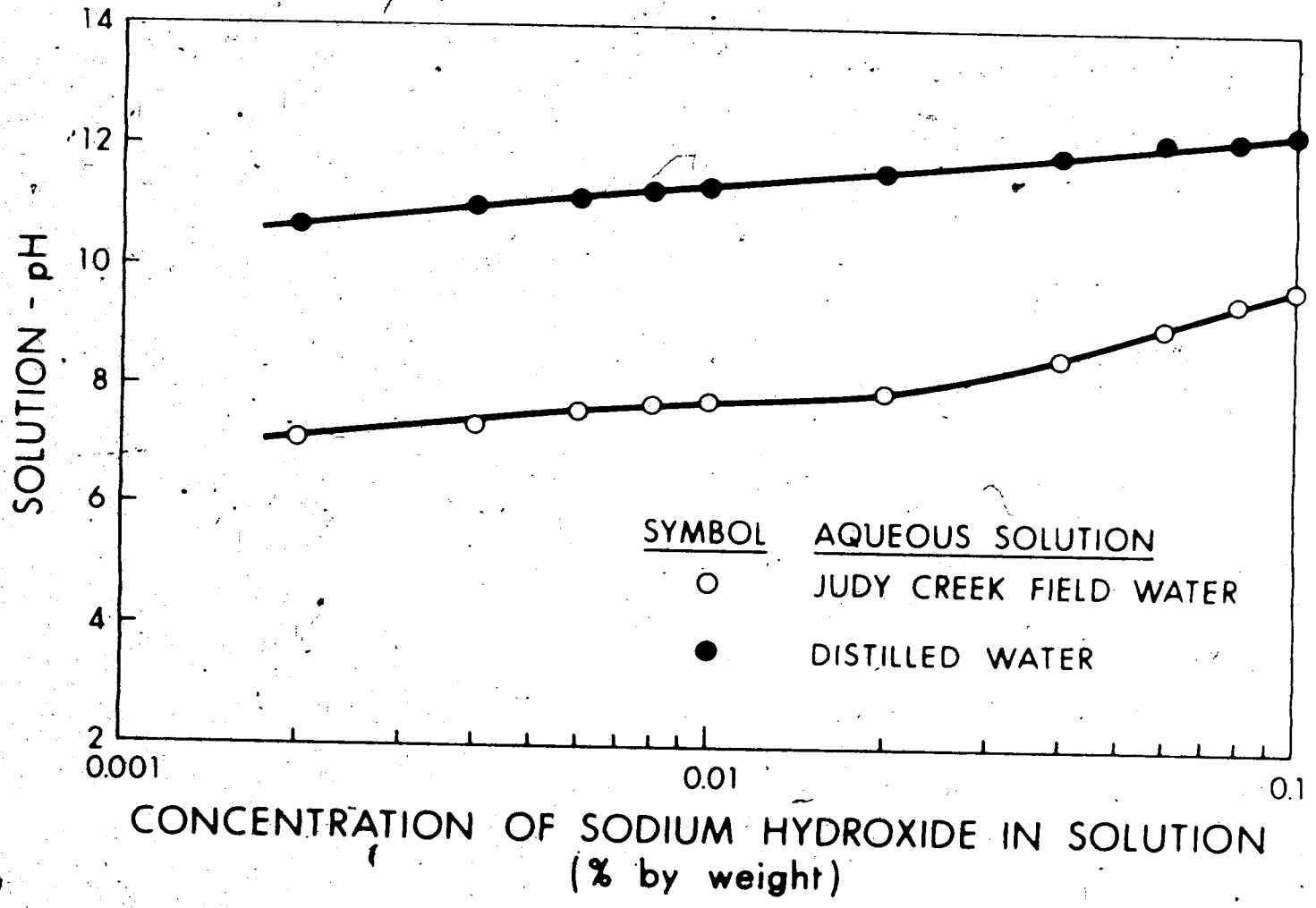

FIGURE 13 - Influence of Sodium Hydroxide Concentration on the pH of Solutions

sodium hydroxide and a lot worse than those of the non-ionic surfactants. However, although the anionic surfactants have proved ineffective in reducing interfacial tensions, nevertheless they are known to be good wetting agents. They could therefore be used in combination with non-ionics to provide some complementary wetting activity to the interfacial tension reduction effect during displacement tests.

The effect of sodium hydroxide on the pH of various solutions is shown in Fig. 13. The pH of solutions of sodium hydroxide in both field water and distilled water increased steadily as the concentration of sodium hydroxide increased. The pH of solutions of sodium hydroxide in field water increased from 7.10 to 9.80 and the pH of the same solutions in distilled water increased from 10.48 to 12.36. Fig. 14 shows the influence of a surfactant concentration on the pH of solutions. Commercial surface active agents are usually of low pH and do not show pH variation with concentration. The pH of solutions of sodium hydroxide in both field water and distilled water is a function of concentration, but the pH of surfactant solutions does not show such dependence.

Fig. 15 shows the relationship between aqueous solution pH and interfacial tension for sodium hydroxide in distilled water. It was observed that for a distilled water solution of sodium hydroxide, a reduction in interfacial tension between the crude oils and the solution correlated with an increase in the solution pH. When the interfacial tension between the viscous crude oils and the sodium hydroxide solu-

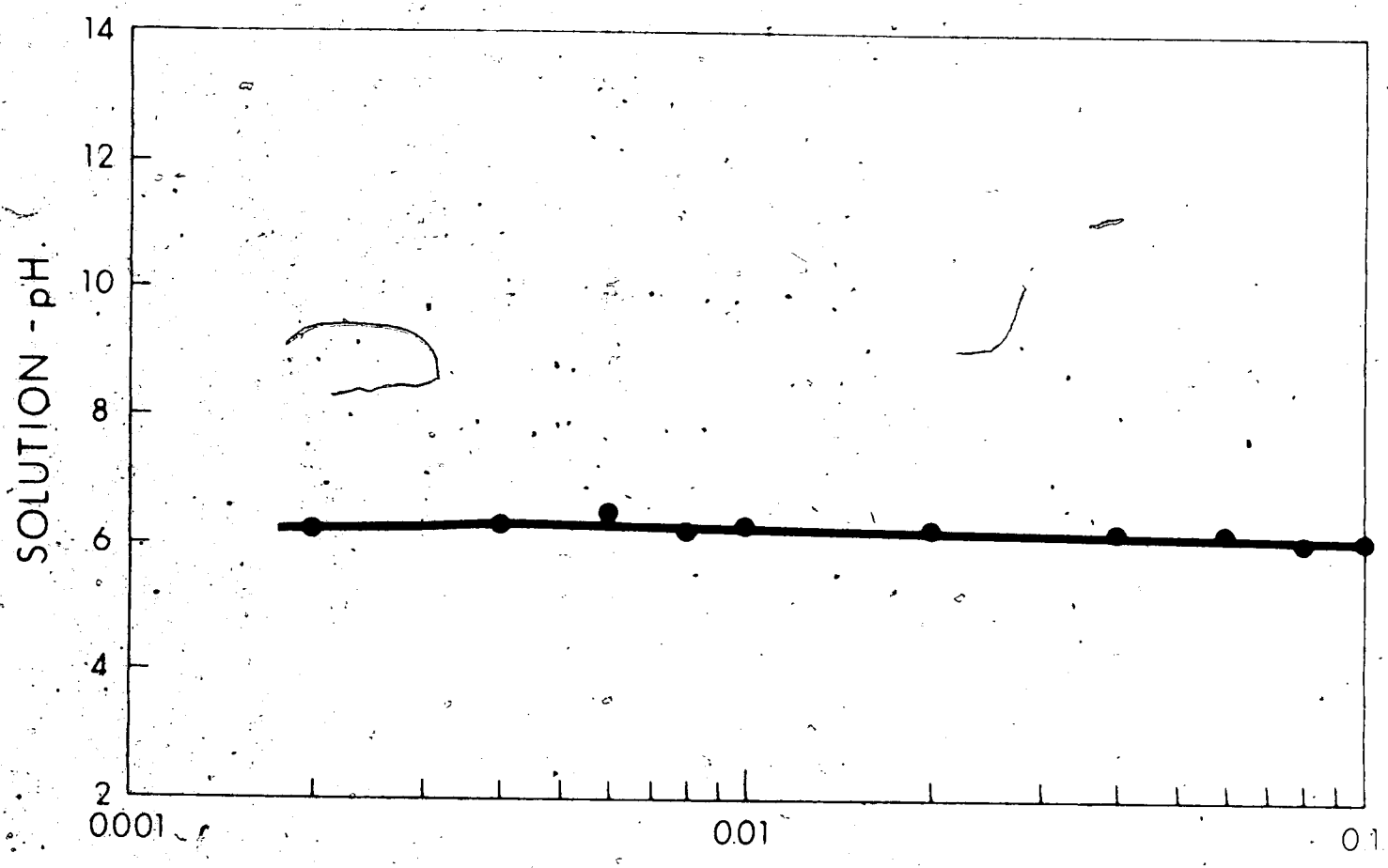

FIGURE 14 - Influence of a Surfactant Concentration on the pH of Solutions

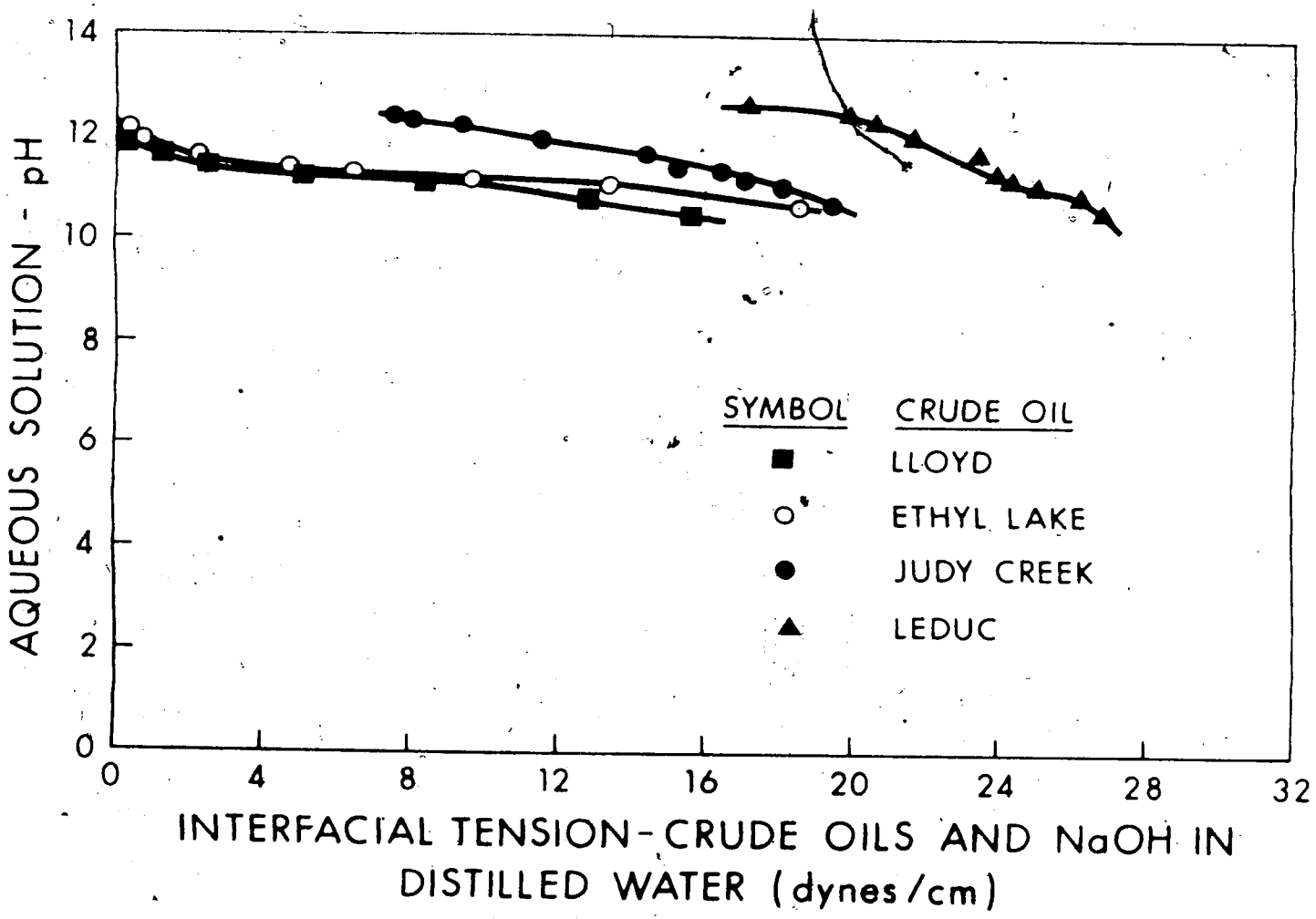

FIGURE 15 - Relationship of Aqueous Solution pH and Interfacial Tension for NaOH Solution

tions was reduced essentially to zero, the pH of the solutions was over 12. It is expected that at a pH of 13 and above, the interfacial tension between the light crude oils and solutions of sodium hydroxide in distilled water should be reduced to zero.

Fig. 16 shows the relationship of aqueous solution pH and interfacial tension for a surfactant solution. It was observed that interfacial tension is not a function of solution pH.

The relationship of aqueous solution pH and interfacial tension for sodium hydroxide in field water is shown in Fig. 17. This figure shows interfacial tension as a function of pH. It is noted that the relationship here between pH and interfacial tension is weaker than the case of solution of sodium hydroxide in distilled water. The pH values of sodium hydroxide in field water were also generally lower than the pH values obtained at all concentrations of sodium hydroxide in distilled water.

Some trace clouding was observed at low concentrations of sodium hydroxide in field water, and at 0.02 per cent concentration and above, a milky white precipitate was observed. Simulation tests showed that the white precipitate was a combination of hydroxides of calcium and magnesium.

ATOMIC ABSORPTION TEST RESULTS

The aqueous portions of mixtures of Lloydminster crude oil in distilled water and Ethyl Lake crude in distilled water were analyzed on the atomic absorption apparatus and

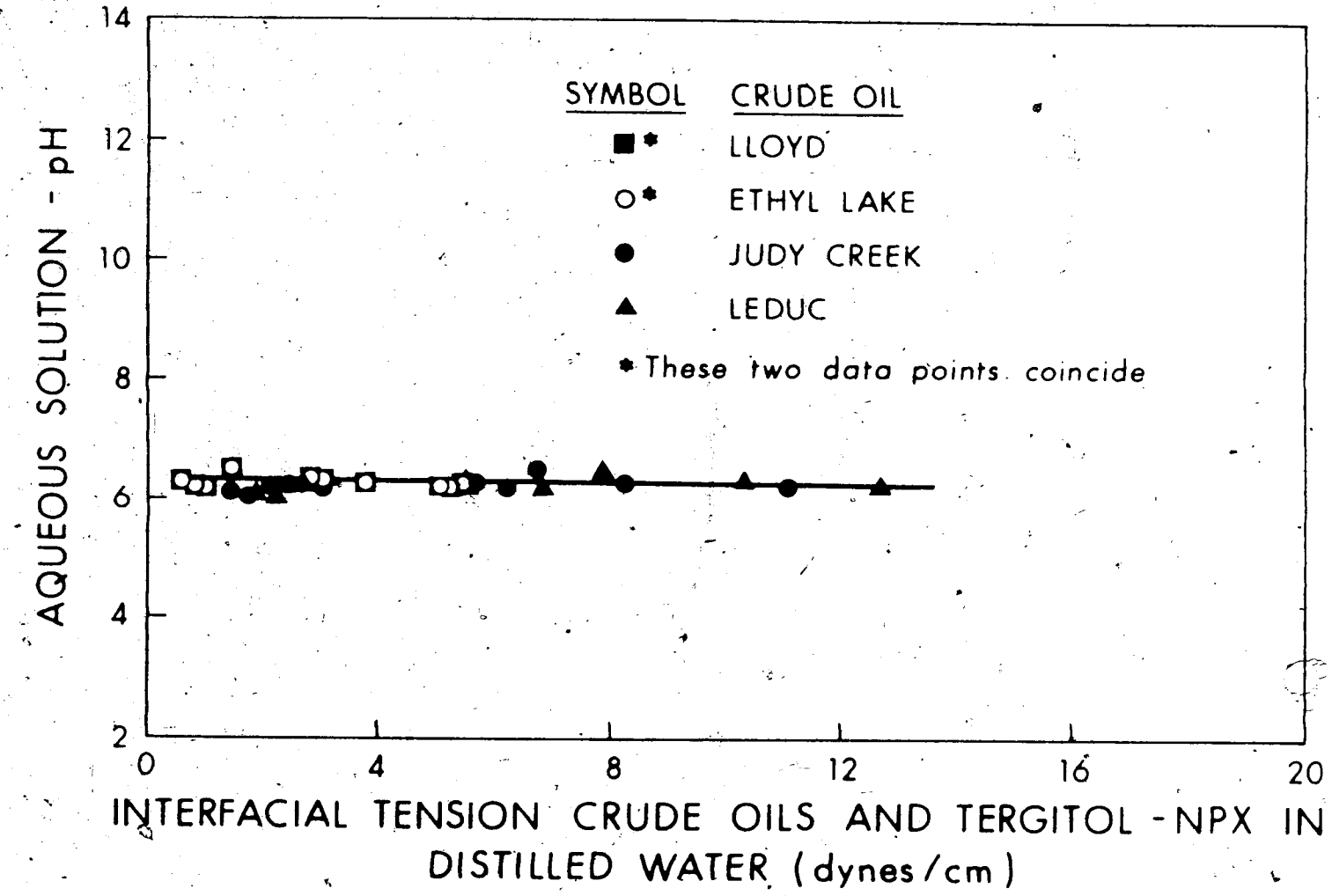

FIGURE 16 - Relationship of Aqueous Solution pH and Interfacial Tension for a Surfactant Solution

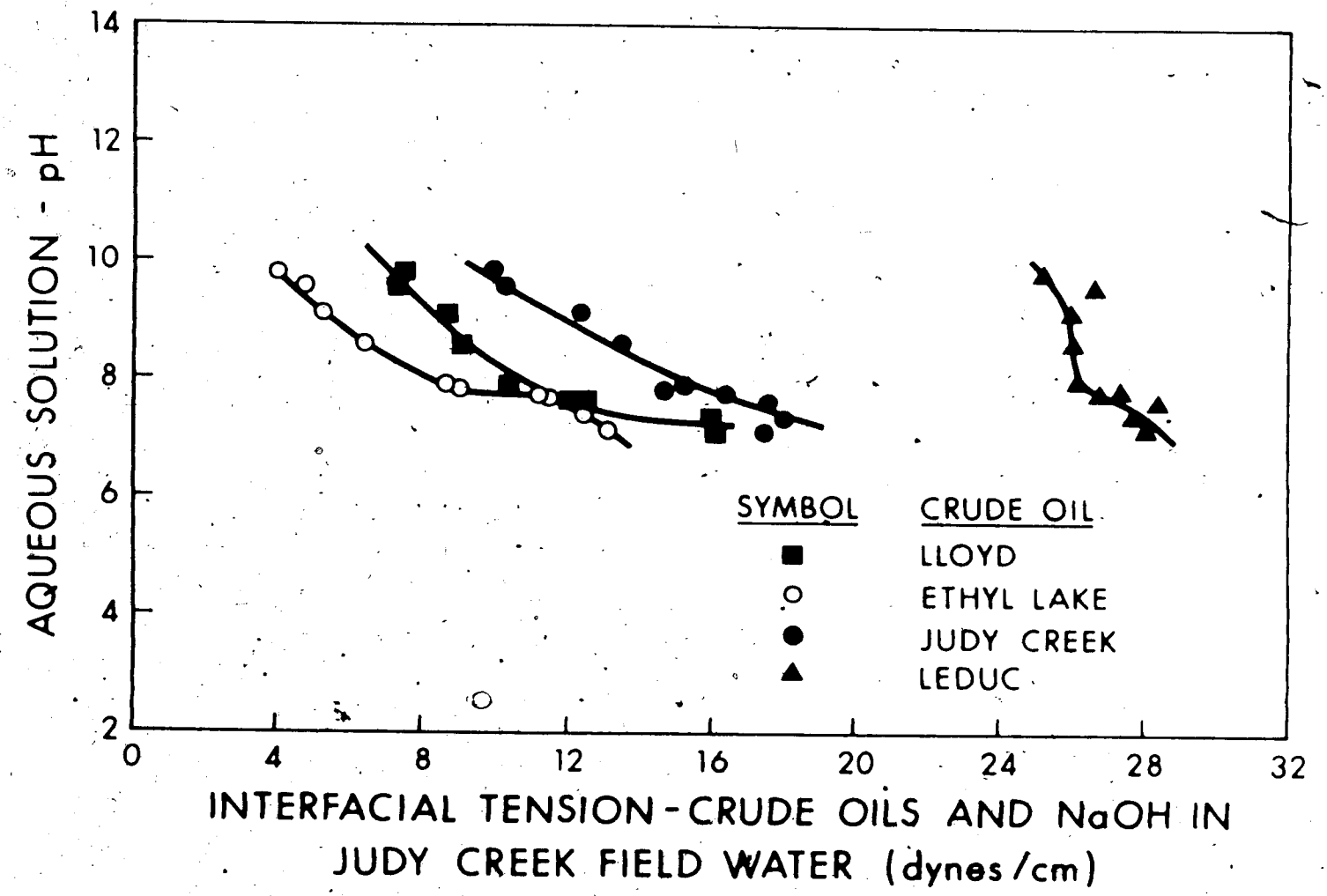

FIGURE I7 - Relationship of Aqueous Solution pH and Interfacial Tension for NaOH Solution

no trace of any metallic complexes were observed. Similar aqueous portions of the same crude oils in 0.01 per cent solution of surfactant--Tergitol NPX--were also analyzed on the atomic absorption equipment and there was no indication of the presence of any metallic complexes in those fractions. The result of this analysis shows that there was no chemical interaction between the crude oils and the solutions. Except in the case of sodium hydroxide, any interaction between the crudes and solutions used in this work is purely interfacial and physical in nature. The concentration of the crude oil polar constituents at the interface between crude oils and solutions of different concentrations may be attributed to purely surface concentration effect in which adsorption is possibly the only factor.

FOAMING TECHNIQUE RESULTS

The result of the interfacial tension tests before and after bubbling nitrogen through the crude oils are shown in Figs. 18, 19, 20 and 21.

Effect on Heavy Crudes

Fig. 18 shows the nitrogen bubbling effect on interfacial tension between Lloydminister viscous crude oil and surfactant-Tergitol NPX solution. The interfacial tensions obtained after foaming were significantly higher than those before foaming. This indicates some difference in concentration of surface active compounds in the crude oil before and after the foaming process. The interfacial tension between

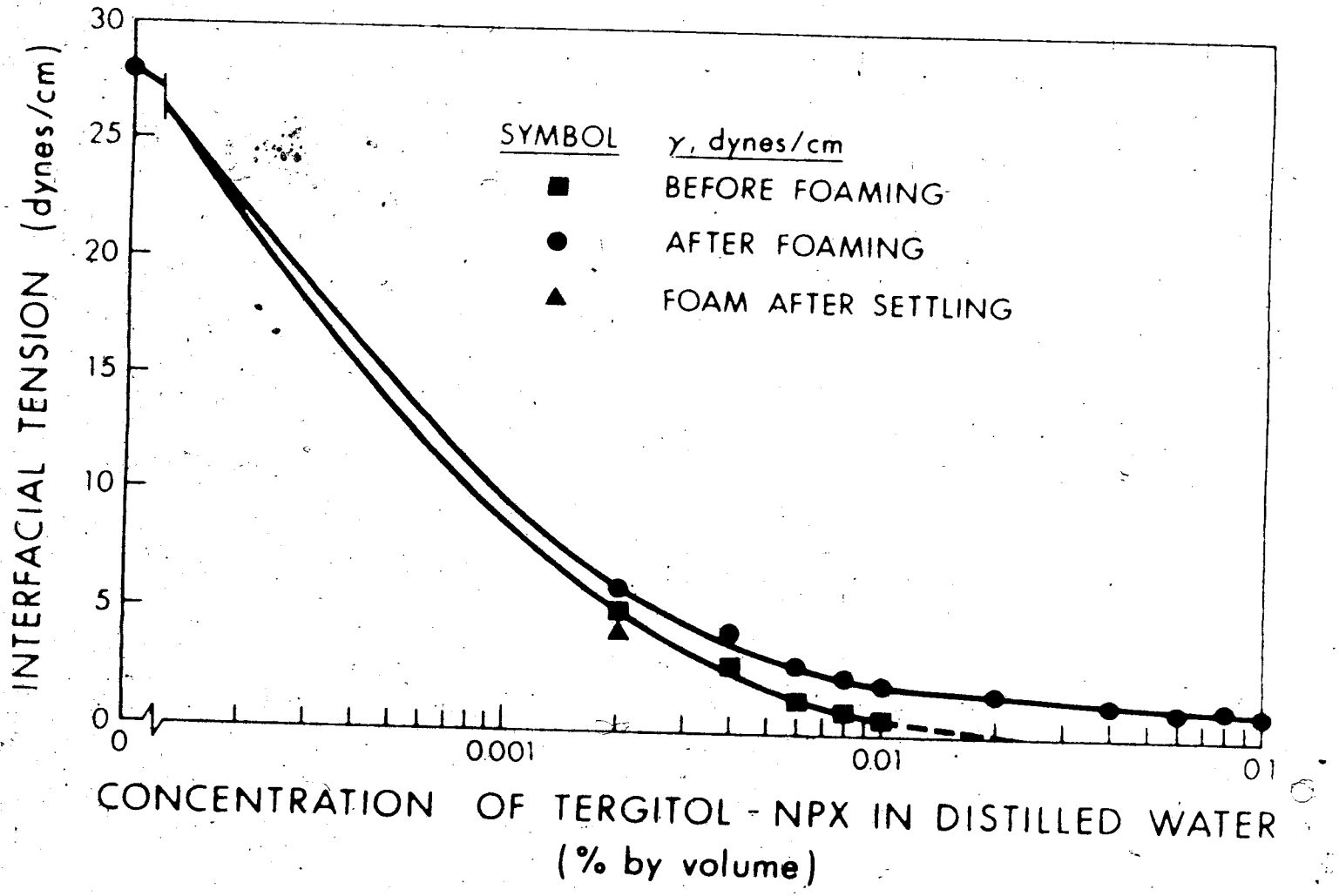

FIGURE 18 - Effect of Nitrogen Foaming on Interfacial Tension of Surfactant Solution and Lloydminster Crude Oil

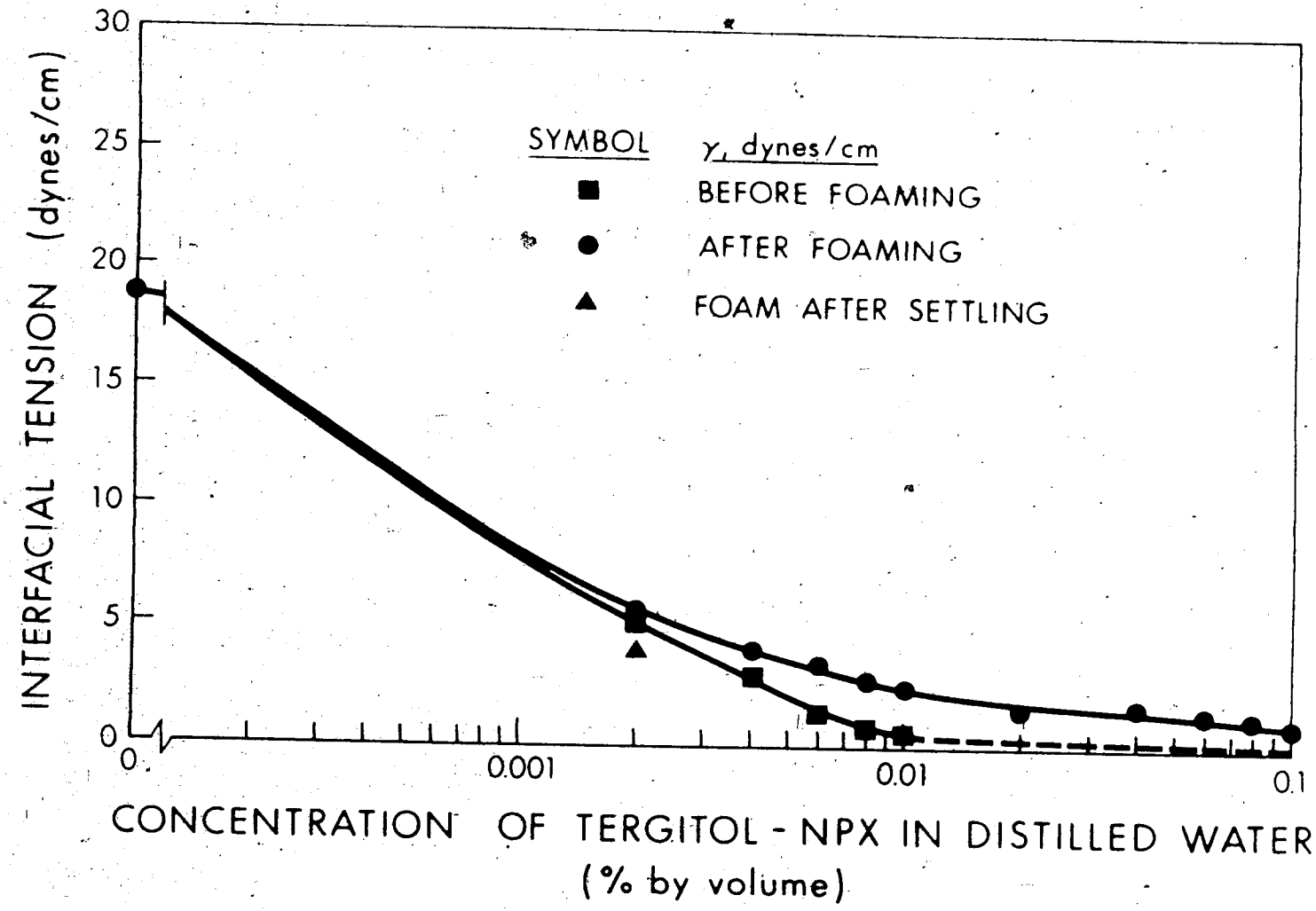

FIGURE 19 - Effect of Nitrogen Foaming on Interfacial Tension of Surfactant Solution and Ethyl Lake Crude Oil

the skimmed-off foam which was allowed to settle, and 0.002 per cent surfactant concentration was measured. The result of this single measurement was lower than that of same concentration measurement made before the foaming process, and considerably lower than that of the measurement made after foaming. This suggests that the scum had a higher concentration of the surface active compounds than the original crude oil. This can be explained by adsorption. The scum is the skimmed-off froth containing almost all of the bubbles formed by the nitrogen. The polar constituents adsorb to the greatly extended surface area of the bubbles. This foam, after settling, will have higher concentration of surface active compounds which will consequently lower the interfacial tension between the crude oil and surfactant solution. Similar interfacial tension results as explained above were also obtained for Ethyl Lake crude oil and surfactant solutions - Fig. 19.

Effect on Light Crudes

Figs. 20 and 21 show that, for light crudes, bubbling nitrogen had little or no effect on the interfacial tension. The slight discrepancies observed are due mainly to experimental errors. It may thus be concluded that the light crude oils were devoid of surface active compounds.

An important observation made in the course of the nitrogen foaming experiments was that the interfacial tension between distilled water and each crude oil before and after

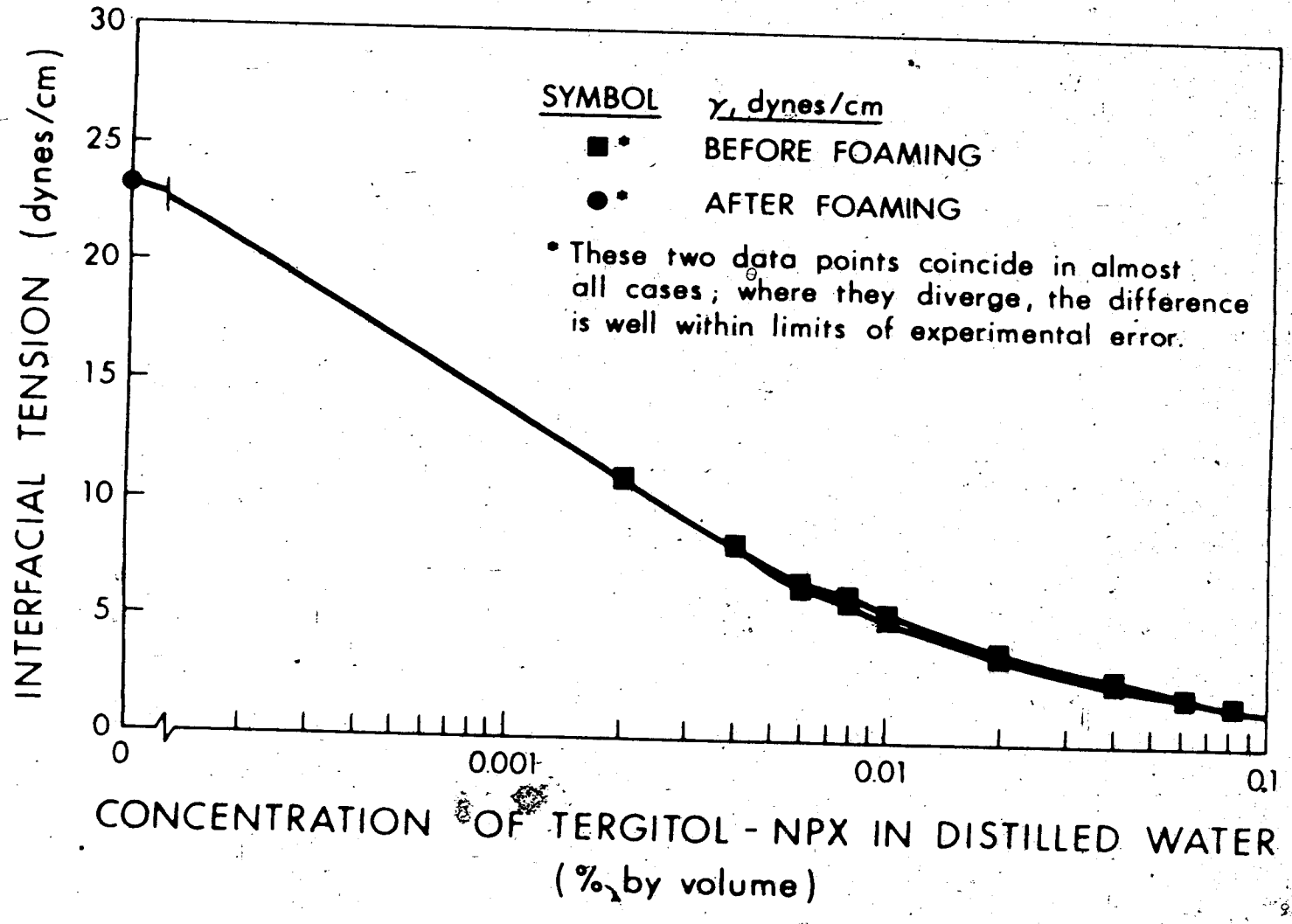

FIGURE 20 - Effect of Nitrogen Foaming on Interfacial Tension of Surfactant Solution and Imperial Judy Creek Crude Oil

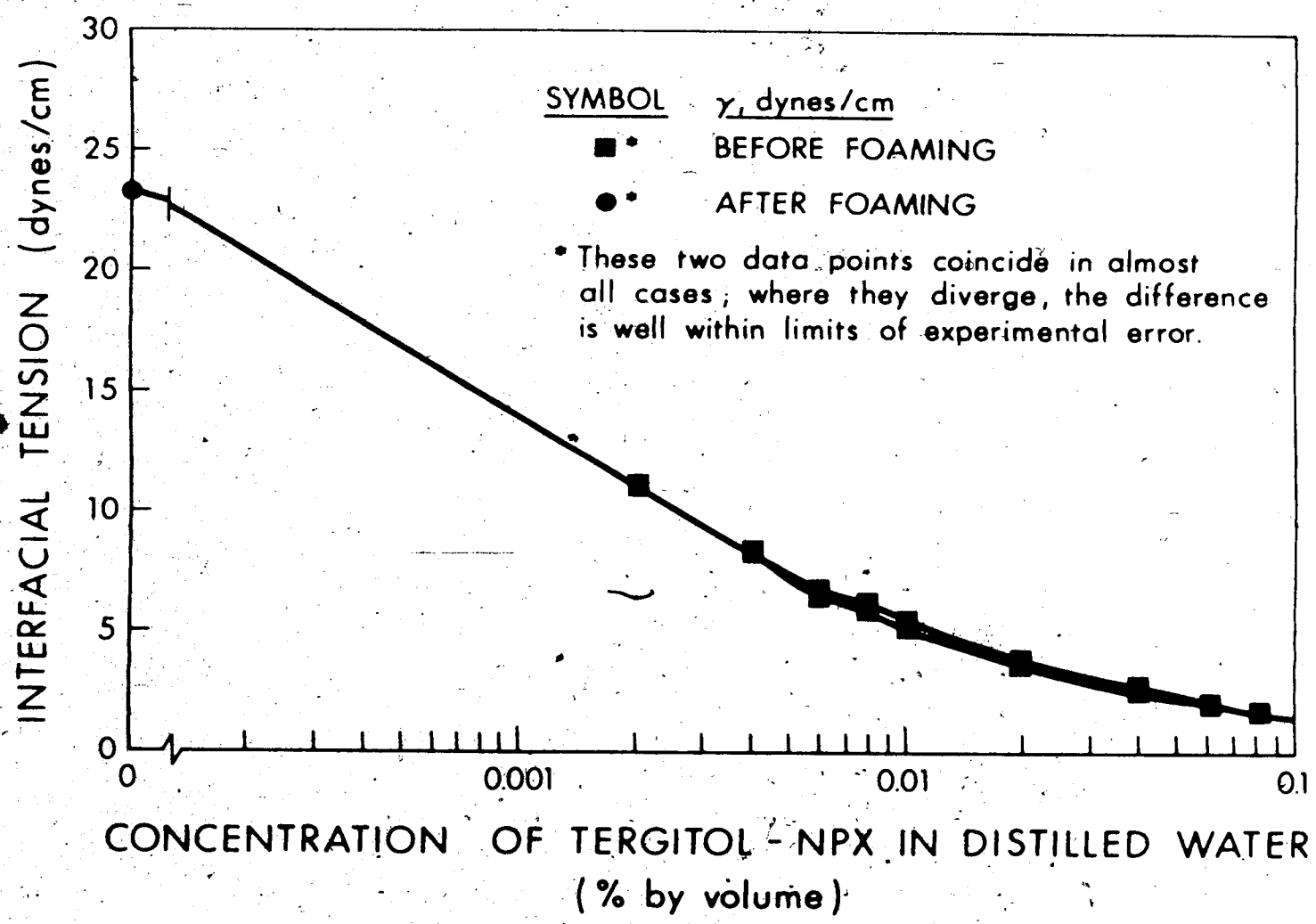

FIGURE 20 - Effect of Nitrogen Foaming on Interfacial Tension of Surfactant Solution and Imperial Judy Creek Crude Oil

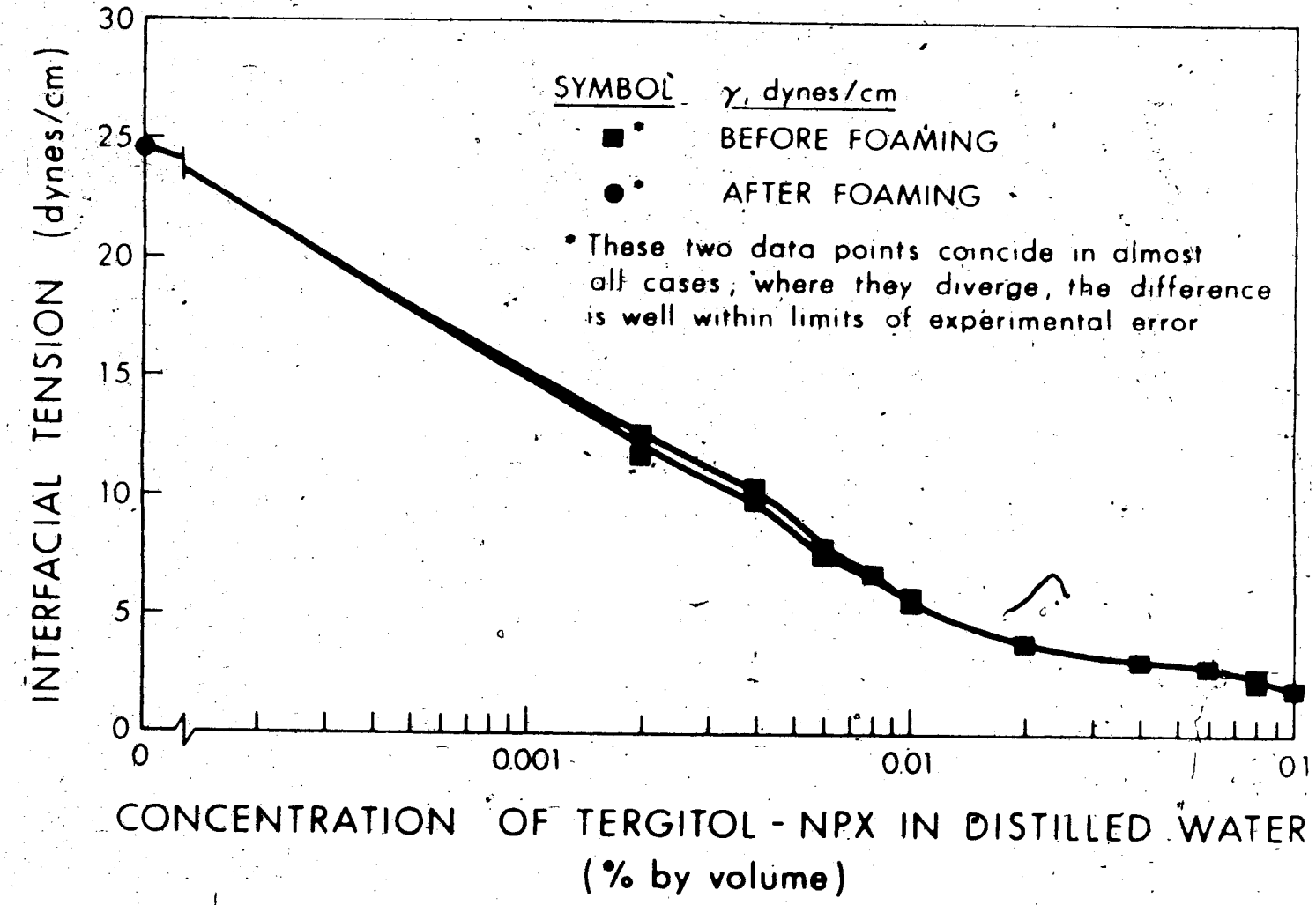

FIGURE 21 - Effect of Nitrogen Foaming on Interfacial Tension of Surfactant Solution and Leduc-Woodbend Crude Oil

foaming was the same for the particular crude oil used. Thus it may be concluded that there is no interaction between crude oils and distilled water. When some surface active agent is added to distilled water, the lowering of interfacial tension is brought about by the additive activities of these surface active materials contained in both crude oil and water phases.

MASS SPECTOMETRY RESULTS

Due to a possibly improper extraction procedure; the result of the mass spectometry analysis was inconclusive. The peaks of the metal porphyrin complexes could not be clearly indentified within the range of the visible spectra. However, metal porphyrin complexes of nickel, vanadium and iron of the same crudes have been identified by other investigators.

DISCUSSION

EFFECT OF SURFACTANTS

The interfacial tension data indicate that interfacial tension between viscous crude oils and surfactant solutions is quickly reduced to zero at very low concentrations of non-ionic surfactants in distilled water. Light crude oils require much higher non-ionic surfactant concentration in distilled water before the interfacial tension is progressively reduced to zero. The ability of the surfactants to reduce interfacial tension between the viscous crude oils and surfactant solutions at very low concentrations is aided by the additive actions of the surface active agents contained in both the crude oil and the surfactant solutions.

Interfacial tension data also show that concentrations higher than 0.1 per cent by volume of anionic surfactants would be required in order to reduce the interfacial tension of the crude oils measured against the surfactant solutions.

EFFECT OF pH

It is widely recognized that the properties of interfacial films show a striking dependence on the pH of the substrate. This investigation indicates such a dependence for interfacial films formed between the four crude oils and solutions of sodium hydroxide. Such a dependence was not

observed in the case of interfacial films formed between the crude oils and the surfactant solutions.

Reisberg and Dorscher (26), and Harkins and Zollman (60) reported extremely low oil-water interfacial tensions when working with highly alkaline solutions. Reisberg and Dorscher (26), in pendant drop work on Ventura crude, observed visually that rigid film formation became negligible at a pH in excess of 8. The data on pH and interfacial tension between crude oils and sodium hydroxide solutions presented in this work indicate a major change in interfacial properties at high values of pH.

THE INFLUENCE OF SODIUM CHLORIDE

Some authors (26,53,59,60) have shown that substantial reduction in interfacial tension is realized by the presence of sodium chloride in the aqueous solution. The present state of knowledge indicates that the presence of ions in a substrate may alter the physical characteristics of surface films by a number of mechanisms:

(1) The ions may react chemically with hydrophilic groups to form insoluble salts.

(2) In the absence of chemical effects, salts act to increase the area of a monolayer (82) and lead to a more expanded phase state.

(3) Ions are negatively adsorbed at a water surface. This effect leads to a layer of pure water, the thickness of which is inversely proportional to the ionic concentra-

tion. As a result, electrostatic effects may become more pronounced as the ionic concentration is increased.

(4) Where surface films are charged, a charged surface exists below the interface (Donnan effect). A diffuse layer of counter-ions will exist below this surface and result in an electrostatic contribution to the surface energy (10).

(5) Differing degrees of hydration may possibly make some ions more effective than others.

The above effects are usually associated with the air-water interface and the extent to which they apply to an oil-water interface is not clear. With complex organic and ionic systems, several mechanisms may be operative simultaneously (61). It is therefore considered inappropriate for the results of air-water surface studies to be applied unconditionally to crude oil-water interfacial behaviour. Supporting evidence may be found in the data of Table D-51 which shows the effect of sodium chloride in sodium hydroxide concentrations on interfacial tension. One volume of 10 per cent solution of sodium chloride was added to various concentrations of sodium hydroxide in distilled water. In Fig. 22 it is observed that the addition of sodium chloride slightly reduced interfacial tension of Imperial Judy Creek crude oil measured against low concentrations of sodium hydroxide. However, beyond 0.06 per cent concentration of sodium hydroxide in distilled water it was observed that interfacial tension between the crude oil and the solution containing sodium

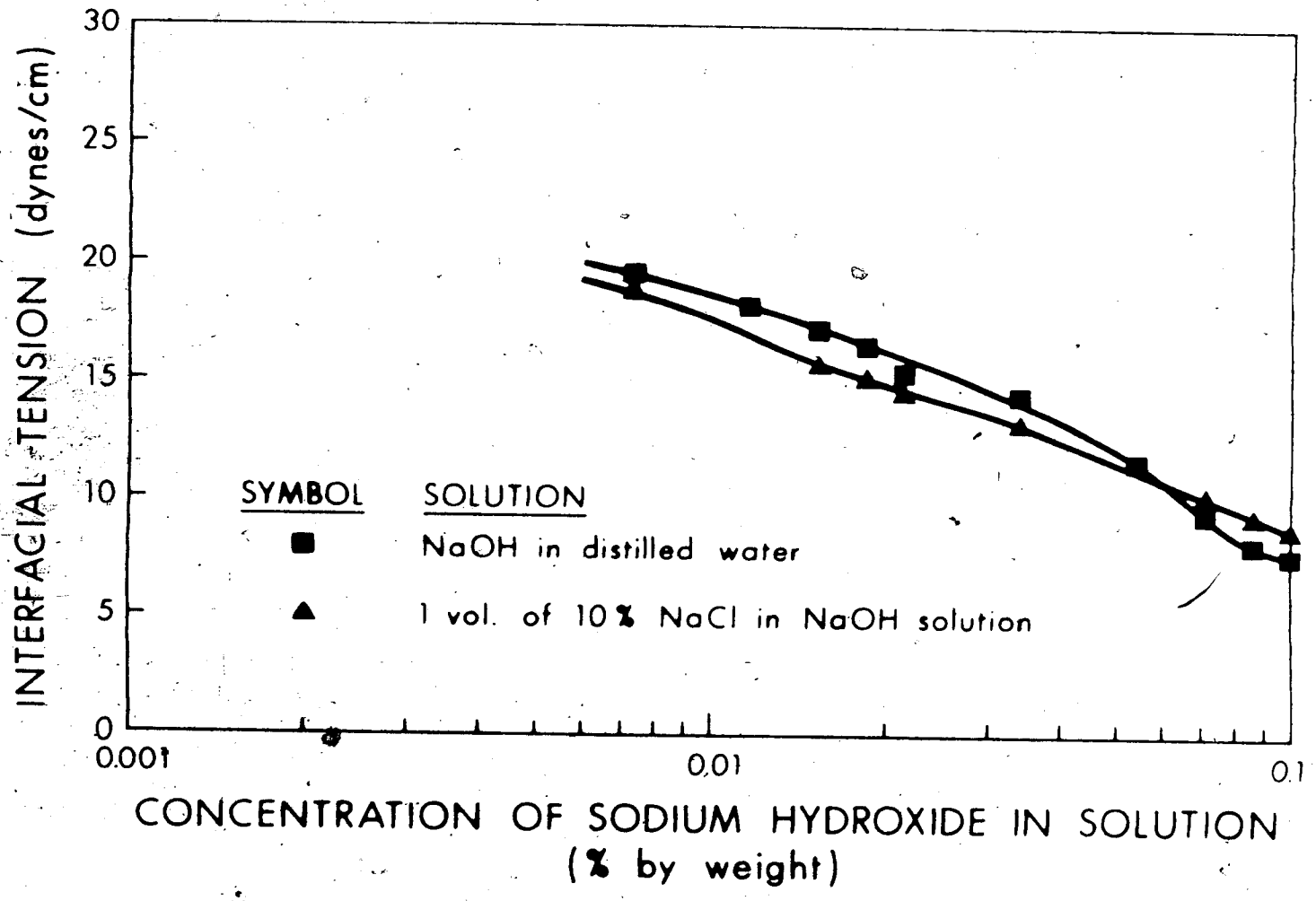

FIGURE 22 - Effect of Ionic Composition of Solution on Interfacial Tension

chloride progressively increased above the values obtained in the absence of sodium chloride.

PRACTICAL APPLICATION

The economics of waterflooding requires that as low a concentration as possible be used in the project. In accordance with this requirement, this investigation specifically used low concentration solutions in obtaining interfacial tension data. Such data obtained with the use of anionic surfactants indicate that effective reduction in interfacial tension becomes possible only at concentrations higher than those used in this investigation. This would involve higher cost. However, although the anionic surfactants investigated are not good interfacial tension reducers at low concentrations, nevertheless, they could be used in combination with non-ionic surfactants to provide characteristic wetting effect with which the anionics are commonly associated.

By means of the nitrogen foaming technique viscous crude oil polar constituents were induced to concentrate at the extended surface area of the nitrogen bubbles. As the froth of these surface active compounds aggregating at the bubble surface was periodically skimmed off the total concentration of the compounds in the crude oil apparently progressively decreased. Consequently, the interfacial activity correspondingly decreased. This simple technique could be used for the removal of a good fraction of crude oil

polar impurities for purposes of small scale laboratory investigations. It is a unique method whereby no heat is applied and crude oil components are not reconstituted.

CONCLUSIONS

The results of this experimental investigation led to the following conclusions:

(1) The visual observation of the interfacial films formed by various crude oils showed that they differ markedly in their physical characteristics.

(2) Physical characteristics of interfacial films are a function of crude oil composition; presence of non-ionic polar molecules in the solution; extent of adsorption; concentration of polar type constituents in the oil phase; and, in the case of alkaline solutions, ionic composition and pH of the substrate.

(3) Interfacial tension between heavy crude oils and water can be reduced to zero at very low surfactant concentrations in the water.

(4) Nonionic surfactant solutions were the most efficient in reducing interfacial tension at very low concentrations.

(5) Anionic surfactant solutions did not reduce interfacial tension between the crude oils and water at low anionic surfactant concentrations.

(6) The interfacial tension between the crude oils and field water was not reduced to zero within the range of sodium hydroxide concentrations studied.

(7) The interfacial tension between the crude oils and

sodium hydroxide is a function of pH, but the interfacial tension between the crude oils and surfactant solutions was independent of the pH of the surfactant substrate.

(8) The addition of sodium chloride to alkaline solution like sodium hydroxide did not reduce interfacial tension monotonically as reported by some earlier investigators, rather it reduced interfacial tension at low sodium hydroxide concentration while increasing it at higher concentrations.

(9) The milky white precipitates formed by the addition of sodium hydroxide to Imperial Judy Creek field water were a combination of insoluble hydroxides of calcium and magnesium.

(10) Atomic absorption tests indicated that any interaction between crude oils and distilled water was purely physical.

(11) A simple, new technique -- nitrogen foaming technique -- was used to reduce the concentration of surface active agents contained in the heavy (viscous) Lloydminster and Ethyl Lake crudes.

(T2) The foaming technique had no discernible effect on the constitution of Imperial Judy Creek and Leduc-Woodbend light crudes.

RECOMMENDATIONS

Further studies involving laboratory flood tests should be conducted in order to determine possible chemical loss and mechanisms for such loss. The degree of chemical loss, if any, will determine the chemical requirements and applicability of the range of concentrations studied.

In view of the fact that the nonionic surfactants have been found to be a powerful interfacial tension reducer and the anionics a good wetting agent, it may prove most advantageous to use a combination of these chemicals in displacement tests in order to fully investigate the effect of their complementary action.

The effect of sodium chloride on interfacial behavior should be more fully investigated. Other inorganic electrolytes, especially those high up in the electrochemical series, should also be tested.

The influence of temperature and pressure on the interfacial tension between aqueous surfactant solutions and crude oils should be investigated.

In some instances, terms specific to the field of surface chemistry have been used without definition, or a discussion of the term does not appear before they are formally used in this work. Some of the terms are either confused, misused or not properly understood in the petroleum industry. Such terms are defined here.

Adsorption: The adhesion of a thin film of molecules to a solid or liquid surface.

Amphoteric Surfactant: A surface-active material that ionizes in aqueous solution. The surface-active ion may bear a negative or a positive charge, depending upon the pH of the solution.

Anionic Surfactant: A surface-active material that ionizes in aqueous solution. The ion that bears a negative charge has a pronounced tendency to concentrate at the interface between two phases.

Cationic Surfactant: A surface-active agent that ionizes in aqueous solution, with the surface-active ion bearing a positive charge.

Contact Angle: The angle formed by a droplet in contact with a solid surface measured from within the droplet. An advancing contact angle is formed when the droplet advances on a fresh surface. A receding contact angle is formed when the droplet is withdrawn from a portion of the surface on

which it has been in contact.

Critical Surface Tension: The value of the liquid surface tension below which liquids will spread on a given solid.

Emulsion: A system consisting of two immiscible liquids, with one dispersed as small droplets in the other. In certain complex emulsions, a portion of the liquid constituting the external phase may also be found dispersed within droplets of the second liquid.

Free Surface Energy: A two-dimensional free energy term applied to a hyopthetical surface phase. Used interchangeably with surface free energy.

Hydrophilic: Having an affinity for water. A hydrophilic surface is one that is wet by water. A hydrophilic emulsifier is soluble in water and promotes the formation of an oil-in-water emulsion.

Hydrophobic: The opposite of hydrophilic.

Interface: The region between two contacting phases, generally two condensed phases.

Interfacial Tension: A force with the dimensions of dynes/cm. A measure of the work required to enlarge the interface by one square centimeter.

Non-ionic Surfactant: A surface-active agent that does not ionize in water.

Surface: The region between two contacting phases, generally a condensed and a gaseous phase.

Surface-active Agent: A substance that exhibits a

marked tendency to adsorb at a surface or interface.

Surface Tension: A force with the dimension of dynes/cm that is a measure of the work required to increase the area of a surface by one square centimeter.

Surfactant: A surface-active agent.

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APPENDIX A

FLUID PROPERTIES

TABLE A-1

CRUDE OIL PROPERTIES

LLOYD - Lloydminster Sparky Pool

ETHYL LAKE - Ethyl Lake Clearwater Formation

JUDY CREEK - Imperial Judy Creek Beaverhill Lake

LEDUC - Leduc-Woodbend 16-30-50-26W4M

Crude	API Gravity °API*	Density gm/cc	Bottom Sediment & Water % by Volume
LLOYD	15.10	0.9635	1.04
ETHYL LAKE	13.10	0.9769	0.18
JUDY CREEK	37.84	0.8340	<0.05
LEDUC	40.90	0.8191	<0.05

* @ 70°F.

TABLE A-2

PROPERTIES OF FIELD WATERS

Field Water N1	-	From Lloydminster Sparky Pool, Alberta Density - 1.052 gm/cc at 60°F pH - 7.56 @ 76.6°F
Field Water N2	-	From Ethyl Lake Clearwater Formation, Alberta Density - 0.999 gm/cm at 60°F pH - 7.65 @ 76.6°F
Field Water N3	-	From Sparky Pool, Chauvian South Unit #1 Density - 1.047 gm/cc at 60°F pH - 7.20 @ 76.6°F
Field Water N4*	-	From well Imperial Judy Creek 2-29BL-63-10W5M Beaverhill Lake Density - 1.110 gm/cc at 60°F pH - 7.15 @ 76.6°F

* Field Water N4 was used for all the testing not for reasons of any unique property but by virtue of its availability in larger quantity.

TABLE A-3

CHEMICAL ANALYSES OF FIELD WATERS

	Solids Content Milligrams/Litre			
Sample	N1	N2	N3	N4
Chlorides	44,400	2,320	40,900	97,000
Sulphates	7	88	8.0	1,007
Calcium	2,660	39	1,200	3,483
Magnesium	1,150	14	820	525
Sodium	23,000	858	23,000	55,167
Potassium	1,100	60	1,150	1,683
Copper	0.08	<0.05	0.07	0.15
Zinc	0.10	<0.05	0.05	0.10
Iron	18.94	--	3.28	13.50
Manganese	0.40	0.15	0.25	0.40
Total Solids	73,218	4,020	66,600	162,235
Conductivity	87,000	6,300	79,000	152,000
Hardness	9,883	234	5,910	9,178
Alkalinity	47	250	323	95
Nature of Alkalinity*	BCM	BCMS	BCM	BCM

* BCM - Bicarbonate of Calcium and Magnesium.
BCMS - Bicarbonate of Calcium, Magnesium and Soda.

TABLE A-4

IDENTIFICATION OF CHEMICALS TESTED

Chemical Name	Chemical Formula
Sodium Hydroxide	NaOH
Tergitol Nonionic 15-S-12	(Linear Alcohol C_{11} to C_{15})*
Tergitol Nonionic 15-S-7	(Linear Alcohol C_{11} to C_{15})*
Tergitol NPX	(Nonylphenol)*
Tergitol NP 35	(Nonylphenol)*
Tergitol Nonionic 15-S-9	(Linear Alcohol C_{11} to C_{15})*
Triton X-100 (Alkylaryl Polyether Alcohol)	
Tergitol 4 (Sodium Tetradecyl Sulfate)	
Tergitol 7 (Sodium Heptadecyl Sulfate)	

* Chemical formulae not known.

APPENDIX B

TEMPERATURE-VISCOSITY RESULTS

TABLE B-1

TEMPERATURE-VISCOSITY RESULTS

Temperature °F	Viscosity, cp — Crude Oil			
	LLOYD	ETHYL LAKE	JUDY CREEK	LEDUC
70	2,720	8,450	4.2	3.1
100	755.4	1,495.4	3.6	2.3
130	241.9	370	1.9	1.7
170*	--	119.2	1.4	1.3
210*	31.6	--	---	---

* Stream of bubbles escaping from the crude; an indication of possible loss of some light ends.

APPENDIX C

SURFACE TENSION TEST RESULTS

TABLE C-1

SURFACE TENSION DATA FOR WATER SAMPLES AND CRUDE OILS

Water Sample	Surface Tension (dynes/cm) Apparent	Corrected	Temperature °F
Distilled Water	76.00	71.06	72
Lloydminster Sparky Pool	62.40	57.41	74
Ethyl Lake Clearwater Formation	55.30	50.60	74
Sparky Pool, Chauvian South, Unit #1	46.80	42.35	74
Imperial Judy Creek Beaverhill Lake	55.10	50.14	74
Crude Oil Sample			
Lloydminster Sparky Pool	35.50	31.74	73
Ethyl Lake Clearwater Formation	37.80	33.94	73
Imperial Judy Creek	31.40	27.95	73
Leduc-Woodbend	29.50	26.26	73

TABLE C-2

SURFACE TENSION DATA ON SURFACE-AGEING PHENOMENON

Time Minutes	0.1% NaOH Concentration (Percent by Weight)		0.1% Tergitol NP-35 (Percent by Volume.)		0.1% Triton X-100 (Percent by Volume)	
	Surface Tension					
	Apparent (dynes/cm)	Corrected (dynes/cm)	Apparent (dynes/cm)	Corrected (dynes/cm)	Apparent (dynes/cm)	Corrected (dynes/cm)
1	62.50	57.69	40.80	36.72	34.70	31.06
3	72.00	67.10	40.50	36.45	34.60	30.97
5	75.25	70.40	40.50	36.45	34.60	30.97
7	76.40	71.50	40.50	36.45	34.50	30.88
10	75.60	70.72	40.40	36.40	34.30	30.66
12	76.50	71.60	40.40	36.40	34.35	30.68
15	76.30	71.40	40.50	36.45	34.50	30.88
20	75.80	71.90	40.50	36.45	34.35	30.68
25	75.70	70.81	40.40	36.40	34.50	30.88
30	76.10	71.20	40.50	36.45	34.10	30.45
60	75.60	70.72	40.50	36.45	34.00	30.33
90	75.80	70.90	40.30	36.38	33.85	30.16
120	76.10	71.20	40.40	36.40	33.90	30.21

APPENDIX D

INTERFACIAL TENSION TEST RESULTS

TABLE D-1

INTERFACIAL TENSION DATA FOR HEAVY CRUDE OILS AND DISTILLED WATER

Temperature °F	Interfacial Tension Apparent (dynes/cm)	Corrected (dynes/cm)
LLOYD CRUDE and Distilled Water		
77	22.56	28.04
87	21.80	27.25
100	21.60	26.14
120	20.20	23.76
130	20.00	23.20
ETHYL LAKE CRUDE and Distilled Water		
75	24.95	45.60
100	22.40	30.70
120	18.60	24.17
130	16.90	20.96
150	15.70	18.92
164	14.90	17.43

TABLE D-2

INTERFACIAL TENSION DATA FOR LIGHT CRUDE OILS AND DISTILLED WATER

Temperature °F	Interfacial Tension Apparent (dynes/cm)	Interfacial Tension Corrected (Dynes/cm)
JUDY CREEK CRUDE and Distilled Water		
79	26.76	27.03
90	26.80	27.87
110	26.10	26.07
130	26.00	25.87
150	24.40	24.06
164	21.60	21.04
LEDUC CRUDE and Distilled Water		
76	28.41	29.26
90	28.20	28.76
105	27.95	27.94
125	27.80	27.80
140	27.80	27.70
160	27.50	27.20
164	25.10	24.60

TABLE D-3

pH AND INTERFACIAL TENSION DATA FOR SOLUTIONS OF NaOH

IN DISTILLED WATER AND LLOYDMINSTER CRUDE OIL

NaOH Concentration* (Weight Percent)	pH Measured	Surface Tension		Interfacial Tension		Temperature (°F)
		Apparent (dynes/cm)	Corrected (dynes/cm)	Apparent (dynes/cm)	Corrected (dynes/cm)	
0	5.94	76.20	71.25	22.30	28.10	72
0.002	10.48	75.25	70.36	13.70	15.72	72
0.004	10.80	76.20	71.25	11.60	12.93	72
0.006	11.10	75.16	70.28	8.00	8.48	74
0.008	11.25	76.18	71.23	5.20	5.20	74
0.01	11.38	76.30	71.34	2.70	2.54	74
0.02	11.65	75.80	70.87	1.45	1.31	76
0.04	11.92	75.75	70.83	0.35	0.30	76
0.06	12.12	76.00	71.06	<0.35	<0.30	76
0.08	12.25	75.60	70.69	<0.35	<0.30	76
0.1	12.36	76.10	71.15	<0.35	<0.30	76

* No precipitate formed at any NaOH concentration.

TABLE D-4

pH AND INTERFACIAL TENSION DATA FOR SOLUTIONS OF NaOH IN DISTILLED WATER AND ETHYL LAKE CRUDE OIL

NaOH Concentration* (Weight Percent)	pH Measured	Surface Tension		Interfacial Tension		Temperature (°F)
		Apparent (dynes/cm)	Corrected (dynes/cm)	Apparent (dynes/cm)	Corrected (dynes/cm)	
0	5.94	76.20	71.25	14.60	18.72	77
0.002	10.68	75.25	70.36	14.55	18.62	77
0.004	11.00	76.20	71.25	11.10	13.43	77
0.006	11.15	75.16	70.28	8.45	9.73	77
0.008	11.30	76.18	71.23	6.00	6.54	77
0.01	11.38	76.30	71.34	4.55	4.78	77
0.02	11.60	75.80	70.87	2.35	2.28	72
0.04	11.90	75.75	70.83	0.85	0.77	72
0.06	12.12	76.00	71.06	0.43	0.38	75
0.08	12.25	75.60	70.69	<0.35	<0.35	75
0.1	12.36	76.10	71.15	<0.35	<0.35	75

* No precipitate formed at any NaOH concentration.

TABLE D-5

pH AND INTERFACIAL TENSION DATA FOR SOLUTIONS OF NaOH IN DISTILLED WATER AND IMPERIAL JUDY CREEK CRUDE OIL

NaOH Concentration* (Weight Percent)	pH Measured	Surface Tension		Interfacial Tension		Temperature (°F)
		Apparent (dynes/cm)	Corrected (dynes/cm)	Apparent (dynes/cm)	Corrected (dynes/cm)	
0	5.94	76.20	71.25	23.50	23.36	74
0.002	10.68	75.25	70.36	20.00	19.50	74
0.004	11.00	76.20	71,25	18.70	18.14	74
0.006	11.15	75.16	70:28	17.75	17.15	74
0.008	11.30	76.18	71.23	17.15	16.50	74
0.01	11.38	76.30	71.34	16.00	15.30	74
0.02	11.65	75.80	70.87	15.20	14.44	74
0.04	11.95	75.75	70.83	12.40	11.60	74
0.06	12.12	76.00	71.06	10.20	9.42	74
0.08	12.25	75.60	70.69	8.90	8.14	74
0.1	12.36	76.10	71.15	8.40	7.64	74

* No precipitate formed at any NaOH concentration.

TABLE D-6

pH AND INTERFACIAL TENSION DATA FOR SOLUTIONS OF NaOH IN DISTILLED WATER AND LEDUC-WOODBEND CRUDE OIL

NaOH Concentration* (Weight Percent)	pH Measured	Surface Tension		Interfacial Tension		Temperature (°F)
		Apparent (dynes/cm)	Corrected (dynes/cm)	Apparent (dynes/cm)	Corrected (dynes/cm)	
0	5.94	76.20	71.25	25.00	24.80	72
0.002	10.55	75.25	70.36	26.90	26.85	72
0.004	10.90	76.20	71.25	26.40	26.29	72
0.006	11.05	75.16	70.28	25.30	25.10	72
0.008	11.20	76.18	71.23	24.60	24.35	72
0.01	11.30	76.30	71.34	24.25	23.93	72
0.02	11.70	75.80	70.87	23.80	23.44	72
0.04	11.98	75.75	70.83	22.20	21.76	72
0.06	12.28	76.00	71.06	21.20	20.67	72
0.08	12.45	75.60	70.69	20.60	20.00	72
0.1	12.65	76.10	71.15	17.90	17.10	72

* No precipitate formed at any NaOH concentration.

TABLE D-7

pH AND INTERFACIAL TENSION DATA FOR SOLUTIONS OF TERGITOL 15-S-7 IN DISTILLED WATER AND LLOYDMINSTER CRUDE OIL

Tergitol 15-S-7 Concentration* (Weight Percent)	pH Measured	Surface Tension		Interfacial Tension		Temperature (°F)
		Apparent (dynes/cm)	Corrected (dynes/cm)	Apparent (dynes/cm)	Corrected (dynes/cm)	
0	6.17	76.10	71.15	22.30	28.10	72
0.002	7.65	36.60	32.76	9.10	9.78	72
0.004	6.15	34.45	30.84	5.40	5.43	72
0.006	6.10	33.50	29.82	3.50	3.36	72
0.008	6.25	32.70	29.10	2.00	1.84	72
0.01	6.30	32.30	28.75	0.90	0.80	72
0.02	6.29	31.80	28.30	<0.40	<0.40	72
0.04	5.85	31.30	27.83	<0.40	<0.40	72
0.06	6.10	31.50	28.00	<0.40	<0.40	72
0.08	6.09	31.10	27.65	<0.40	<0.40	72
0.1	5.75	31.30	27.83	<0.40	<0.40	72

* No precipitate formed at any Tergitol 15-S-7 concentration.

TABLE D-8

pH AND INTERFACIAL TENSION DATA FOR SOLUTIONS OF TERGITOL 15-S-7 IN DISTILLED WATER AND ETHYL LAKE CRUDE OIL

Tergitol 15-S-7 Concentration* (Weight Percent)	pH Measured	Surface Tension		Interfacial Tension		Temperature (°F)
		Apparent (dynes/cm)	Corrected (dynes/cm)	Apparent (dynes/cm)	Corrected (dynes/cm)	
0	6.17	76.10	71.15	14.60	18.72	72
0.002	7.65	36.60	32.76	6.10	6.67	72
0.004	6.15	34.45	30.84	4.00	4.14	72
0.006	6.10	33.50	29.82	3.40	3.44	72
0.008	6.25	32.70	29.10	2.10	2.02	72
0.01	6.30	32.30	28.75	1.20	1.11	72
0.02	6.29	31.80	28.30	0.50	0.44	72
0.04	5.85	31.30	27.83	<0.40	<0.40	72
0.06	6.10	31.50	28.00	<0.40	<0.40	72
0.08	6.09	31.10	27.65	<0.40	<0.40	72
0.1	5.75	31.30	27.83	<0.40	<0.40	72

* No precipitate formed at any Tergitol 15-S-7 concentration.

TABLE D-9

pH AND INTERFACIAL TENSION DATA FOR SOLUTIONS OF TERGITOL 15-S-7 IN DISTILLED WATER AND IMPERIAL JUDY CREEK CRUDE OIL

Tergitol 15-S-7 Concentration* (Weight Percent)	pH Measured	Surface Tension		Interfacial Tension		Temperature (°F)
		Apparent (dynes/cm)	Corrected (dynes/cm)	Apparent (dynes/cm)	Corrected (dynes/cm)	
0	6.17	76.10	71.15	23.50	23.36	72
0.002	7.65	36.60	32.76	15.00	14.25	72
0.004	6.15	34.45	30.84	13.80	13.04	72
0.006	6.10	33.50	29.82	11.70	10.88	72
0.008	6.25	32.70	29.10	11.50	10.71	72
0.01	6.30	32.30	28.75	11.20	10.39	72
0.02	6.29	31.80	28.30	9.30	8.56	72
0.04	5.85	31.30	27.83	5.80	5.19	72
0.06	6.10	31.50	28.00	5.50	4.91	72
0.08	6.09	31.10	27.65	4.70	4.17	72
0.1	5.75	31.30	27.83	2.50	2.18	72

* No precipitate formed at any Tergitol 15-S-7 concentration.

TABLE D-10

pH AND INTERFACIAL TENSION DATA FOR SOLUTIONS OF TERGITOL 15-S-7 IN DISTILLED WATER AND LEDUC-WOODBEND CRUDE OIL

Tergitol 15-S-7 Concentration (Weight Percent)	pH Measured	Surface Tension		Interfacial Tension		Temperature (°F)
		Apparent (dynes/cm)	Corrected (dynes/cm)	Apparent (dynes/cm)	Corrected (dynes/cm)	
0	6.17	76.10	71.15	25.05	24.80	74
0.002	7.65	36.60	32.76	16.30	15.49	74
0.004	6.15	34.45	30.84	14.20	13.38	74
0.006	6.10	33.50	29.82	12.35	11.49	74
0.008	6.25	32.70	29.10	11.65	10.78	74
0.01	6.30	32.30	28.75	11.50	10.63	74
0.02	6.29	31.80	28.30	9.50	8.68	74
0.04	5.85	31.30	27.83	7.30	6.57	74
0.06	6.10	31.50	28.00	6.00	5.35	74
0.08	6.09	31.10	27.65	5.50	4.88	74
0.1	5.75	31.30	27.83	4.70	4.16	74

* No precipitate formed at any Tergitol 15-S-7 concentration.

TABLE D-11

pH AND INTERFACIAL TENSION DATA FOR SOLUTIONS OF TERGITOL NPX IN DISTILLED WATER AND LLOYDMINSTER CRUDE OIL

Tergitol NPX Concentration* (Weight Percent)	pH Measured	Surface Tension		Interfacial Tension		Temperature (°F)
		Apparent (dynes/cm)	Corrected (dynes/cm)	Apparent (dynes/cm)	Corrected (dynes/cm)	
0	5.90	76.20	71.15	22.30	28.10	74
0.002	6.23	37.40	33.51	5.10	5.10	74
0.004	6.30	35.60	31.83	3.00	2.85	74
0.006	6.50	34.40	30.79	1.60	1.45	74
0.008	6.20	34.20	30.47	1.10	0.98	74
0.01	6.28	34.10	30.45	0.70	0.61	74
0.02	6.24	34.60	30.86	<0.40	<0.40	74
0.04	6.20	34.20	30.47	<0.40	<0.40	74
0.06	6.20	34.80	31.15	<0.40	<0.40	74
0.08	6.05	34.40	30.79	<0.40	<0.40	74
0.1	6.10	34.50	30.81	<0.40	<0.40	74

* No precipitate formed at any Tergitol NPX concentration.

TABLE D-12

pH AND INTERFACIAL TENSION DATA FOR SOLUTIONS OF TERGITOL NPX IN DISTILLED WATER AND ETHYL LAKE CRUDE OIL

Tergitol NPX Concentration* (Weight Percent)	pH Measured	Surface Tension		Interfacial Tension		Temperature (°F)
		Apparent (dynes/cm)	Corrected (dynes/cm)	Apparent (dynes/cm)	Corrected (dynes/cm)	
0	5.90	76.20	71.15	14.60	18.72	72
0.002	6.23	37.40	33.51	4.90	5.19	72
0.004	6.30	35.60	31.83	3.00	3.00	72
0.006	[illegible].50	34.40	30.79	1.50	1.40	72
0.008	6.20	34.20	30.47	0.80	0.72	72
0.01	6.28	34.10	30.45	0.60	0.53	72
0.02	6.24	34.60	30.86	<0.40	<0.40	72
0.04	6.20	34.20	30.47	<0.40	<0.40	72
0.06	6.20	34.80	31.15	<0.40	<0.40	72
0.08	6.05	34.40	30.79	<0.40	<0.40	72
0.1	6.10	[illegible].50	30.81	<0.40	<0.40	72

* No precipitate formed at any Tergitol NPX concentration.

TABLE D-13

pH AND INTERFACIAL TENSION DATA FOR SOLUTIONS OF TERGITOL NPX IN DISTILLED WATER AND IMPERIAL JUDY CREEK CRUDE OIL

Tergitol NPX Concentration* (Weight Percent)	pH Measured	Surface Tension		Interfacial Tension		Temperature (°F)
		Apparent (dynes/cm)	Corrected (dynes/cm)	Apparent (dynes/cm)	Corrected (dynes/cm)	
0	5.90	76.20	71.15	23.50	23.36	72
0.002	6.23	37.40	33.51	11.90	11.10	72
0.004	6.30	35.60	31.83	9.00	8.24	72
0.006	6.50	34.40	30.79	7.40	6.70	72
0.008	6.20	34.20	30.47	6.90	6.21	72
0.01	6.28	34.10	30.45	6.00	5.38	72
0.02	6.24	34.60	30.86	4.35	3.84	72
0.04	6.20	34.20	30.47	2.80	2.44	72
0.06	6.20	34.80	31.15	2.45	2.13	72
0.08	6.05	34.40	30.79	2.00	1.73	72
0.1	6.10	34.50	30.82	1.70	1.46	72

* No precipitate formed at any Tergitol NPX concentration.

TABLE D-14

pH AND INTERFACIAL TENSION DATA FOR SOLUTIONS OF TERGITOL NPX IN DISTILLED WATER AND LEDUC-WOODBEND CRUDE OIL

Tergitol NPX Concentration* (Weight Percent)	pH Measured	Surface Tension		Interfacial Tension		Temperature (°F)
		Apparent (dynes/cm)	Corrected (dynes/cm)	Apparent (dynes/cm)	Corrected (dynes/cm)	
0	5.90	76.20	71.15	25.05	24.85	75
0.002	6.23	37.40	33.51	13.50	12.62	75
0.004	6.30	35.60	31.83	11.10	10.27	75
0.006	6.50	34.40	30.79	8.70	7.83	75
0.008	6.20	34.20	30.47	7.55	6.81	75
0.01	6.28	34.10	30.45	6.20	5.54	75
0.02	6.24	34.60	30.86	4.30	3.78	75
0.04	6.20	34.20	30.47	3.50	3.07	75
0.06	6.20	34.80	31.15	3.20	2.79	75
0.08	6.05	34.40	30.79	2.60	2.26	75
0.1	6.10	34.50	30.81	2.20	1.91	75

* No precipitate formed at any Tergitol NPX concentration.

TABLE D-15

pH AND INTERFACIAL TENSION DATA FOR SOLUTIONS OF TRITON X-100 IN DISTILLED WATER AND LLOYDMINSTER CRUDE OIL

Triton X-100 Concentration* (Weight Percent)	pH Measured	Surface Tension		Interfacial Tension		Temperature (°F)
		Apparent (dynes/cm)	Corrected (dynes/cm)	Apparent (dynes/cm)	Corrected (dynes/cm)	
0	5.90	76.20	71.15	22.30	28.10	72
0.002	5.94	43.45	39.24	4.40	4.33	72
0.004	6.75	39.20	35.10	2.90	2.74	72
0.006	5.84	37.80	33.91	1.85	1.69	72
0.008	5.93	36.10	32.35	1.20	1.07	72
0.01	6.07	35.10	31.38	0.80	0.70	72
0.02	6.65	33.30	29.74	0.42	0.36	72
0.04	6.20	33.90	30.24	<0.40	<0.35	72
0.06	6.39	33.80	30.14	<0.40	<0.35	72
0.08	6.51	34.00	30.36	<0.40	<0.35	72
0.1	6.45	34.10	30.46	<0.40	<0.35	72

* No precipitate formed at any Triton X-100 concentration.

TABLE D-16

pH AND INTERFACIAL TENSION DATA FOR SOLUTIONS OF TRITON X-100 IN DISTILLED WATER AND ETHYL LAKE CRUDE OIL

Triton X-100 Concentration* (Weight Percent)	pH Measured	Interfacial Tension		Temperature (°F)
		Apparent (dynes/cm)	Corrected (dynes/cm)	
0	5.90	14.60	18.72	72
0.002	6.78	7.50	8.48	72
0.004	6.51	6.00	6.54	72
0.006	6.36	4.90	5.19	72
0.008	6.10	3.80	2.90	72
0.01	6.08	2.80	2.77	72
0.02	7.10	1.80	1.71	72
0.04	6.50	1.00	0.91	72
0.06	6.30	0.40	0.35	72
0.08	6.40	<0.40	<0.35	72
0.1	6.60	<0.40	<0.35	72

* No precipitate formed at any Triton X-100 concentration.

TABLE D-17

pH AND INTERFACIAL TENSION DATA FOR SOLUTIONS OF TRITON X-100 IN DISTILLED WATER AND IMPERIAL JUDY CREEK CRUDE OIL

Triton X-100 Concentration* (Weight Percent)	pH Measured	Interfacial Tension		Temperature (°F)
		Apparent (dynes/cm)	Corrected (dynes/cm)	
0	5.90	23.50	23.36	72
0.002	6.78	14.70	13.97	72
0.004	6.51	13.90	13.14	72
0.006	6.36	11.60	10.81	72
0.008	6.10	10.35	9.55	72
0.01	6.08	9.80	9.02	72
0.02	7.10	7.10	6.30	72
0.04	6.50	5.20	4.63	72
0.06	6.30	3.70	3.26	72
0.08	6.40	3.00	2.63	72
0.1	6.60	2.50	2.18	72

* No precipitate formed at any Triton X-100 concentration.

TABLE D-18

pH AND INTERFACIAL TENSION DATA FOR SOLUTIONS OF TRITON X-100 IN DISTILLED WATER AND LEDUC-WOODBEND CRUDE OIL

Triton X-100 Concentration* (Weight Percent)	pH Measured	Interfacial Tension		Temperature (°F)
		Apparent (dynes/cm)	Corrected (dynes/cm)	
0	5.90	25.00	24.80	72
0.002	5.94	17.00	16.24	72
0.004	6.75	15.50	14.69	72
0.006	5.84	13.30	12.44	72
0.008	5.93	11.70	10.82	72
0.01	6.07	10.90	10.03	72
0.02	6.65	7.65	6.90	72
0.04	6.20	5.60	4.93	72
0.06	6.39	4.85	4.30	72
0.08	6.51	4.10	3.61	72
0.1	6.45	3.50	3.10	72

**No precipitate formed at any Triton X-100 concentration.

TABLE D-19

pH AND INTERFACIAL TENSION DATA FOR SOLUTIONS OF TERGITOL NP-35 IN DISTILLED WATER AND LLOYDMINSTER CRUDE OIL

Tergitol NP-35 Concentration* (Weight Percent)	pH Measured	Surface Tension		Interfacial Tension		Temperature (°F)
		Apparent (dynes/cm)	Corrected (dynes/cm)	Apparent (dynes/cm)	Corrected (dynes/cm)	
0	5.90	76.20	71.15	22.30	28.10	72
0.002	6.40	45.15	40.86	5.10	5.10	72
0.004	5.72	44.85	40.59	4.00	3.90	72
0.006	5.20	41.40	37.26	2.20	2.04	72
0.008	5.45	40.40	36.36	1.50	1.36	72
0.01	5.28	39.30	35.17	1.00	0.89	72
0.02	5.30	40.30	36.32	0.60	0.52	72
0.04	5.15	40.20	36.30	0.37	0.32	72
0.06	5.20	39.60	35.44	<0.37	<0.32	72
0.08	5.25	40.10	36.10	<0.37	<0.32	72
0.1	5.15	40.60	36.54	<0.37	<0.32	72

* No precipitate formed at any Tergitol NP-35 concentration.

TABLE D-20

pH AND INTERFACIAL TENSION DATA FOR SOLUTIONS OF TERGITOL NP-35 IN DISTILLED WATER AND ETHYL LAKE CRUDE OIL

Tergitol NP-35 Concentration* (Weight Percent)	pH Measured	Interfacial Tension		Temperature (°F)
		Apparent (dynes/cm)	Corrected (dynes/cm)	
0	5.90	14.60	18.72	72
0.002	6.42	4.90	5.19	72
0.004	6.22	3.60	3.67	72
0.006	6.10	2.00	1.92	72
0.008	6.38	1.30	1.20	72
0.01	7.22	1.00	0.91	72
0.02	6.11	0.60	0.53	72
0.04	6.22	0.40	0.35	72
0.06	5.98	<0.40	<0.35	72
0.08	5.96	<0.40	<0.35	72
0.1	6.16	<0.40	<0.35	72

* No precipitate formed at any Tergitol NP-35 concentrations.

TABLE D-21

pH AND INTERFACIAL TENSION DATA FOR SOLUTIONS OF TERGITOL NP-35 IN DISTILLED WATER AND IMPERIAL JUDY CREEK CRUDE OIL

Tergitol NP-35 Concentration (Weight Percent)	pH Measured	Interfacial Tension		Temperature (°F)
		Apparent (dynes/cm)	Corrected (dynes/cm)	
0	5.90	23.50	23.36	72
0.002	6.42	11.30	10.51	72
0.004	6.22	8.10	7.47	72
0.006	6.10	6.80	6.12	72
0.008	6.38	5.80	5.19	72
0.01	7.22	5.00	4.45	72
0.02	6.11	3.60	3.16	72
0.04	6.22	3.00	2.62	72
0.06	5.98	2.80	2.42	72
0.08	5.96	2.55	2.22	72
0.1	6.16	2.33	2.02	72

* No precipitate formed at any Tergitol NP-35 concentration.

TABLE D-22

pH AND INTERFACIAL TENSION DATA FOR SOLUTIONS OF TERGITOL NP-35 IN DISTILLED WATER AND LEDUC-WOODBEND CRUDE OIL

Tergitol NP-35 Concentration* (Weight Percent)	pH Measured	Interfacial Tension		Temperature (°F)
		Apparent (dynes/cm)	Corrected (dynes/cm)	
0	5.90	25.00	24.80	72
0.002	6.40	13.90	13.07	72
0.004	5.72	10.75	9.91	72
0.006	5.20	8.80	8.01	72
0.008	5.45	8.10	7.33	72
0.01	5.28	6.65	5.96	72
0.02	5.30	4.95	4.38	72
0.04	5.15	4.35	3.84	72
0.06	5.20	3.50	3.07	72
0.08	5.25	3.10	2.71	72
0.1	5.15	2.90	2.52	72

* No precipitate formed at any Tergitol NP-35 concentration.

TABLE D-23

pH AND INTERFACIAL TENSION DATA FOR SOLUTIONS OF TERGITOL 15-S-12 IN DISTILLED WATER AND LLOYDMINSTER CRUDE OIL

Tergitol 15-S-12 Concentration* (Weight Percent)	pH Measured	Surface Tension		Interfacial Tension		Temperature (°F)
		Apparent (dynes/cm)	Corrected (dynes/cm)	Apparent (dynes/cm)	Corrected (dynes/cm)	
0	5.90	76.20	71.15	22.30	28.10	72
0.002	5.39	38.40	34.48	4.85	4.81	72
0.004	5.30	38.00	34.10	3.95	3.85	72
0.006	5.28	36.50	32.67	3.15	3.01	72
0.008	5.40	36.55	32.71	1.75	1.60	72
0.01	5.40	35.65	31.91	1.10	0.98	72
0.02	5.28	35.10	31.44	0.75	0.66	72
0.04	5.20	35.30	31.59	0.40	0.35	72
0.06	5.10	35.40	31.68	<0.40	<0.35	72
0.08	5.05	35.20	31.52	<0.40	<0.35	72
0.1	5.10	35.30	31.59	<0.40	<0.35	72

* No precipitate formed at any Tergitol 15-S-12 concentration.

TABLE D-24

pH AND INTERFACIAL TENSION DATA FOR SOLUTIONS OF TERGITOL 15-S-12 IN DISTILLED WATER AND ETHYL LAKE CRUDE OIL

Tergitol 15-S-12 Concentration* (Weight Percent)	pH Measured	Interfacial Tension		Temperature (°F)
		Apparent (dynes/cm)	Corrected (dynes/cm)	
0	5.90	14.60	18.72	72
0.002	5.39	5.00	5.33	72
0.004	5.30	3.80	3.90	72
0.006	5.28	3.10	3.10	72
0.008	5.40	1.70	1.61	72
0.01	5.40	0.95	0.86	72
0.02	5.28	0.70	0.63	72
0.04	5.20	0.40	0.35	72
0.06	5.10	<0.40	<0.35	72
0.08	5.05	<0.40	<0.35	72
0.1	5.10	<0.40	<0.35	72

* No precipitate formed at any Tergitol 15-S-12 concentration.

TABLE D-26

pH AND INTERFACIAL TENSION DATA FOR SOLUTIONS OF TERGITOL 15-S-12 IN DISTILLED WATER AND LEDUC-WOODBEND CRUDE OIL

Tergitol 15-S-12 Concentration* (Weight Percent)	pH Measured	Interfacial Tension		Temperature (°F)
		Apparent (dynes/cm)	Corrected (dynes/cm)	
0	5.90	25.00	24.80	72
0.002	5.39	16.50	15.68	72
0.004	5.38	13.45	12.58	72
0.006	5.28	11.65	10.78	72
0.008	5.40	10.40	9.57	72
0.01	5.40	9.65	8.83	72
0.02	5.28	7.20	6.48	72
0.04	5.20	5.35	4.75	72
0.06	5.10	4.60	4.05	72
0.08	5.05	3.85	3.38	72
0.1	5.10	2.95	2.57	72

* No precipitate formed at any Tergitol 15-S-12 concentration.

TABLE D-27

pH AND INTERFACIAL TENSION DATA FOR SOLUTIONS OF TERGITOL 15-S-9 IN DISTILLED WATER AND LLOYDMINSTER CRUDE OIL

Tergitol 15-S-9 Concentration* (Weight Percent)	pH Measured	Surface Tension		Interfacial Tension		Temperature (°F)
		Apparent (dynes/cm)	Corrected (dynes/cm)	Apparent (dynes/cm)	Corrected (dynes/cm)	
0	5.90	76.20	71.15	22.30	28.10	72
0.002	5.80	36.40	32.54	5.90	5.99	72
0.004	5.62	35.00	31.22	3.85	3.73	72
0.006	5.62	34.50	30.81	2.65	2.49	72
0.008	5.70	34.60	30.90	1.85	1.69	72
0.01	5.70	34.75	31.03	1.20	1.07	72
0.02	6.10	33.30	29.64	0.85	0.75	72
0.04	5.70	33.10	29.46	0.50	0.44	72
0.06	5.65	33.45	29.77	<0.40	<0.35	72
0.08	5.71	33.70	30.00	<0.40	<0.35	72
0.1	5.70	33.50	29.80	<0.40	<0.35	72

* No precipitate formed at any Tergitol 15-S-9 concentration.

TABLE D-28

pH AND INTERFACIAL TENSION DATA FOR SOLUTIONS OF TERGITOL 15-S-9 IN DISTILLED WATER AND ETHYL LAKE CRUDE OIL

Tergitol 15-S-9 Concentration* (Weight Percent)	pH Measured	Interfacial Tension		Temperature (°F)
		Apparent (dynes/cm)	Corrected (dynes/cm)	
0	5.90	14.60	18.72	72
0.002	5.80	5.70	6.16	72
0.004	5.62	3.80	3.90	72
0.006	5.62	2.40	2.34	72
0.008	5.70	1.70	1.61	72
0.01	5.70	1.40	1.30	72
0.02	6.10	0.70	0.63	72
0.04	5.70	0.40	0.35	72
0.06	5.65	<0.40	<0.35	72
0.08	5.71	<0.40	<0.35	72
0.1	5.70	<0.40	<0.35	72

* No precipitate formed at any Tergitol 15-S-9 concentration.

TABLE D-29

pH AND INTERFACIAL TENSION DATA FOR SOLUTIONS OF TERGITOL 15-S-9 IN DISTILLED WATER AND IMPERIAL JUDY CREEK CRUDE OIL

Tergitol 15-S-9 Concentration* (Weight Percent)	pH Measured	Interfacial Tension		Temperature (°F)
		Apparent (dynes/cm)	Corrected (dynes/cm)	
0	5.90	23.50	23.36	72
0.002	5.80	12.30	11.50	72
0.004	5.62	11.10	10.32	72
0.006	5.62	10.90	9.46	72
0.008	5.70	9.80	9.00	72
0.01	5.70	9.50	8.74	72
0.02	6.10	7.00	6.30	72
0.04	5.70	5.60	5.01	72
0.06	5.65	3.80	3.34	72
0.08	5.71	3.40	3.00	72
0.1	5.70	3.10	2.71	72

* No precipitate formed at any Tergitol 15-S-9 concentration.

TABLE D-30

pH AND INTERFACIAL TENSION DATA FOR SOLUTIONS OF TERGITOL 15-S-9 IN DISTILLED WATER AND LEDUC-WOODBEND CRUDE OIL

Tergitol 15-S-9 Concentration* (Weight Percent)	pH Measured	Interfacial Tension		Temperature (°F)
		Apparent (dynes/cm)	Corrected (dynes/cm)	
0	5.90	25.00	24.80	72
0.002	5.80	18.50	17.76	72
0.004	5.62	15.10	14.27	72
0.006	5.62	12.40	11.53	72
0.008	5.70	11.30	10.44	72
0.01	5.70	10.35	9.52	72
0.02	6.10	8.60	7.83	72
0.04	5.70	6.15	5.50	72
0.06	5.65	5.00	4.44	72
0.08	5.71	4.55	4.02	72
0.1	5.70	4.00	3.51	72

* No precipitate formed at any Tergitol 15-S-9 concentration.

TABLE D-31

pH AND INTERFACIAL TENSION DATA FOR SOLUTIONS OF TERGITOL 4 IN DISTILLED WATER AND LLOYDMINSTER CRUDE OIL

Tergitol 4 Concentration* (Weight Percent)	pH Measured	Surface Tension		Interfacial Tension		Temperature (°F)
		Apparent (dynes/cm)	Corrected (dynes/cm)	Apparent (dynes/cm)	Corrected (dynes/cm)	
0	5.90	76.20	71.15	22.30	28.10	72
0.002	6.20	61.80	56.98	14.30	16.52	72
0.004	6.15	66.80	62.46	14.70	17.08	72
0.006	6.95	57.80	53.18	14.30	16.52	72
0.008	6.33	62.80	58.03	14.20	16.37	72
0.01	6.45	67.30	62.59	14.70	17.08	74
0.02	6.65	65.40	60.50	14.90	17.34	74
0.04	6.65	65.70	60.77	14.00	16.14	74
0.06	6.92	62.90	57.99	14.60	16.94	74
0.08	7.10	61.70	56.46	14.70	17.08	74
0.1	7.35	63.20	58.33	13.90	15.99	74

* No precipitate formed at any Tergitol 4 concentration.

TABLE D-32

pH AND INTERFACIAL TENSION DATA FOR SOLUTIONS OF TERGITOL 4 IN DISTILLED WATER AND ETHYL LAKE CRUDE OIL

Tergitol 4 Concentration* (Weight Percent)	pH Measured	Interfacial Tension		Temperature (°F)
		Apparent (dynes/cm)	Corrected (dynes/cm)	
0	5.90	14.60	18.72	72
0.002	6.20	12.70	15.70	72
0.004	6.15	12.80	15.87	72
0.006	6.95	12.60	15.60	72
0.008	6.33	12.50	15.42	72
0.01	6.45	12.80	15.87	72
0.02	6.65	12.70	15.70	72
0.04	6.65	12.60	15.60	72
0.06	6.92	12.80	15.87	72
0.08	7.10	12.70	15.70	72
0.1	7.35	11.80	14.49	72

* No precipitate formed at any Tergitol 4 concentration.

TABLE D-33

pH AND INTERFACIAL TENSION DATA FOR SOLUTIONS OF TERGITOL 4 IN DISTILLED WATER AND IMPERIAL JUDY CREEK CRUDE OIL

Tergitol 4 Concentration* (Weight Percent)	pH Measured	Surface Tension		Interfacial Tension		Temperature (°F)
		Apparent (dynes/cm)	Corrected (dynes/cm)	Apparent (dynes/cm)	Corrected (dynes/cm)	
0	5.90	76.20	71.15	23.50	23.36	72
0.002	6.20	60.30	55.48	24.30	24.30	72
0.004	6.15	57.80	53.18	24.60	24.60	72
0.006	6.95	59.80	55.08	24.70	24.70	72
0.008	6.33	57.10	52.53	24.20	24.20	72
0.01	6.45	58.60	53.91	24.40	24.40	72
0.02	6.65	57.70	53.16	24.60	24.60	72
0.04	6.65	56.40	51.66	23.80	23.66	72
0.06	6.92	56.40	51.66	23.60	23.46	72
0.08	7.10	57.80	53.18	23.30	23.07	72
0.1	7.35	54.80	50.14	23.50	23.30	72

* No precipitate formed at any Tergitol 4 concentration.

TABLE D-34

pH AND INTERFACIAL TENSION DATA FOR SOLUTIONS OF TERGITOL 4 IN DISTILLED WATER AND LEDUC-WOODBEND CRUDE OIL

Tergitol 4 Concentration* (Weight Percent)	pH Measured	Interfacial Tension		Temperature (°F)
		Apparent (dynes/cm)	Corrected (dynes/cm)	
0	5.90	25.00	24.80	76
0.002	6.20	27.70	27.78	76
0.004	6.15	27.75	27.81	76
0.006	6.95	27.20	27.20	76
0.008	6.33	27.30	27.30	76
0.01	6.45	27.75	27.81	76
0.02	6.65	27.60	27.66	76
0.04	6.65	27.50	27.56	76
0.06	6.92	26.70	26.70	76
0.08	7.10	27.60	27.66	76
0.1	7.35	27.00	27.00	76

* No precipitate formed at any Tergitol 4 concentration.

TABLE D-35

pH AND INTERFACIAL TENSION DATA FOR SOLUTIONS OF TERGITOL 7 IN DISTILLED WATER AND LLOYDMINSTER CRUDE OIL

Tergitol 7 Concentration* (Weight Percent)	pH Measured	Surface Tension		Interfacial Tension		Temperature (°F)
		Apparent (dynes/cm)	Corrected (dynes/cm)	Apparent (dynes/cm)	Corrected (dynes/cm)	
0	5.90	76.20	71.15	22.30	28.10	72
0.002	6.05	58.90	54.20	13.30	15.03	72
0.004	5.48	59.10	54.37	13.60	15.57	72
0.006	5.40	55.50	50.78	13.40	15.34	72
0.008	6.22	54.60	50.00	13.75	15.79	72
0.01	5.80	53.60	49.04	13.60	15.57	72
0.02	6.33	58.00	53.36	13.40	15.34	72
0.04	6.46	51.80	47.24	11.40	12.71	72
0.06	6.78	47.20	42.80	8.50	9.10	72
0.08	6.60	44.00	39.78	6.70	6.93	72
0.1	6.95	42.70	38.43	4.70	4.65	72

* No precipitate formed at any Tergitol 7 concentration.

TABLE D-36

pH AND INTERFACIAL TENSION DATA FOR SOLUTIONS OF TERGITOL 7 IN DISTILLED WATER AND ETHYL LAKE CRUDE OIL

Tergitol 7 Concentration* (Weight Percent)	pH Measured	Interfacial Tension		Temperature (°F)
		Apparent (dynes/cm)	Corrected (dynes/cm)	
0	5.90	14.60	18.72	72
0.002	6.05	13.30	16.69	72
0.004	5.48	12.40	15.34	72
0.006	5.40	12.60	15.65	72
0.008	6.22	12.30	15.19	72
0.01	5.80	12.70	15.80	72
0.02	6.33	12.60	15.65	72
0.04	6.46	12.70	15.80	72
0.06	6.78	10.60	12.72	72
0.08	6.60	10.40	12.27	72
0.1	6.95	8.60	9.93	72

* No precipitate formed at any Tergitol 7 concentration.

TABLE D-37

pH AND INTERFACIAL TENSION DATA FOR SOLUTIONS OF TERGITOL 7 IN DISTILLED WATER AND IMPERIAL JUDY CREEK CRUDE OIL

Tergitol 7 Concentration* (Weight Percent)	pH Measured	Interfacial Tension		Temperature (°F)
		Apparent (dynes/cm)	Corrected (dynes/cm)	
0	5.90	23.50	23.36	72
0.002	6.05	24.60	24.60	72
0.004	5.48	23.90	23.78	72
0.006	5.40	24.50	24.50	72
0.008	6.22	24.00	23.93	72
0.01	5.80	23.90	23.78	72
0.02	6.33	24.50	24.50	72
0.04	6.46	22.20	21.91	72
0.06	6.78	21.30	20.96	72
0.08	6.60	19.70	19.21	72
0.1	6.95	18.00	17.41	72

* No precipitate formed at any Tergitol 7 concentration.

TABL[redacted]

pH AND INTERFACIAL [redacted]NSION DATA FOR SOLUTIONS OF TERG[redacted]

IN DISTILLED WATER AND LEDUC-WOODBEND CRUDE OIL

Tergitol 7 Concentration* (Weight Percent)	pH Measured	Interfacial Tension		Temperature (°F)
		Apparent (dynes/cm)	Corrected (dynes/cm)	
0	5.90	25.00	24.80	74
0.002	6.05	28.70	28.84	74
0.004	5.48	29.60	29.90	74
0.006	5.40	28.60	28.77	74
0.008	6.22	29.00	29.20	74
0.01	5.80	29.00	29.20	74
0.02	6.33	29.00	29.20	74
0.04	6.46	27.20	27.20	74
0.06	6.78	24.00	23.64	74
0.08	6.60	22.60	22.15	74
0.1	6.95	20.60	19.98	74

* No precipitate formed at any Tergitol 7 concentration.

TABLE D-39

pH AND INTERFACIAL TENSION DATA FOR SOLUTIONS OF NaOH IN FIELD WATER AND LLOYDMINSTER CRUDE OIL

NaOH Concentration* (Weight Percent)	pH Measured	Surface Tension		Interfacial Tension		Temperature (°F)
		Apparent (dynes/cm)	Corrected (dynes/cm)	Apparent (dynes/cm)	Corrected (dynes/cm)	
0	5.90	76.20	71.15	22.30	28.10	72
0.002	7.10	56.60	51.51	16.70	16.20	72
0.004	7.35	50.00	45.25	16.60	16.10	72
0.006	7.60	57.30	52.14	12.90	12.23	72
0.008	7.73	48.40	43.80	12.20	11.49	72
0.01	7.80	45.50	40.95	12.30	11.58	72
0.02	7.90	44.10	39.69	11.20	10.47	72
0.04	8.58	45.70	41.13	9.90	9.20	72
0.06	9.10	50.00	45.25	9.50	8.79	72
0.08	9.55	58.50	53.35	8.10	7.41	72
0.1	9.80	56.70	51.60	8.30	7.60	72

* Trace clouding observed; milky white precipitate formed at 0.02% NaOH concentration.

TABLE D-40

pH AND INTERFACIAL TENSION DATA FOR SOLUTIONS OF NaOH IN FIELD WATER AND ETHYL LAKE CRUDE OIL

NaOH Concentration (Weight Percent)	pH Measured	Interfacial Tension		Temperature (°F)
		Apparent (dynes/cm)	Corrected (dynes/cm)	
0	5.90	14.60	18.72	72
0.002	7.10	13.70	13.15	72
0.004	7.35	13.10	12.55	72
0.006	7.60	13.10	12.55	72
0.008	7.73	11.90	11.31	72
0.01	7.80	9.70	9.05	72
0.02	7.90	9.40	8.74	72
0.04	8.58	7.10	6.49	72
0.06	9.10	5.90	5.34	72
0.08	9.55	5.30	4.77	72
0.1	9.80	4.50	4.03	72

* Trace clouding observed; milky white precipitate formed at 0.02% NaOH concentration.

TABLE D-41

pH AND INTERFACIAL TENSION DATA FOR SOLUTIONS OF NaOH IN FIELD WATER AND IMPERIAL JUDY CREEK CRUDE OIL

NaOH Concentration* (Weight Percent)	pH Measured	Interfacial Tension		Temperature (°F)
		Apparent (dynes/cm)	Corrected (dynes/cm)	
0	5.90	23.50	23.36	72
0.002	7.10	18.90	17.58	72
0.004	7.35	19.40	18.06	72
0.006	7.60	19.00	17.67	72
0.008	7.73	17.80	16.47	72
0.01	7.80	16.10	14.81	72
0.02	7.90	16.60	15.32	72
0.04	8.58	14.80	13.53	72
0.06	9.10	13.60	12.38	72
0.08	9.55	11.50	10.37	72
0.1	9.80	11.10	9.99	72

* Trace clouding observed; milky white precipitate formed at 0.02% NaOH concentration.

TABLE D-42

pH AND INTERFACIAL TENSION DATA FOR SOLUTIONS OF NaOH IN FIELD WATER AND LEDUC-WOODBEND CRUDE OIL

NaOH Concentration* (Weight Percent)	pH Measured	Interfacial Tension		Temperature (°F)
		Apparent (dynes/cm)	Corrected (dynes/cm)	
0	5.90	25.00	24.80	72
0.002	7.10	29.30	28.13	72
0.004	7.35	29.00	27.78	72
0.006	7.60	29.60	28.42	72
0.008	7.73	28.10	26.81	72
0.01	7.80	28.80	27.51	72
0.02	7.90	27.50	26.24	72
0.04	8.58	27.40	26.14	72
0.06	9.10	27.30	26.00	72
0.08	9.55	28.00	26.70	72
0.1	9.80	26.60	25.27	72

* Trace clouding observed; milky white precipitate formed at 0.02% NaOH concentration.

TABLE D-43

pH AND INTERFACIAL TENSION DATA FOR SOLUTIONS OF TERGITOL NPX IN DISTILLED WATER AND LLOYDMINSTER CRUDE OIL

Tergitol NPX Concentration* (Percent by Volume)	pH Measured	Interfacial Tension				Temperature (°F)
		Before N_2 Foaming		After N_2 Foaming		
		Apparent (dynes/cm)	Corrected (dynes/cm)	Apparent (dynes/cm)	Corrected (dynes/cm)	
0	5.90	22.30	28.10	22.20	28.00	72
0.002	6.23	5.10	5.10	6.00	6.12	72
0.004	6.30	3.00	2.85	4.30	4.22	72
0.006	6.50	1.60	1.45	3.00	2.85	72
0.008	6.20	1.10	0.98	2.60	2.44	72
0.01	6.28	0.70	0.61	2.30	2.14	72
0.02	6.24	<0.40	<0.35	1.90	1.74	72
0.04	6.20	<0.40	<0.35	1.60	1.45	72
0.06	6.20	<0.40	<0.35	1.28	1.15	72
0.08	6.05	<0.40	<0.35	1.40	1.26	72
0.1	6.10	<0.40	<0.35	1.10	0.98	72

* No precipitate formed at any Tergitol NPX concentration.

TABLE D-44

pH AND INTERFACIAL TENSION DATA FOR SOLUTIONS OF TERGITOL NPX IN DISTILLED WATER AND ETHYL LAKE CRUDE OIL

Tergitol NPX Concentration* (Percent by Volume)	pH Measured	Interfacial Tension				Temperature (°F)
		Before N_2 Foaming		After N_2 Foaming		
		Apparent (dynes/cm)	Corrected (dynes/cm)	Apparent (dynes/cm)	Corrected (dynes/cm)	
0	5.90	14.60	18.72	14.70	18.85	72
0.002	6.23	4.90	5.19	5.25	5.65	72
0.004	6.30	3.00	3.00	4.00	4.14	72
0.006	6.50	1.50	1.40	3.45	3.49	72
0.008	6.20	0.80	0.72	2.85	2.82	72
0.01	6.28	0.60	0.53	2.50	2.45	72
0.02	6.24	<0.40	<0.35	1.65	1.55	72
0.04	6.20	<0.40	<0.35	1.85	1.76	72
0.06	6.20	<0.40	<0.35	1.60	1.51	72
0.08	6.05	<0.40	<0.35	1.45	1.35	72
0.1	6.10	<0.40	<0.35	1.10	1.01	72

* No precipitate formed at any Tergitol NPX concentration.

TABLE D-45

pH AND INTERFACIAL TENSION DATA FOR SOLUTIONS OF TERGITOL NPX IN DISTILLED WATER AND IMPERIAL JUDY CREEK CRUDE OIL

Tergitol NPX Concentration* (Percent by Volume)	pH Measured	Interfacial Tension				Temperature (°F)
		Before N_2 Foaming		After N_2 Foaming		
		Apparent (dynes/cm)	Corrected (dynes/cm)	Apparent (dynes/cm)	Corrected (dynes/cm)	
0	5.90	23.50	23.36	23.70	23.56	72
0.002	6.23	11.90	11.10	12.00	11.20	72
0.004	6.30	9.00	8.24	9.10	8.37	72
0.006	6.50	7.40	6.70	7.20	6.52	72
0.008	6.20	6.90	6.24	6.60	5.94	72
0.01	6.28	6.00	5.38	5.80	5.19	72
0.02	6.24	4.35	3.84	4.15	3.67	72
0.04	6.20	2.80	2.44	3.10	2.71	72
0.06	6.20	2.45	2.13	2.35	2.05	72
0.08	6.05	2.00	1.73	2.10	1.82	72
0.1	6.10	1.70	1.46	1.74	1.50	72

* No precipitate formed at any Tergitol NPX concentration.

TABLE D-46

pH AND INTERFACIAL TENSION DATA FOR SOLUTIONS OF TERGITOL NPX IN DISTILLED WATER AND LEDUC-WOODBEND CRUDE OIL

Tergitol NPX Concentration* (Percent by Volume)	pH Measured	Interfacial Tension				Temperature (°F)
		Before N_2 Foaming		After N_2 Foaming		
		Apparent (dynes/cm)	Corrected (dynes/cm)	Apparent (dynes/cm)	Corrected (dynes/cm)	
0	5.90	25.00	24.80	25.20	25.00	72
0.002	6.23	13.50	12.62	12.60	11.72	72
0.004	6.30	11.10	10.27	10.70	9.85	72
0.006	6.50	8.70	7.83	8.35	7.56	72
0.008	6.20	7.55	6.81	7.50	6.75	72
0.01	6.28	6.20	5.54	6.40	5.73	72
0.02	6.24	4.30	3.78	4.40	3.89	72
0.04	6.20	3.50	3.07	3.50	3.07	72
0.06	6.20	3.20	2.79	3.20	2.79	72
0.08	6.05	2.60	2.26	2.40	2.10	72
0.1	6.10	2.20	1.91	2.10	1.82	72

* No precipitate formed at any Tergitol NPX concentration.

TABLE D-47

pH AND INTERFACIAL TENSION DATA FOR LLOYDMINSTER CRUDE OIL AND FIELD WATERS

Field Water	pH	Interfacial Tension		Temperature (°F)
		Apparent (dynes/cm)	Corrected (dynes/cm)	
Lloydminster Sparky Pool	7.56	19.60	20.50	78
Ethyl Lake-Clearwater Formation	7.65	15.30	16.10	76
Sparky Pool, Chauvian South Unit #1	7.20	25.80	25.16	74
Imperial Judy Creek-Beaverhill Lake	7.15	27.70	26.87	73

TABLE D-48

pH AND INTERFACIAL TENSION DATA FOR ETHYL LAKE CRUDE OIL AND FIELD WATERS

Field Water	pH	Interfacial Tension		Temperature (°F)
		Apparent (dynes/cm)	Corrected (dynes/cm)	
Lloydminster Sparky Pool	7.56	17.40	20.45	78
Ethyl Lake-Clearwater Formation	7.65	12.20	14.64	75
Sparky Pool, Chauvian South Unit #1	7.20	20.70	20.29	75
Imperial Judy Creek-Beaverhill Lake	7.10	23.80	23.44	74

TABLE D-49

pH AND INTERFACIAL TENSION DATA FOR IMPERIAL JUDY CREEK CRUDE OIL AND FIELD WATERS

Field Water	pH	Interfacial Tension		Temperature (°F)
		Apparent (dynes/cm)	Corrected (dynes/cm)	
Lloydminster Sparky Pool	7.56	18.20	18.69	78
Ethyl Lake-Clearwater Formation	7.65	14.40	14.69	75
Sparky Pool, Chauvian South Unit #1	7.20	22.50	21.60	75
Imperial Judy Creek-Beaverhill Lake	7.10	25.00	24.05	74

TABLE D-50

pH AND INTERFACIAL TENSION DATA FOR LEDUC-WOODBEND CRUDE OIL AND FIELD WATERS

Field Water	pH	Interfacial Tension		Temperature (°F)
		Apparent (dynes/cm)	Corrected (dynes/cm)	
Lloydminster Sparky Pool	7.56	21.40	21.27	78
Ethyl Lake-Clearwater Formation	7.65	16.20	15.80	75
Sparky Pool, Chauvian South Unit #1	7.20	25.10	23.85	75
Imperial Judy Creek-Beaverhill Lake	7.10	29.20	28.00	74

TABLE D-51

pH AND INTERFACIAL TENSION DATA FOR SOLUTIONS OF 1 VOL. OF 10% NaCl IN NaOH IN DISTILLED WATER AND JUDY CREEK CRUDE OIL

1 Vol. 10% NaCl in NaOH Solution, Concentration* (Weight Percent)	pH	Interfacial Tension		Temperature (°F)
		Apparent (dynes/cm)	Corrected (dynes/cm)	
0	5.95	23.50	23.36	72
0.002	10.55	19.25	18.73	72
0.004	10.85	18.65	18.09	72
0.006	11.10	16.30	15.65	72
0.008	11.18	15.85	15.14	72
0.01	11.32	15.30	14.55	72
0.02	11.60	14.00	13.23	72
0.04	11.90	12.45	11.65	72
0.06	12.22	10.90	10.08	72
0.08	12.33	10.10	9.30	72
0.1	12.60	9.50	8.74	72

* No precipitate formed at any solution concentration.

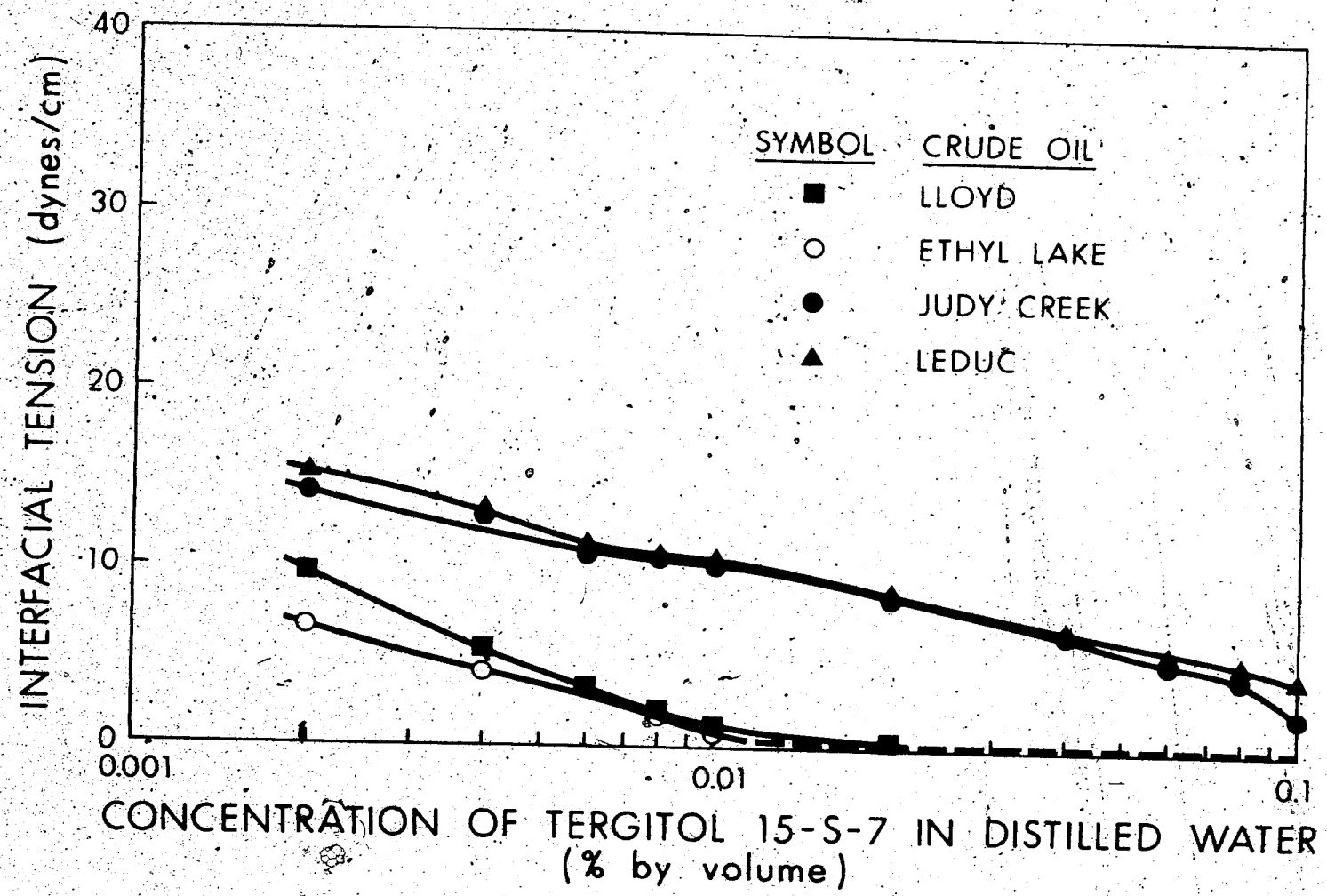

FIGURE D-1 Influence of Tergitol 15-S-7 Concentration on Interfacial Tension

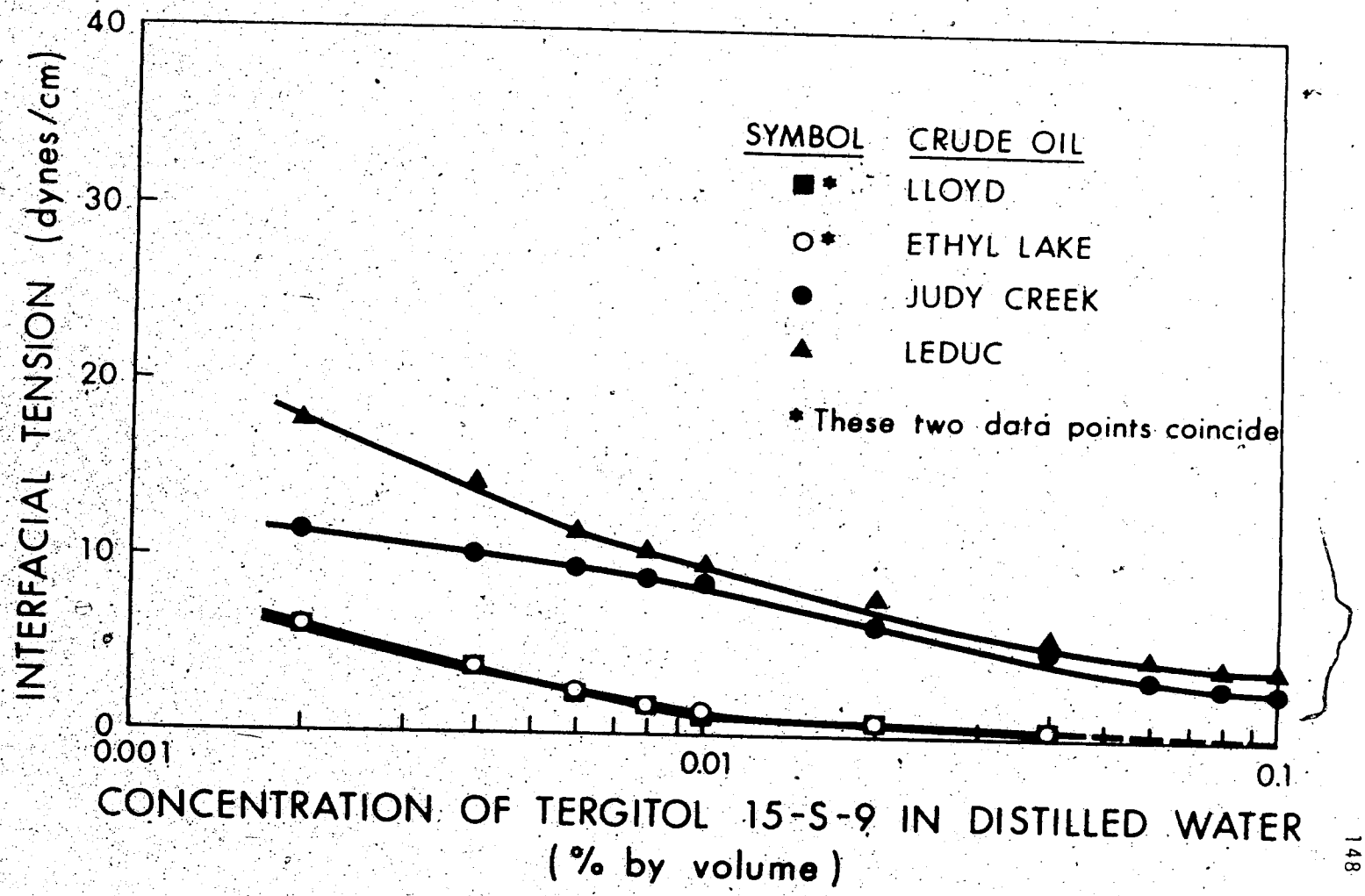

FIGURE D-2 Influence of Tergitol 15-S-9 Concentration on Interfacial Tension

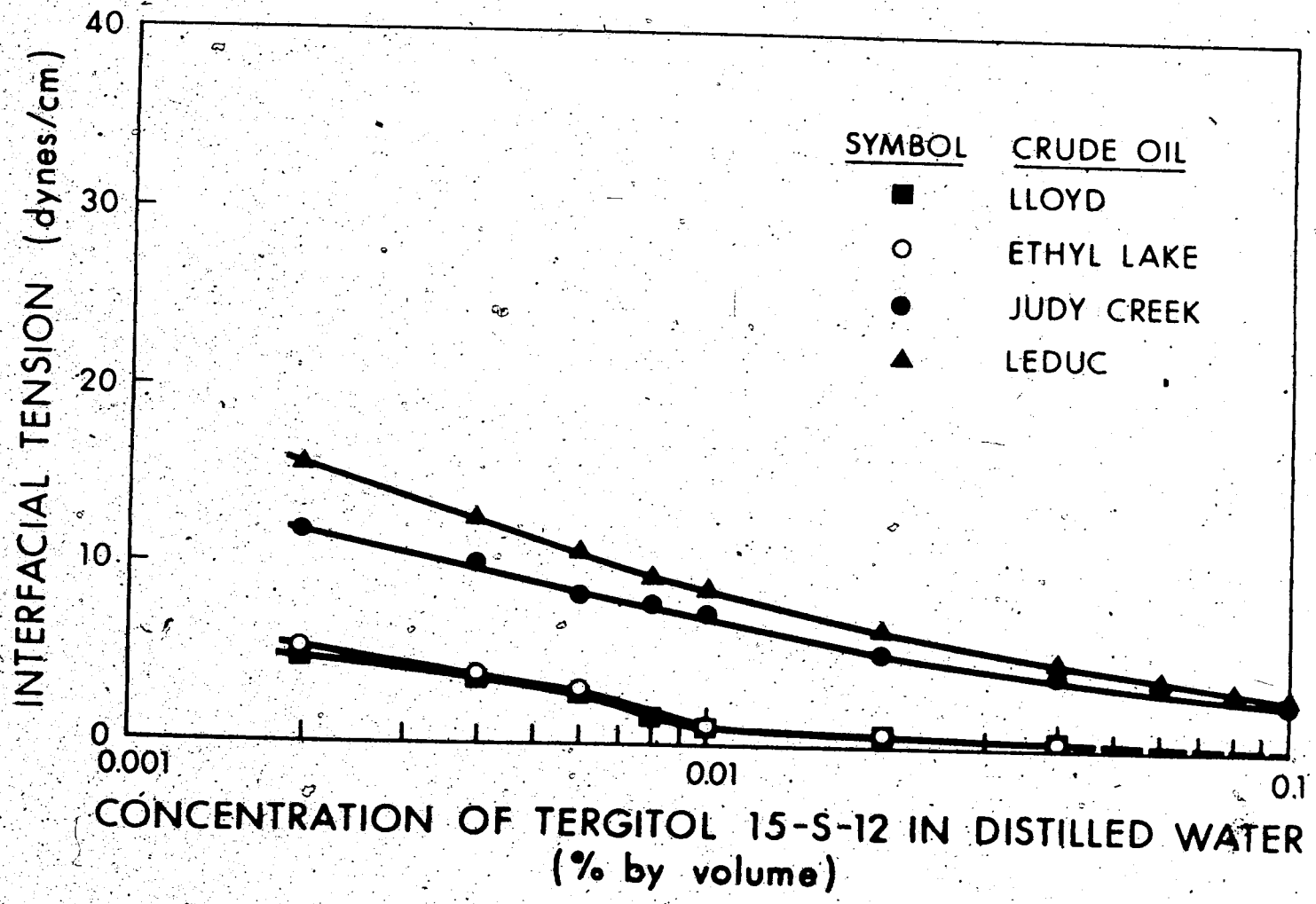

FIGURE D-3 Influence of Tergitol 15-S-12 Concentration on Interfacial Tension

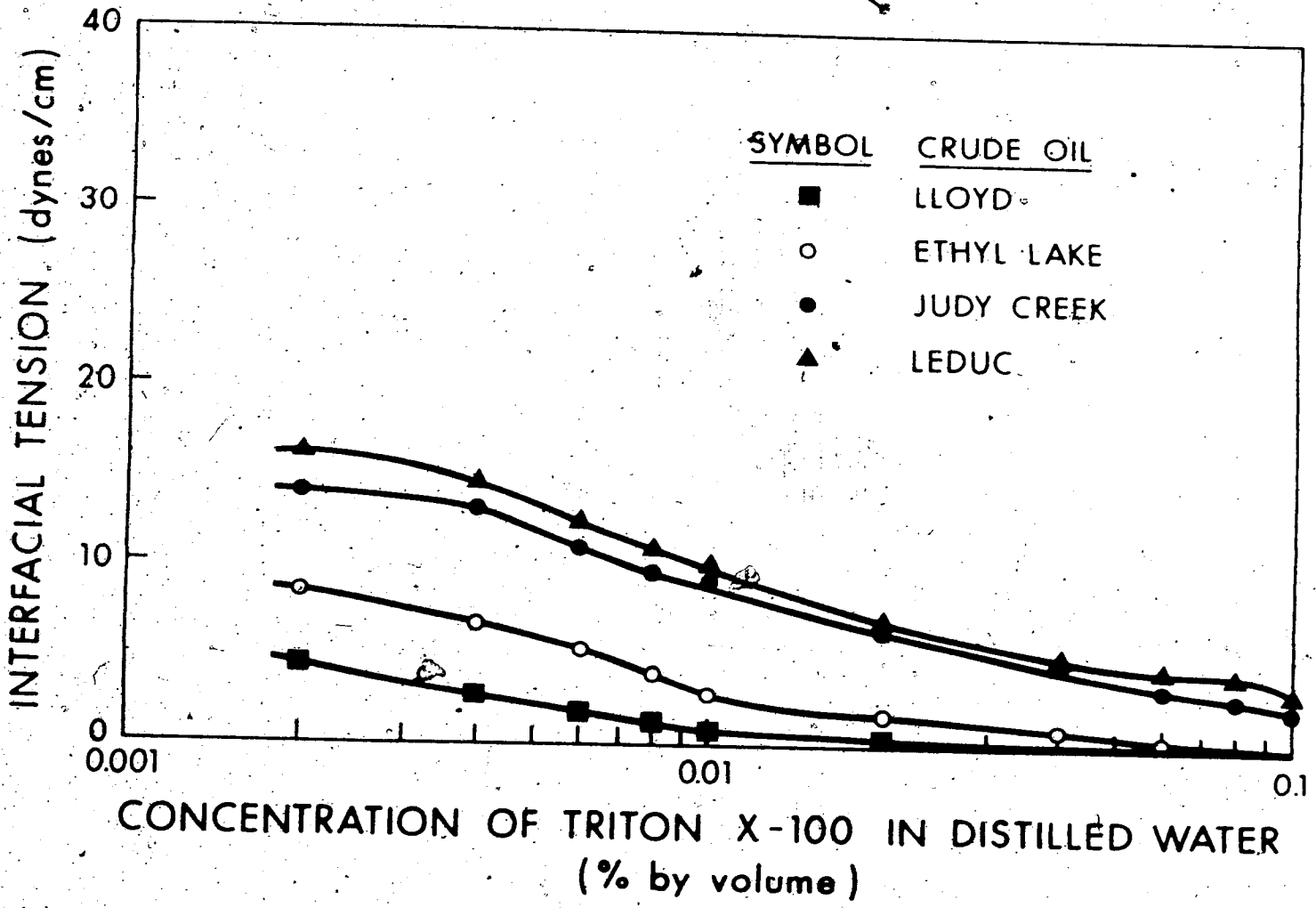

FIGURE D-4 Influence of Triton X-100 Concentration on Interfacial Tension

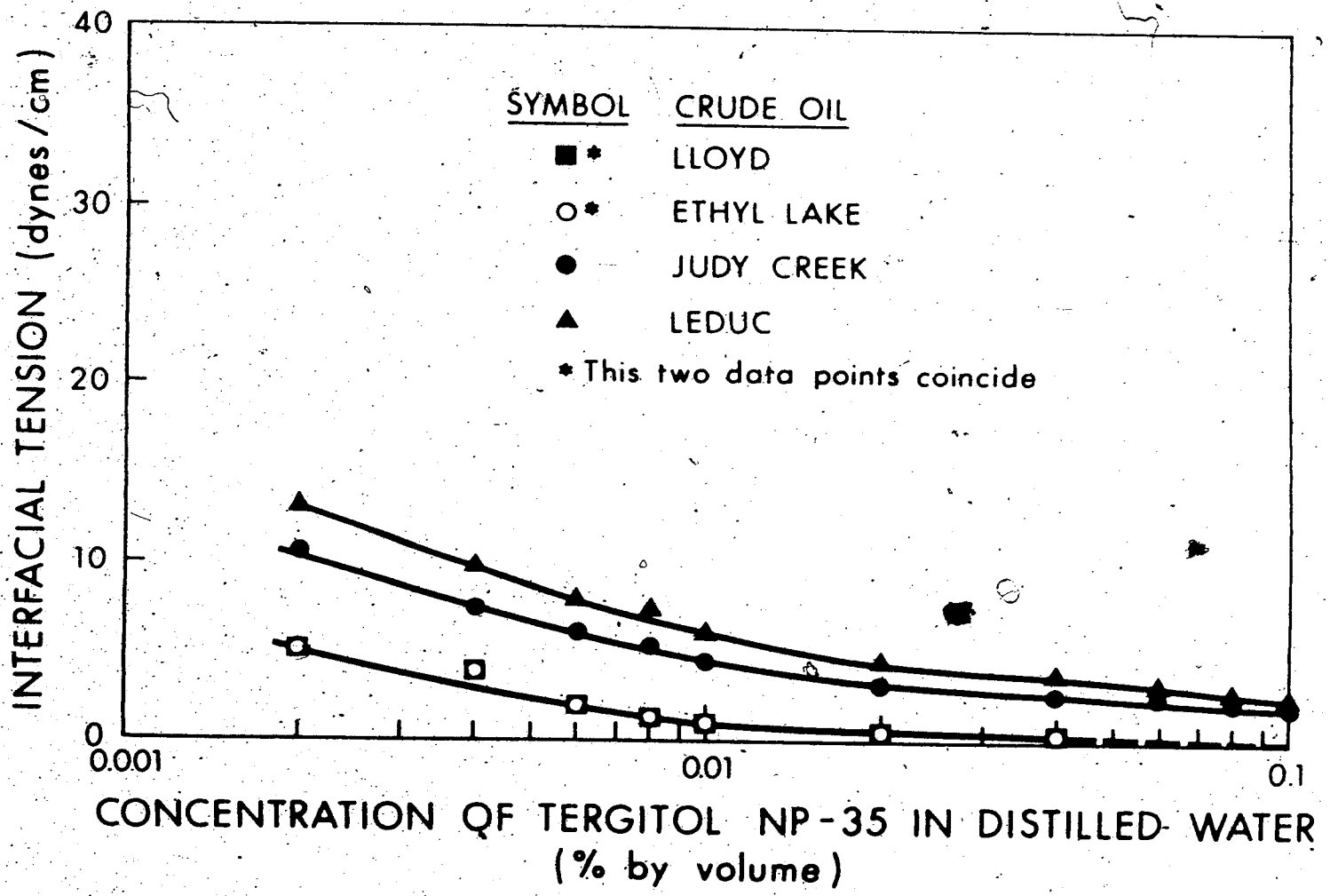

FIGURE D-5 Influence of Tergitol NP-35 Concentration on Interfacial Tension

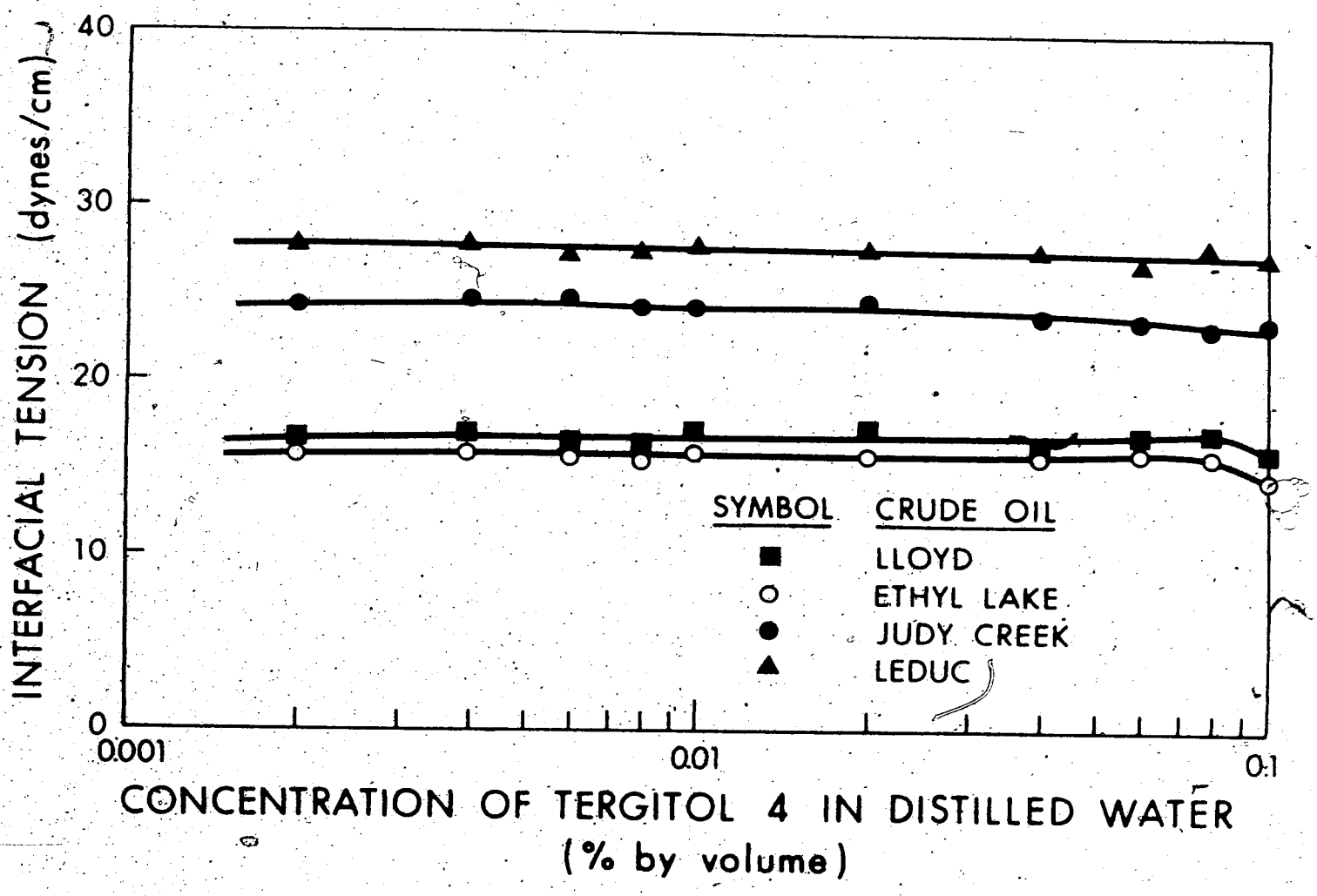

FIGURE D-6 Influence of Tergitol 4 Concentration on Interfacial Tension

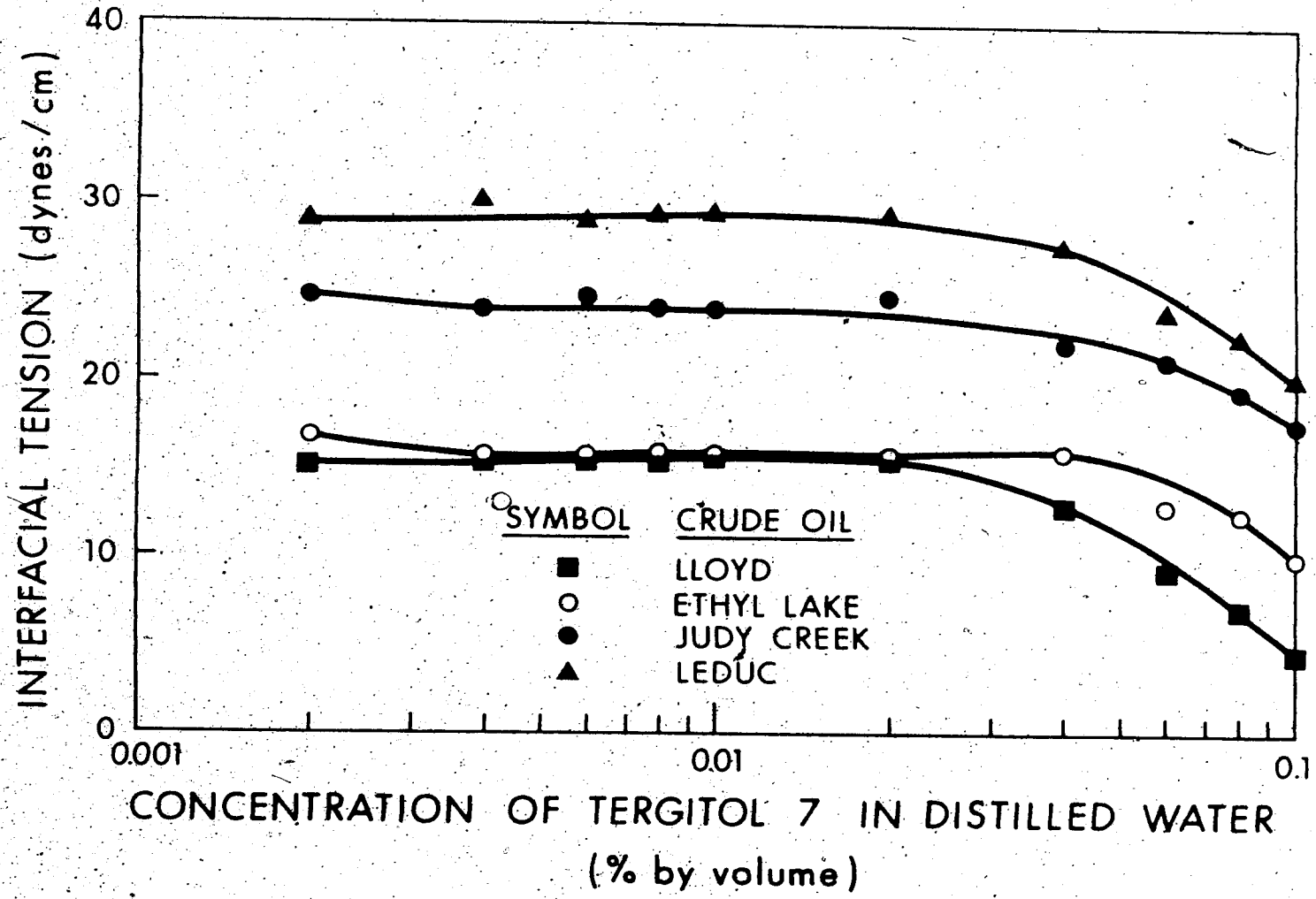

FIGURE D-7 Influence of Tergitol 7 Concentration on Interfacial Tension

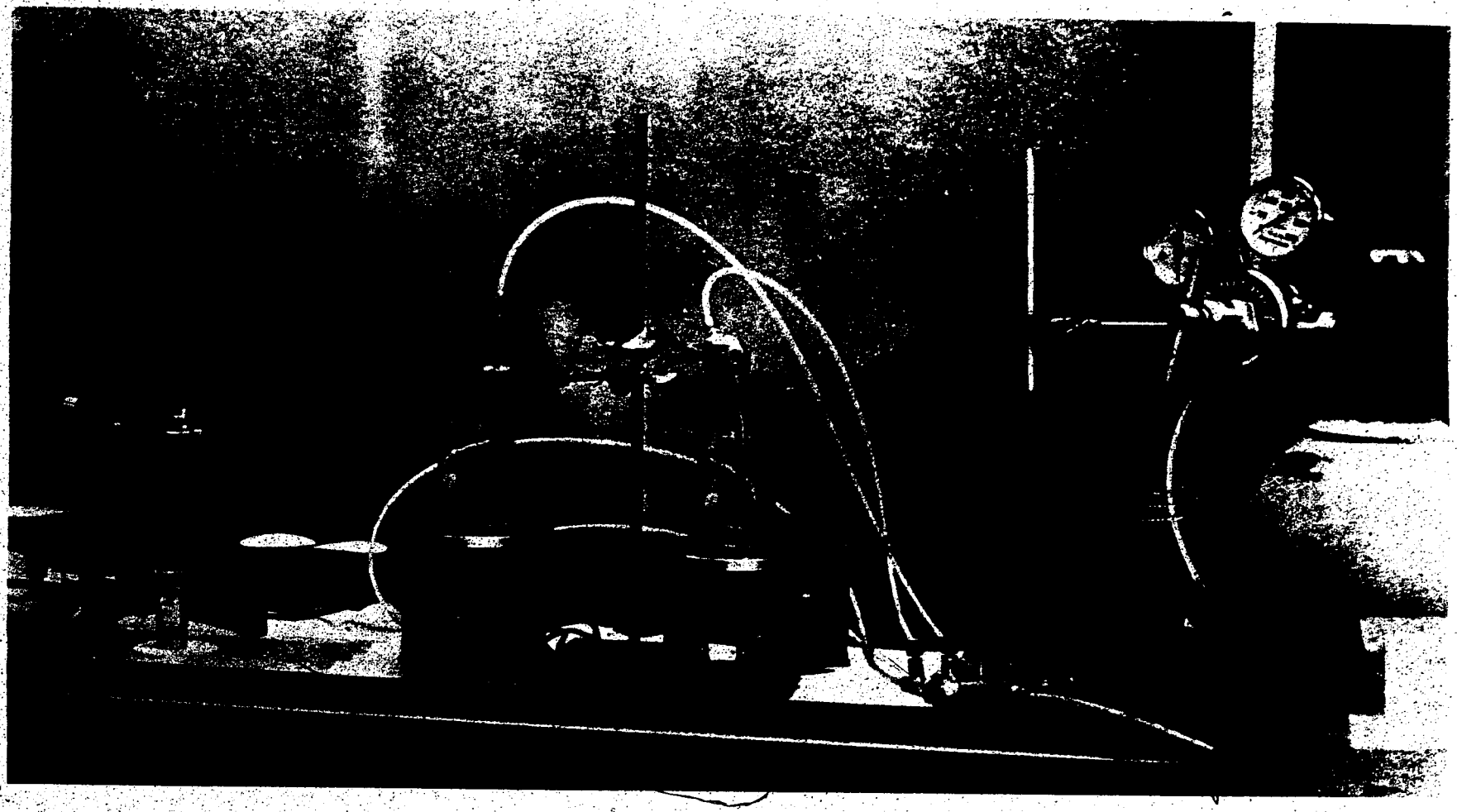

PLATE 1 - Frothing Apparatus, Consisting of Nitrogen Cylinder, Pressure Gauge (Matheson Type), Manifold, Poly-Flo Tubing 44-P-1/4 (Imperial Eastman), Lucite Bubblers, Beakers and Regulated Rotators.

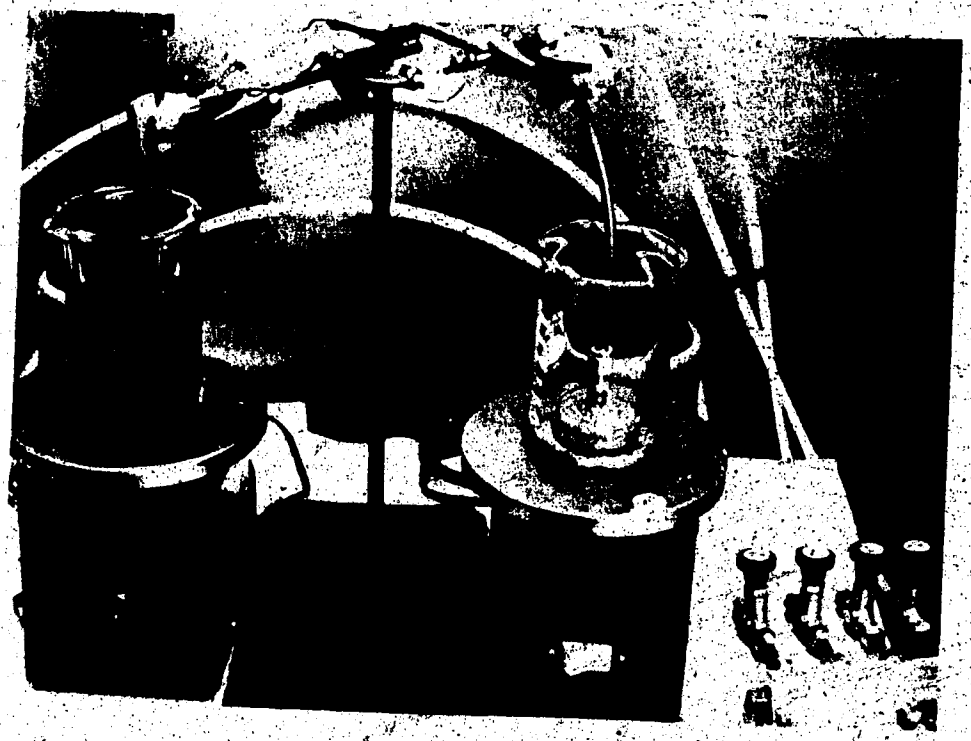

PLATE 2 - Frothing Apparatus: Beakers being Filled with Crude Oil Prior to Nitrogen Foaming

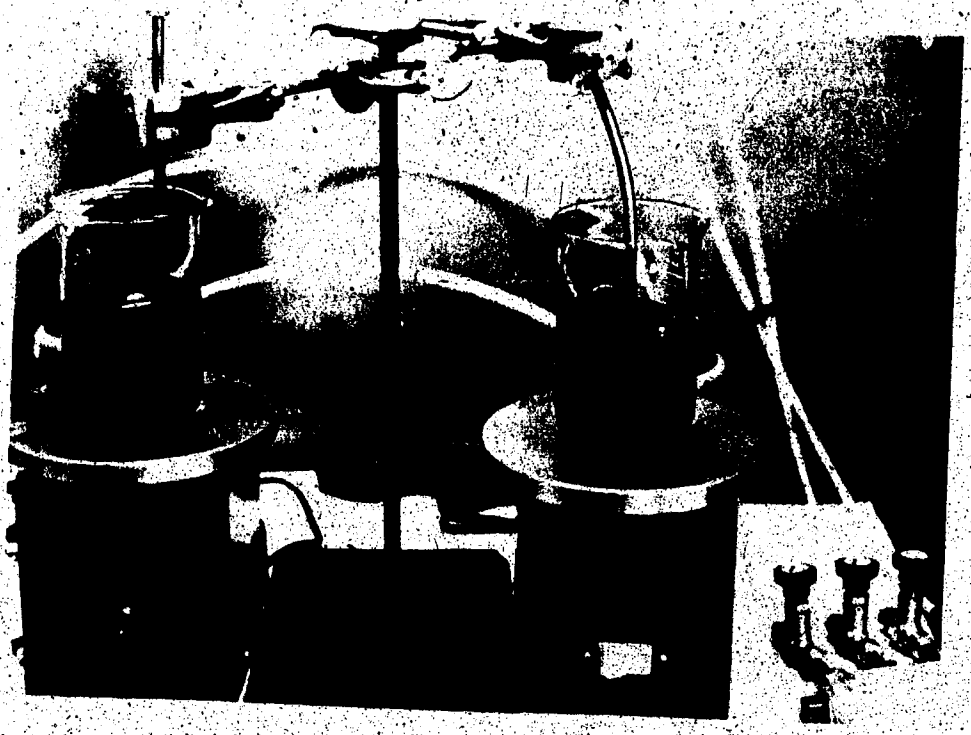

PLATE 3 - Frothing Apparatus: Nitrogen Foaming in Progress. A large buble can be observed in the beaker on the right.