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Interfacial Tension Behaviour of a Canadian Heavy Oil against Caustic Solutions

by

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Ottawa, Ontario, 1985

A thesis
presented to the University of Ottawa
in fulfillment of the
thesis requirement for the degree of
Master of Applied Science
in
Chemical Engineering

UNIVERSITÉ D'OTTAWA
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ABSTRACT

At the present rate of consumption, the proven reserves of conventional (light) crude oil in Canada will soon be depleted. For a continued supply of petroleum, alternative sources must be developed. One of these sources is heavy oil.

Heavy oils are usually defined as those crudes having a density of 0.95 g/cm³ or higher. In addition to a density close to that of water, these crudes are highly viscous at reservoir conditions and contain a large amount of carboxylic and phenolic acids. Due to the presence of these acids, contacting heavy oils with caustic solutions produces surfactants in-situ at the crude oil-caustic interface. The surfactants thus generated act to lower the interfacial tension between the two phases to ultralow values.

The interfacial tension (IFT) between an important Canadian heavy oil (from Lloydminster, Saskatchewan) and various caustic solutions was measured using a University of Texas Model 500 Spinning Drop Interfacial Tensiometer. The effects of salinity and alkalinity of the aqueous phase and system temperature were studied. The effect of oil acidity on IFT was also investigated through the use of a series of dilutions of the Lloydminster crude oil with dodecane.

It was found that the interfacial tension was highly dependent upon interfacial age, and exhibited a dynamic minimum. The lowest IFT observed was obtained using a 0.05% NaOH solution. Also, with this aqueous phase the IFT remained at this ultralow minimum for contact times of over 10,000 seconds. The presence of sodium chloride in the aqueous phase had two main effects. The magnitude of the IFT increased with increasing salinity for constant pH aqueous phases. Also, the rate of rise in IFT subsequent to the minimum was greater and the rise commenced at shorter times as the salinity was increased.

Temperature had a much larger effect on the time at which the minimum IFT was attained than on the magnitude of this minimum. Also, the decrease in the minimum IFT observed and the time of this minimum were significantly greater for an increase in temperature from 25°C to 40°C than one from 40°C to 55°C.

The dilution of Lloydminster oil with dodecane resulted in higher IFT values than those for the pure crude oil. With these dilutions, the minimum IFT was reached at shorter times and the rate of increase in IFT following the minimum was greater than for the Lloydminster oil. The effect of temperature on IFT values was not as substantial for the oil-dodecane mixtures as for the pure crude oil.

ACKNOWLEDGEMENTS

Foremost, I would like to thank my research supervisors, Drs. G. Neale and V. Hornof, for their invaluable suggestions and advice and for freely giving their time to help in the preparation of this thesis.

Also, I wish to thank Messrs. G. Gasperetti, D. Lefebvre, and A. Bonaldo for their excellent technical assistance whenever it was asked.

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Chapter I

INTRODUCTION

Ever since the Industrial Revolution in the late nineteenth century, the world has been dependent upon fossil fuels. Coal, oil, and natural gas are used in such diverse fields as transportation, electrical generation, and the manufacture of a myriad of goods ranging from steel to gasoline to children's plastic toys. Indeed, the high standard of living enjoyed today in Canada and other industrialized nations could not have been attained without the use of petroleum and petroleum products.

However, the traditional sources of petroleum are quickly being depleted. The estimated proven world reserves of crude oil (those recoverable with present technology) amount to only a thirty year supply at present consumption rates(1). The Canadian situation is even worse, as shown in Table 1. Only a 13.5 year supply of proven reserves exists. Thus it is imperative that alternative sources of petroleum be developed to meet future needs. In Canada, two of these new sources are tar sands and heavy oils.

Heavy oils are usually defined as those crudes having a gravity of 20 °API or less. These oils are acidic in nature

Table 1 Crude Oil Reserves and Demand

	10³ bbl
LIGHT CRUDE OIL	
Proven Reserves	
Canada	7,020,000
Total World	668,262,406
Annual Demand	
Canada	518,300
Total World	21,325,539 (1)
HEAVY CRUDE OIL	
Proven Reserves	
Lloydminster Area	612,360
Total Canada	2,305,800
Potential Additions	
Lloydminster Area	1,360,800
Total Canada	2,400,300 (2)

and have a high viscosity at reservoir conditions. One of the largest deposits of heavy oil in Canada is situated near Lloydminster on the Alberta-Saskatchewan border. The established reserves contained in this deposit are 27 per cent of the total heavy oil reserves in Canada. The Lloydminster area represents an even greater percentage of the potential additions to heavy oil reserves. The National Energy Board has estimated that fully 57 per cent of the additional ultimate potential of heavy oil in Canada will be from the Lloydminster deposit(2). However, for this potential to be realized significant advances in recovery technology must be made.

1.1 Stages of Oil Production

A typical oil reservoir, as shown in Figure 1, consists of a layer of porous rock, such as sandstone, bounded both above and below by an impervious rock formation, usually granite or shale. Over a period of many million years, water, oil, and gas have accumulated in the porous medium, and have separated into fairly distinct layers due to gravity effects. The crude oil is trapped in the pores of the rock by natural forces resulting from viscosity, interfacial tension, and capillarity. These forces must be overcome in order for the oil to be produced.

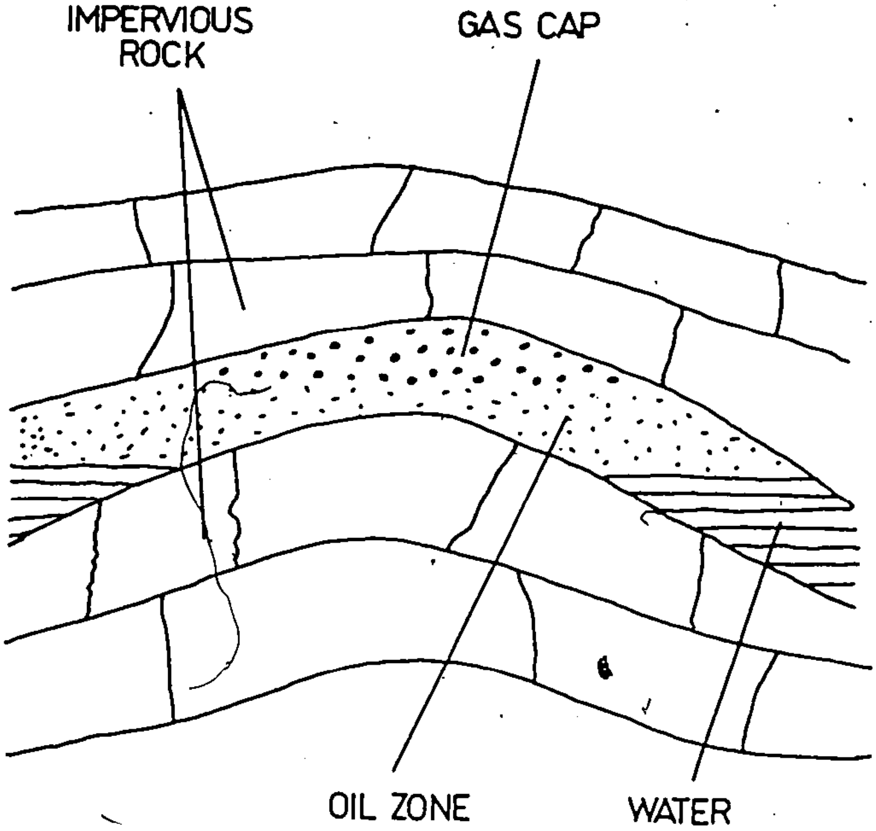

Figure 1: A Typical Oil Reservoir

1.1.1 Primary Recovery

When a well is drilled through the impervious cap of an oil reservoir, a pressure sink is formed and the reservoir contents are able to flow to the wellhead at the surface due to the expansion of reservoir fluids. This production of oil by natural energy is called primary recovery and can occur by one of three principal drive mechanisms: solution gas drive, gas cap drive, or water drive.

In a solution gas drive reservoir, the gases dissolved in the crude oil expand and come out of solution as the pressure in the reservoir drops. This expansion of gases causes the oil to be driven towards the wellbore. As production continues, the pressure in the reservoir decreases until the energy available from the expanding gas is no longer sufficient to cause the oil to flow to the surface, and pumping is required for further oil production. In a solution gas drive reservoir, the primary recovery is usually quite low, only 5 to 25% of the original oil-in-place(OOIP)(3), and other recovery techniques are necessary to recover more oil.

A water drive reservoir is one in which the predominant source of energy for the production of oil is water encroachment from an adjoining aquifer, caused by the expansion of water and rock in the aquifer as a result of the lower pressure at the wellbore. The aquifer associated with a water drive reservoir is often much larger than the reservoir itself, and thus the energy supplied by the aquifer results in continued oil production over a long period of time. An effective water drive reservoir is characterised by a slow drop in reservoir pressure with time, and thereby a high recovery efficiency.

When the pressure in the reservoir is not high enough to maintain all the light hydrocarbons in solution, free gas collects in the porous medium above the oil, creating a gas cap just below the impervious rock layer. In such a gas cap drive reservoir, the drop in pressure at the wellbore causes the gas cap to expand and displace oil towards the production well. Also, this drop in pressure allows the gas dissolved in the oil to come out of solution which aids in forcing the oil to the wellbore. Because the gas cap can expand a considerable amount, the decline in reservoir pressure occurs more slowly than in a solution gas drive reservoir, and thus the oil recovery is higher, usually 20 to 40% OOIP(3).

1.1.2 Secondary Recovery

Production of oil by the natural reservoir energy continues until this energy is depleted to the point where there is not sufficient force to drive the oil to the surface. At this point, it is necessary to supply energy from an external source for further production. This is accomplished by a technique known as pressure maintenance, in which a large volume of water, or sometimes gas, is injected into the reservoir through a separate well(4). The injected fluid restores pressure in the reservoir, helps to keep the dissolved gases in solution (which maintains a low oil viscosity), and forces the oil through the porous rock to the production well. The injection of water results in a second harvest of oil, hence the name secondary recovery.

In a waterflooding operation, injection wells are drilled in a pattern around the production wells. Some typical patterns of well placement are shown in Figure 2. The most commmon pattern is the five-spot, which is actually a staggered line drive with the spacing between adjacent production wells and injection wells being the same. When water is injected into an oil reservoir, it displaces some of the oil remaining in the pores of the rock. This oil forms an oil bank which is then pushed towards the producing well. Secondary recovery techniques may produce 15 to 30% OOIP, which means that substantial quantities of oil are still trapped in the reservoir. This remaining oil can often be produced by various other methods, collectively known as enhanced oil recovery techniques.

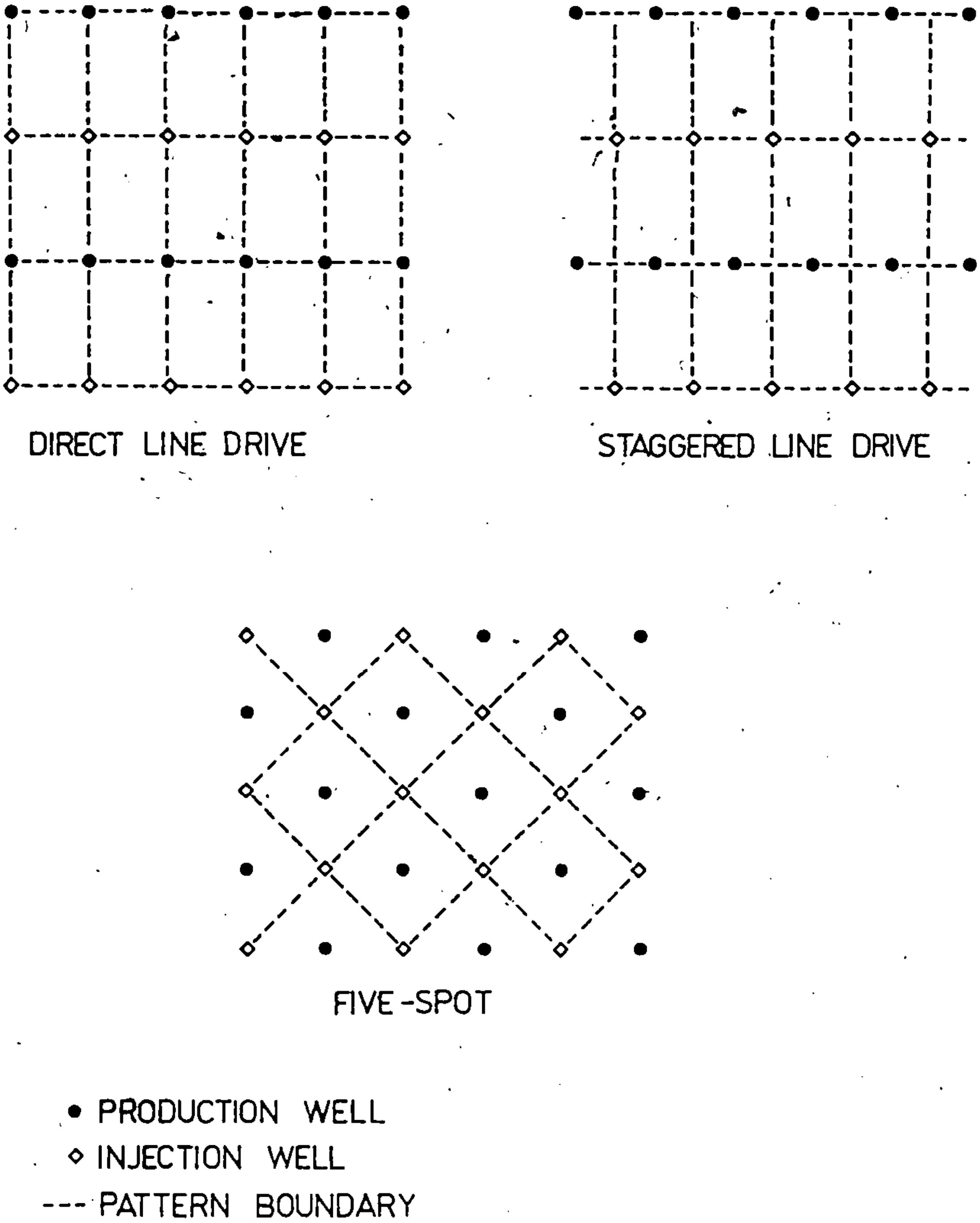

Figure 2: Patterns of Well Placement for Waterflooding

1.1.3 Enhanced Oil Recovery

The term Enhanced Oil Recovery(EOR) has been defined in many ways. Jha(4) uses this term to describe all the techniques used to increase the amount of oil obtained after primary recovery, thereby including waterflooding as an EOR process. However, a broader definition is more applicable to the recovery of heavy oils. This definition, which has been adopted by the Alberta Energy Resources Conservation Board, states that EOR is any oil production via artificial supplementation of natural reservoir energy(3).

The technical and economic viability of an EOR process is dependent upon three key factors: the oil saturation after primary recovery, the microscopic displacement efficiency of the fluid being used, and the volumetric sweep efficiency(4). These factors are in turn influenced by the past production history of the reservoir.

The microscopic displacement efficiency is the fraction of the oil contacted by the injected fluid that is displaced or forced out of the pores in the reservoir rock. The oil left in the reservoir is called the residual oil and occurs in one of two forms. In a water-wet reservoir, the residual oil takes the form of droplets of oil surrounded by water and trapped in the pore spaces by interfacial forces. In an oil-wet reservoir the residual oil exists as a thin film spread on the reservoir rock.

The volumetric sweep efficiency, the product of the areal and vertical sweep efficiencies, is determined by the physical properties of the reservoir (permeability and porosity) as well as the mobility ratio of the injected fluid to the displaced fluid. The mobility of a fluid in a porous medium is a measure of the ease with which the fluid flows through the medium, and is defined as the permeability of the formation to that fluid divided by the viscosity of the fluid, i.e.

$$\text{Mobility} = \frac{\text{Permeability}}{\text{Viscosity}}$$

If the mobility of the injected fluid (such as water) is greater than that of the displaced fluid (oil), the water can by-pass parts of the reservoir instead of driving the oil towards the production well in a bank, a phenomenon known as viscous fingering.

In light of these factors affecting the yield from an oil reservoir, any EOR process should be concerned with two main objectives (3):

1. to improve the microscopic displacement efficiency either by altering the forces that trap the oil in the rock pores, or by increasing the potential energy of the oil by increasing the pressure gradient in the reservoir or by solubilization of injected gas.
2. to improve the sweep efficiency, and thus the portion of the reservoir contacted by the displacing fluid, by

altering the mobility ratio or the flow paths developed during primary recovery.

In many cases, techniques which increase the displacement efficiency can actually reduce the sweep efficiency and therefore an optimal mix of these two objectives is required for a successful EOR application(4). The choice of an EOR process for a given reservoir depends on many factors, such as the geology and physical properties of the reservoir, and past production methods. EOR techniques can be divided into three classes: thermal processes, miscible displacement processes, and chemical processes.

1.1.3.1 Role of Capillary Forces in EOR

As mentioned previously, one of the key parameters in determining the feasibility of an EOR process is the microscopic displacement efficiency. This efficiency can be defined as(5)

$$E_m = \frac{1 - S_{or} - S_{wi}}{1 - S_{wi}}$$

where S_{or} is the residual oil saturation and S_{wi} is the irreducible water saturation, the fraction of the pore space containing water at infinite capillary pressure.

It has long been recognized that capillary forces are responsible for trapping the residual oil in the rock(6), and that this phenomenon can be explained by the pore-doublet model, as shown in Figure 3. In this model, two parallel capillaries, representing pores in the water-wet reservoir rock, are initially saturated with oil. During a displacement process such as waterflooding, the injected fluid will move faster through the smaller capillary if the displacement velocity is lower than the imbibition rate (the usual case in an actual flood). When the water reaches the point in the formation where the two pores reconverge, recovery of oil from the larger pore will stop and some of the oil will be trapped in that pore(7).

Melrose and Brandner(6) state that the mobilization of the oil thus trapped will occur only if the capillary forces dominate the macroscopic displacement process. For this to occur, it is necessary for a dimensionless ratio called the capillary number to exceed a critical value. The capillary number represents the ratio of the magnitude of the viscous forces to the magnitude of the capillary forces and is defined as

$$N_{Ca} = \frac{\mu V}{\phi \gamma}$$

where μ and V are the water viscosity and flow rate per unit cross-sectional area respectively, ϕ the porosity of the medium, and γ the oil-water interfacial tension(IFT).

A correlation of microscopic displacement efficiency with capillary number indicated that the critical capillary number necessary for residual oil mobilization ranged between

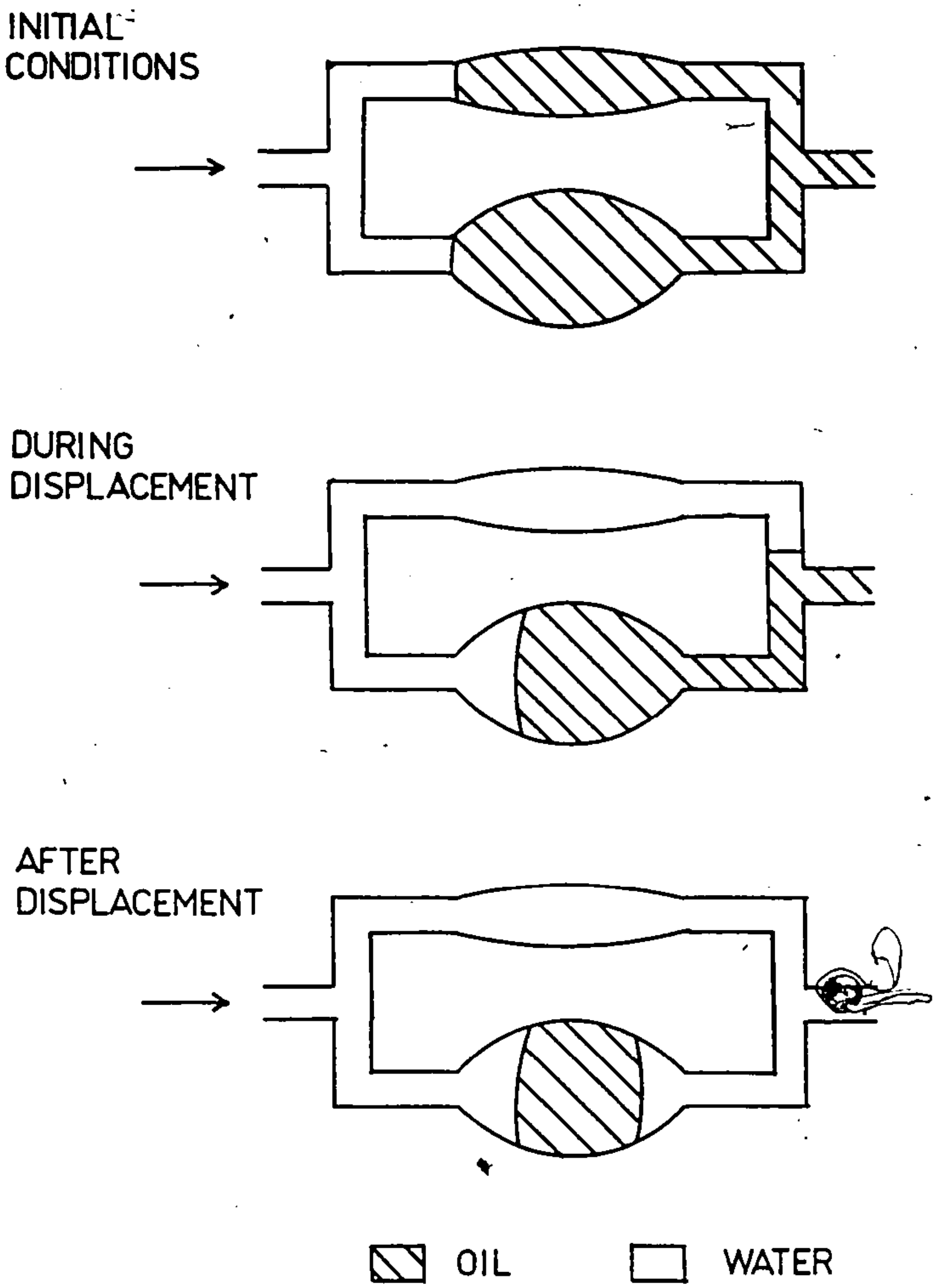

Figure 3: Stranding of Residual Oil

10^{-4} and 10^{-2}(6). For values of the capillary number as high as this to be attained, ultra-low values of interfacial tension are required. These ultra-low values are of the order of 10^{-2} to 10^{-3} mN/m, much lower than the interfacial tensions normally encountered under reservoir conditions.

1.2 Heavy Oil Recovery

In contrast with the data mentioned above for the recovery of conventional (light) crude oils, primary recovery of heavy oils produces only 3 to 8% OOIP, with waterflooding adding just a few per cent more(8). Therefore the successful recovery of heavy oils is dependent on the choice of an appropriate EOR technique. Due to the high viscosity of heavy oils, thermal processes are usually used for heavy oil recovery. In these processes, heat is applied to the reservoir in order to raise the temperature of the rock and reservoir fluids. The application of heat serves to decrease the crude oil viscosity, causes thermal expansion of the oil and therefore increases relative permeability, and causes distillation and thermal cracking of the oil(9). There are three types of thermal techniques being used today - in-situ combustion, steam stimulation, and steamflooding.

1.2.1 In-Situ Combustion

In the in-situ combustion process, also known as fireflooding, air is injected into the oil reservoir through an injection well, and the crude oil ignites either spontaneously or with the aid of a gas burner or resistance heater. As air injection continues, the combustion front moves away from the injection well, heating and displacing oil and water to the surrounding wells. At the combustion front, the connate (interstitial) water is vapourized and the oil is cracked leaving a residue of coke on the rock to maintain combustion. The steam produced in this manner moves ahead of the combustion front, condenses and mobilizes the oil into an oil bank which is pushed towards the production well. The portion of the reservoir swept by the front is then burned clean.

Often water is injected along with the air, a process known as wet combustion. The advantage of this is that the amount of heat transported to the region ahead of the combustion front is significantly increased(9). As a result of this, the oil viscosity is greatly reduced, improving oil recovery. Also, much less air is needed in the wet combustion process.

1.2.2 Steam Stimulation

In this process, also called cyclic steam injection, steam soak, or huff and puff, steam is injected into the reservoir through a production well (huff) for a period of several weeks to heat up the reservoir. The well is then shut-in for several days or weeks before production is resumed. During the shut-in period, the heat from the steam increases the reservoir temperature which decreases the oil viscosity and makes the mobility ratio more favourable. The oil is then produced (puff) until economic factors necessitate another steam injection. The production period is often up to one year in length, and this cycle of injection and production is usually repeated several times. Steam stimulation has been successfully applied in many cases, and is often followed by steamflooding.

1.2.3 Steamflooding

Steamflooding, alternatively known as steam drive or steam displacement, is quite similar to waterflooding in many respects. Steam is injected into the reservoir through injection wells laid out in a pattern around the producing wells. The steam mobilizes the oil and drives it towards the production wells. At the steam front, condensation occurs and a hot water bank is formed. The hot water causes thermal expansion of the crude oil and brings about a decrease in oil viscosity. Behind the steam front, oil is displaced by the vapourization of the lighter hydrocarbons and the resultant gas drive. Much of the heat injected in a steamflooding operation is lost to the reservoir rock, but this can sometimes be regained by following the steamflood with a cold waterflood(3).

1.2.4 Additives in Steamflooding

Currently, the use of additives injected simultaneously with steam is being tested for possible effects on recovery efficiency. The main purpose of these additives is threefold: to reduce the initial oil viscosity near the wellbore thus improving the injectability of the steam, to reduce oil viscosity out in the reservoir increasing the steam contact area, and to supplement the steam drive mechanism behind the steam front(10). The additives under consideration are solvents and gases, such as iso-propyl alcohol and carbon dioxide respectively, and surfactants which reduce oil-water interfacial tension and promote emulsification of the oil.

Chapter II

LITERATURE SURVEY

The beneficial effects of caustic solutions on oil recovery have long been known. In 1917, Squires(11) noted that "The displacement of oil may be made more complete by introducing an alkali into the water...". In 1925, Nutting(12) described the use of alkaline salts such as sodium carbonate and sodium silicate for improved waterflood recovery. He dismissed the use of stronger bases, such as sodium hydroxide, in field applications due to excessive reactivity with crude oil. However, in 1927 Atkinson(13) was issued a patent detailing the flooding of oil-bearing sands with water containing caustic alkali. This patent described the benefits of strongly basic solutions, such as sodium and potassium hydroxide, on oil recovery.

Also in 1927, Beckstrom and Van Tuyl(14) reported improved oil recovery with the use of solutions of alkaline compounds. Although they emphasized the use of sodium carbonate, dilute solutions of sodium hydroxide and potassium hydroxide were also shown to increase the yield of oil.

The next significant advance in the use of caustic solutions occurred in 1942 when Subkow(15) patented the injection of aqueous emulsifying agents, including sodium hydroxide, for recovering heavy oil or bitumen.

2.1 Mechanisms of Alkaline Oil Recovery

These early workers were unsure of the mechanisms by which caustic solutions acted to increase oil recovery. Nutting(12) believed that alkaline solutions released residual oil from adherence to sand surfaces. Also, he reported that caustic inhibited the formation of semi-solid, crude oil-water interfacial films, but he did not believe that this was a factor in the improved yield of oil.

Atkinson(13) hypothesized that residual oil was held in the intergranular spaces by capillary forces, viscous resistance to flow, and adhesion of the oil to the sand. He stated that caustic solutions had the ability to overcome these forces and release the oil. Beckstrom and Van Tuyl(14) also believed that adhesion of the oil to the reservoir rock was an important parameter in oil recovery. They felt that emulsification of the oil was to be avoided, thus their preference for the use of sodium carbonate instead of stronger bases.

Contrary to these conclusions, Subkow(15) maintained that the formation of an oil-in-water emulsion in the pore spaces was essential for improved oil recovery. He postulated that a two-step process was responsible for this improved yield of oil. The first step was the in-situ emulsification of the crude oil. The second step was the entrainment of the emulsion in the flowing alkaline solution, with both being produced concurrently. Subkow also described the reaction of caustic solutions, particularly those of sodium hydroxide, with the organic acids present in some crude oils to produce emulsifying soaps.

2.1.1 Emulsification and Entrainment

Subkow's findings form the basis of one of the four fundamental mechanisms outlined by Johnson(16), that of emulsification and entrainment. Reisberg and Doscher(17) believed that this process was the result of a lowering of interfacial tension between the crude oil and the displacing alkaline solution. However, they concluded that caustic flooding was not economically feasible due to the large amount of caustic necessary because of adsorption and reaction with the reservoir rock.

2.1.2 Wettability Reversal (Oil-Wet to Water-Wet)

The second mechanism responsible for improved oil recovery presented by Johnson(16) is a change in rock wettability from oil-wet to water-wet. Wagner and Leach(18) concluded that this change in wettability during a waterflood will result in an increase in oil recovery over that obtained where no wetting change occurs. They achieved this wettability reversal through the addition of certain chemicals, including acids, bases, and some salts, that changed the injection water pH. They also found that the higher the oil viscosity the greater the percentage improvement obtained with this wettability reversal over conventional waterflood recovery.

Johnson(16) concluded that this improvement in oil recovery results from changes in relative oil and water permeability that accompany a wettability reversal from oil-wet to water-wet in a region where oil is still flowing. This permeability change causes the mobility ratio to be reduced, thus better recovery. Johnson further stated that in reservoirs where viscous fingering occurs, the water-oil ratio may also be lowered for a time by this wettability reversal.

2.1.3 Wettability Reversal (Water-Wet to Oil-Wet)

A third mechanism by which caustic solutions might improve oil recovery was first reported in 1974 by Cooke et al(19). Their investigation showed that some types of porous media could be changed from water-wet to oil-wet by the adjustment of injection water pH, salinity, and temperature. They also observed that certain combinations of caustic and salt were able to both cause this wettability change and lower the crude oil-water interfacial tension to very low values.

This change in wettability from water-wet to oil-wet causes the trapped residual oil, originally discontinuous in the porous medium, to be converted to a continuous wetting phase, thereby making a flow path for the trapped oil to the production well. Due to the low interfacial tensions present, an emulsion of water droplets in the now continuous oil phase forms(16). These emulsion droplets tend to become trapped in the porous medium and thus induce a high pressure gradient which is able to overcome the capillary forces retaining the oil in the reservoir, these forces having been already reduced by the low interfacial tension.

2.1.4 Emulsification and Entrapment

Jennings et al(20) proposed an alternative to the wettability reversal mechanism by which the injection of caustic solutions can significantly improve the recovery of certain oils. This mechanism involves the drastic reduction of oil-water interfacial tension by the caustic activation of potentially surface-active organic acids naturally occurring in some crude oils. This reduction in interfacial tension causes in-situ emulsification of residual oil. The emulsion thus formed tends to move downstream with the flowing caustic and becomes entrapped by pores that are too small for the emulsion droplets to penetrate.

The entrapment of the emulsion droplets lowers the injection water mobility, controls the tendency towards viscous fingering, and improves both vertical and areal sweep efficiencies. The emulsified oil, once trapped in the pore throats, is not recovered and the ultimate residual oil saturation is not significantly affected by caustic injection(20). Therefore this mechanism would be primarily of importance in reservoirs containing highly viscous oils where sweep efficiency is poor. In these types of reservoirs, any improvement in sweep efficiency, caused by a more favourable mobility ratio, would be more important economically than the recovery of residual oil left after a waterflood.

The results of Jennings et al(20) show a clear dependence of oil recovery efficiency on interfacial tension with an optimum oil recovery at the lowest value of interfacial tension. Their results also indicated that interfacial tensions below 0.01 mN/m are necessary to obtain significant oil recovery increases by the in-situ emulsification and entrapment mechanism. They further stated that the required concentration of sodium hydroxide for in-situ emulsification usually ranges between 0.05 and 0.50 weight percent, approximately one-fifth the concentration required for a wettability reversal.

2.1.5 Emulsification and Coalescence

A fifth mechanism for alkaline oil recovery, that of emulsification and coalescence, was proposed by Castor et al(21). As with the emulsification and entrainment and emulsification and entrapment mechanisms, the first stage in this mechanism is accomplished by the in-situ formation of surfactants which promote emulsification of the oil. However, in the emulsification and coalescence mechanism unstable water-in-oil emulsions are formed by the injection of calcium hydroxide. The calcium hydroxide acts to swell the residual oil and increase its apparent saturation. Because of this swelling, adjacent oil ganglia contact each other and coalesce to form localized regions of high oil saturation that have an increased oil permeability. These local regions then combine to form a mobile oil bank which improves the oil recovery efficiency. There is also evidence that the emulsification and entrainment and the emulsification and entrapment mechanisms can aid the coalescence phenomena to increase oil recovery.

2.2 Interfacially Active Components in Crude Oil

The fact that certain crude oils contain naturally occurring acidic components has long been recognized. However, it was not until 1955 that the interfacial activity of some crude oils was shown to be caused by these acidic components(17). In 1964, Neumann(22) reported that phenols were the main interfacially active constituents of a West German crude oil. While nc chemical analysis of Lloydminster oil has been reported, various researchers(23,24) have studied the chemical composition of other crudes, most notably those from California. Seifert and Howells(23), working with Midway Sunset oil from California, isolated the interfacially active components by a combination of extractions, two-stage ion exchange, and repeated silica gel chromatography. They found that the polar constituents of this oil were responsible for its high interfacial activity. They further isolated these polar components into carboxylic acid fractions, phenolic fractions, and fractions containing mixtures of phenolic and carboxylic groups, probably indicative of carboxyphenols. The carboxylic acids were the most prevalent type of interfacially active component, comprising 2.5% by weight of the oil. Although most of these acids were saturated aliphatics, the number average molecular weight ranged from 300 to 400, suggesting the presence of unsaturated, substituted, or aromatic acids.

Jang et al(24) separated a Long Beach crude into various fractions by vacuum distillation and silica gel chromatography. The only fraction that showed interfacial activity with alkali was an asphalt-like solid. Further analysis of this substance by gas chromatography and mass spectroscopy identified various long chain carboxylic acids, both confirming the results of Seifert and Howells and demonstrating that more than one species is involved in the diffusion and reaction process that occurs at the crude oil-caustic interface. Sharma et al(25) suggested that the reduction in interfacial tension is probably caused by two different components, one being an acid with a low molecular weight and the other having a significantly higher molecular weight.

2.3 System Chemistry

Even though the findings of Seifert and Howells(23) and Sharma et al(25) indicate that more than one acidic species is responsible for the lowering of IFT, for simplicity's sake all of the species that lead to the formation of surfactants can be considered to be one component, HA(26,27,28). This acid distributes itself between the oleic and aqueous phases according to the equilibrium relationship

$$HA_o \rightleftharpoons HA_w$$

and

$$K_D = \frac{C_{HA_o}}{C_{HA_w}}$$

where HA_o is the acid in the oleic phase, HA_w the aqueous-phase acid, and C_i the concentration of species i at equilibrium. The distribution ratio, K_D, will be very large due to the extremely low concentration of acid in the aqueous phase under normal conditions.

The dissociation of the acid in the aqueous phase to form hydronium ions and the surface-active species A^- can be represented by

$$HA_w + H_2O \rightleftharpoons H_3O^+ + A^-$$

and

$$K_A = \frac{(C_{H_3O^+})(C_{A^-})}{(C_{HA_w})}$$

where K_A is the dissociation constant of HA.

With the addition of NaOH an undissociated salt, represented as NaA, can form at the interface(26). This salt is soluble in crude oil, due to the hydrophobic nature of the hydrocarbon chain of A, and dissociates almost completely in the aqueous phase to produce sodium ions and the surface-active species A^-. The formation of this salt in the aqueous phase and its transfer to the oleic phase can be represented as

$$Na^+ + A^- \rightleftharpoons NaA_w$$

$$NaA_w \rightleftharpoons NaA_o$$

where

$$K_S = \frac{(C_{Na^+})(C_{A^-})}{(C_{NaA_o})}$$

is the equilibrium constant for these two reactions. Figure 4 shows all of these crude oil-caustic interactions.

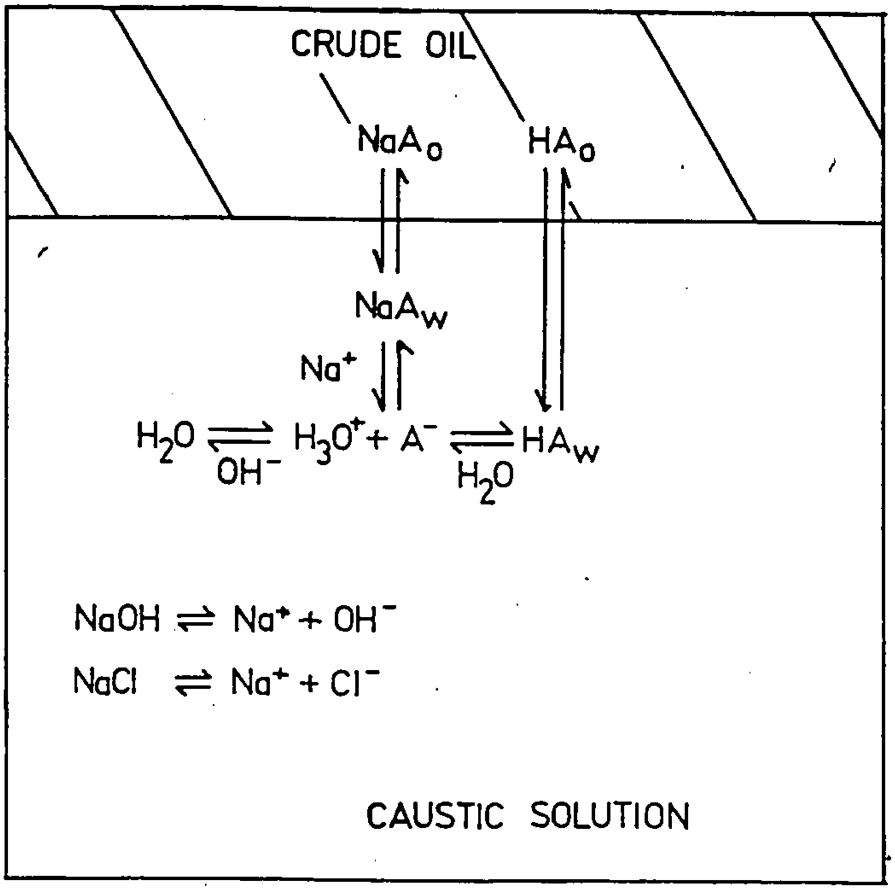

Figure 4: Crude Oil-Caustic Interactions

2.4 Interfacial Resistances and Dynamic IFT Minima

As mentioned in the previous section, upon contacting an acidic crude oil with alkali the acids transport out of the oil and react to produce surface-active salts which can initiate oil mobilization and thus improve oil recovery. This production of surfactants leads to a dramatic reduction in interfacial tension to ultralow values (< 0.01 mN/m) followed by a slow rise to higher values (2-10 mN/m). Because of this large change in IFT with time, it is often difficult to decide which tension value is indicative of reservoir conditions.

The transfer of the surface-active species from the oil to the aqueous phase may be considered to occur in six distinct steps: convective-diffusion from the oil phase to the interface, adsorption at the interface, reaction at the interface to produce the surfactant, desorption from the interface, and convective-diffusion into the aqueous phase(29). It is this sequence of events that determines the dynamic nature of the interfacial tension between acidic crude oils and alkaline solutions. Since the hydrolysis reaction to produce the surfactant is ionic in nature, it is thought to occur instantaneously(30). The remaining five steps determine the kinetics of the overall process.

Rubin and Radke(29) state that the IFT minimum must occur concurrently with a maximum in surface-active species adsorption to satisfy theoretical considerations. Bansal et al(31) stated this observation somewhat differently, their investigation showing that a maximum in charge density (or electrophoretic mobility) at the crude oil/caustic interface corresponds to the minimum IFT. Thus, any process that leads to a net accumulation of surface-active species of charge at the interface would result in a lowering of IFT. For this net accumulation to occur, one of two conditions must be met : either the net rate of adsorption is significantly higher than the net rate of desorption, or the convective-diffusion resistance of the aqueous phase exceeds that of the oil phase.

Due to the high viscosity of most heavy oils, it would seem that the mass-transfer resistances could significantly inhibit the extraction of the acids out of the oil phase. It was originally thought that this diffusion of the acids towards and away from the interface gave rise to the transient minimum in IFT(32). However, the second condition mentioned above has been shown to have no direct influence on the dynamic tension minima due to a lack of consistent behaviour in IFT, measured by the spinning drop method, with changes in oil viscosity and aqueous phase pH and salinity(29). Other researchers have reached the same conclusion that mass-transfer resistances are not important in the case of linear alkaline flooding (30). Therefore it would seem that the rate of desorption of the surfactant from the oil-caustic interface controls the overall kinetics of the process. Both theoretical and experimental evidence has been presented to confirm this assertion(29).

As previously mentioned, there is some confusion about which tension value best represents the IFT that would be operative in an alkaline flood of an actual reservoir. Since the minimum IFT is reached shortly after the initial oil-caustic contact, McCaffery(33) believed that this ultralow IFT would be unlikely to lead to any sustained oil mobilization during the course of an alkaline flood. However, Rubin and Radke state that "... the spinning drop tension minimum for acid crude oils is indicative of the lowest achievable reservoir equilibrium value"(29). This is due to the great disparity in the ratio of the volume of water to oil in a spinning drop tensiometer and that in a partially depleted (non-producing) oil reservoir. The model they presented showed that the rise in IFT that occurs after attaining the minimum is highly dependent on this water-to-oil ratio, with a larger ratio yielding a larger rise in IFT. As this ratio is between several hundred and a thousand to one in a spinning drop apparatus and usually no more than three to one in an oil reservoir, It is quite likely that the rise in IFT observed with the spinning drop method would never occur in a field application.

2.5 Previous Work

Many researchers have studied crude oil-caustic interfacial tensions. However, most of this work has been concerned with equilibrium tensions and not the dynamic nature of the IFT between an acidic oil and an alkaline solution.

Jennings(34) used the pendent-drop method to study the interfacial tension between caustic solutions and 164 crude oil from 78 different fields. He noticed a change in IFT with interfacial age but chose to report tension values at an interfacial age of 10 seconds as most of the reduction in IFT had occurred by then. The results presented have two important implications with respect to the present work. First of all, ultralow interfacial tensions were possible with almost all of the crude oils with gravities of 20°API or lower- i.e. the heavy oils. Secondly, 90% of the oils that showed any interfacial activity on contact with alkali did so at a caustic concentration of close to 0.1% by weight. Both sodium and potassium hydroxides were used in this investigation, with no appreciable difference in the results.

Jennings(34) also found that sodium chloride in solution reduces the amount of caustic necessary to achieve maximum surface activity (i.e. minimum IFT). Calcium chloride had the opposite effect in that it suppressed surface activity. This detrimental effect of calcium, as well as other divalent ions, was also noted by Sharma et al(25) and Dranchuk et al(35).

Campbell(36) measured IFT between various alkaline solutions and a Long Beach(California) crude oil using the spinning drop technique. The values he reported were those obtained after 5 minutes rotation, and no explanation of the choice of this measurement time was given. The results therefore could be misleading, but are still interesting. Caustic concentrations ranging from 0.05% to 0.25%, in a 1% NaCl solution, resulted in the minimum IFT values of 0.01 to 0.025 mN/m, when either sodium orthosilicate or sodium hydroxide was used as the base. When produced brine was used as the aqueous phase, it was found that the caustic concentration necessary for a reduction in IFT increased to approximately 0.5%. McCaffery(33) also observed that a higher caustic concentration was required to reduce IFT when injection water, instead of distilled water, was used as the aqueous phase in a spinning drop apparatus. In both cases, it was theorized that the presence of dissolved solids, especially calcium and magnesium, were responsible for the higher concentrations of alkali necessary to reduce IFT to ultralow values.

2.6 Objectives of the Present Research

The present research was concerned with the dynamic nature of the interfacial tension between caustic solutions and an important Canadian heavy oil, that from the Lloydminster deposit. The transient behaviour of the IFT was studied with particular attention being paid to three parameters : the absolute value of the minimum IFT attained, the time at which this minimum was attained, and the length of time for which the minimum was sustained.

It was decided that the main variables to be considered would be the composition of the aqueous phase (varying both alkalinity and salinity) and the temperature of the system. The effect of the acidity of the oil was also investigated, this being done through the use of a series of dilutions of the Lloydminster crude oil with dodecane.

Chapter III

EXPERIMENTAL

3.1 Materials

The heavy oil used in this work was supplied by Esso Resources Canada Ltd., Calgary, Alberta, directly from the Lloydminster deposit, specifically well A2-12-49-23 W3. This well is in the Golden Lake area, approximately 60 km east of Lloydminster, Saskatchewan. This is a Lower Cretaceous Waseca sand reservoir, with typical properties shown in Table 2. The oil was used as received, i.e. dewatered but otherwise untreated. The gravity of the oil was measured to be 14.3°API.

Stock solutions of sodium chloride, sodium hydroxide, and potassium hydroxide were prepared using distilled water. The sodium chloride and potassium hydroxide were supplied by Fisher Scientific Ltd., and were "A.C.S" grade. Sodium hydroxide was supplied by BDH Chemicals and dodecane by Matheson, Coleman, and Bell, and both of these chemicals were 99% pure. All dilutions were on a weight per cent basis as this is most applicable to field conditions. Therefore throughout this work the units of concentration for aqueous solutions are <u>weight percent.</u> For the mixtures of

Table 2: Reservoir Properties of the Waseca Formation

Depth, m	460-475
Temperature, °C	22-24
Initial Pressure, kPa	3450
Net Pay, m	3-9
Tank Oil Viscosity at Reservoir Temperature, mPa·s	3500-6500
Air Permeability of Core, md	2000
Porosity, %	31-35
Water Saturation, %	13-19
Gas Saturation, %	0

oil and dodecane, a volume percent basis was used to compensate for the density differences. All densities in this work were measured using 2 mL density flasks. The densities of the oil:dodecane mixtures are shown in Table 3.

Table 3: Densities of Oleic Phases @ 25 °C

Oleic Phase	Density(g/cm³)
100% Lloydminster	0.9705
90% Lloydminster	0.9225
75% Lloydminster	0.8890
50% Lloydminster	0.8325

3.2 Interfacial Tension Measurements

All IFT measurements were performed using a University of Texas Model 500 Spinning Drop Interfacial Tensiometer. The design and mechanics of this instrument are described elsewhere (37,38). This apparatus is capable of temperature control of +/-0.1°C up to about 60°C. In the spinning drop tensiometer, a small droplet of oil is introduced into a glass capillary tube, approximately 2 mm in diameter and 10 cm long, which has been filled with an aqueous solution. When spun in the tensiometer, this droplet elongates due to the rotational forces until a balance is struck between these forces and the interfacial forces.

3.2.1 Sample Loading Procedure

The procedure for loading the aqueous solution and oil droplet into the capillary tube is fairly simple and is as follows.

1. The capillary tube was filled with the aqueous solution to be used, set aside for a few moments, and then shaken to remove the aqueous solution. This pre-flush served two purposes - first, to remove any water left from the previous washing of the tube and secondly to fill any possible adsorption sites on the glass capillary. Thus, when the IFT measurement was made, any adsorption would have already occurred and would not cause the measurement to be inaccurate.

2. The cap assembly, consisting of a Teflon cap, a rubber O-ring, and a rubber septum, was put together. The septum was not pushed completely into the end of the cap but rather only until the top of the septum was slightly above the O-ring. A small quantity of the aqueous solution was then placed in the cap to cover the septum and O-ring.

3. The capillary tube was refilled with the solution to be used. Care was taken to ensure that no air bubbles were present, either floating at the open end of the tube or trapped against the side of the glass tube. If air bubbles were present, more liquid was injected into the tube in order to force the bubbles out.

4. The next step in loading was the actual injection of the oil droplet. A Hamilton Gas-Tight syringe was used for this due to the high viscosity of the crude oil. Any residual air and a small quantity of oil were first expelled from the syringe. The needle tip was then touched against a lint-free wiper to remove any excess oil outside of the needle cavity. The needle was then quickly inserted into the filled capillary tube to minimize any evaporation of oil which would lead to air being introduced into the tube. A small amount of the oil was forced out of the syringe near the centre of the tube by depressing the plunger. Since the oil clung to the end of the needle, the syr-

inge was rotated and quickly withdrawn to detach the oil droplet. The timer was then started to record the initial oil-caustic contact.

5. With the tube in a horizontal position to prevent the oil droplet from drifting to the open end of the capillary tube, additional aqueous solution was added to the tube until a small pendant drop of solution appeared on the tube mouth.

6. The tube was then held in a vertical position and quickly inserted into the cap assembly, pushing the septum into the cap end to firmly seat it. Air bubbles sometimes appeared at this step and it was usually necessary to repeat the whole procedure, especially if the air bubbles came into contact with the oil droplet.

7. Any excess aqueous solution was removed from the tube and cap, and the entire assembly was screwed into the rotating sleeve of the spinning drop tensiometer.

8. IFT measurements were recorded as soon as possible, usually 100 seconds from the initial oil-caustic contact. These measurements were continued at regular intervals up to a time of 6000 seconds.

9. Once the experiment was finished, the tube was removed from the tensiometer and taken apart. The cap assembly was disassembled and rinsed with distilled water, and then placed in a beaker of distilled water

for storage. The tube was shaken to remove its contents and then rinsed with approximately 5 mL of hexane, followed by the same volume of acetone, and then by 10 to 15 mL of distilled water.

3.2.2 Calculation of IFT

The calculation of IFT is dependent upon drop shape and volume, as detailed by Cayias et al(37). However, if the droplet elongates so that its length is 4 or more times its diameter, then the Vonnegut infinite length approximation can be used. With this approximation, the droplet is said to be cylindrical with rounded ends, and the IFT can be calculated from

$$\gamma = \frac{1}{4} \Delta\rho \ \omega^2 \ r^3 \qquad (3-1)$$

where γ is the IFT, $\Delta\rho$ the density difference between the two phases, ω the angular velocity, and r the droplet radius.

As some of the terms in Equation (3-1) are difficult to measure, substitutions can be made to facilitate the calculations. The angular velocity can be expressed in terms of the frequency, ν, since

$$\omega = 2\pi\nu \qquad (3-2)$$

The Spinning Drop Interfacial Tensiometer measures the period of revolution, T, in msec/rev, where

$$\nu = \frac{10^3}{T} \qquad (3\text{-}3)$$

Combining these last two equations yields

$$\omega = \frac{2\pi \times 10^3}{T} \qquad (3\text{-}4)$$

In the tensiometer, the drop diameter rather than the drop radius is measured. Therefore Equation (3-1) becomes

$$\gamma = \frac{1}{4} \Delta\rho \left(\frac{2\pi \times 10^3}{T}\right)^2 \left(\frac{d}{2}\right)^3 \qquad (3\text{-}5)$$

A further complication to this equation is that the glass in the capillary tube magnifies the droplet width. Thus a correction factor is needed since the true diameter of the droplet is required in Equation (3-5). This correction factor is.

$$d(\text{true}) = \frac{d(\text{measured})}{1.332} \qquad (3\text{-}6)$$

Equation (3-5) therefore becomes

$$\gamma = 5.222 \times 10^5 \, \frac{\Delta\rho \, (d')^3}{T^2} \qquad (3\text{-}7)$$

where d' is the measured diameter.

The diameter of the droplet is measured through an eyepiece with units of measurement of 10^{-2} cm. Thus the final equation for the calculation of IFT is

$$\gamma = 0.522 \frac{\Delta\rho \ (d')^3}{T^2} \qquad (3\text{-}8)$$

with γ in units of mN/m, $\Delta\rho$ in g/cm³, d' in 10^{-2} cm (read directly from the tensiometer) and T in msec/rev (also read directly from the tensiometer).

Chapter IV

CRUDE OIL ACID NUMBER DETERMINATION

As previously mentioned, the surfactants responsible for the lowering of IFT are produced by reaction between the acids in the oil, mostly carboxylic and phenolic acids (23), and the surrounding caustic solution.

An important parameter in identifying the reactivity of a crude oil is the acid number, defined as the number of milligrams of potassium hydroxide required to neutralize the acid in one gram of the oil. The exact value of the acid number depends upon the measurement procedure used (34). An American Society for Testing and Materials procedure exists (ASTM Designation D-664-81)(39), but facilities for this method are not available at the University of Ottawa.

A modification of this standard procedure, simply dissolving the oil in iso-propanol, was tried. A large part of the oil seemed to dissolve (this being inferred from a colour change in the iso-propanol from clear to brown), but portions of the oil did not. Since it was unclear as to whether or not the acidic components would have dissolved, this method was discarded.

The procedure used in the determination of the acid number involves contacting a known amount of potassium hydroxide with a sample of the oil, and calculating the amount of base left after a set period of time. The acid number of the Lloydminister crude, as well as that of a conventional crude from Chatham, Ontario, and blanks of dodecane and toluene, were determined using the following procedure.

1. 5 g of 1N KOH were added to 195 g of distilled water in a 500 mL Erlenmeyer flask.
2. 20 g of the oleic phase were poured on top of the KOH-water mixture.
3. The flask was shaken vigorously once a day for a week.
4. A 20 mL sample of the aqueous phase was extracted and titrated with 0.056N HCl using phenolphthalein as indicator.
5. The amount of KOH used in neutralizing the oil sample was calculated by subtraction.

Steps 4 and 5 were repeated for each oil to determine the reproducibility of the procedure. The result of this procedure will henceforth be called the acid content to distinguish it from the acid number of the ASTM procedure.

This method yielded a significant acid content for dodecane, an acid-free substance. Toluene was then tried and again the value was not negligible. As the acid contents of toluene and dodecane were close (average values of 0.6 and

0.5 respectively), it was postulated that these values were due to reaction of the potassium hydroxide with dissolved carbon dioxide or to adsorption of the potassium hydroxide onto the glass flask or into the oil phase. Based on these findings it was decided to "adjust" the acid contents of the crude oils by subtracting the average value for the toluene and dodecane blanks.

The Lloydminister crude oil had an average acid content of 1.46, thus an "adjusted" acid content of 0.9 mg KOH/g oil. The acid content for the Chatham crude was 0.75, yielding an "adjusted" value of 0.2 mg KOH/g oil.

Chapter V

PHASE BEHAVIOUR

When an externally produced surfactant, such as petroleum sulphonate, is used in an enhanced oil recovery process, precipitates and so-called third phases have been observed to occur(41). Therefore, a phase behaviour study was undertaken to determine if the surfactants generated in-situ by the reaction of an acidic crude oil with alkaline solutions caused any significant change in either the aqueous or oleic phase.

The procedure used in this investigation was quite simple and follows the method of Son et al(41). The technique is as follows:

1. 30 mL of the aqueous phase to be used was placed in a large test tube.
2. 15 mL of the oleic phase was poured on top of the aqueous phase, taking care to prevent any mixing.
3. The tubes were placed on their sides (horizontally) to maximize interfacial area and were left undisturbed for a period of one week.
4. The tubes were then returned to a vertical position and were observed after a settling time of two days.

Four different oleic phases and three different aqueous phases were used in this study. The oleic phases were the Lloydminster crude oil and dilutions of this oil with dodecane, containing 10%, 25%, and 50% dodecane by volume. The aqueous phases were 0.02% NaOH, 0.10% NaOH, and a solution containing 0.05% NaOH and 0.50% NaCl. The combinations of aqueous and oleic phases are shown in Table 4.

Table 4: Sample Labelling in Phase Behaviour Study

AQUEOUS PHASE	OLEIC PHASE (% CRUDE OIL)			
	100	90	75	50
0.05% NaOH 0.50% NaCl	1	2	3	4
0.10% NaOH	5	6	7	8
0.02% NaOH	9	10	11	12

Tubes #1 to #4 showed no change in appearance at all. The aqueous phases remained clear and colourless even after several months of contact time. The aqueous phase of Tube #5 turned orangish-brown in colour and had a darker brown precipitate that was concentrated near the oil-water interface. This precipitate was milky in texture and had "arms" that swirled to the bottom of the test tube. Tube #6 was much the same as #5, except that the colour was lighter and there was less precipitate. Tube #7 was lighter in colour than #6 and had no precipitate. Tube #8 was even lighter in colour, a yellowish-brown, and was clear whereas tubes #5 to #7 were translucent. Tubes #9 to #12 were light brown in colour, with #11 being the darkest. These tubes were all transparent and had no signs of any precipitate.

The change in colour noticed in eight of the twelve samples is probably due to one of two major factors. First of all, solubilization of the oil into the aqueous phase would be accompanied by a darkening of the aqueous phase. Secondly, the presence of the surfactant generated in-situ could be reponsible for the colour change. This explanation is more likely, considering that a precipitate was noticed in two of the samples. These two samples contained the strongest base used (0.10% NaOH), and also the two least diluted oil mixtures (100% oil and 90% oil). The oleic phase of these samples had a high acid content and the aqueous phase was presumably basic enough that most of the acids in the oil would be extracted, thereby forming surfactants.

The presence of sodium chloride in the aqueous phase inhibited the formation of surfactants, as the aqueous phase of those samples remained clear and colourless. Thus it would seem that chloride ions somehow interfere with the extraction process. It is unclear as to whether or not the formation of micelles by the surfactants would contribute to the colour change. While the formation of micelles is possible, it is unlikely as the surface-active species are very large branched molecules, and the close packing required to form a micelle would be difficult to achieve.

Chapter VI

RESULTS AND DISCUSSION

6.1 Effect of System Operating Variables

The reproducibility of the measurement of interfacial tension as a function of interfacial age (henceforth denoted as "time") is shown in Figure 5 and Figure 6. From these figures it can be seen that the variability in the IFT measurements at a specific time is approximately 20%, which is in good agreement with other researchers(33). It is also fairly evident that the variability in measurements decreases with increasing time of contact (and thus time of spinning in the tensiometer).

There are two major reasons for the above behaviour. First of all, the time is measured from the initial oil-caustic contact and not the start of spinning in the tensiometer, usually 60 to 120 seconds after the initial contact. As the dramatic reduction in IFT occurs at low times, a small difference in the time of introduction into the tensiometer could make an appreciable difference. Secondly, the oil droplets were not always perfectly cylindrical or had small surface aberrations at low times, probably due to the high viscosity of the Lloydminster crude. When either

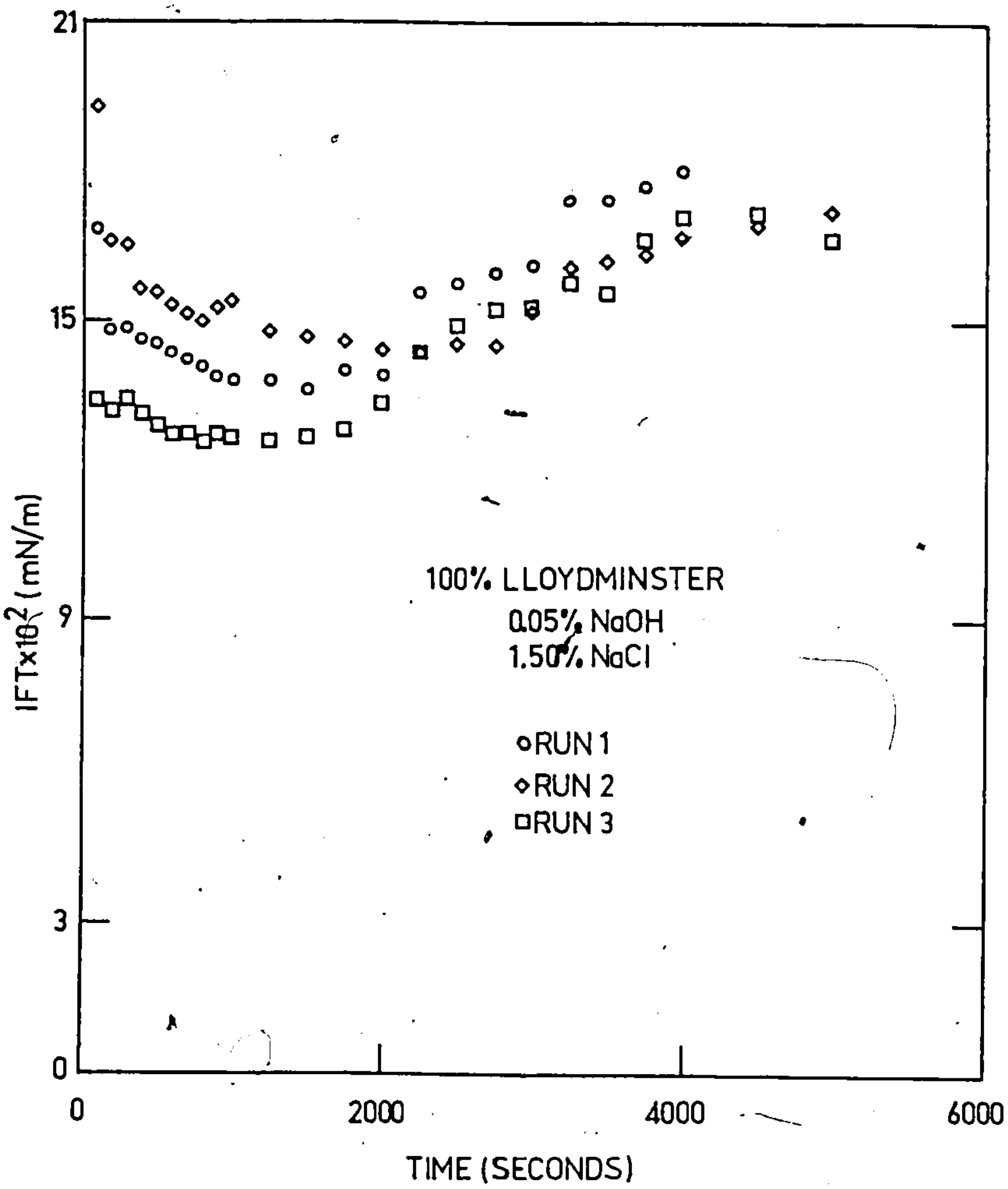

Figure 5: Replicate Runs (0.05% NaOH 1.50%NaCl)

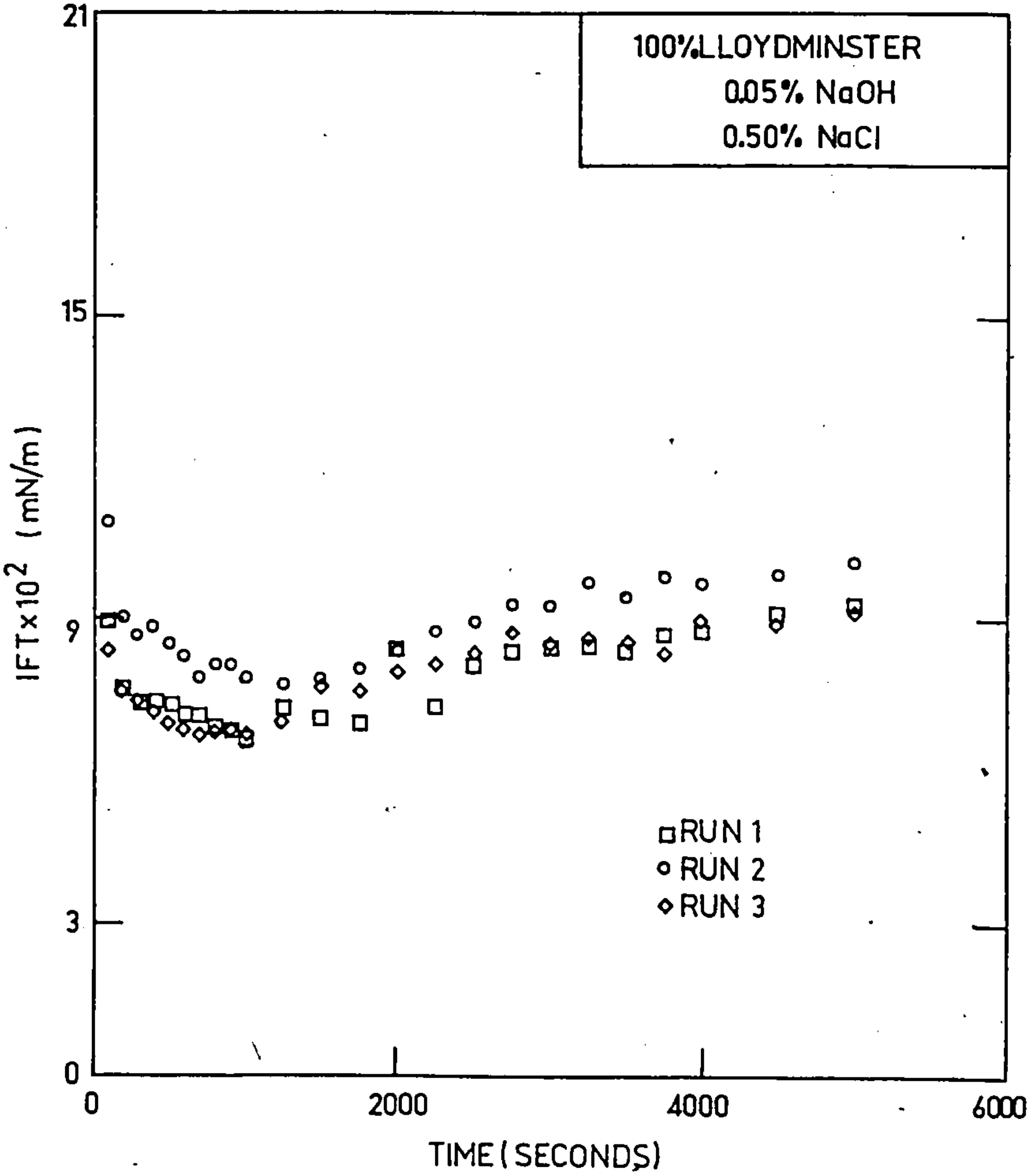

Figure 6: Replicate Runs (0.05% NaOH 0.50% NaCl)

of these deviations occurred, the drop diameter, hence IFT, was dependent upon the place of measurement on the drop. Thus the calculated IFT could vary from one end of the drop to the other.

6.1.1 The Effect of Rotational Speed

The effect of the rotational operating speed on IFT was investigated, as it is an important variable in the calculation of IFT. As the rotational speed of the apparatus is increased, the oil droplet becomes more elongated due to increased centrifugal force. Princen et al(41) presented photographs of this elongation and found no effect of operating speed on IFT for a n-hexadecane droplet in glycerol. Contrary to this observation, Cappelle(42) noted a large dependence of IFT on rotational velocity for a German crude oil-surfactant system. His results suggested a minimum in interfacial tension at a rotational speed of approximately 8000 rpm. The present work, as illustrated in Figure 7, shows ~~no~~ significant effect of rotational speed on interfacial tension. This is in concordance with the findings of Babu et al(43) and Currie and van Nieuwkoop(44) for low tension systems. Based on Figure 7, it was decided to use an operating speed of 7500 rpm for all experiments, as this was the highest stable speed possible (i.e. at higher rotational velocities, the speed fluctuated).

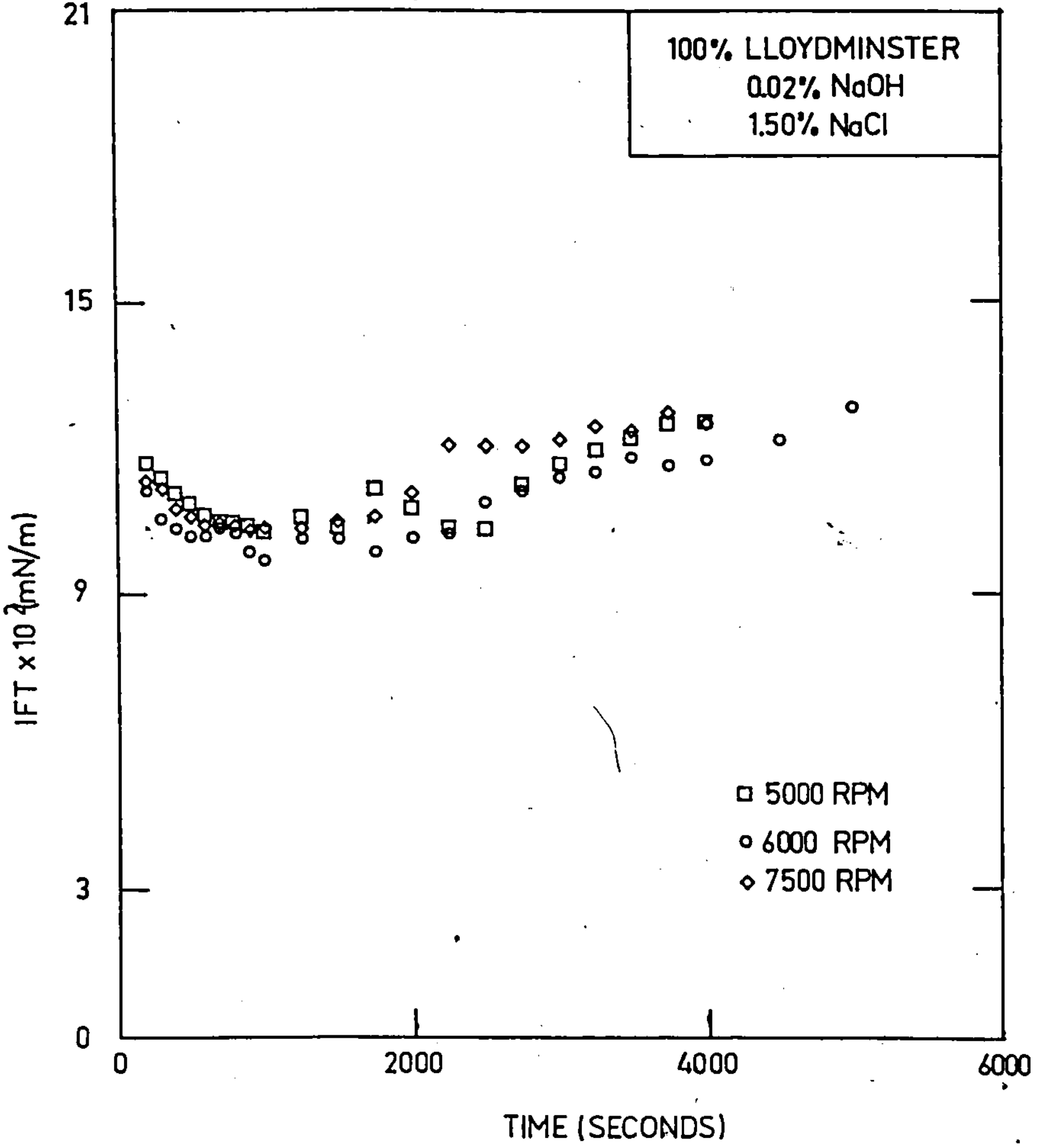

Figure 7: The Effect of Rotational Speed on IFT

6.1.2 The Effect of Drop Volume

The effect of oil drop volume on interfacial tension was also investigated. Theoretical considerations based on the Vonnegut infinite length approximation predict no effect of drop volume on IFT. However, McCaffery(33) reported that the aging period (the period of time for which an ultralow IFT is sustained) increased with the size of oil drop used in the measurement. Babu et al(43) observed a small variation in minimum IFT and no variation in the time of this minimum with droplet volume. The present work seems to suggest the opposite, as shown in Figure 8. The minimum IFT was attained sooner for a drop of volume 1 μL than for one of 5 μL (1750 seconds and 2750 seconds respectively). However, the scatter in IFT values was no greater than that for replicate runs. It was therefore decided that a droplet volume of between 2 μL and 3 μL would be used in all subsequent experiments, as droplets of this volume presented the fewest difficulties during the injection procedure.

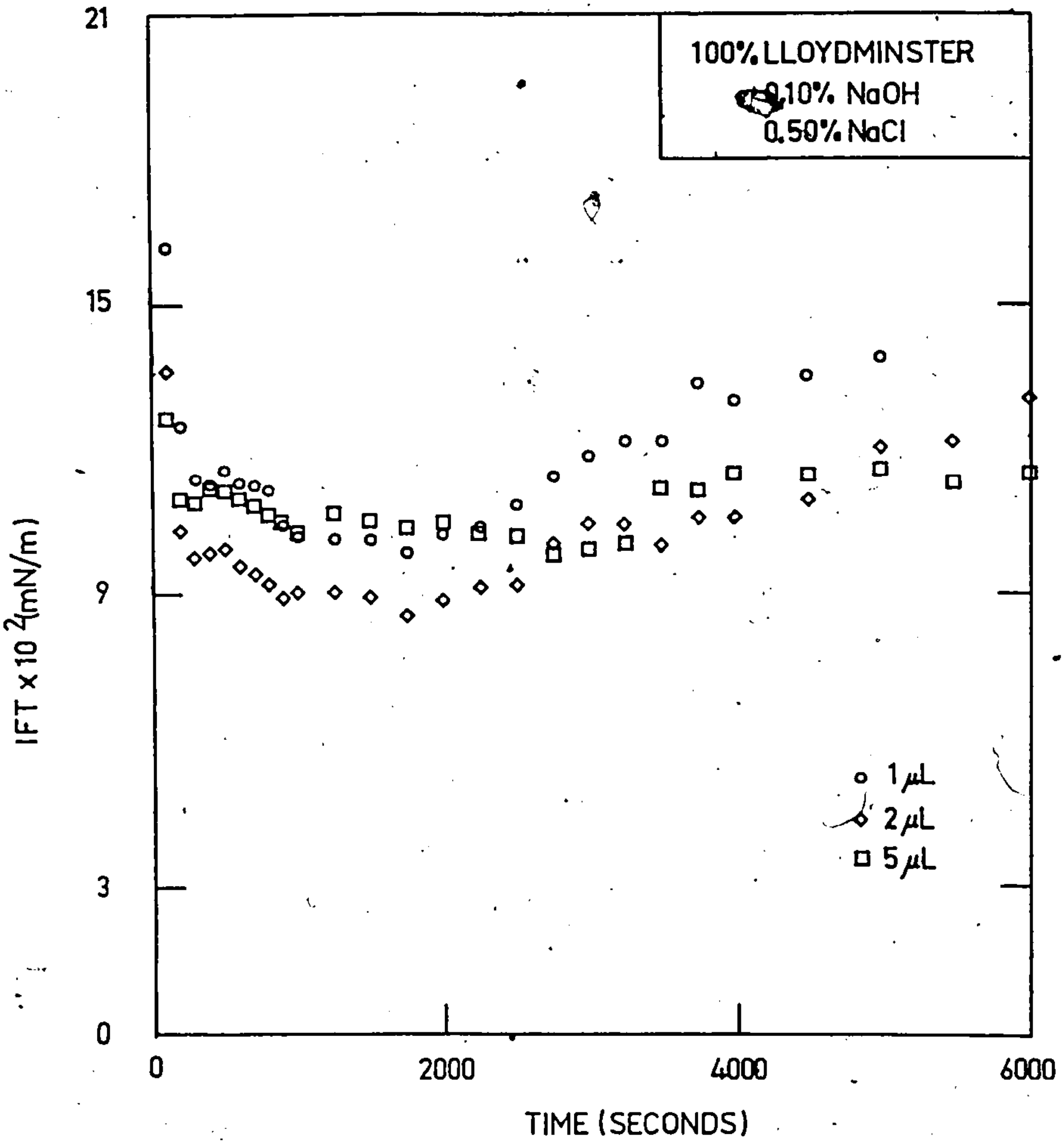

Figure 8: The Effect of Drop Volume on IFT

6.2 Dependence of IFT on Alkalinity

It has been noted that the interfacial potential between acidic crude oils and caustic solutions passes through a maximum as the concentration of sodium hydroxide is increased(26). Other researchers(33,34) have shown that ultra-low interfacial tensions are only obtained over a small range of caustic concentrations. Chan and Yen(45) thought that this behaviour was due to the pH of the oil-caustic interface being equal to the pK_A of the acids contained in the oil.

As can be seen in Figure 9, the lowest interfacial tension values were obtained with a sodium hydroxide concentration of 0.05%. With this aqueous phase, the IFT did not increase appreciably from the minimum even at very long times (10,000 seconds). For all other aqueous phase compositions, the IFT had generally begun to rise by 3000 seconds. This would seem to indicate that the pH of a 0.05% NaOH solution is equal to the pK_A of the acids in the Lloydminster oil. However, simple calculations reveal that the amount of base present in the capillary tube was approximately five times larger than that required to neutralize the acids in the oil based on the calculated acid number.

A possible explanation for this discrepancy would be the presence of a large boundary layer surrounding the oil droplet. This boundary layer could impede the diffusion of

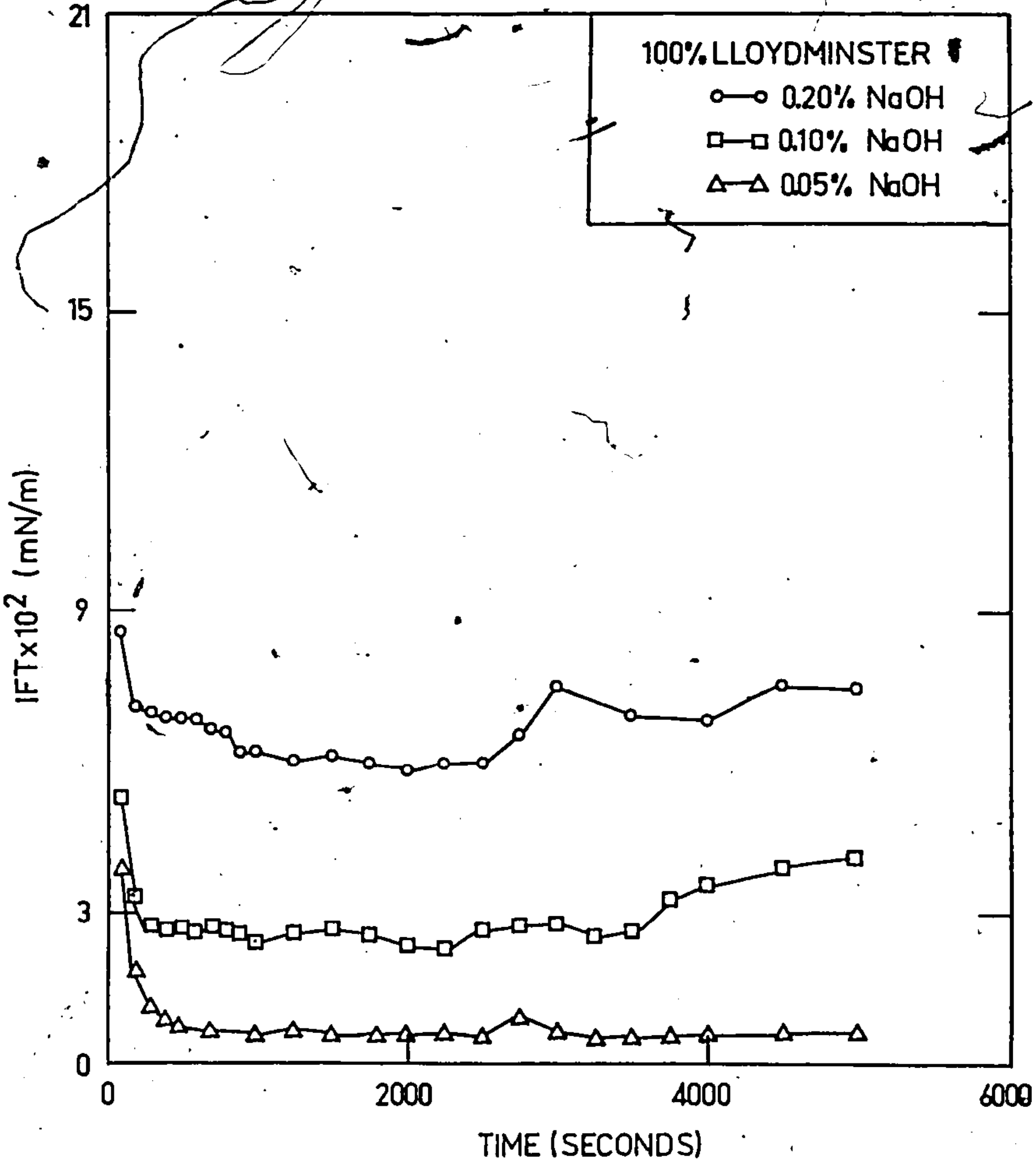

Figure 9: IFT Behaviour for Different Alkalinities (no NaCl)

ions to the oil-caustic interface, resulting in an interfacial pH much lower than the pH of the bulk aqueous phase. Manning and Scriven(46) noticed that the rotational speed of the droplet and that of the capillary tube could be substantially different and that this difference resulted in a viscous shear layer surrounding the drop. Mayer et al(47) postulated that the formation of a film at the oil-water interface would result in diffusional barriers which could inhibit reaction of the acidic components of the oil with the alkali in the bulk aqueous phase.

The formation of a film at the oil-water interface could also explain the very long time for which the IFT is at a minimum for an aqueous phase of 0.05% NaOH. If such a film were present, the rate of desorption of the surface-active species from the interface could be so slow that these species would still be present at very long times.

The curves of Figure 9 and Figure 11 show that both increasing and decreasing the sodium hydroxide concentration from 0.05% yielded higher IFT values. Although alkalinity has a profound effect on the value of IFT, it does not seem to affect the shape of the IFT curves in any significant way. The rise in IFT after the minimum follows no consistent pattern, as illustrated in Figure 10.

Due to experimental difficulties, it was not possible to measure the interfacial tension of Lloydminster crude

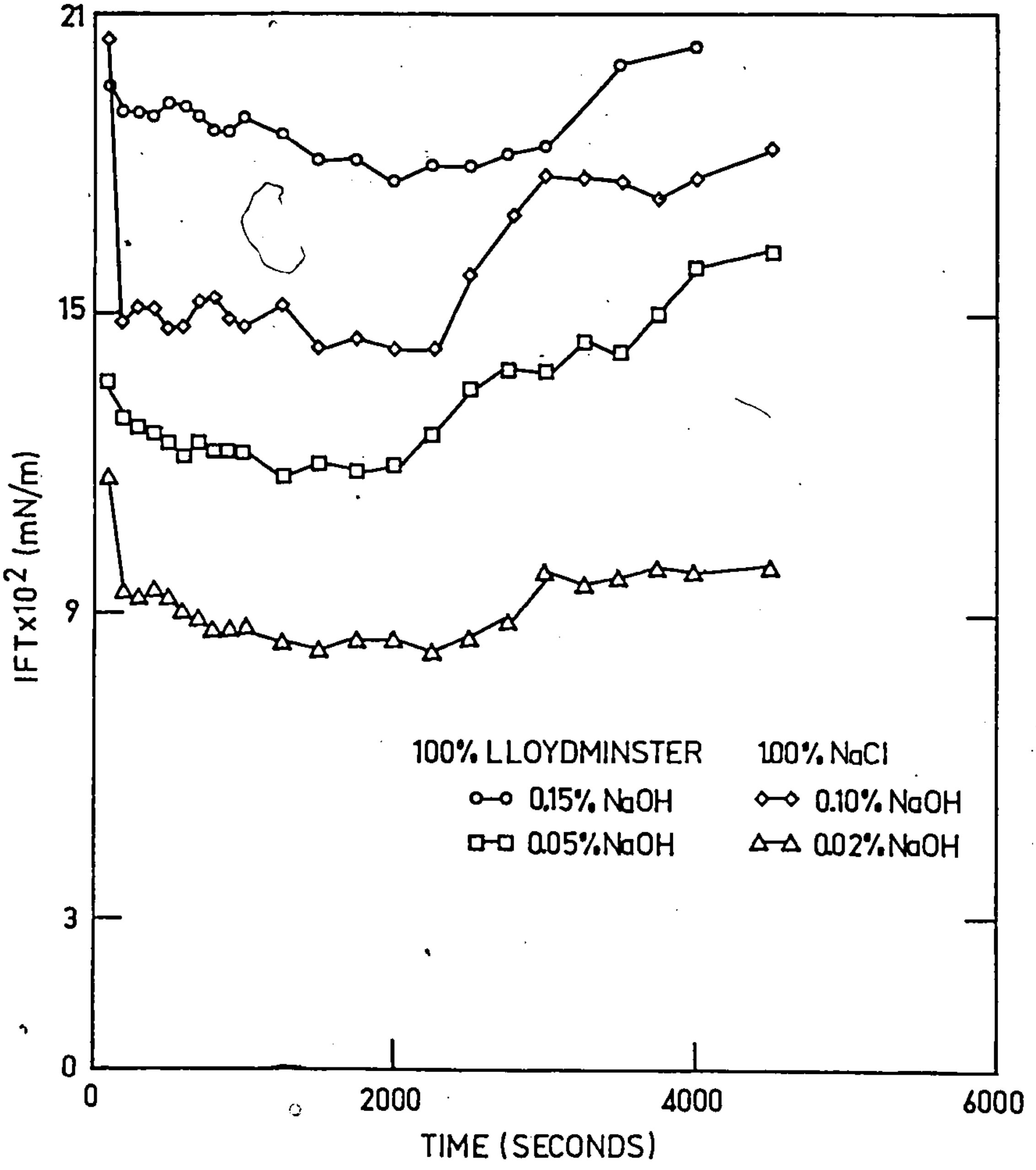

Figure 10: IFT Behaviour for Different Alkalinities (1.00% NaCl)

against pure water using the spinning drop technique. When the aqueous phase was distilled water, the oil droplet adhered strongly to the glass capillary tube even when the drop size was reduced. This adherence was probably due to either a change in wettability of the glass upon contact with alkali or electrostatic attraction between the oil droplet and the glass tube wall.

6.3 Effect of Salinity

The effect of salinity on the equilibrium IFT between crude oils and alkaline solutions has been studied by various researchers(27,34,48). Jennings(34) used the pendent drop method and measured the IFT of 164 different crude oils against caustic solutions. He observed that the amount of sodium hydroxide required to lower the interfacial tension decreased with increasing sodium chloride concentration up to 20,000 ppm. However, other researchers(27,49) have shown that the addition of sodium chloride increases IFT at constant pH. Sharma et al(27) developed a thermodynamic theory based on chemical potentials to model the effects of salinity and alkalinity on IFT. This theory was able to predict the above experimental results - i.e., that higher tensions are obtained at higher salinities at the same pH and that the minimum IFT occurs at lower pH values with increasing salinity. It must be stressed that these results are for equilibrium or pseudo-equilibrium conditions and may not be directly applicable to transient IFT behaviour.

The curves in Figure 11 show the different IFT responses produced with different sodium chloride concentrations in the aqueous phase. It is evident that sodium chloride not only increases the value of the minimum interfacial tension obtained but also causes the subsequent rise in IFT to occur at a shorter time. With a NaCl concentration of 1.50% the rise in IFT begins around 2000 seconds whereas for a NaCl concentration of 0.50% it does not increase until approximately 3500 seconds.

A comparison of Figure 9 with Figure 10 shows the effect of sodium chloride in the bulk aqueous phase even more dramatically. In the absence of NaCl, the interfacial tension for a 0.05% NaOH solution decreased to very low values (0.006 mN/m) and did not increase even at long times (10,000 seconds). When the aqueous phase contained 1.00% NaCl, the minimum IFT attained was almost twenty times higher (0.118 mN/m) and the rise in IFT began at a time of 2000 seconds.

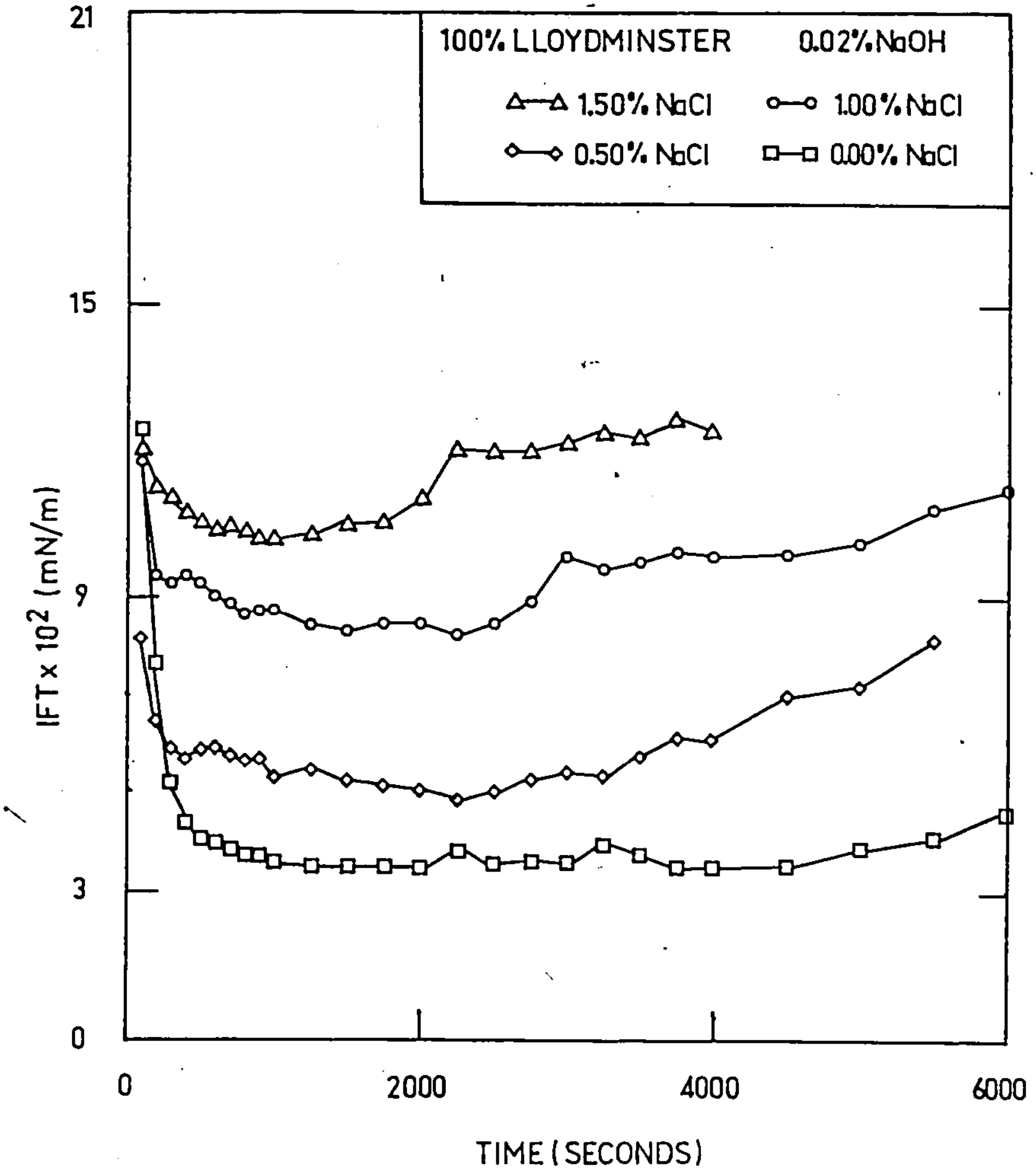

Figure 11: The Effect of Salinity

6.4 Effect of Oil Acidity

As previously mentioned, experiments were performed in which the Lloydminster heavy oil was diluted with dodecane to determine the effect of the acidity of the oil on interfacial tension. Dodecane was chosen for these dilutions on the assumption that the equivalent alkane carbon number(50) for the Lloydminster oil would be approximately twelve. The dilutions were on a volume per cent basis so that the amount of acid in the droplet could be easily calculated - e.g. a droplet of a mixture of 50% dodecane and 50% Lloydminster oil contained one-half the amount of acid in a droplet of 100% Lloydminster crude oil of equal volume (such a droplet is denoted as 50% oil on all figures).

The transient IFT behaviour of the dodecane-diluted oil is shown in Figure 12 and Figure 13. It is evident that the shape of the IFT curves is highly dependent upon the degree of dilution. In the case of the most dilute system (50% oil), no minimum in interfacial tension was observed and the IFT increased very rapidly. When the oleic phase contained 75% oil, the transient IFT curve was peculiarly shaped. The IFT reached a minimum at a short time (generally 200 to 350 seconds), rose moderately quickly to a plateau, and then rose extremely rapidly to high values (0.20 mN/m). The plateau was less evident at higher temperatures, as in Figure 13, but was still present. The rapid rise in IFT following this plateau is indicative of all of the acidic

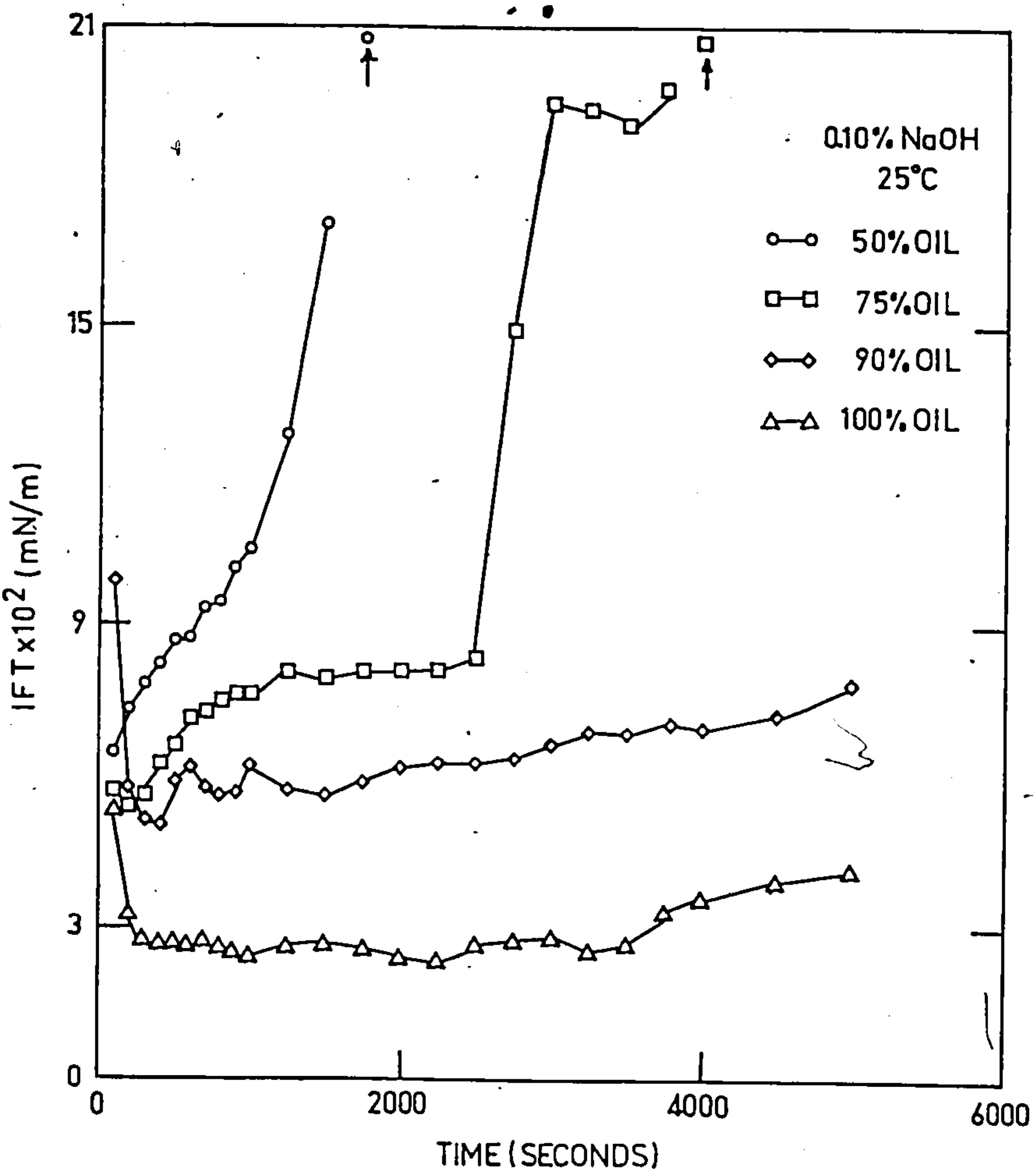

Figure 12: Effect of Dilutions (25°C)

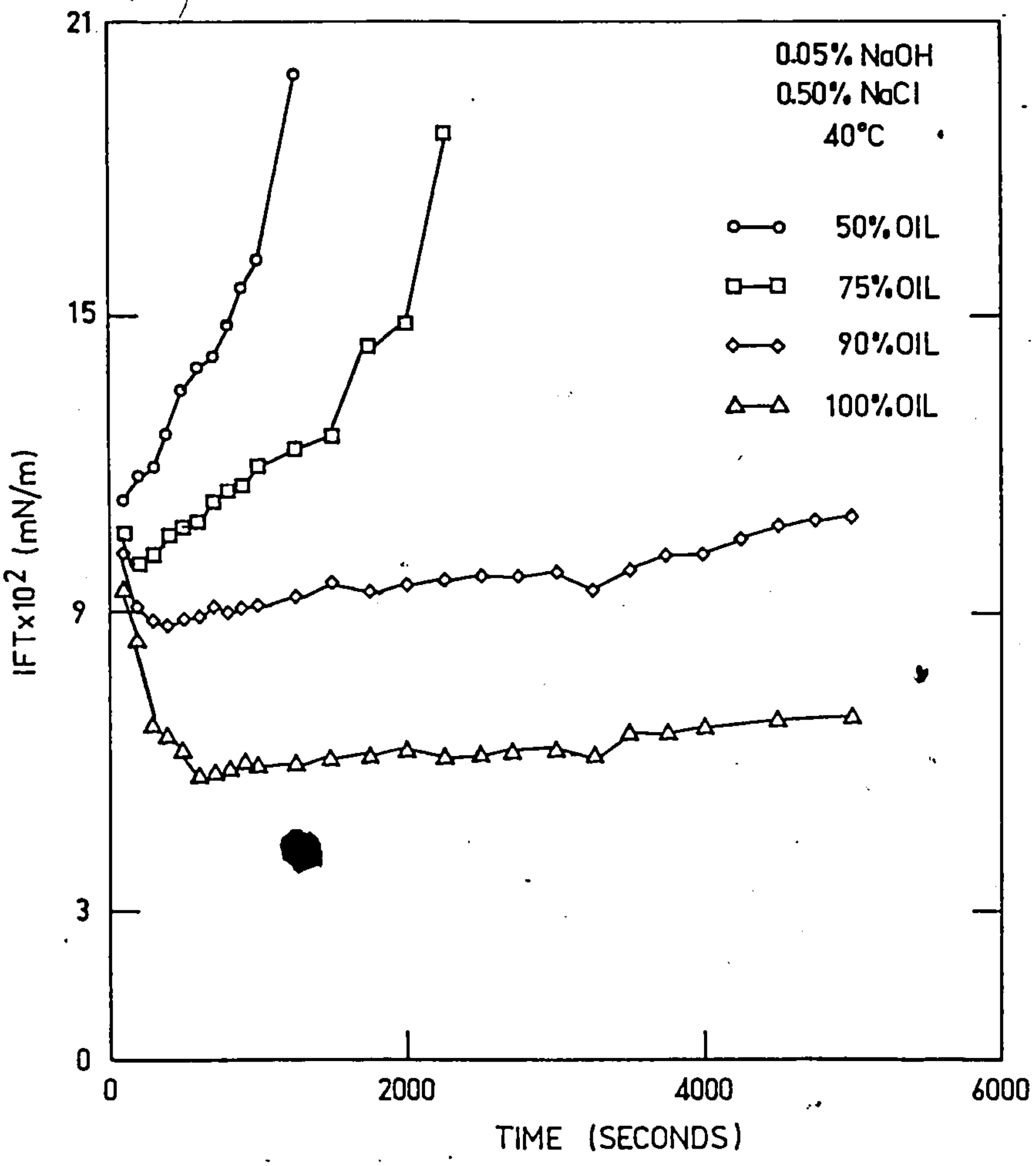

Figure 13: Effect of Dilutions (40°C)

components having been extracted out of the oleic phase. Thus the reaction to produce the surface-active species subsequently slowed, and the IFT rose.

As the viscosities of the oil-dodecane mixtures were much lower than that of the Lloydminster oil, it is possible that the surface-active species could diffuse much faster through the mixtures than through the Lloydminster oil. However, as previously noted, it is the rate of desorption of the surfactant from the interface, and not mass transfer resistances, that controls the lowering of IFT(29). Thus it can be safely assumed that the reduction in viscosity, and the inherent increase in diffusivity, has no effect on interfacial tension.

6.5 Effect of Temperature

The effect of temperature on interfacial tension has not been extensively studied. Jennings(34) found temperature to have a second-order effect on the IFT between acidic crude oils and caustic solutions. Babu et al(43) observed that interfacial tension values for Lloydminster oil-caustic systems showed a slight decreasing trend with increasing temperature. Isaacs and Smolek(50), working with bitumen and petroleum sulphonate, concluded that interfacial tension-temperature behaviour cannot be predicted accurately, as for some systems IFT actually increased with temperature.

Figures 14 to 19 present both the minimum interfacial tension and the time at which minimum occurred as a function of temperature for the oil-dodecane mixtures studied and various aqueous phases. The combination of these two parameters relays the most important information about the time-dependent interfacial tension behaviour and allows for greater simplicity in the reporting of this data.

As can be seen from Figures 14, 16, and 18, the minimum in IFT generally decreases with increasing temperature, in accordance with the findings of Babu et al(43). It is evident that an increase in temperature from 25°C to 40°C has a much more profound effect on IFT than an increase from 40°C to 55°C. This suggests that there is a kinetic "activation temperature" beyond which further increases in temperature have little effect. The temperature-dependent behaviour of the time of occurrence of the minimum in IFT follows exactly the same pattern, as shown in Figures 15, 17, and 19. For 100% Lloydminster crude oil, an increase in temperature from 25°C to 40°C decreases the time of the occurrence of the minimum IFT from approximately 1000 seconds to 400 seconds. Further increases in temperature do not yield as dramatic a decrease. Also, the decrease in the time of occurrence of the minimum IFT with increasing temperature is much smaller for the oil-dodecane mixtures than it is for the pure Lloydminster oil.

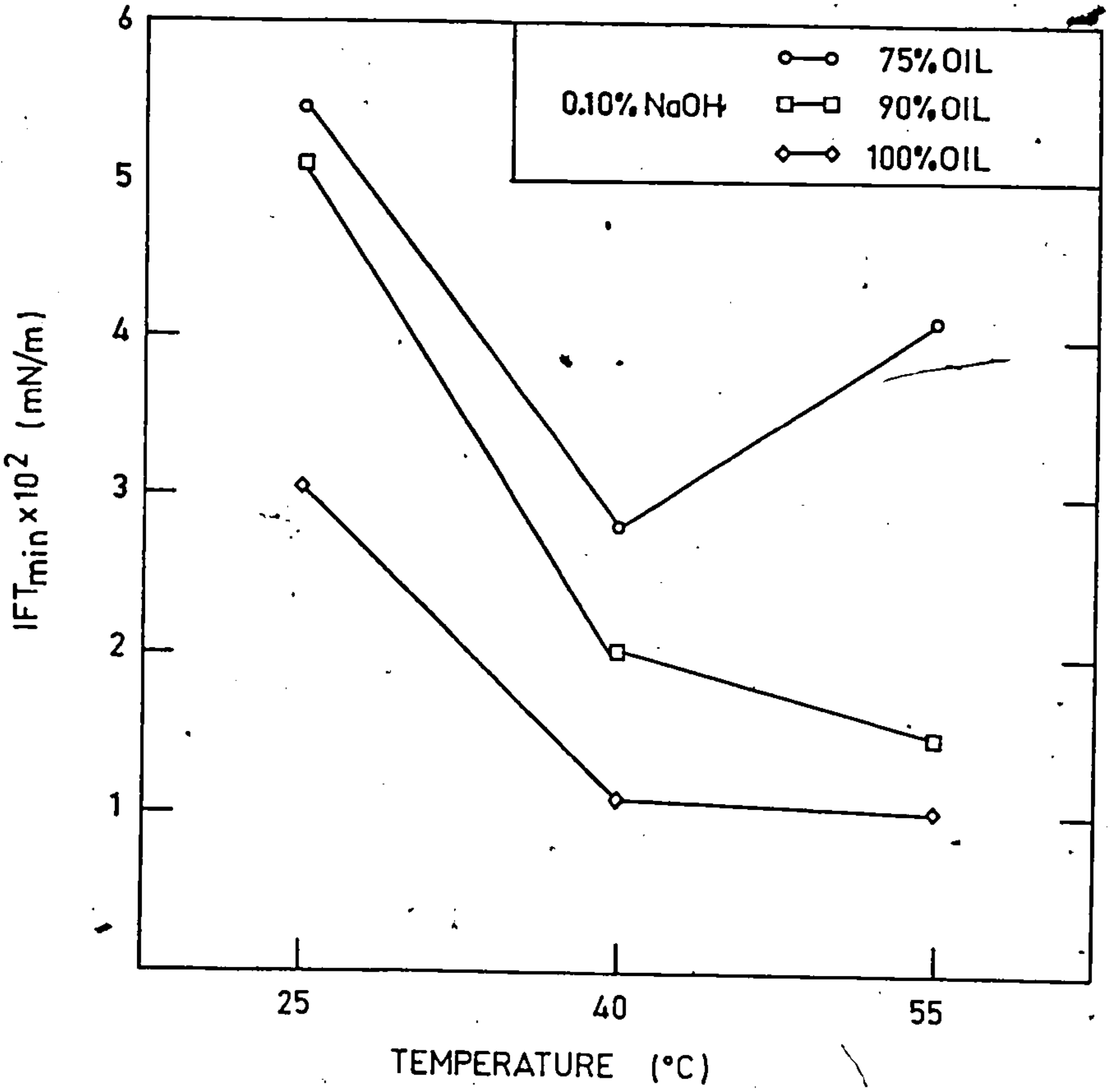

Figure 14: Minimum IFT vs. Temperature (0.10% NaOH)

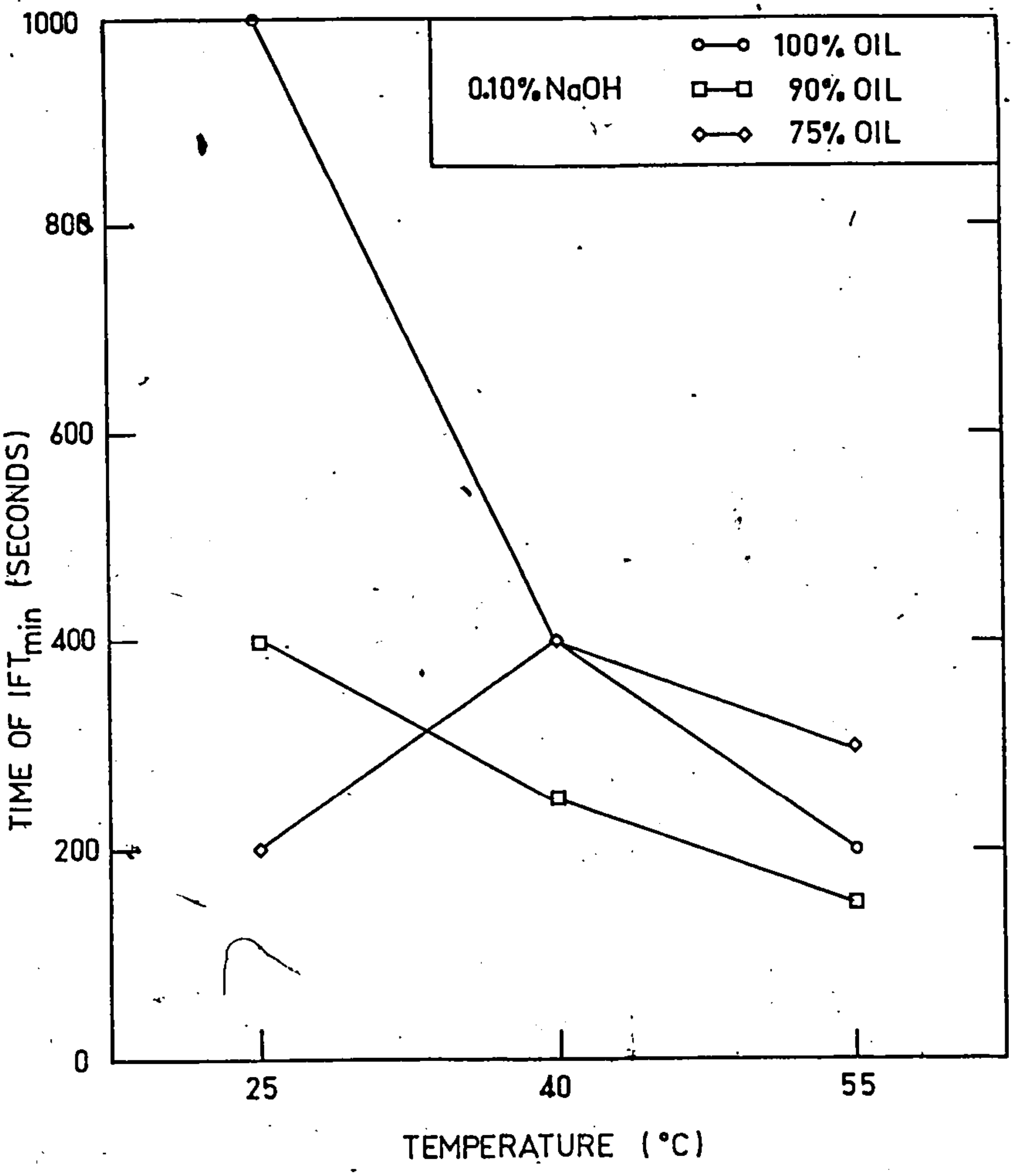

Figure 15: Time of Occurrence of Minimum IFT vs. Temperature (0.10% NaOH)

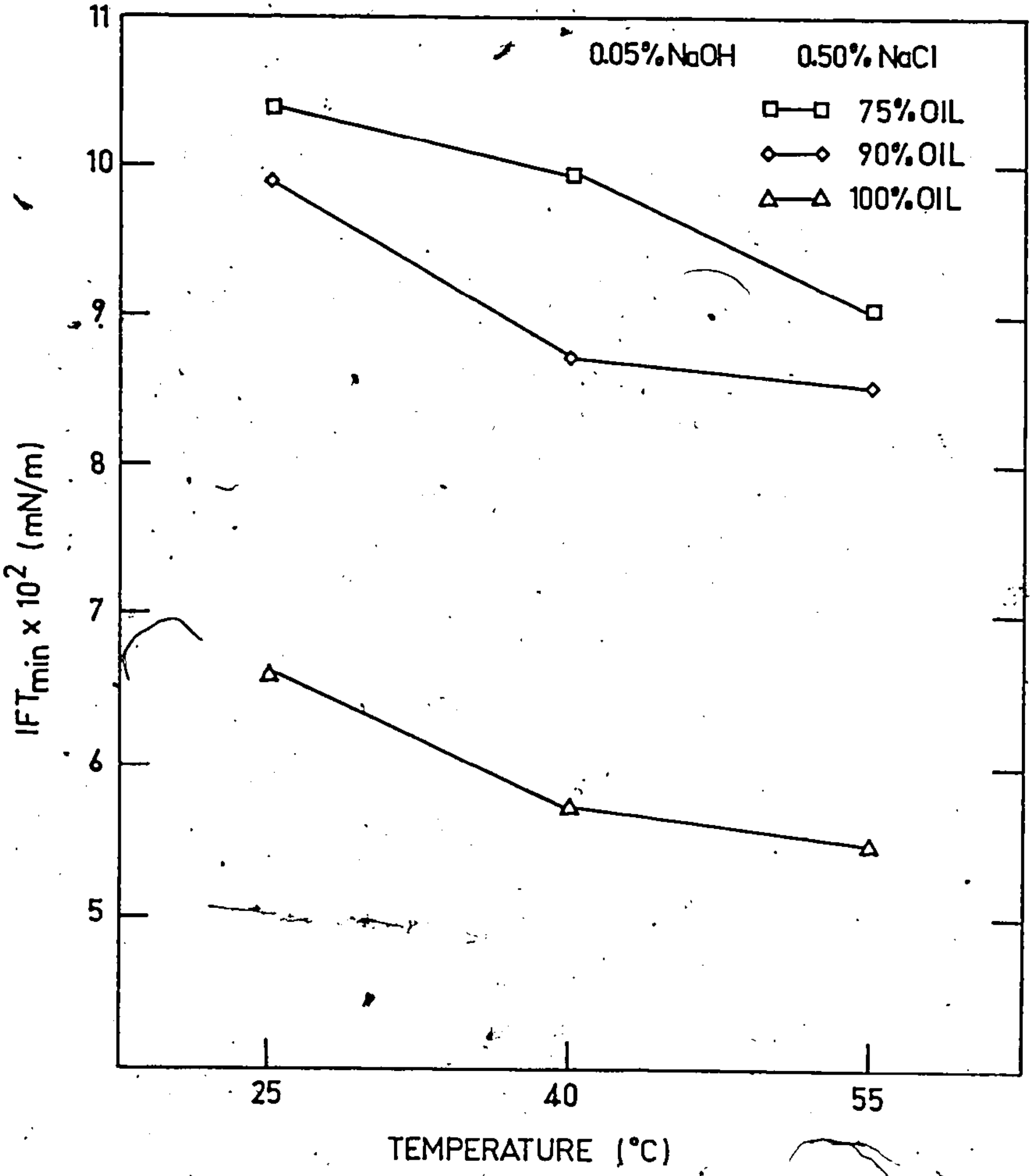

Figure 16: Minimum IFT vs Temperature (0.05% NaOH 0.50% NaCl)

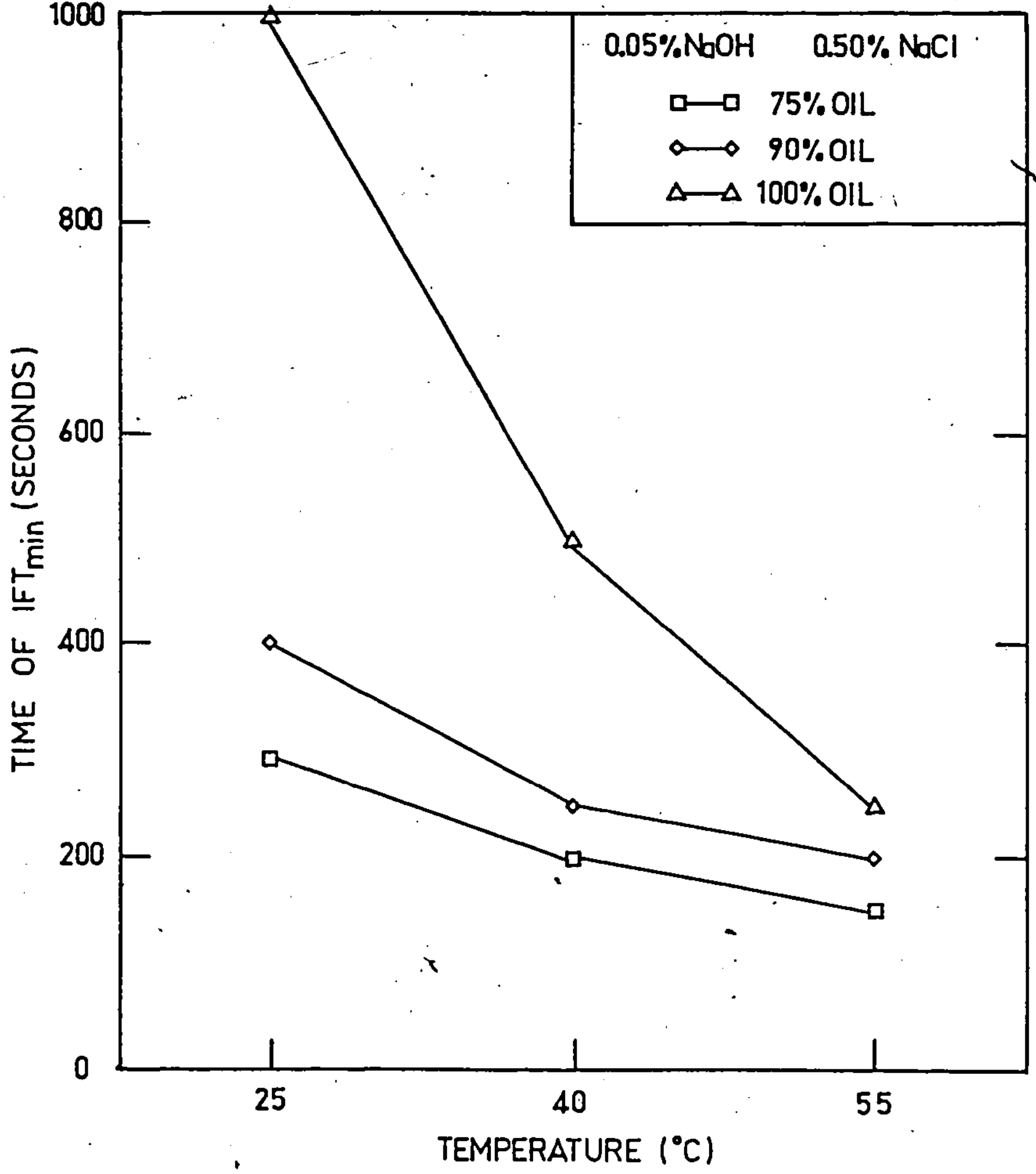

Figure 17: Time of Occurrence of Minimum IFT vs. Temperature (0.05% NaOH 0.50% NaCl)

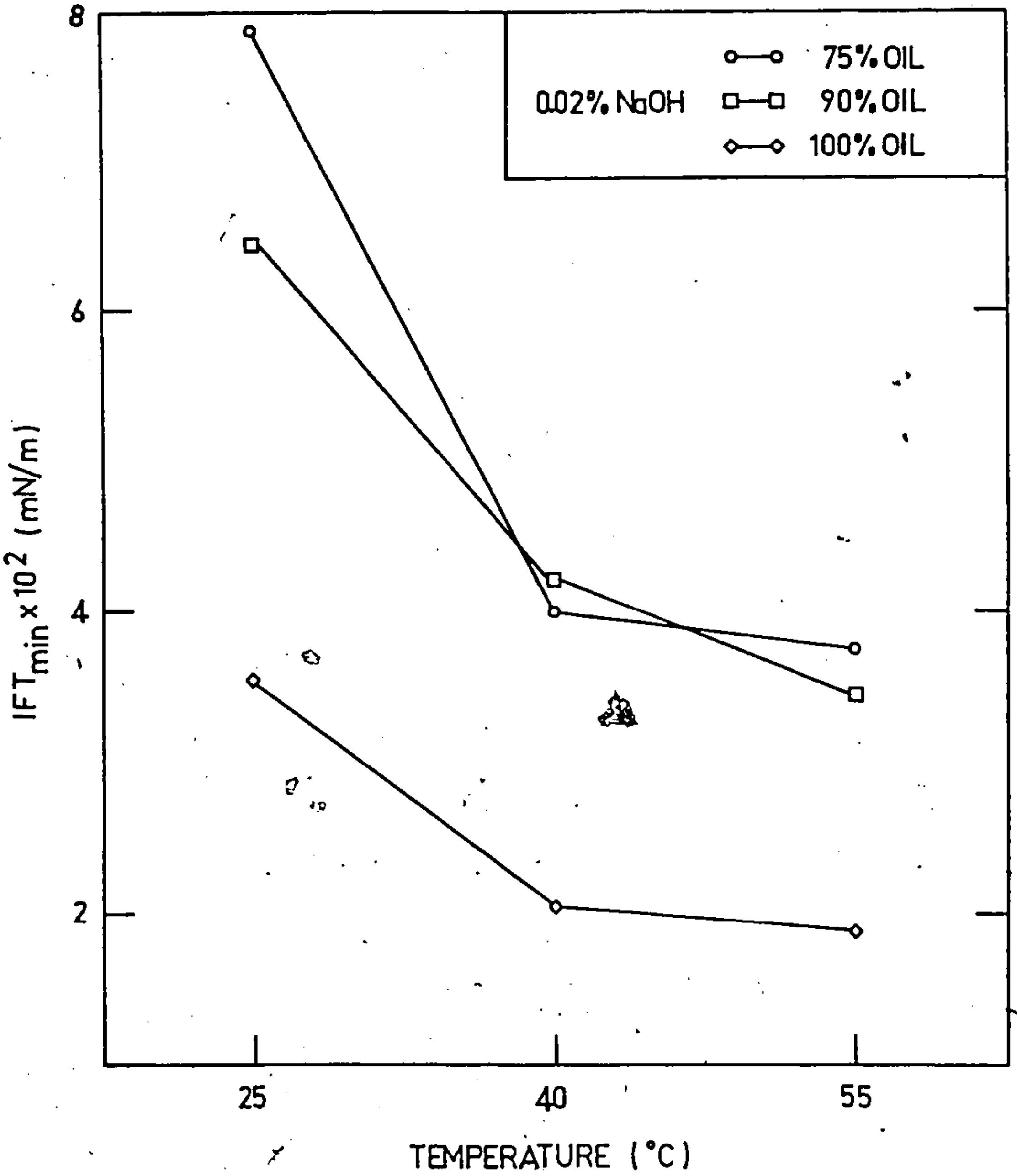

Figure 18: Minimum IFT vs. Temperature (0.02% NaOH)

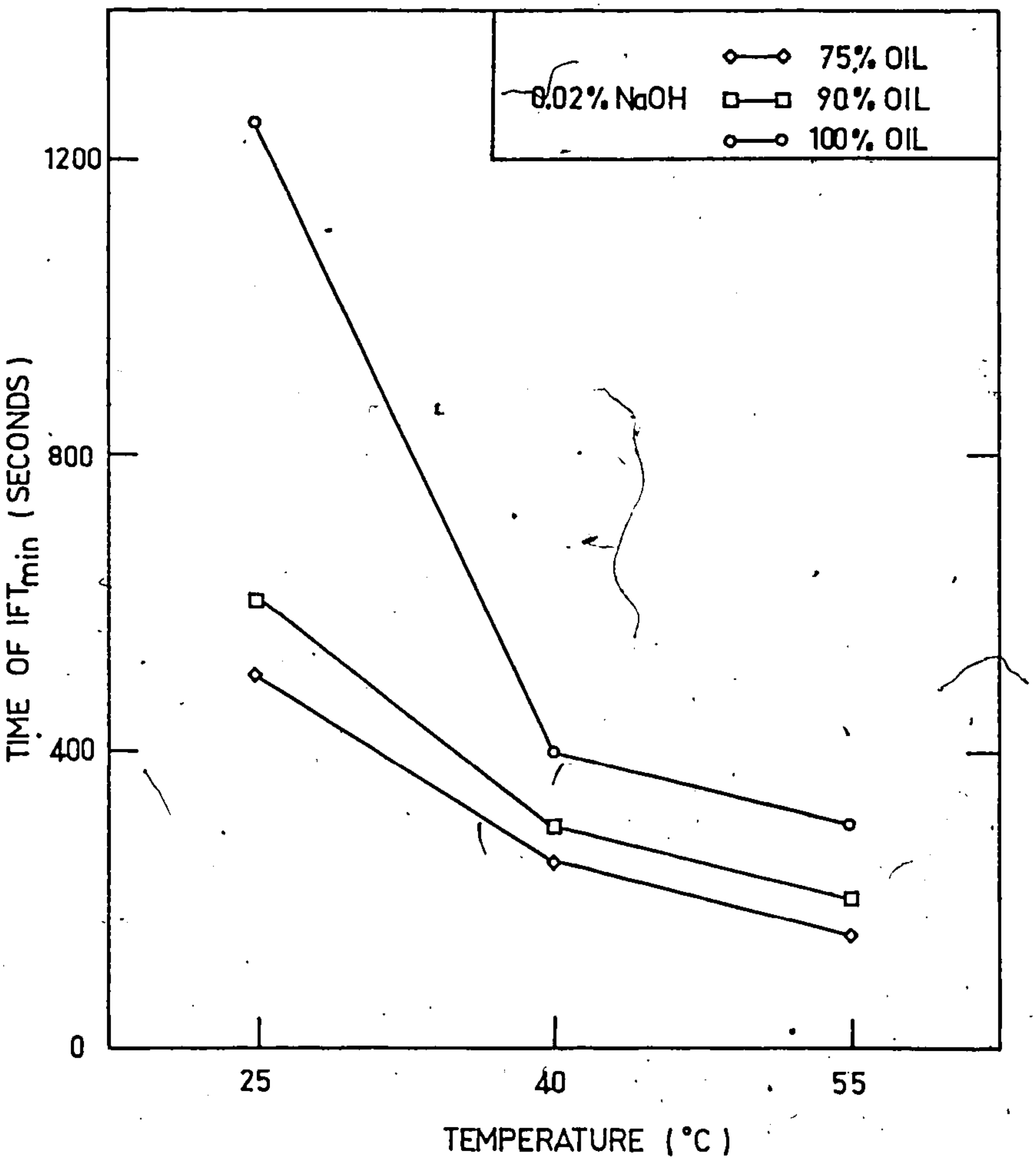

Figure 19: Time of Occurrence of Minimum IFT vs. Temperature (0.02% NaOH)

The decrease in the time of occurrence of the minimum interfacial tension with increasing temperature has more important implications than the decrease in the magnitude of the minimum IFT itself. In an actual reservoir situation, the caustic at the oil-water front would be constantly replenished by fresh injected alkali. Thus it is desirable for the minimum IFT to be attained as soon as possible after the contact of the fresh alkali with the oil bank. Any decrease in the time required to reach the minimum IFT will result in improved oil recovery. Therefore, thermal EOR processes such as steamflooding will benefit not only from reduced oil viscosity but also from a quicker reduction in interfacial tension if alkali is added to the steam.

It is also important to note that the composition of the aqueous phase has a greater effect on IFT than does temperature or the percentage of dodecane in the oil-dodecane mixtures. This is especially evident in Figure 16, in which the aqueous phase contained sodium chloride in solution. The minimum IFT's attained in this case were substantially higher than those for systems with no sodium chloride. The time at which the minimum IFT was attained is not significantly affected by the presence of sodium chloride, as shown in Figure 17. However, the minimum was not sustained for as long as it was in systems with no sodium chloride.

Chapter VII

CONCLUSIONS

1. Ultralow values of interfacial tension are possible between Lloydminster crude oil and alkaline solutions. The interfacial tension is highly dependent upon interfacial age, and exhibits a dynamic minimum.

2. The lowest IFT observed was obtained using a 0.05% NaOH solution. With this aqueous phase, the IFT decreased to a value of 0.006 mN/m and showed no increase from this value during the time period studied.

3. The presence of sodium chloride in the aqueous phase had two main effects. First of all, higher IFT's were obtained at higher salinities for constant pH aqueous phases. Secondly, sodium chloride caused the rate of rise in IFT subsequent to the minimum to increase.

4. When the Lloydminster crude oil was diluted with dodecane, the minimum interfacial tension was higher than for the pure crude oil and it was reached at shorter times. The rate of increase in IFT following the minimum was greater and much higher ultimate IFT's were obtained for these dilutions than for the Lloydminster oil.

5. Temperature had a much larger effect on the time at which the minimum IFT was attained than on the magnitude of this minimum. Also, the decrease in the minimum IFT associated with an increase in temperature from 25°C to 40°C was considerably greater than that for an increase from 40°C to 55°C. The time of the minimum IFT also [illegible]creased in the same way.

6. The effect of temperature on IFT values was not as substantial for the oil-dodecane mixtures as for the pure Lloydminster oil. However, the dilutions had no appreciable effect on the variation of the time of occurrence of the minimum IFT with temperature.

Chapter VIII

RECOMMENDATIONS

1. An analysis of the Lloydminster crude oil could be performed in order to isolate the surface-active components. Also, an analysis of aqueous phases that have been contacted with the Lloydminster oil would provide a clearer understanding of the system chemistry.

2. The crude oil-caustic system could be modelled using a pure high viscosity oleic phase, such as paraffin oil, to [illegible] acids representative of those in the crude oil [illegible] been added. This would yield a more quantitative description of the effect of oil acidity on interfacial tension, and perhaps a model capable of predicting the effects of alkali and salt.

3. Core flooding experiments should be performed using those aqueous phases for which the IFT was the lowest to determine the potential increase in oil recovery using caustic flooding over simple waterflooding. Also, it would be interesting to see if the time at which the minimum interfacial tension was attained affects the ultimate oil recovery.

NOMENCLATURE

C_i	concentration of species i
d	actual drop diameter
d'	measured drop diameter
E_m	macroscopic displacement efficiency
EOR	enhanced oil recovery
IFT	interfacial tension
K_A	dissociation constant of HA
K_D	distribution ratio of HA
K_S	equilibrium constant of NaA
OOIP	original-oil-in-place
r	drop radius
S_{or}	residual oil saturation
S_{wi}	irreducible water saturation
T	period of revolution
V	linear displacement velocity

γ	interfacial tension
μ	viscosity
ν	frequency of revolution
$\Delta\rho$	density difference
ϕ	porosity
ω	angular velocity

Subscripts

o	oil
w	water

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