A STUDY OF BRINE - CRUDE OIL INTERFACIAL TENSION

by

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ABSTRACT

This Thesis is concerned with relating accepted laboratory brine-crude oil interfacial tension measuring techniques to petroleum reservoir conditions. The interfacial tension between selected brines and a low API gravity crude oil was measured as a function of brine concentration, interface contact time, brine-crude agitation time, and interface contact time after agitation.

In all cases, the interfacial tension was found to be a function of brine composition and concentration. Of the three brines tested, sodium chloride was found to influence interfacial tension the most, calcium chloride somewhat, and magnesium chloride the least.

The effect of interface contact time was found to be dependent upon brine composition and concentration. Sodium chloride brines continued to reduce interfacial tension at long interface contact times; whereas, calcium chloride and magnesium chloride affected only a slight increase in interfacial tension at long contact times.

In all cases, agitation of a mixture of crude oil and brine affected an increase of the interfacial tension. After the initial increase, the brines exhibited characteristics similar to those observed under static conditions.

Contact time after agitation increased the interfacial tension with sodium chloride and calcium chloride brines, but showed no effect with the magnesium chloride brine.

The du Nouy ring, considered the standard method for oil-water interfacial tension measurement by the American Society for Testing and Materials, was used for all interfacial tension determinations. Lloydminster crude (15.3° API) was used as the oil phase of the interface in all experimental procedures.

TABLE OF CONTENTS

LIST OF FIGURES

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INTRODUCTION

Low API gravity, viscous petroleum fields are known to contain millions of barrels of oil not currently economically produceable by secondary recovery techniques.[1] Some production of economic significance, however, has resulted from injecting sodium hydroxide into the waterflood to reduce brine-crude oil interfacial tension.[2] Laboratory studies predicted that the Lloydminster Field of Canada would produce significantly if subjected to caustic waterflooding techniques. Pilot flood results, however, were disappointing.[3]

A possible explanation for the disparity between laboratory prediction and Lloydminster Field results is that the brine-crude oil interfacial tension measured in the laboratory is smaller than the interfacial tension existing in the reservoir. Researchers have related interfacial tension measurements made at laboratory temperatures and pressures to reservoir conditions;[4,5] however, the effects of reservoir fluid composition, concentration, interface contact time, agitation time, and contact time after agitation have been left largely untouched. This investigation will attempt to establish the influence of common reservoir fluid components, component concentration, interface contact time, agitation time, and contact time after agitation upon accepted laboratory interfacial tension measuring techniques.

REVIEW OF LITERATURE

"Surface tension is defined as a force with the dimensions of dynes per cm that is a measure of the work required to increase the area of a surface by one square centimeter."[6] A measurable quantity existing in all liquid surfaces, surface tension occurs as a result of the imbalance of cohesive forces existing between the molecules of the liquid. Because many of the concepts of surface properties were developed prior to 1900, a short chronological history, as abstracted from Matijevic,[7] is presented to develop the principles upon which this thesis is based.

> Leonardo da Vinci (1452-1519) is believed to have been the first to observe and record the rise of a liquid in a tube of small bore. The phenomenon became known as capillarity because the tubes that were used possessed a bore as "fine as hair" (Latin: capillus = hair). Sir Isaac Newton (1642-1727) refers to the forces of cohesion and adhesion that produce the rise of a liquid in a capillary tube. He recognized that the forces were intermolecular in origin and that the mutual attraction gave rise to a pressure inside the liquid.
>
> At the end of the 17th century, Hawksbee performed the first "accurate" observations of the ascent of liquids in capillary tubes and between glass plates. He observed ...that attraction forces arose from the matter near the inside surface of his glass tubes. Some 50 years later von Segner brought together Newton's concept of cohesive forces and Hawksbee's idea of surface matter giving rise to them, by proposing the first theory of capillarity. It was that cohesive forces created a pressure which was resisted by a uniform tension in the surface. This tension was called

surface tension and was thought to explain capillarity. "Surface tension" thus came to denote the supposed presence of a contractile skin at the surface of a liquid.

Chronologically, the next stop was provided by the simultaneous publication by Thomas Young and by Viscompte Pierre S. de Laplace, of theoretical treatments of the effect of cohesive forces on the contractile skin of a liquid.

Young ...supposed that particles of matter act on one another with two kinds of forces, attraction and repulsion, the former acting over greater distances than the latter. The attractive force was thought to be constant throughout the minute distance to which it extended, but the repulsion force was thought to increase rapidly as the distance diminished. Young's attraction force was shown to give rise to a pressure on surface particles, the magnitude of which was proportional to the sum of the curvatures of the surface in two normal planes at right angles to each other.

The main step forward in the treatments of Laplace and Young was that the pressure across a curved surface was a consequence of two radii of curvature and not of just one radius, as suggested by von Segner. Thus, their equation connecting curvature with the change in pressure, ΔP, and surface tension, γ, enabled the height of capillary rise to be related experimentally to the radius of the capillary tube. Their equation was

$$\gamma \, (1/R_1 + 1/R_2) = \Delta P \qquad (1)$$

where R_1 and R_2 represent the two principal radii of curvature.

Bashforth and Adams tested eq. 1 rigorously 60 years later by applying it to the calculation of the shape of a sessile drop of liquid on a level solid plate and then comparing the calculated and measured shapes. Their experimental work ... forms an extensive set of tables ... used for correcting values of surface tension obtained by the capillary height and the drop weight methods.

> The historical development and the concepts concerning surface forces and surface tension were clearly laid down by the turn of the century. At this time, most of the principles had been worked out qualitatively, and quantitative relationships between the energetics of surface formation and intensive properties of the liquid were set out rigorously in Gibbs' thermodynamic treatment. The existence of physical forces of attraction between molecules had been shown by van der Waals and their relationship to surface tension was treated extensively in papers by Lord Rayleigh in which he indicated the ability of particles of matter to repel each other in the manner envisaged by Thomas Young.

This brief chronology of the development of surface tension concepts provides the background to begin the study of surface tension influences in petroleum reservoirs. In applying the principles of surface tension to interfacial tension, one merely replaces the air or vapor phase with another liquid. The same concepts of molecular interaction still apply. These concepts, however, are complicated by the fact that they now act across phase boundaries or interfaces.

Interfacial tension between water and oil became of interest during the early 1920's. Johansen,[8] writing in 1924, reported interfacial tensions between petroleum and similar oils, and related surface and interfacial tension values. At about the same time Howard and Sollman[9] developed a formula for calculating the interfacial tension of a solution against an oil, taking into account the concentration of the solute within the solution.

In 1928 Bartell and Miller[10] devised a simple apparatus to measure the interfacial tension of water against oil. They also reported adhesion tensions of various oils against silica, the values of which ranged from 58 to 72 dynes per cm. About the same time Vellinger[11] was making experimental determinations of the interfacial tension between mineral oils and aqueous solutions of electrolytes. He found that the interfacial tension between water and oil is increased by neutral salts and decreased by organic dyes in the water phase.

The first work relating interfacial tension specifically to the petroleum industry appeared in the French publication Petroleum Z in 1935. In this article Vellinger[12] reported that surface tension is nearly independent of molecular weight. He also reported that the interfacial tension of light oils against aqueous solutions is independent of the solution pH, but that the interfacial tension of heavy oils against aqueous solutions decreases rapidly with increasing pH.

As efforts to recover higher percentages of crude from petroleum reservoirs became more rewarding, research into the mechanism of fluid movement through these reservoirs became more popular.

Hocott[13] in 1938 investigated the interfacial tension between salt water and crude oil containing dissolved gases

at reservoir pressures. He determined that the interfacial tension between water and most sweet crudes: (a) varies between 27 and 35 dynes per cm; (b) increases slightly with an increase in the amount of dissolved gas; (c) decreases slightly with an increase of pressure; and (d) varies directly with the density of the crude oil.

Working independently, Livingston[14] reported the range of variation of crude oil surface tension as plus (+) or minus (-) 11 percent from an average value of 30.4 dynes per cm. He determined the standard deviation of interfacial tension of naturally occurring oil-water systems is 7.3 dynes per cm from an average of 20.4 dynes per cm. Livingston also reported that (a) there is no correlation between surface or interfacial tensions and geologic formation; (b) interfacial tension varies directly with the surface tension of the crude oil; and (c) interfacial tension increases as viscosity, specific gravity, and paraffin content of the crude increase.

During the participation of the United States in World War II, and immediately thereafter, a distinct lack of research publications in the field of interfacial tension is noticed.

The first new work to appear after World War II was in 1949 when Bartell and Niederhauser[15] conducted their classic investigations of naturally occurring crude oil-water

interfacial films. These researchers concluded that the films were a result of an adsorption process and responsible for lowering crude oil-water interfacial tensions. The films, composed of minute amounts of asphaltic material, were considered a result of oxidation of the crude by air, and therefore not normally present in natural petroleum reservoirs.

Writing in 1951 Hough et al.[5] described a new apparatus for determining interfacial tension at reservoir pressures and temperatures. His data show changes in interfacial tension in the 15 to 15,000 psi pressure range from 70 to 22 dynes per cm at 100°F and from 53 to 21 dynes per cm at 280°F. About the same time, Glogoczowski and Czaplicka[16] reported interfacial tension values for eighteen Polish crudes against sodium chloride, sodium sulfate, calcium chloride, and magnesium chloride brines. The values for sodium sulfate were proportional to concentration; however, the other salts showed unexplained maxima and minima.

Film-forming and surface-active constituents naturally present in crude petroleum were isolated by Denekas, et al.[17] in 1951. A major portion of the film-forming material was found to be a non-polar, normal paraffin hydrocarbon containing up to 70 or 80 carbon atoms. Also in 1951, Burcik and Vaughn[18] published experimental

results dealing with the rate of surface tension lowering as effected by solution pH. They found that anionic surface-active agents increased the rate of surface tension lowering with increasing pH, and that cationic surface-active agents decrease the rate of surface tension lowering with increasing pH.

The discovery of metallic elements in film-forming and surface-active constituents of petroleum were reported in 1952 by Dodd, et al.[19] Zinc, copper, nickel, titanium, calcium, and magnesium were found to be selectively adsorbed at petroleum-water interfaces.

The effect of electrolytes on the initial time rate of surface tension lowering of ionic surface-active agents was investigated by Burcik[20] in 1953. He observed that for anionic surface-active agents the increase in rate is largely determined by the charge of the added positive ion; for cationic surface-active agents the increase in rate is largely determined by the charge of the added negative ion.

Writing in 1953, Muskat[21] recognized the importance of understanding interfacial forces by stating:

> It is believed that interactions between the water and oil, in the presence of the peculiar internal surface area and structure of the porous rock, and their immiscibility control and limit oil recovery by water displacement....If agents could be found or formulated which, when added to water, give vanishing interfacial tensions with respect to the crude, and do not suffer appreciable

> adsorption on the solid (rock) surface...substantially increased if not complete recovery of the oil should be obtained.

In contradiction to Muskat's theories, Kennedy and Guerrero[22] found that lowering the oil-water interfacial tension had a tendency toward reducing the recovery of oil, and that lowering the surface tension of the brine had little or no effect on the oil recovery.

As more interest was generated in understanding and measuring the oil-water interfacial tension under reservoir conditions, new measuring apparatus became available. One of these devices, described by Kusakov, et al.,[23] is capable of measuring liquid-liquid interfacial tensions up to pressures of 400 kg per sq cm and at temperatures up to 100°C.

In Japan, Fukushima and Ichimura[24] reported interfacial tension values for crude oils against sodium chloride, sodium sulfate, and sodium carbonate solutions. In all cases the interfacial tension decreased as the salt concentration increased. When the concentration of the salt solution was held constant and interfacial tension was measured as a function of pH, a maximum interfacial tension was found in the pH range of 6 through 9. Rapid reduction of interfacial tension was recorded at pH values less than 6 or greater than 9.

The first voluminous measurement of crude oil-water interfacial tension was made by Everett and Weinaug[25] in 1955 when they determined physical properties for 453 samples of eastern Kansas crude oils. These tests indicated that no correlation existed between the API gravity and the interfacial tension.

An investigation of the effects of wettability by Kennedy[26] on the recovery of oil by waterflooding in 1955, showed that if the wettability was changed while the interfacial tension was not controlled, oil recovery was increased; however, if the wettability was changed while the interfacial tension was maintained at a constant level, oil recovery was not significantly affected. In all cases wetting properties were controlled by the addition of surface-active chemicals, and wetting properties were measured by the sessile drop method.

Concurrent work by Newcombe[27] disclosed that for both oil-wet and water-wet systems and a low viscosity oil, recoveries were a function of the oil-water interfacial tension. High interfacial tension floods were more efficient than low interfacial tension floods on water-wet systems, but low interfacial tension floods were more efficient on oil-wet systems. Systems of intermediate or neutral wettability were less sensitive to the rate of flood advance and interfacial tension than either oil-wet

or water-wet systems.

Classification of crude oils and ground waters by their surface activity and interfacial tension was reported in 1956 by Malyshek.[28] Malyshek determined the organic acid content and the interfacial tension of the crude in contact with an alkaline ground water and classified the oils as inactive, normally active, or highly active. Interfacial tension was found to decrease proportionally to the increase in organic acid content of the crude oil.

The interfacial behavior of crude oil-water systems was investigated by Reisberg and Doscher[29] in 1956. Their investigations showed that the interfacial tension was affected by aging, contraction and expansion of the interface, and the pH of the aqueous phase. Rigid films were observed at the interface between anaerobic crude oils and water. The formation of these films resulted in the adhesion of crude oil to a water-wetted hydrophilic surface and the serious distortion of the fluid-flow pattern in small capillaries. The recovery of crude oil was shown to be strongly dependent upon the ability of the displacing fluid to lower the interfacial tension and simultaneously overcome the effects of the rigid films. Aqueous solutions of sodium hydroxide together with nonionic surfactants were found to be most effective in accomplishing this.

In the same year, Kusakov and Kosheleva[30]

reported the interfacial tension of four crudes in contact with connate and distilled waters as a function of temperature. All but one crude exhibited an increase in interfacial tension with an increase in temperature.

Cerchez and Negoescu[31] reported that sulfonic acids and sodium sulfonates noticeably decreased the interfacial tension between crude oil and water.

Fukishima and Ichimura[32] determined the interfacial tension between moisture free crude oils and distilled water, and found that it varies with the pH of the aqueous phase. For pH values of 1, 7, and 11, interfacial tensions of 15, 30, and 18 dynes per cm were reported. Water separated from the crudes had sodium chloride contents of 1.18 to 1.38 percent by weight and pH values of 7.4 to 8.2.

During the late 1950's, Harvey[33] investigated the crude oil-water interfacial films first observed by Bartell and Niederhauser,[15] and later studied by Reisberg and Doscher.[29] As a result of his investigation, Harvey concluded that the films are formed by the adsorption at the interface of a slightly soluble, surface-active component. This component, originally present in the crude oil, constitutes a molecular layer or film at the interface. Upon rapid shrinkage of the interface area, the molecular layer becomes a rigid, insoluble film. By use of the pendant drop method of interfacial tension measurement, Harvey

determined the ratio of interfacial areas at the beginning of film formation and at the start of shrinkage. He designated this ratio as the film factor "F". This film factor is used in Harvey's proposed mathematical expressions for calculating crude oil-water interfacial tension and its variation with time and film-forming component concentration.

Dodd[34] developed the first interfacial film viscometer designed especially for rheological investigations at oil-water interfaces in 1960. The viscometer was used to study diffusion-controlled reactions at crude oil-water interfaces and the non-equilibrium, time-dependent rheological properties acquired by films as a result of such interactions. Evidence was presented which indicated that the film structures involve free naphthenic acids, acid anions and their salts.

The recovery of oil from various types of porous media was studied by Burtsev[35] as a function of wettability, oil-water interfacial tension, and the ratio of the viscosity of oil to that of water. He determined that the lowering of the interfacial tension at a viscosity ratio of 1.46 resulted in a slight increase in the oil yield, but at ratios of 35.8 and 296.0 the yield was unchanged. At a viscosity ratio of 1.46 the over-all oil yield increased in a hydrophobic medium, but decreased slightly in a hydrophilic medium. As opposed to the water-free yield, the

over-all oil yield from a hydrophilic porous medium increased substantially with a rise in the interfacial tension.

In 1961 Glumov[36] reported variations in oil and water physical properties as determined in laboratory apparatus at 200-atm pressure and 40°C. Oil-water interfacial tension was found to decrease during prolonged contact between oil and water. Analysis of initial and residual oils showed that a considerable portion of nitrogen, methane, and other light hydrocarbons had migrated from the oil into the water.

The interfacial tension of some heavy petroleum fractions with water was investigated by Abas-Zade and Pashaev[37] in 1961. In all fractions investigated, with an increase of the molecular weight, the surface tension of the fractions at the boundary with air became lower than the interfacial tension at the boundary with water. This is apparently due to a decrease in the solubility of these products with an increase of their molecular weight.

De Saint-Palais and Leandre[38] studied the variation of oil-water interfacial tension with time. Using the du Nouy ring method of measurement, the oil-water interfacial tension at 24°C and atmospheric pressure was found to decrease exponentially between zero and 200 hours.

The variation of surface tension with depth was reported by Kuliev[39] in 1963. He determined the interfacial tension of petroleum and formation waters at six

locations between 1690- and 1970-meter depth. The interfacial tension at 20°C decreased with depth from 8.5 to 2.1 dynes per cm.

Interfacial tension at reservoir conditions was further studied by Casanova and Leandri,[40] who in 1963 built an experimental apparatus capable of determining interfacial tension at pressures of 10,000 psi and temperatures of 200°C.

In 1965 Neumann[41] reported that the higher the specific gravity of crude oil the higher the surface tension, but the lower the interfacial tension of the oil-water interface. He also published crude oil-water interfacial tension determinations as a function of aqueous phase pH. The interfacial tension was found to reach a maximum value at a pH of 6 and usually decreased rapidly, reaching near zero values at a pH of 11.

Mungan[42] conducted experiments to determine the effects of wettability, interfacial tension, and viscosity ratio on the immiscible displacement of a liquid by another liquid in porous media. His laboratory results showed that oil recovery by water injection into strongly oil-wet porous media is inefficient. Recovery can be improved by lowering the interfacial tension, increasing the viscosity of the injection water, and changing the matrix wettability.

Interfacial tension at the oil-water interface may be altered by the formation of interfacial films as reported by

Kimbler, et al.[43] These films result from the adsorption of high molecular weight polar oil molecules at the interface. The phase state of the film is influenced by the pH of the aqueous phase, contact time allowed for adsorption, concentration of polar molecules in the oil phase, and the presence of nonionic polar molecules in the water phase.

Hough and Warren[44] reported the use of digital computers to estimate the interfacial tension values of binary systems by the modified Weinaug-Katz equation. Their method required that the mole fractions, molal volumes, and densities of the phases be known.

Wagner and Leach[45] studied the effect of interfacial tension from 0.01 to 5.0 dynes per cm on displacement efficiency under oil-wet and water-wet conditions. Under both conditions displacement efficiency was improved by reducing the interfacial tension to less than 0.07 dynes per cm. Below 0.07 dynes per cm, small reductions in interfacial tension generated large increases in displacement efficiency.

Interfacial properties of hydrocarbon-water systems were studied by Gillap et al.[46] in 1967. Gillap found that the interfacial tension of aliphatic hydrocarbon-water systems increased linearly as a function of the log of hydrocarbon chain length.

The control of interfacial tension in waterflooding

operations was recognized as of economical significance in 1968 when Treiber et al.[47] applied for a U.S. patent on a process using NaOH to control oil-water interfacial tension.

Experiments were run by Taber[48] in 1969 to investigate the dynamic and static forces required to remove residual oil from porous media containing both oil and water. In every case, the oil removed was a function of the ratio $\Delta P/L\sigma$, where ΔP is the pressure drop across the distance L and σ is the interfacial tension between the oil and the water. No residual oil could be removed until a critical value of $\Delta P/L$ was exceeded. Above the critical value of the ratio, further increases in the ratio produced more of the residual oil. Good recovery was obtained at ratios 5 to 10 times greater than the critical value. In translating laboratory results to reservoir conditions, extremely low values of oil-water interfacial tension, obtainable by using surface active agents, must be used to avoid high waterflooding pressures that could possibly fracture the formation.

EXPERIMENTAL PROCEDURE

The experimental procedure will be discussed under three titles:

Equipment

Reservoir Fluids

Oil-Water-Time Correlation

Equipment

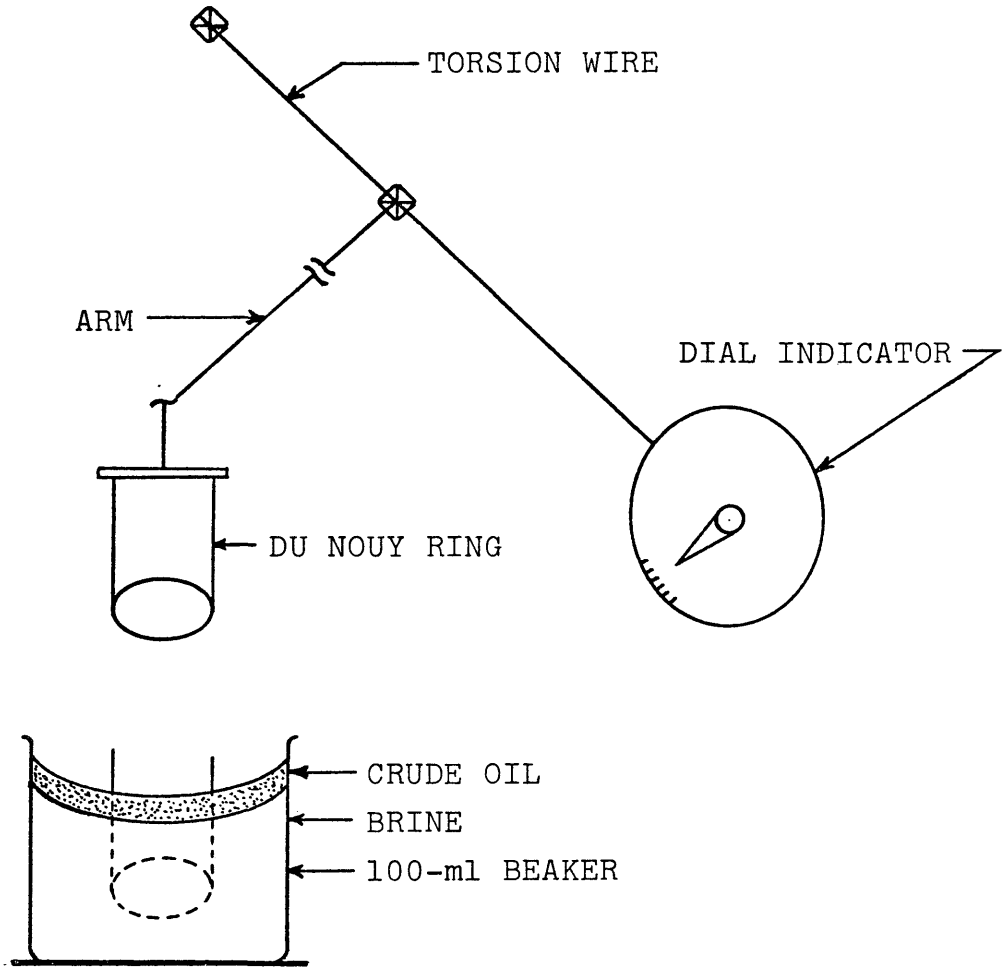
The choice of an interfacial tension measuring device was based upon the American Society for Testing Materials Method D-971 (Interfacial Tension of Oil against Water), in which the du Nouy ring is the prescribed method of measurement. This method utilizes the principles of operation originally devised by Dr. Pierre Lecomte du Nouy for studies of biological fluids.(7) In the du Nouy method, a platinum-iridium ring of precisely known dimensions is suspended from a counterbalanced lever arm. The arm is held horizontal by torsion applied to a taut steel wire, to which it is clamped. Increasing the torsion in the wire raises the arm and the ring, that carries with it a film of the liquid in which it was immersed. The force necessary to pull the test ring free from this film is measured.

The "Tensiometer" shows this "apparent" interfacial

tension on a calibrated dial. The dial reading must then be converted to "true" values by applying a correction factor which relates the density difference of the fluids, the dial reading, the radius of the ring, and the diameter of the wire used to form the ring.[49]

An additional correction had to be applied to the tensiometer used, Fisher Surface Tensiometer (Model 20), due to the unavailability of the manufacturer's prescribed ring. Substitute rings from other laboratory tensiometers were used in all measurements. The configuration of these substitute rings required that the measurements be made from the more dense (brine) to the less dense (oil) liquid. This prevented the visual observation of the interface rupture. Use of the proper ring would have made measurements from the less dense (oil) to the more dense (brine) liquid possible, and would have increased the accuracy of the measurements by observing the first sign of rupture.

The crude-brine emulsion was prepared by placing the fluids in a small, screw-lid container. The container was shaken to accomplish the initial emulsification. Continuous agitation was then performed by the electric shaking device described in Figure 2. After agitation a small portion of agitated brine was placed in the measuring beaker to cover the du Nouy ring. The emulsion was then added above the brine and the interfacial tension was determined



INTERFACIAL TENSION = (Mg/2L)F dynes per centimeter

where:

M = weight expressed in grams

g = acceleration due to gravity in centimeters per second^2

L = mean circumference of the ring in centimeters

F = correction factor dependent upon the size of the ring, the size of wire used in the ring, the instrument reading, and the densities of the two phases.

Figure 1. Fisher Surface Tensiometer (Model 20)[49]

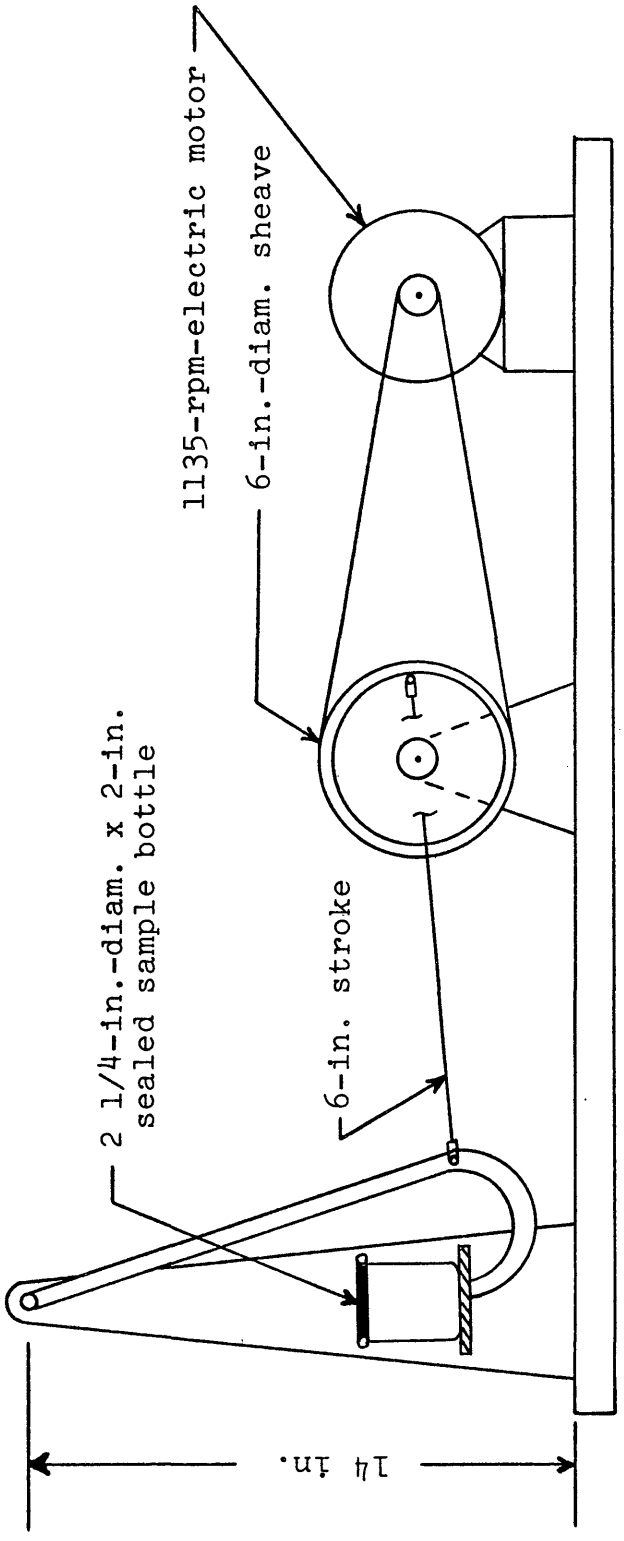


Figure 2. Hydrocarbon Shaker, Parr Instrument Co.

in the normal manner.

Reservoir Fluids

Of the three fluids present in petroleum reservoirs, crude oil, gas, and water, the discussion here will be limited to crude oil and its associated "connate" or interstitial water.

Crude Oil -- The crude oil selected for experimental purposes is a viscous, low-gravity (15.3° API) Canadian oil known as Lloydminster crude. This crude is most probably a complex mixture of high molecular weight, straight-chain hydrocarbons. These hydrocarbons are thought to be mostly saturated although some cyclic or naphthene hydrocarbons may be present. The crude also probably contains small amounts of combined oxygen, nitrogen, and sulfur.

Water -- Petroleum reservoir water almost always contains dissolved salts. Chemical analysis of water from many reservoirs has disclosed the presence of a variety of dissolved ions. Cations most commonly present are sodium, potassium, calcium, and magnesium; however, barium, lithium, and iron are also found. The anions most commonly present are chloride, sulfate, and bicarbonate; however, carbonate, nitrate, bromide, iodide, and sulfide have also been reported.[50] Sodium chloride, calcium chloride, and magnesium chloride were selected as the salts of interest for this thesis because of the widespread occurrence of sodium,

calcium, magnesium, and chloride ions.

To gain as realistic a study as possible, a literature search was conducted to ascertain the maximum concentrations of the selected salts found in formation brines. From this literature review the following salt concentrations were determined as being "representative" of brines found in petroleum reservoirs:

a) Sodium chloride - maximum value 278,000 ppm.[51] Increments of 50,000 ppm from zero to 300,000 ppm were selected for experimental work.

b) Calcium chloride - maximum value 68,700 ppm.[52] Increments of 20,000 ppm from zero to 80,000 ppm were selected for experimental work.

c) Magnesium chloride - maximum value 42,700 ppm.[53] Increments of 10,000 ppm from zero to 50,000 ppm were selected for experimental work.

Oil-Water-Time Correlation

The formation and migration of crude oil and its associated "connate" water takes place over a period of many years; thus, the "contact time" between crude oil and water may be quite long. Although it is impossible to duplicate this long "contact time" in the laboratory, an insight into the relationship can be gained by allowing Lloydminster crude to remain in contact with selected salt solutions for a period of time, and measuring the interfacial tension at

regular intervals.

The second stage of the time investigation was conducted by simulating natural reservoir oil-water contact conditions. This was accomplished by shaking an oil-water mixture until water droplets were dispersed throughout the oil media. "Agitation times" and "contact times" after agitation were varied, to determine whether emulsification of the crude with reservoir brines had any effect upon interfacial tension.

BRINE - CRUDE OIL INTERFACES

The molecular structure of brine-crude oil interfaces will be discussed under three titles:

Molecular Structure of Brine

Molecular Structure of Crude Oil

Molecular Structure at the Interface

Molecular Structure of Brine

Of the natural forces existing between molecules of water in its pure state, only the dipole force will be considered. These forces, electrical in nature, occur because of the unsymmetrical distribution of the atoms and electrons in molecules which make one part of the molecule more negative than the remainder. The two hydrogen atoms in water, being on the same side of the oxygen atom, make this side more positive, leaving the opposite side more negative. This charged "end" condition, called dipolar, constitutes an important binding force between the molecules by attracting the oppositely charged "ends" of neighboring molecules. This attraction/repulsion effect between the molecules extends throughout the liquid.

When a salt such as sodium chloride is brought into contact with water, the crystal lattice breaks down and the ions drift off into solution independent of each other.

However, due to the polar nature of water, the ions become hydrated shortly after contacting the solvent. Several water molecules, clustering around each ion of the salt, will create large composite ions. In the case of the sodium ion, the negative ends of the water molecule are adjacent to the positively charged ion; whereas with the chloride ions, the positive ends of the water molecules are adjacent to the negatively charged ion. Thus, the sodium and the chloride ions are able to break completely away from each other despite the attractive forces between them. Because of the envelope of water molecules which shields each ion from its neighbors, the separated hydrated ions can move through the solvent with considerable freedom.(54)

Molecular Structure of Crude Oil

Petroleum deposits vary widely in chemical composition. Those obtained from different localities may have entirely different physical and chemical properties. In spite of this diversity, the bulk of the chemical compounds found in crude oil are hydrocarbons. These hydrocarbons are classed according to the structure of the molecule and are designated as paraffin, naphthene, or aromatic hydrocarbons. The discussion here will be limited to the "simplest case" or paraffin series although the principles developed could be applied to the other classes of hydrocarbons with little difficulty.

The paraffin series is characterized by the fact that the carbon atoms are arranged in open chains and are joined by single bonds. That is, one valence of each carbon is used to form the chemical bond between adjacent carbon atoms in the chain. The open chain terminology does not mean that all the hydrogen atoms are in one plane nor the carbon atoms in one straight chain. The structural formula merely represents the fact that a certain number of carbons are joined together by single bonds to form an open chain, and the remaining valences form bonds with hydrogen.

Crude oil generally consists of a mixture of these straight-chain hydrocarbons. In the low-gravity crude used for experimental purposes we shall assume the presence of unknown percentages of paraffins ranging from low molecular weight pentane through some undetermined high molecular weight hydrocarbon. The important element of molecular structure relating to our experiments is the fact that many hydrogen atoms are bonded to a few carbon atoms, and that these hydrogen atoms are outside or protruding from the molecule's central carbon chain.(50)

Molecular Structure at the Interface

Molecular structure at the interface will be discussed on the basis of axioms developed by Michaels.(55) In his discussion, Michaels explains interfacial activity by relating the energy level of a molecule solely to its

distance from another molecule. Since energy determined by position with respect to some point in space is considered "potential energy," Michaels designates his relation a "potential-distance function."

If it is assumed that A and B are present as immiscible liquids in contact, the presence of B molecules at the A surface (and vice versa) will reduce the potential energy of an interfacial molecule relative to a surface molecule. In other words, the interfacial tension between two immiscible phases will always be less than the surface tension of the higher cohesive energy-density phase.

Adsorption -- If, to a system comprised of two immiscible liquids A and B in contact, a third component soluble in A or B or both is added, adsorption of that component at the interface may occur with a corresponding reduction of the interfacial tension. Since interactions between dissimilar molecules at the liquid-liquid interface (in the absence of solute) are weaker than those between molecules in the higher cohesive energy-density liquid, the interface is generally more favorable for concentration of solute than is the solvent surface. For interfacial adsorption of solute to occur, it is necessary that the interactions between A and the solute, and B and the solute be greater than the interaction between A and B. More simply, a condition of low potential energy must exist at the interface.

The extent to which a solute adsorbs at a liquid-liquid interface is primarily governed by the magnitude of the interfacial tension in the absence of solute. Interfacial tension, in the absence of solute, is an inverse measure of the deterioration of the phase boundary (mixing) or the potential energy of interaction between molecules of the two liquid components. When interfacial tension is low, molecular interactions between the two liquids are high and their separation at the interface is unfavorable for the admission of a potentially adsorbable solute molecule. The converse is true for liquids exhibiting high interfacial tension.

Electric Double Layer -- If a water immiscible liquid is placed in contact with water containing an electrolyte, one ionic species may be selectively adsorbed on the surface of the non-aqueous phase. This adsorption causes the build-up of an electrostatic potential at the interface. An equivalent number of ions of opposite charge (counterions) will accumulate in the aqueous phase near the charged interfacial layer to maintain electrostatic neutrality. These counterions tend to be distributed randomly about the interface in a thick layer (relative to molecular dimensions) whose depth is influenced by the dielectric constant of dispersing media. Electrostatic rather than molecular attractive forces act upon these counterions to hold them in the

vicinity of the interface. These layers of charge imbalance constitute the "diffuse double layer"[55] or the more commonly recognized "electric double layer."[56,57] The electric double layer generally retards ionic and molecular diffusion between phases since ions of the same charge as the adsorbed layer are electrostatically prevented from reaching the interface.

DISCUSSION

The preceding synopsis of brine-crude oil interface theory has established:

a) that anions and cations are present in the substrate proportional to the concentration of the solution.

b) that there exists an electric double layer at the interface composed of anions and cations.

c) that these anions or cations may be surrounded by dipole molecules of water, or may exist in a free ionic state.

d) that the oil phase of the system is composed mostly of paraffin hydrocarbons of high molecular weight.

The experimental results will be discussed under three headings:

Sodium Chloride Substrate

Calcium Chloride Substrate

Magnesium Chloride Substrate

Sodium Chloride Substrate

Figure 3 illustrates the effect of increasing aqueous phase sodium chloride concentration on brine-crude oil interfacial tension. This graph has two points of interest: (1) the pronounced flattening of the curve at 50,000 ppm, and (2) the minimum value of the curve at 150,000 ppm. In regard to the flattening it may be assumed that at

concentrations less than 50,000 ppm the ions in the electrolyte are spaced far enough apart that they will not interfere with diffusion across the interface. At 50,000 ppm the concentration of ions becomes great enough that free movement is curtailed and the rate of interfacial tension reduction is slowed by the inability of all available ions to gain immediate access to the interface. This is the first indication of the formation of the electric double layer. As the ion concentration is increased, the spacing at the interface is further reduced until we reach a saturation point where a closely packed layer of chloride ions prevents free interfacial ion exchange. The anion portion of the electric double layer is now complete. During this same period of time the cation portion of the electric double layer is forming.

The reduction of interfacial tension was based on the electric potential difference between the oil and the anions of the electrolyte. Thus, as the cation concentration increases, the potential of the anion layer decreases and a slight rise in the curve is observed. This rise is a function of the availability of sodium ions which increases with concentration.

The next set of curves (Figure 4) depicts the reduction of interfacial tension as a function of time under static conditions. Returning to the electric double layer

configuration one may predict a reaction between the chloride ions and the hydrogen ions bound to the hydrocarbon. This reaction would result in the formation of hydrochloric acid and a free carbon valence bond. The close proximity of sodium ions presents favorable conditions for sodium's being absorbed into the hydrocarbon as a replacement for the hydrogen. Evidence for this replacement reaction was indicated by the distinct lowering of the pH of the substrate after prolonged contact. The stabilization of the 50,000-ppm curve indicates that all the available chloride ions had reacted; whereas, the continuing slope of the 150,000-ppm curve indicates that replacement reactions were still occurring at 20 contact hours.

Figure 5 illustrates the variation of brine-crude oil interfacial tension as a function of agitation time and contact time. These curves were obtained by dispersing the sodium chloride solution throughout the oil media by shaking (agitation time), and then allowing the emulsion to set undisturbed for a period of contact time.

From the graph it is observed that agitation of the fluids increases the interfacial tension. The original 150,000-ppm sodium chloride solution now exhibits interfacial tension values of the same general magnitude as the 50,000-ppm solution. This indicates a decrease in the salt concentration. An attempt will be made to explain this

apparent decrease in salt concentration.

Electrolytic solutions in the static state contain sodium and chloride ions intermixed with water molecules and ions to which water dipoles have affixed themselves. Upon agitation, the sodium and chloride ions are quickly forced into contact with a large number of hydrocarbon molecules. The agitation also decreases the probability that the ions will remain in a hydrated condition; thus the possibility of a chemical reaction between the ions and the hydrocarbon is increased. After emulsification the sodium and chloride ions again function as previously discussed, but at lower concentrations. The preceding statements are strengthened by the measured decrease in pH after agitation.

The interfacial tension readings were noted to increase with contact time after agitation. This increase is attributed to the coalescence of the water droplets[58] with time. As the water drops become larger, more "pull" is required to raise the tensiometer ring through the emulsion.

The measured values recorded in Figure 5 are subject to slight deviation due to the increased density of the upper phase of the interface. This increase in density upon emulsification was not taken into consideration because of the questionable percentage of water present. The magnitude of the error is considered of minor importance.

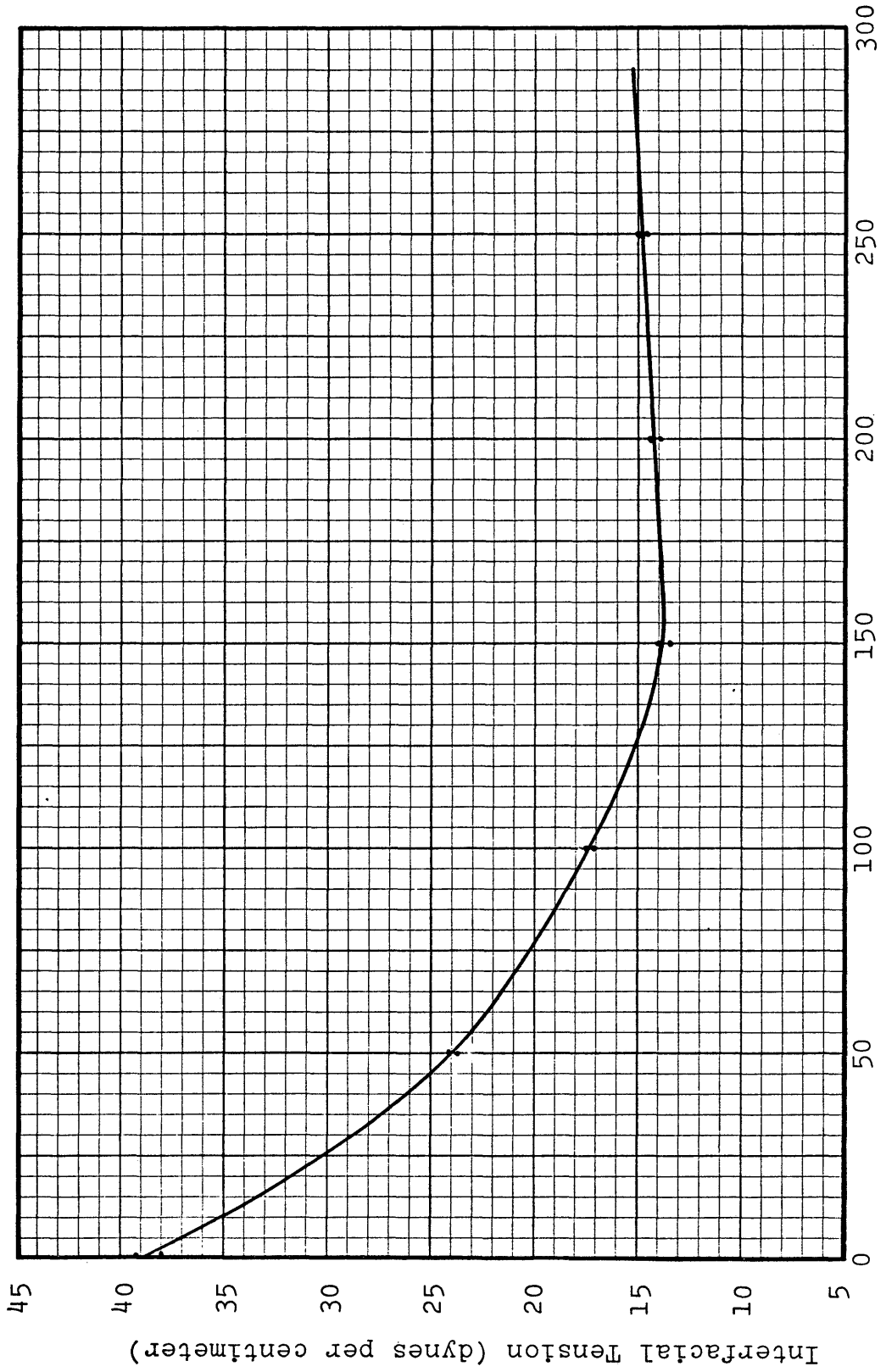


Figure 3. Sodium chloride brine concentration effect on brine-crude oil interfacial tension.

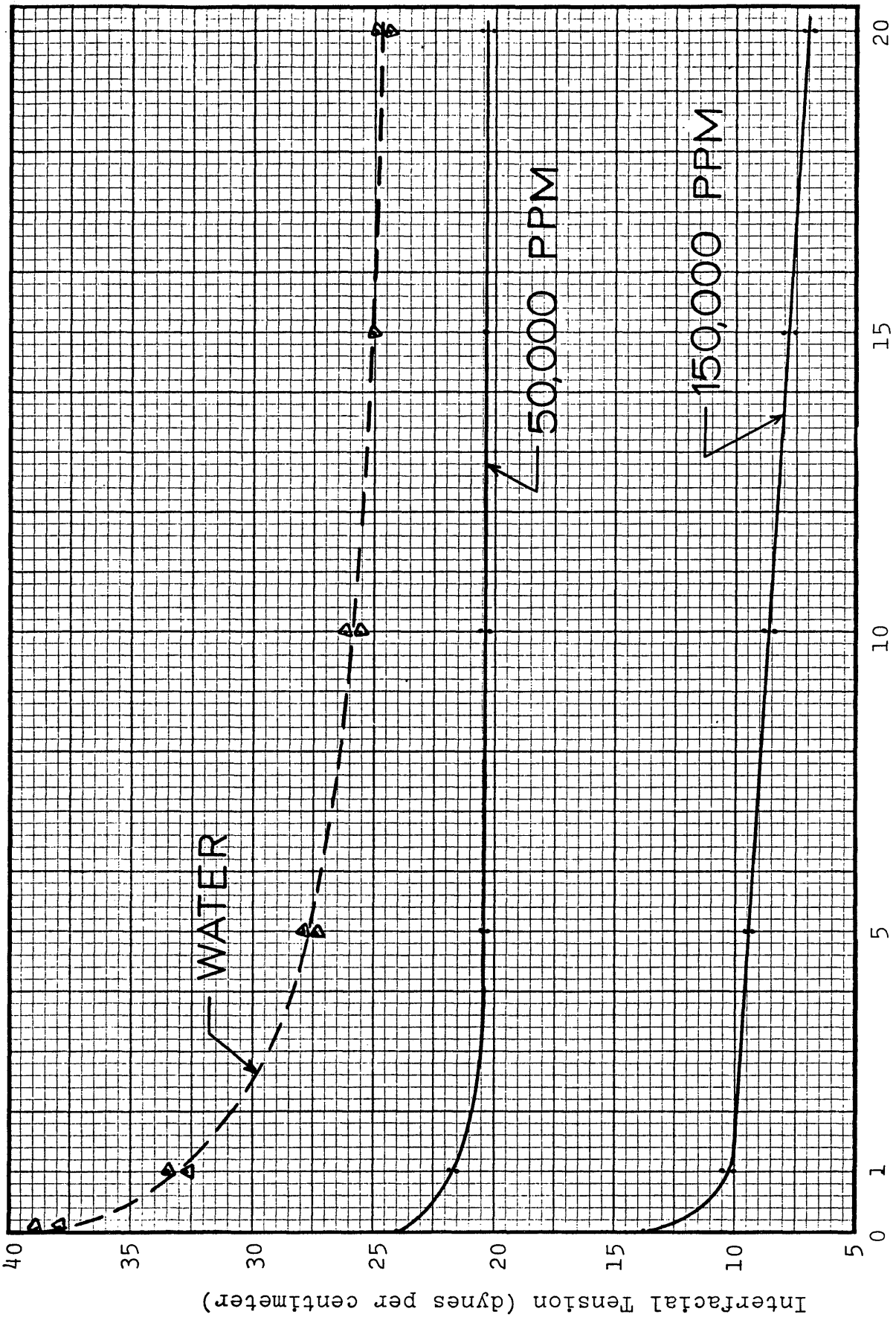


Figure 4. Static contact effect on brine-crude oil interfacial tension. Water and sodium chloride brines of 50,000- and 150,000-ppm concentration.

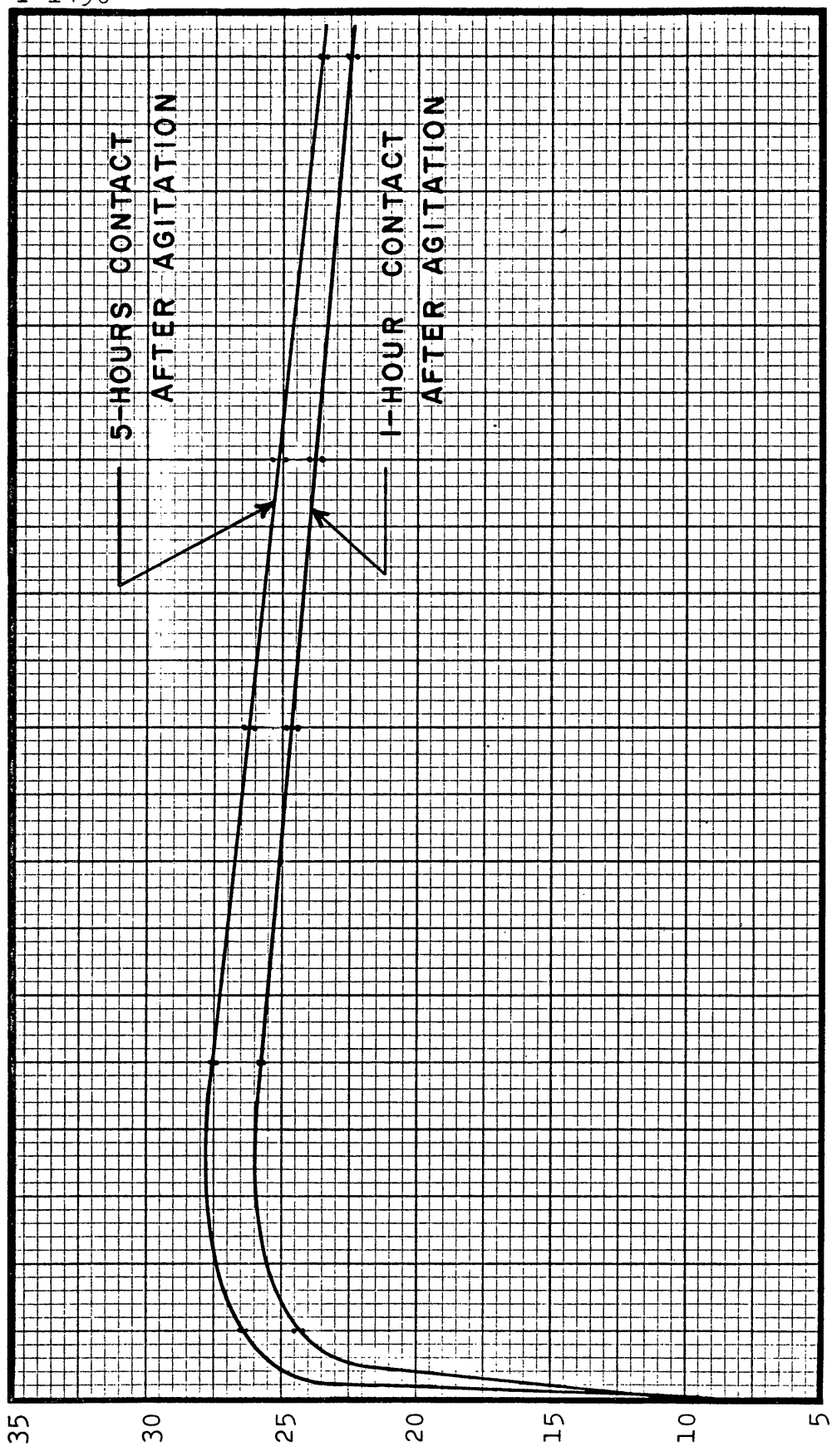


Figure 5. Dynamic disturbance effect on brine-crude oil interfacial tension. Sodium chloride, 150,000-ppm brine, at 1- and 5-hour contact times after agitation.

Calcium Chloride Substrate

Like sodium chloride, calcium chloride, Figure 6, exhibits both a pronounced flattening of the curve and a minimum value when the concentration of the salt is plotted against brine-crude oil interfacial tension. The explanations for these points are the same; however, two anions are now available for each cation, and the salt solution concentration is considerably lower. It would be expected, therefore, that the curve flattening and the minimum value would be obtained at one-half the values recorded for sodium chloride. Considering the large increments used in the salt solution preparation and the limits of experimental accuracy, a rather large variation in the two-to-one ratio is still found. This variation can be explained by the fact that calcium ions are larger and, due to hydration, less reactive than sodium ions, and therefore less likely to transfer across the interface and react with the hydrocarbon.

Figure 7 shows that the interfacial tension-time relationship is almost linear. This is explained by the fact that the calcium ion exhibits two free valence bonds, and is therefore more strongly contained within its water envelope. The ion is, therefore, less likely to transfer across the interface to react with the hydrocarbon even though an open valence bond may exist on the hydrocarbon.

The slight rise in the curve at zero through five hours is due to the early reaction of the chloride ions with the hydrocarbon and the steady replacement of chloride ions by calcium ions until a stabilizing layer of calcium ions is formed.

From Figure 8 it is observed that agitation of the 40,000-ppm brine has increased the interfacial tension to values usually obtained from 10,000-ppm brines. This apparent decrease in brine concentration is attributed to reduction of the calcium ion concentration during emulsification. After emulsification the interfacial tension curves are similar to those determined under static conditions.

The decision whether a replacement reaction had occurred between the hydrocarbon and the brine was based on the determination of brine pH before and after agitation. A decrease in pH from 7.0 before to 5.8 after agitation was recorded. This reduction of pH is evidence that some calcium ions replaced hydrogen ions in the hydrocarbon.

Magnesium Chloride Substrate

The effects of increasing concentrations of magnesium chloride on brine-crude oil interfacial tensions are shown in Figure 9. The explanations for the flattening of the curve at 10,000 ppm and the minimum value at 30,000 ppm are the same as previously stated for sodium chloride and calcium chloride. From the consistently higher values recorded

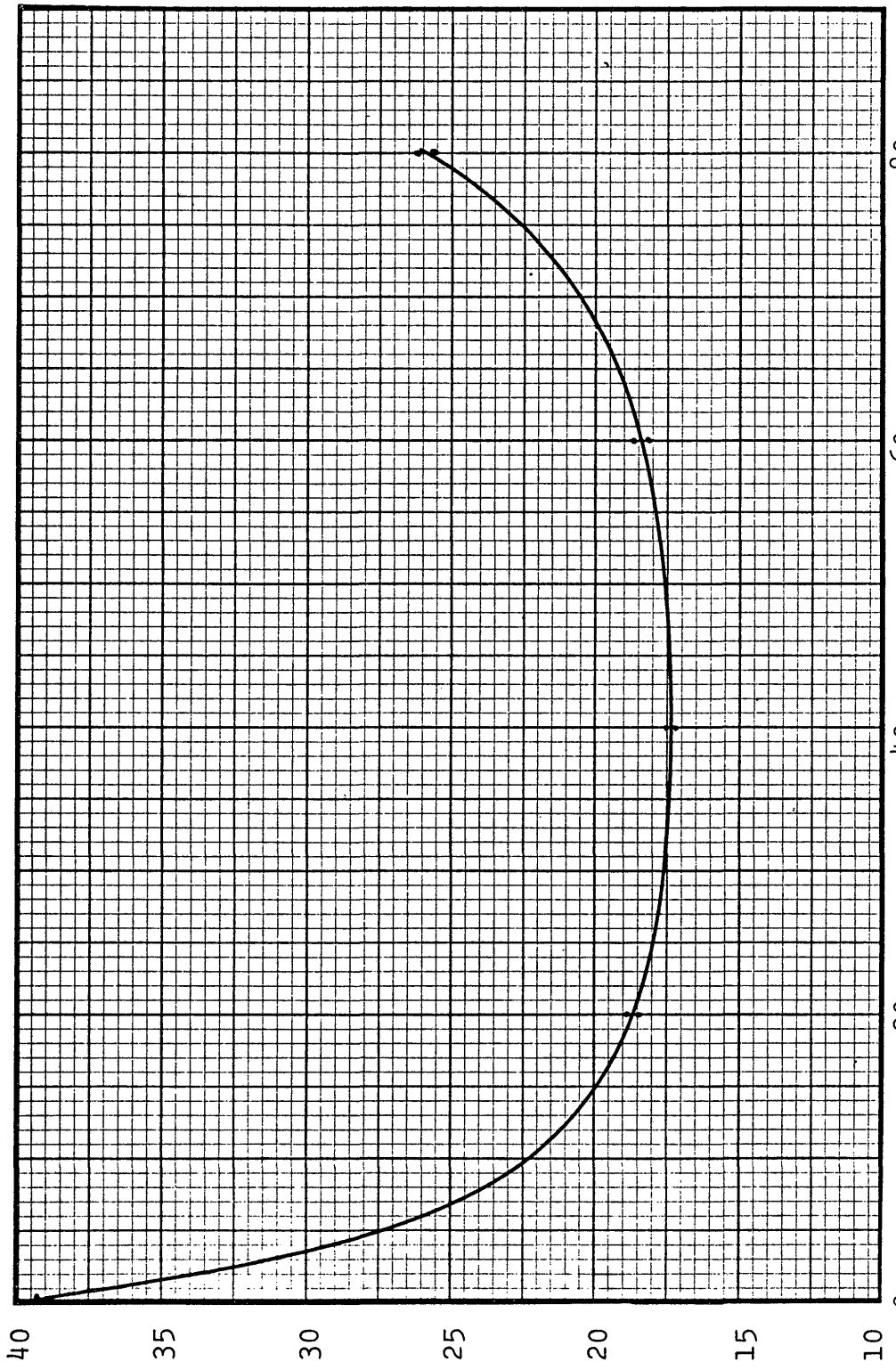


Figure 6. Calcium chloride brine concentration effect on brine-crude oil interfacial tension.

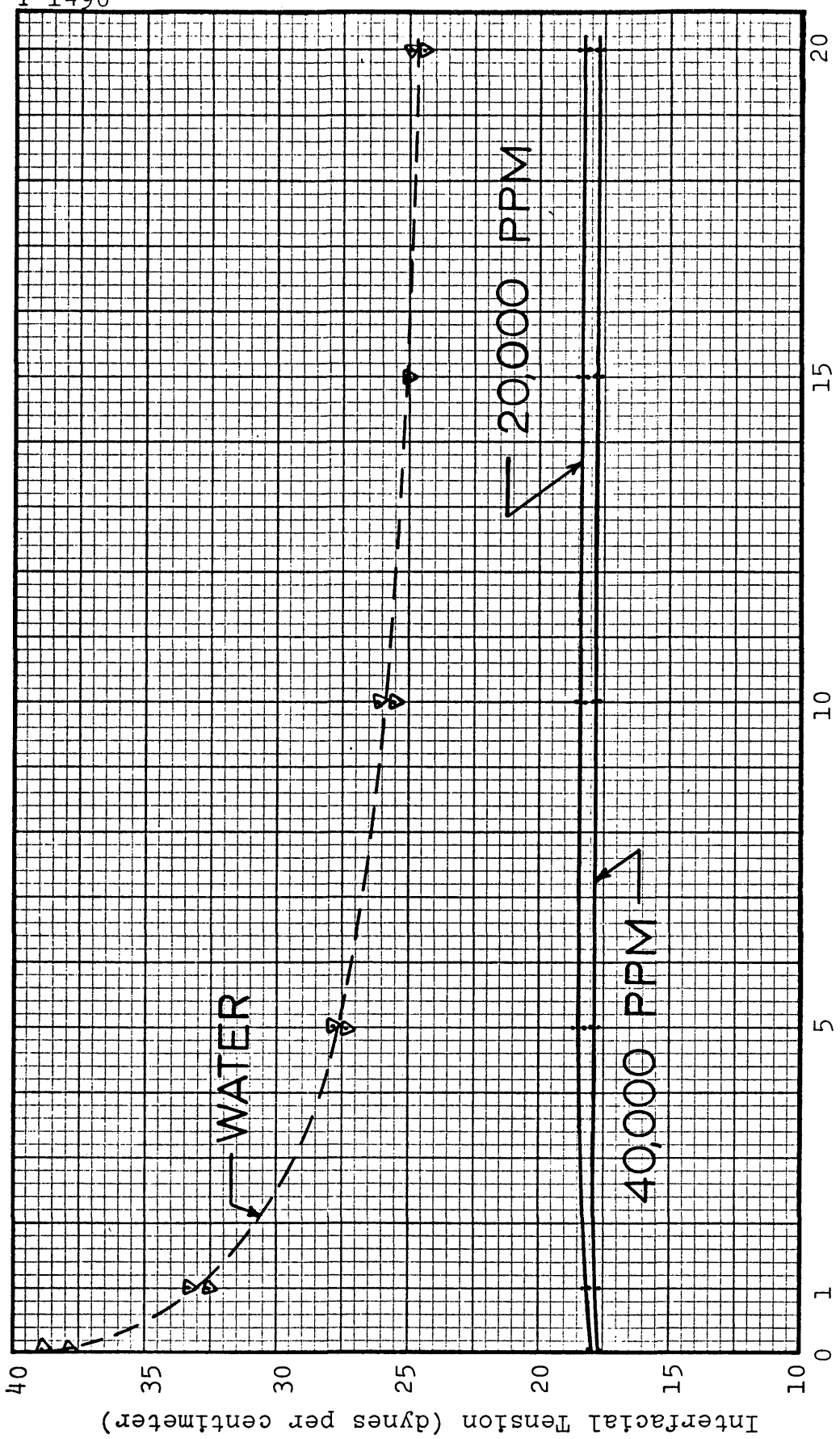


Figure 7. Static contact effect on brine-crude oil interfacial tension. Water and calcium chloride brines of 20,000- and 40,000-ppm concentration.

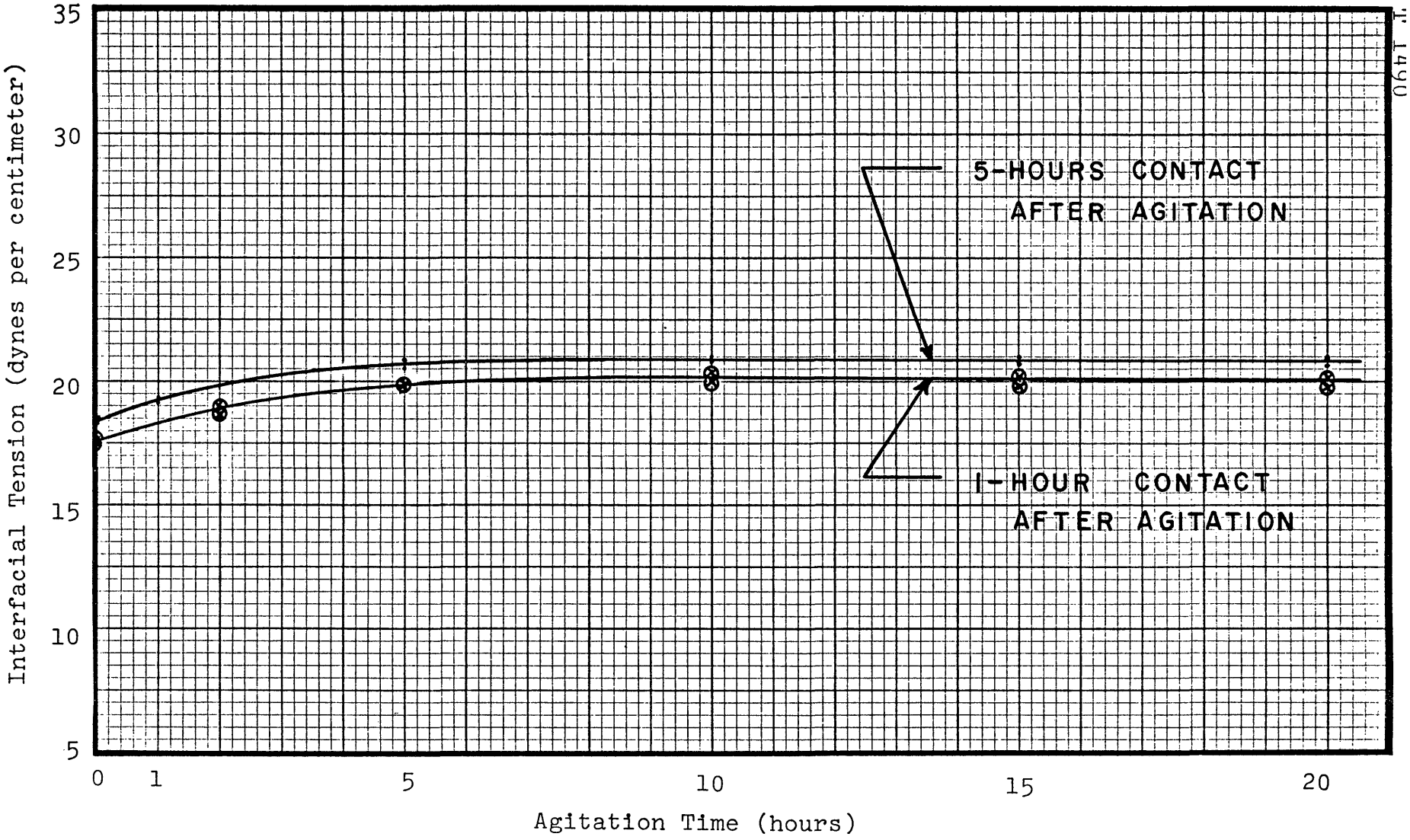


Figure 8. Dynamic disturbance effect on brine-crude oil interfacial tension. Calcium chloride, 40,000-ppm brine, at 1- and 5-hour contact times after agitation.

for magnesium chloride, as compared with those for calcium chloride, it may be concluded that magnesium chloride is not so interfacially active as calcium chloride.

Figure 10 illustrates the effect of static contact conditions upon magnesium chloride brine-crude oil interfacial tension. The curve, quite similar to that of calcium chloride (Figure 7), is caused by adsorption of the hydrated magnesium ion at the interface in sufficient quantities to prevent further diffusion between the brine and the crude oil.

Upon agitation of the 30,000-ppm magnesium chloride brine with crude oil, a distinct increase in interfacial tension was again observed. The pH was recorded before (7.5) and after (5.2) agitation to determine whether a replacement reaction had occurred. The lowering of the pH indicates an increase in the hydrogen ion concentration, which in turn can be taken as evidence of replacement of the hydrocarbon hydrogen by the magnesium ion. Additional evidence for this replacement is the interfacial tension values now being nearly equal to the values recorded for the 10,000-ppm magnesium chloride brine.

Contact time after agitation had no effect on magnesium chloride brine-crude oil interfacial tension. The prevention of water droplet coalescence, or the breakdown of the emulsion, reinforces the stabilizing effect of the hydrated magnesium ion indicated by the static contact graph, Figure 10.

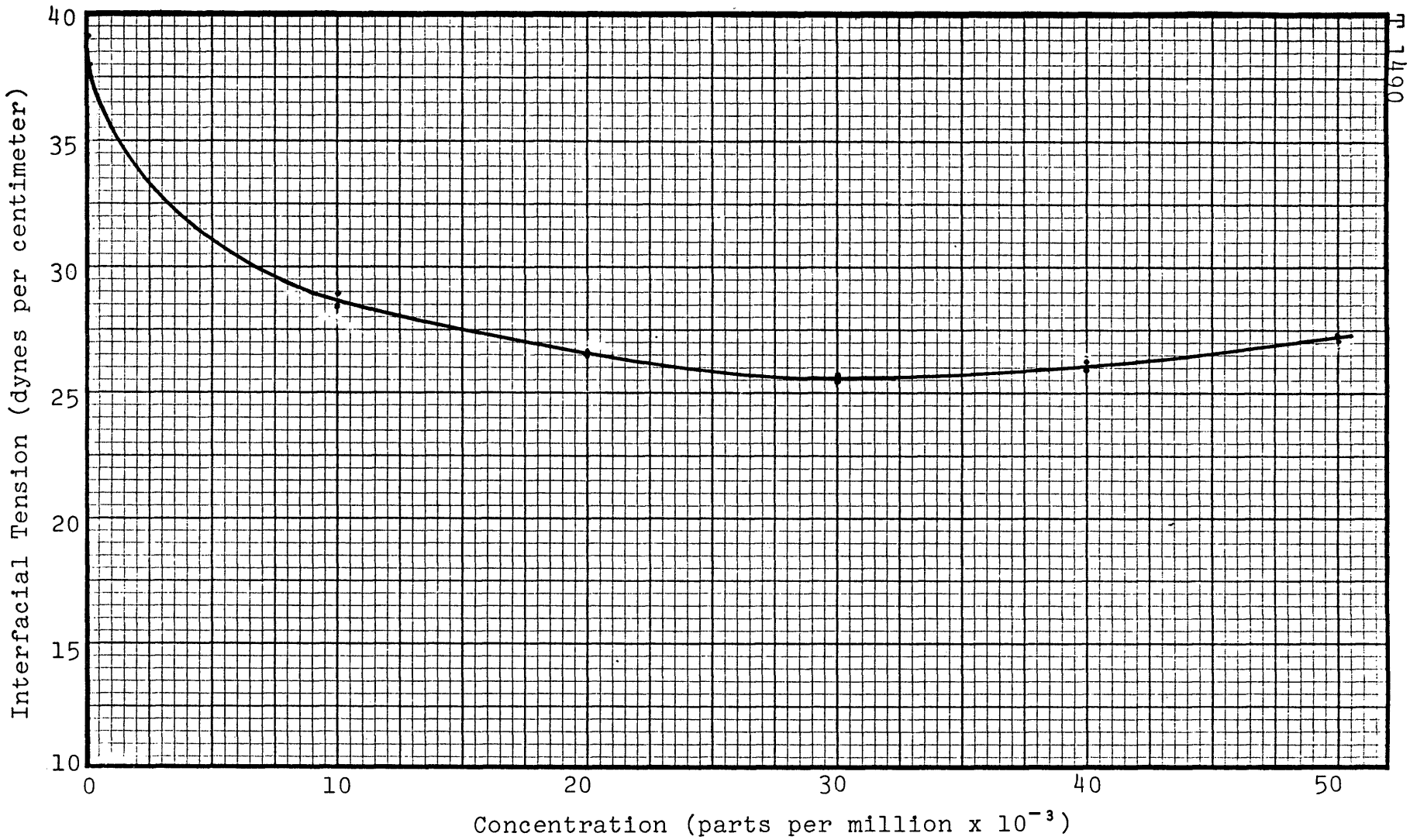


Figure 9. Magnesium chloride brine concentration effect on brine-crude oil interfacial tension.

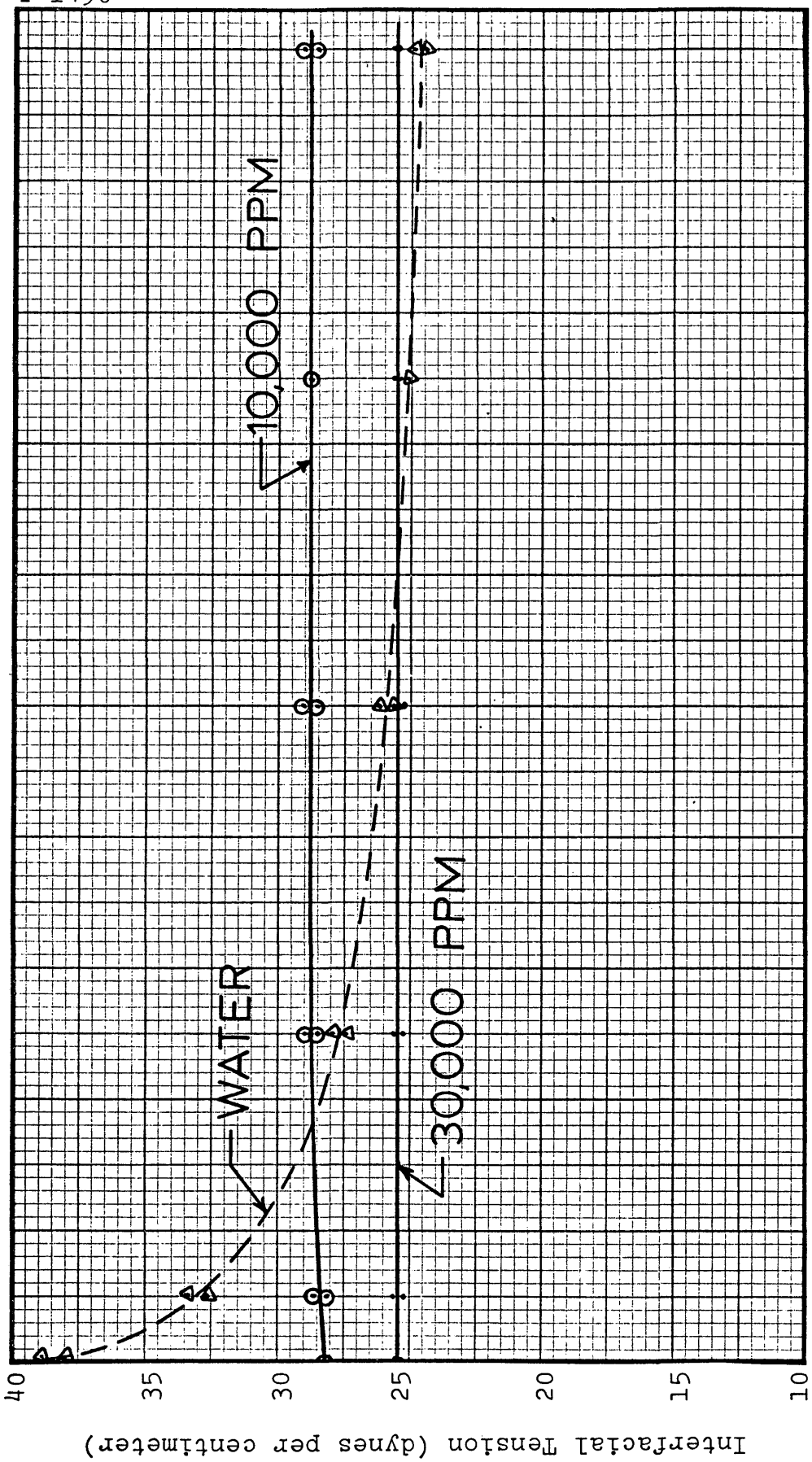


Figure 10. Static contact effect on brine-crude oil interfacial tension. Water and magnesium chloride brines of 10,000- and 30,000-ppm concentration.

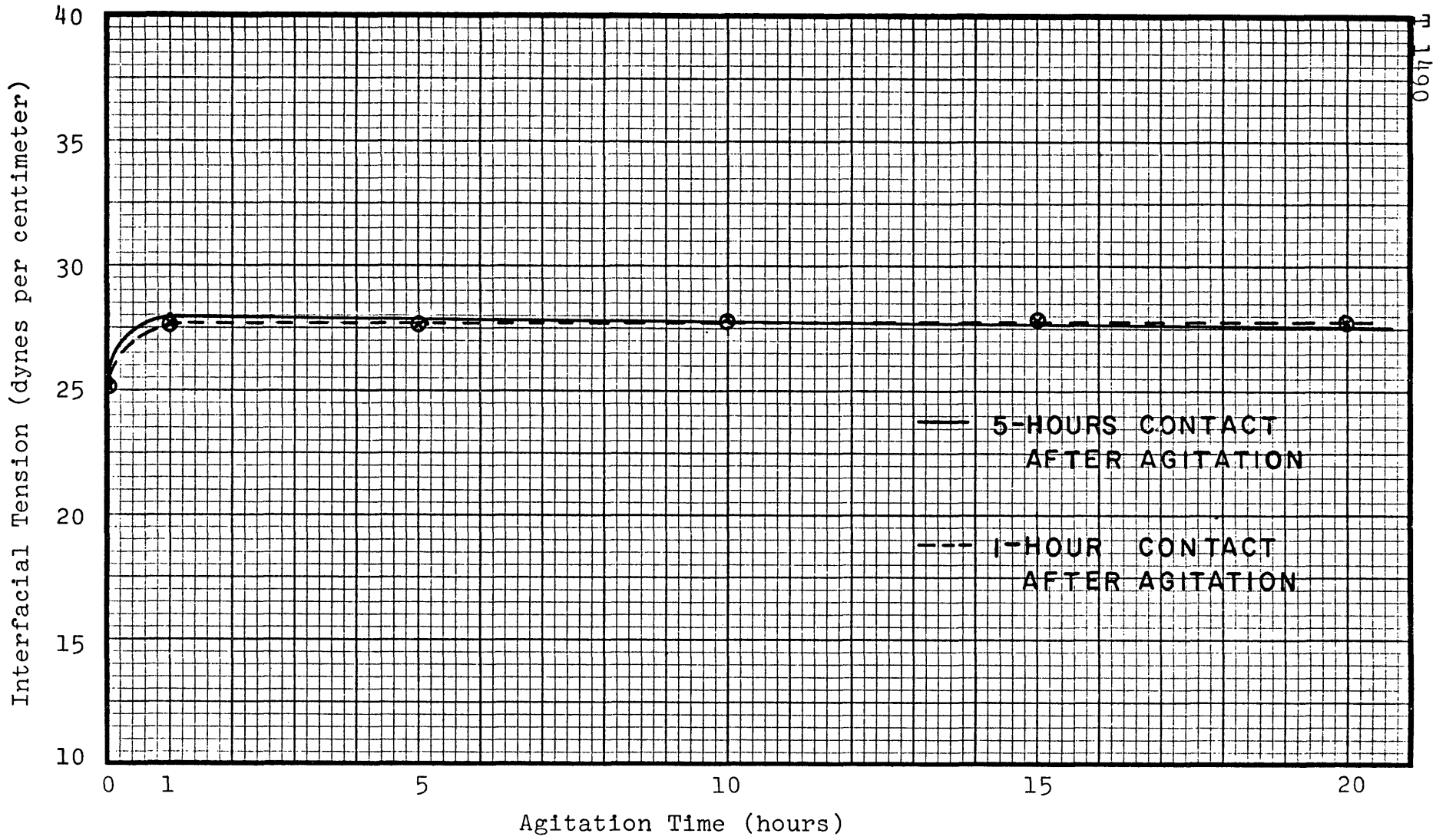


Figure 11. Dynamic disturbance effect on brine-crude oil interfacial tension. Magnesium chloride, 30,000-ppm brine, at 1- and 5-hour contact times after agitation.

CONCLUSIONS

The following conclusions may be drawn from the experimental results:

1) The interfacial tension between low-gravity Lloydminster crude oil and reservoir brines is a function of the composition and concentration of the brine. At common reservoir concentrations, sodium chloride causes the greatest reduction of interfacial tension; magnesium chloride causes the least reduction.

2) The effect of contact time on brine-crude oil interfacial tension is dependent upon the specific salt used and its concentration. Prolonged contact of crude oil against sodium chloride solutions produces marked decreases in interfacial tension values; whereas, prolonged contact against calcium chloride and magnesium chloride brines produces a slight increase in interfacial tension values. Higher brine concentrations effect lower interfacial tension values regardless of which salt is present in the brine.

3) In all cases agitation of a mixture of crude oil and brine effects an increase of the brine-crude oil interfacial tension. After the initial increase, the brines exhibit characteristics similar to those observed under static

conditions. The sharp rise in interfacial tension values is attributed to a replacement reaction between the cations and the hydrocarbon. This replacement reaction has the effect of lowering the salt concentration. Contact time after agitation increases the interfacial tension against sodium chloride and calcium chloride brines, but has no effect with the magnesium chloride brine.

4) Of the three salts tested, sodium chloride is interfacially the most active, calcium chloride noticeably less active, and magnesium chloride the least active.

5) When relating laboratory interfacial tension measurements to reservoir conditions, two factors must be considered. First, the cation present and its concentration. If sodium chloride is present at high concentrations, over 100,000 ppm, determinations after long periods of static contact are advisable. Calcium chloride and magnesium chloride effects are essentially dependent upon concentration only, and contact time studies are not considered necessary. The second factor to be considered is the physical state of the crude oil. If the crude is in an emulsified condition, interfacial tension determinations after agitation of a brine-crude oil mixture are necessary due to the consistently higher values obtained from the emulsified crude.

RECOMMENDATIONS

This research has indicated that reservoir interfacial tension between Lloydminster crude and brine may be as much as three-hundred per cent (sodium chloride brine after agitation) higher than laboratory methods predict. This large discrepancy between laboratory and reservoir values may be considered at least partly responsible for the disparity between oil recovery prediction and pilot water flood results. The completed research has also raised some unanswered questions pertaining to the influence of brine pH on interfacial tension measurements. Therefore, the following recommendations are offered relative to continuing the research:

1) Further investigative effort should be directed toward determining the influence of brine pH on interfacial tension. The first new measurements should again be made with the brine concentration which effected the minimum interfacial tension value (150,000 ppm for sodium chloride) for the salt under consideration. It is expected that the maximum interfacial tension will be found in a narrow range of pH values near neutral, and that interfacial tension will decline rapidly on both sides of the maximum values. Using the inflection points from these curves to determine experimental pH values, and the same brine concentration, a new set of static contact

time versus interfacial tension curves can be obtained. These static contact time versus interfacial tension curves will depict the influence of pH on the rate of interfacial tension lowering. The dynamic disturbance curves should also be repeated using the brine concentration and pH values determined for the static contact graphs. If the same sharp increase in interfacial tension after agitation is again obtained, interfacial tension is a function of brine composition and concentration only. If, however, the sharp increase is reduced or eliminated, interfacial tension must also be a function of brine pH.

2) In the preceding investigation, a distinct drop in pH was noted after agitation of the brine-crude emulsion. This reduction of pH indicates a strong tendency for a chemical reaction to occur between the brine and the crude. To reduce the effect of a brine-crude reaction on experiments for determining the influence of pH on interfacial tension, it is recommended that all experimental brines be buffered to reduce the possibility of a lower pH (chemical reaction result) existing at the brine-crude interface than is measured in the bulk solution.

3) Many authors have reported the presence of a membrane-like film at the interface of some low-gravity crudes and brines.[15,17,29] Although the presence of such a film was not observed during this investigation, its absence should

be verified. This verification can be easily accomplished by making some interfacial tension determinations with a pendant drop apparatus. Any film formation can be visually detected in this apparatus by simply retracting the drop after a period of brine-crude contact. A wrinkled surface appearing on the drop as it is retracted indicates the presence of an insoluble film.

APPENDIX

ANALYSIS OF CRUDE OIL

Field: Lloydminster
Well: Royalties No. 1
Location: Ls. 4, sec. 36, tp. 49, rge. 1, W. 4th
Depth: 1,925 feet

Province: Alberta
Sample from: E. Swain
Date: January 28, 1939

Characteristics

Specific gravity at 60°F.: 0·985
Sulphur, % by weight: 3·92
Water and sediment, % by vol.: 4·2 (by centrifuge)
Viscosity, Saybolt Furol, at 122°F., 475 secs.

Degrees A.P.I. at 60°F.: 12·2
Colour: Black
Pour point: 35°F.

Distillation, Hempel Method

Distillation* at atmospheric pressure, 774 mm. First drop, 190°C. (374°F.)

Fraction cut No.	at °C.	at °F.	Per cent cut	Sum per cent	Specific gravity of cut	Degrees A.P.I. of cut	Correlation Index	Viscosity Say. Univ. at 100°F.	Cloud test, °F.
1	50	122	.....	.....	.....	.....	.....	.....	.....
2	75	167	.....	.....	.....	.....	.....	.....	.....
3	100	212	.....	.....	.....	.....	.....	.....	.....
4	125	257	.....	.....	.....	.....	.....	.....	.....
5	150	302	.....	.....	.....	.....	.....	.....	.....
6	175	347	.....	.....	.....	.....	.....	.....	.....
7	200	392	0·4	0·4	0·848	35·4	.....	.....	.....
8	225	437	1·9	2·3					
9	250	482	3·3	5·6	0·857	33·6	51	.....	.....
10	275	527	6·9	12·5	0·867	31·7	50	.....	.....

Distillation continued at 40 mm. pressure

11	200	392	3·4	15·9	0·886	28·2	51	41	.....
12	225	437	4·9	20·8	0·897	26·3	52	51	.....
13	250	482	5·6	26·4	0·912	23·7	56	75	.....
14	275	527	6·7	33·1	0·927	21·1	60	137	.....
15	300	572	12·6	45·7	0·939	19·2	63	294	Below −5
Residuum			52·4	98·1	1·026	6·4	.....	.....	.....

Carbon residue of residuum: 22·4% **Carbon residue of crude: 11·7%**

Approximate Summary

—	Per cent by volume	Specific gravity	Degrees A.P.I.	Viscosity Say. Univ. at 100°F.
Light gasoline	.....	.....	.....	.....
Total gasoline and naphtha	.....	.....	.....	.....
Kerosene distillate	.....	.....	.....	.....
Gas oil	18·0	0·869	31·3	Below 50
Nonviscous distillate	8·1	0·896—0·918	26·4—22·6	50—100
Medium distillate	7·4	0·918—0·932	22·6—20·3	100—200
Viscous distillate	12·2	0·932—0·947	20·3—17·9	Above 200
Residuum	52·4	1·026	6·4	.....
Distillation loss	1·9	.....	.....	.....
Base of crude	Naphthene (wax-free)			

*Distillation was made on sample after dehydration.

Field: Lloydminster **Province: Saskatchewan**
Well: Triangle Oil & Gas No. 1 Sample from: E. Swain
Location: Ls. 5, sec. 35, tp. 49, rge. 28, W. 3rd Date: June 2, 1937

Characteristics

Specific gravity at 60°F.: 1·014
Sulphur, % by weight: 3·0
Water, % by vol. (A.S.T.M.): 19·0
Water and sediment, % by vol.: 30·0 (by centrifuge)

Degrees A.P.I. at 60°F.: 8·1
Colour: Brownish black

Distillation, Hempel Method

Distillation* at atmospheric pressure, 760 mm.

Fraction cut No.	at °C.	at °F.	Per cent cut	Sum per cent	Specific gravity of cut	Degrees A.P.I. of cut	Correlation Index	Viscosity Say.Univ. at 100°F.	Cloud test, °F.
1	50	122	.....	.....	.....	.....	.....	.....	.....
2	75	167	.....	.....	.....	.....	.....	.....	.....
3	100	212	.....	.....	.....	.....	.....	.....	.....
4	125	257	.....	.....	.....	.....	.....	.....	.....
5	150	302	0·3	0·3					
6	175	347	0·4	0·7					
7	200	392	0·6	1·3	0·849	35·2	.....	.....	.....
8	225	437	2·0	3·3					
9	250	482	3·4	6·7	0·860	33·0	47	.....	.....
10	275	527	7·0	13·7	0·874	30·4	49	.....	.....

Distillation continued at 40 mm. pressure

11	200	392	4·4	18·1	0·893	27·0	54	43 secs.	.....
12	225	437	6·2	24·3	0·908	24·3	57	59 "	.....
13	250	482	7·3	31·6	0·922	22·0	61	100 "	.....
14	275	527	3·4	35·0	0·932	20·3	62	191 "	.....
15	300	572	6·6	41·6	0·939	19·2	63	362 "	Below 0
Residuum.....			58·0	99·6	.....	.....	.....	.....	.....

Carbon residue of residuum: 24·3% **Carbon residue of crude: 14·1%**

Approximate Summary

—	Per cent by volume	Specific gravity	Degrees A.P.I.	Viscosity Say. Univ. at 100°F.
Light gasoline.....	.....	.....	.....	.....
Total gasoline and naphtha.....	.....	.....	.....	.....
Kerosene distillate.....	.....	.....	.....	.....
Gas oil.....	18·3	0·873	30·6	Below 50
Nonviscous distillate.....	9·7	0·900—0·922	25·7—22·0	50—100
Medium distillate.....	5·7	0·922—0·933	22·0—20·2	100—200
Viscous distillate.....	7·9	0·933—0·943	20·2—18·6	Above 200
Residuum.....	58·0	.....	.....	.....
Distillation loss.....	0·4	.....	.....	.....
Base of crude.....	Naphthene (wax-free)			

*Distillation was made on sample after dehydration.

Field: Lloydminster
Well: Colony Oil & Gas No. 3
Location: Ls. 5, sec. 19, tp. 49, rge. 27, W. 3rd

Province: Saskatchewan
Sample from: E. Swain
Date: 1936

Characteristics

Specific gravity at 60°F.: 0·987
Sulphur, % by weight: 3·05
Water, % by vol. (A.S.T.M.): 16·0
Viscosity, Saybolt Furol, at 100°F.: 662 secs.

Degree A.P.I. at 60°F.: 11·9
Colour: Brownish black
Pour point: 25°F.

Distillation, Hempel Method

Distillation* at atmospheric pressure, 760 mm.

Fraction cut No.	at °C.	at °F.	Per cent cut	Sum per cent	Specific gravity of cut	Degrees A.P.I. of cut	Correlation Index	Viscosity Say. Univ. at 100°F.	Cloud test, °F.
1	50	122	.....	.....	.....	.....	.....	.....	.....
2	75	167	.....	.....	.....	.....	.....	.....	.....
3	100	212	.....	.....	.....	.....	.....	.....	.....
4	125	257	.....	.....	.....	.....	.....	.....	.....
5	150	302	.....	.....	.....	.....	.....	.....	.....
6	175	347	.....	.....	.....	.....	.....	.....	.....
7	200	392	0·5	0·5	0·847	35·6	46	.....	.....
8	225	437	2·0	2·5					
9	250	482	3·7	6·2	0·861	32·8	48	.....	.....
10	275	527	6·8	13·0	0·876	30·0	50	.....	.....

Distillation continued at 40 mm. pressure

11	200	392	2·8	15·8	0·894	26·8	55	44 secs.	.....
12	225	437	6·2	22·0	0·904	25·0	55	55 "	.....
13	250	482	7·2	29·2	0·917	22·8	58	81 "	.....
14	275	527	7·3	36·5	0·932	20·3	62	166 "	5
15	300	572	11·1	47·6	0·938	19·4	62	238 "	25
Residuum			50·9	98·5	.....	.....	.....	.....	.....

Carbon residue of residuum: 22% Carbon residue of crude: 11·2%

Approximate Summary

—	Per cent by volume	Specific gravity	Degrees A.P.I.	Viscosity Say. Univ. at 100°F.
Light gasoline	.....	.....	.....	.....
Total gasoline and naphtha	.....	.....	.....	.....
Kerosene distillate	.....	.....	.....	.....
Gas oil	16·6	0·872	30·8	Below 50
Nonviscous distillate	10·7	0·899—0·921	25·9—22·1	50—100
Medium distillate	9·9	0·921—0·935	22·1—19·8	100—200
Viscous distillate	10·4	0·935—0·942	19·8—18·7	Above 200
Residuum	50·9	.....	.....	.....
Distillation loss	1·5	.....	.....	.....
Base of crude	Naphthene (wax-bearing)			

*Distillation was made on sample after dehydration.

Field: Lloydminster
Well: Colony Oil & Gas No. 3

Province: Saskatchewan
Sample from: E. Swain
Date: July 25, 1938

Characteristics

Specific gravity at 60°F.: 0·975
Sulphur, % by weight: 2·9
Water, % by vol. (A.S.T.M.): 13·0
Viscosity, Saybolt Furol, at 100°F., 410 secs.

Degrees A.P.I. at 60°F.: 13·6
Colour: Black
Pour point: 20°F.

Distillation, Hempel Method

Distillation* at atmospheric pressure, 769 mm.

Fraction cut No.	at °C.	at °F.	Per cent cut	Sum per cent	Specific gravity of cut	Degrees A.P.I. of cut	Correlation Index	Viscosity Say. Univ. at 100°F.	Cloud test, °F.
1	50	122	.....	.....	.....	.....	.....	.....	.....
2	75	167	.....	.....	.....	.....	.....	.....	.....
3	100	212	.....	.....	.....	.....	.....	.....	.....
4	125	257	.....	.....	.....	.....	.....	.....	.....
5	150	302	.....	.....	.....	.....	.....	.....	.....
6	175	347	.....	.....	.....	.....	.....	.....	.....
7	200	392	.....	.....	.....	.....	.....	.....	.....
8	225	437	2·4	2·4	0·840	37·0	43	.....	.....
9	250	482	4·4	6·8	0·855	34·0	45	.....	.....
10	275	527	6·7	13·5	0·870	31·1	47	.....	.....
Distillation continued at 40 mm. pressure									
11	200	392	6·7	20·2	0·893	27·0	54	44	.....
12	225	437	6·5	26·7	0·907	24·5	57	59	.....
13	250	482	6·2	32·9	0·920	22·3	60	94	.....
14	275	527	6·6	39·5	0·934	20·0	63	189	Below 0
15	300	572	10·2	49·7	0·943	18·6	64	427	Below 0
Residuum			49·5	99·2	.....	.....	.....	.....	.....

Carbon residue of residuum: 17·3% Carbon residue of crude: 8·6%

Approximate Summary

—	Per cent by volume	Specific gravity	Degrees A.P.I.	Viscosity Say. Univ. at 100°F.
Light gasoline	.....	.....	.....	.....
Total gasoline and nahptha	.....	.....	.....	.....
Kerosene distillate	.....	.....	.....	.....
Gas oil	19·5	0·870	31·1	Below 50
Nonviscous distillate	10·7	0·898—0·921	26·1—22·1	50—100
Medium distillate	6·4	0·921—0·935	22·1—19·8	100—200
Viscous distillate	13·1	0·935—0·948	19·8—17·8	Above 200
Residuum	49·5	.....	.....	.....
Distillation loss	0·8	.....	.....	.....
Base of crude	Naphthene (wax-free)			

*Distillation was made on sample after dehydration.

Field: Lloydminster **Province: Saskatchewan**
Well: Community Service No. 4 Sample from: E. Swain
Location: Ls. 9, sec. 10, tp. 49, rge. 28, W. 3rd Date: April 4, 1946

Characteristics

Specific gravity at 60°F.: 0·970 **Degrees A.P.I. at 60°F.: 14·4**
Sulphur, % by weight: 3·5 **Colour: Black**
Water, % by vol. (A.S.T.M.): 4·0 **Pour point: 15°F.**
Sediment, % by weight: 0·4
(by extraction)
Viscosity, Saybolt Furol, at 100°F., 379 secs.; at 122°F., 192 secs.

Distillation, Hempel Method

Distillation* at atmospheric pressure, 762 mm.

Fraction cut No.	at °C.	at °F.	Per cent cut	Sum per cent	Specific gravity of cut	Degrees A.P.I. of cut	Correlation Index	Viscosity Say. Univ. at 100°F.	Cloud test, °F.
1	50	122	.....	.....	.....	.....	.....	.....	.....
2	75	167	.....	.....	.....	.....	.....	.....	.....
3	100	212	.....	.....	.....	.....	.....	.....	.....
4	125	257	.....	.....	.....	.....	.....	.....	.....
5	150	302	0·1	0·1					
6	175	347	0·6	0·7	0·837	37·6	42	.....	.....
7	200	392	0·7	1·4					
8	225	437	2·5	3·9					
9	250	482	4·3	8·2	0·854	34·2	44	.....	.....
10	275	527	6·9	15·1	0·870	31·1	47	.....	.....
Distillation continued at 40 mm. pressure									
11	200	392	2·0	17·1	0·888	27·9	52	43 secs.	.....
12	225	437	5·3	22·4	0·897	26·3	52	51 "	.....
13	250	482	6·1	28·5	0·912	23·7	56	72 "	.....
14	275	527	5·7	34·2	0·927	21·1	60	130 "	Minus 5
15	300	572	7·6	41·8	0·940	19·0	63	291 "	30
Residuum			56·6	98·4	1·024	6·7	.....	.....	.....

Carbon residue of residuum: 19·5% **Carbon residue of crude: 11·0%**

Approximate Summary

—	Per cent by volume	Specific gravity	Degrees A.P.I.	Viscosity Say. Univ. at 100°F.
Light gasoline	.....	.....	.....	.....
Total gasoline and naphtha	.....	.....	.....	.....
Kerosene distillate	.....	.....	.....	.....
Gas oil	19·3	0·864	32·3	Below 50
Nonviscous distillate	9·0	0·896—0·919	26·4—22·5	50—100
Medium distillate	5·9	0·919—0·933	22·5—20·2	100—200
Viscous distillate	7·6	0·933—0·948	20·2—17·8	Above 200
Residuum	56·6	1·024	6·7	.....
Distillation loss	1·6	.....	.....	.....
Base of crude	Nathpthene (wax-bearing)			

*Distillation was made on sample after dehydration.

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