Interfacial Tension Measurement on Light Oil from Fang Oilfield with Alkaline Solution

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กระบวนการอัดฉีดสารละลายอัลคาไลน์เป็นหนึ่งในกระบวนทางเคมีซึ่งช่วยเพิ่มปริมาณการผลิตน้ำมันโดยการลดแรงตึงผิวระหว่างน้ำมันและสารละลายน้ำประเภทอัลคาไลน์ ในการศึกษาวิจัยครั้งนี้ได้ศึกษาการวัดค่าแรงตึงผิวของน้ำมันจากแหล่งน้ำมันฝางโดยจะทำการศึกษาตัวแปรต่างๆ เช่น ความดัน อุณหภูมิ ชนิดของสารละลายอัลคาไลน์ ความเข้มข้นของสารละลายอัลคาไลน์ ความเข้มข้นของสารละลายเกลือ และ ปริมาณไดวาเลนต์ไอออน

จากผลการศึกษาพบว่าผลกระทบของแต่ละตัวแปรมีผลต่อแรงตึงผิวระหว่างน้ำมันเบาจากแหล่งน้ำมันฝางและสารละลายอัลคาไลน์ที่แตกต่างกันซึ่ง เมื่อทำการเปลี่ยนแปลงความดันค่าความตึงผิวจะค่อนข้างคงที่เนื่องจากระบบที่ทำการศึกษาเป็นของเหลว

ผลกระทบจากชนิดของอัลคาไลน์ที่มีต่อแรงตึงผิวระหว่างน้ำมันและสารละลายอัลคาไลน์พบว่าสารละลายอัลคาไลน์ที่มีลักษณะของเบสแก่สามารถลดแรงตึงผิวได้มากกว่าสารละลายอัลคาไลน์ที่มีลักษณะของเบสอ่อนที่ความเข้มข้นเท่ากันเนื่องจากความสามารถในการแตกตัวของเบสแก่นั้นสูงกว่าเบสอ่อนทำให้สามารถเกิดปฏิกิริยากับกรดในน้ำมันได้มากกว่าและเกิดเป็นสารลดแรงตึงผิวมากขึ้น ซึ่งค่าแรงตึงผิวของสารละลายอัลคาไลน์เบสแก่สามารถลดค่าแรงตึงผิวได้ต่ำถึง 0.2 ดายน์ต่อเซนติเมตร ส่วนสารละลายอัลคาไลน์เบสอ่อนสามารถลดค่าแรงตึงผิวได้ต่ำถึง 0.6 ดายน์ต่อเซนติเมตร

อุณหภูมิเป็นอีกตัวแปรหนึ่งที่ส่งผลต่อค่าแรงตึงผิวคือ การเพิ่มอุณหภูมิจะทำให้ค่าแรงตึงผิวลดลง ส่วนความเข้มข้นของสารละลายอัลคาไลน์และความเข้มข้นของสารละลายเกลือจะมีผลเหมือนกัน คือ ยิ่งค่าเพิ่มขึ้นค่าแรงตึงผิวระหว่างน้ำมันและสารละลายอัลคาไลน์จะยิ่งลดลง นอกจากนี้ผลจากไดวาเลนต์ไอออนมีน้อยสำหรับการศึกษาในครั้งนี้

ภาควิชา วิศวกรรมเหมืองแร่และปิโตรเลียม ลายมือชื่อนิสิต ....

สาขาวิชา วิศวกรรมปิโตรเลียม ลายมือชื่อ อ.ที่ปรึกษาหลัก ....

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Alkaline flooding is one of the chemical process which help to improve the oil recovery by reducing the interfacial tension between oil and aqueous alkaline solution. In this research, the interfacial tension measurement of oil from Fang oilfield would be studied with various parameters such as pressure, temperature, alkaline types, alkaline concentration, salinity concentration and divalent ion.

From the results, the effects of each parameter are different on the interfacial tension. When the pressure changes, the interfacial tension tend to be constant due to the experimental system are liquid phase.

The effects of alkaline types on the interfacial tension are presented that the strong base alkaline solution can reduce the interfacial tension greater than the weak base alkaline solution at the same concentration because the dissociation of the strong base can completely occur compared to weak base. Therefore, the strong base alkaline can from the in-situ surfactant higher than the weak base alkaline. The strong base alkaline can reduce the interfacial tension down to 0.2 dynes/cm while the weak base alkaline can reduce the interfacial tension down to 0.6 dynes/cm.

Temperature is also one of the parameters that affect the interfacial tension in the opposite direction. The increment of temperature would reduce the interfacial tension. Alkaline concentration and salinity affect the interfacial tension in the same direction. The increment of these two parameters would reduce the interfacial tension. The divalent ion has small effect on the interfacial tension.

Department:	Mining and Petroleum Engineering	Student's Signature	....
		Advisor's Signature	....
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List of Abbreviation

Dyne/cm	Dyne per centimeter
mN/m	Mille newton per meter
IFT	Interfacial tension
EOR	Enhance Oil Recovery
NaOH	Sodium hydroxide
Na_2CO_3	Sodium Carbonate
H_2O	Water
Ca^{2+}	Calcium ion
Mg^{2+}	Magnesium ion
Na^{+}	Sodium ion
CO_3^{2-}	Carbonate ion
OH^{-}	Hydroxide ion
^{o}C	Celsius
kg/cm^3	Kilogram per cubic centimeter
pH	Potential hydrogen
% wt	Percent by weight
ppm	part per million
mg/l	mille gram per liter

List of Nomenclature

ρ	Density
m	Mass
V	Volume
^{o}C	Celsius

CHAPTER 1

INTRODUCTION

1.1 Background

With increasing world energy demand and depleting oil reserve by using primary recovery, enhanced oil recovery (EOR) techniques become more and more significant in order to increase the oil production (Sheng 2011). Oil recovery operations normally have been classified into three stages which are primary, secondary and tertiary. Primary recovery is performed by using only the natural drive energy that exists in the reservoir for the displacement of oil to producing wells. These natural energy sources come from solution gas drive, gas cap drive, natural water, fluid and rock expansion and gravity drainage. Secondary recovery usually applied after the primary recovery declined and there is not enough drive energy to transfer the oil up to the surface. The secondary recovery is mainly used to maintain the reservoir pressure to extend the reservoir life and improve volumetric sweep efficiency. Traditional secondary recovery processes are referred to water flooding and gas injection. After the secondary recovery processes become uneconomical, tertiary recovery would be applied. The tertiary recovery processes or EOR can be subdivided into miscible flooding (carbon dioxide, nitrogen, flue gas, solvent etc.), thermal recovery (in situ combustion, Toe to Heel Air Injection etc.), chemical flooding (polymer, surfactant, alkaline etc.) and microbial flooding. EOR processes involve some types of fluid injection into the reservoir. The injected fluids help to displace oil to producing wells. In addition, the injected fluid interacts with the reservoir rock/oil/brine system to create conditions favorable for oil recovery such as lowering interfacial tension or IFT, oil swelling, oil viscosity reduction, wettability modification etc. (Green and Willhite 1998)

Chemical flooding is one of the most wildly used for enhanced oil recovery processed which have joined in many researches and pilot testings. However, its commercial implementation has been facing several technical, operational and economic challenges (Sarkar 2012).

Chemical processes related to the injection of chemical solution that displaces oil effectively. Chemical flooding consisted of polymer flooding, surfactant flooding, alkaline flooding, miscellar flooding, alkaline-surfactant-polymer (ASP) flooding. For alkaline flooding, in-situ surfactant is created by the in-situ chemical reaction between the alkaline solution and the organic acids in oil. The wettability alteration occurs by surface active reaction products adsorbed on the rock surface in order to reduce the residual oil. Furthermore, the in-situ surfactant causes the lowering of interfacial tension between crude oil and water. At low interfacial tension, surface force tends to form oil in water or water in oil emulsion phase depending on pH, temperature, salinity and concentration. The flow properties of this type of emulsion permit a high, non-uniform pressure gradient to generate across the narrow region in the vicinity of the emulsion front. The pressures are enough to surpass the reduced capillary forces and move the oil from the pore space. The displacement efficiency of alkaline flooding can be higher than the typical water flooding efficiency (Abadli 2012). Furthermore, alkaline can be easily found in the market and cheap comparing with the other kinds of surfactant or polymer which make alkaline flooding is more practical. So alkaline flooding can be selected as a first choice for primitive selection.

With the utilization and importance of alkaline flooding, there are many researches working on this type of flooding and try to apply to use in the practical work like that in Thailand. Furthermore, the effect of types of alkaline, alkaline concentration, salinity and temperature over time play significant roles in alkaline performance on enhanced recovery. Therefore, this will be the objectives of this research as shown in section 1.2 to investigate the effects of these parameters on oil production and to measure the IFT from rising drop method. Moreover, from the results, it can determine the optimal operating conditions to minimize the interfacial tension for oil production in Thailand.

1.2 Objective

1. To measure the interfacial tension of oil from Thailand by using rising drop method.

2. To investigate the effects of parameters on interfacial tension of oil from Thailand.
3. To determine the compatible conditions that can minimize the interfacial tension of light oil.

1.3 Expected usefulness

This study emphasizes on the interfacial tension measurement of the crude oil from Thailand. The interfacial tension behaviors at wide ranges of the operational conditions are determined. These results will be useful as operating conditions that can be applied for further study such as testing core flooding and can be used for simulation in the future.

This thesis composes of six chapters. Chapter I introduces background, objectives and contribution of the thesis. The previous literatures related to the study of alkaline flooding are reviewed in Chapter II. Chapter III provides the related theories including alkaline flooding and effect of various parameters on the interfacial tension. Chapter IV describes the details of the condition used to do experiment, oil properties, produced water properties and alkaline solution. Chapter V presents results and discussions from the experiment of alkaline flooding from various conditions. Finally, chapter VI provides summary of thesis as well as recommendation for the future work.

CHAPTER 2

LITERATURE REVIEW

This chapter reviews previous studies involving alkaline flooding by interfacial tension reduction by changing various parameters such as pressure , temperature, alkaline concentration, salinity.

The alkali flooding has been studied for long time. The previous works have presented as shown below:

(Cooke, William et al. 1974) studied the various factors that effect on the interfacial properties. The experiments were conducted on two different kinds of systems which are the systems using synthetic oil and crude oil. First they studied the effect of pH and salinity value on the IFT. The interfacial tension of acidic oils against alkaline water reaches a very low value in the pH range from about 8.2 to 9.2. It means that at higher pH condition, the interfacial tension reduction has high efficiency. The more concentrations of sodium chloride in the water, lower the pH required to achieve a particular interfacial tension.

Secondly, the effect of divalent ion on the interfacial tension has been studied. Calcium and magnesium salts in the aqueous phase even at low concentration would raise the interfacial tension between an acid component in oil and alkaline solution. The concentration of divalent ion that would effect to the interfacial tension is around 40 ppm or greater. In alkaline aqueous phase, calcium and magnesium ions interact with acid component in oil to create the corresponding calcium and magnesium soaps which are much less surface active. Calcium is much more severe than magnesium in this aspect. In oil in which the calcium soap is more soluble, the concentration of calcium ion that particular oil can tolerate is higher. Some of the crude oils, which have a very complex mixture of organic acids, are more tolerant to calcium in the water than the synthetic system containing only oleic acid.

(Buckley and Fan 2005) studied the interfacial tension of oil-brine system by varying multi-parameter such as pH, salinity, acid number.

Researchers did the experiment by using 42 different oil samples with several aqueous phase compositions. Researchers compared the interfacial tension of high and low acid number in oil at different pH values. When the pH is about 6, the interfacial tension of two conditions is in range of 10-30 mN/m. When the pH is above 6, the trend of the interfacial tension will be more different in the two conditions. The higher acid number in oil has more effective in the interfacial tension reduction than the lower acid number in oil. All of the high acid number can reach the ultra-low interfacial tension when pH about 11.

(Taha and Abdul-Jalil 2009) studied the brine salinity effects to the interfacial tension of the dead oil and live oil system in Arab-D carbonate rock at different temperature and pressure. All high, medium, low salinity brine-oil system demonstrated the reduction of the interfacial tension when the temperature increases. The reduction in the interfacial tension is caused by the weakening of intermolecular force between oil-brine interface at higher temperature. At the low temperature, there is more affect in the divalent ion (calcium and magnesium cations) which deactivated the ionizable species in the oil-brine system. Live oil interfacial tension also has the similar trend as dead oil interfacial tension.

(Wang and Gupta 1995) studied the interfacial tension for three different systems (oil-distillated water, oil and brine from carbonate reservoir, oil and brine from sandstone reservoir). The interfacial tension will be raised when pressure increase for all of three systems. On the other hand temperature has opposite effects to the interfacial tension for all three systems. The interfacial tension will be raised when the temperature increase for mineral oil-distilled water and crude oil-brine from carbonate reservoir but the interfacial tension will be reduced when the temperature increase for crude oil-brine from sandstone reservoir. Therefore, the interfacial tension tend to be increased when the pressure increase but oil composition systems will affect the direction of the interfacial tension when temperature changes.

(Hjelmeland and Larrondo 1983) studied the interfacial tension of crude oil-brine at different temperature and pressure. They found that the interfacial tension increase with pressure. At high pressure and low temperature, there is more surface active material concentration to accumulate at the oil-brine interface that will cause lower in the interfacial tension. At high temperature, there is lower surface active material due to the adsorption process. But in the low pressure condition, oxidation process will be occurred and dominant the adsorption effect that makes the interfacial tension reduced. Oxidation reaction will be occurred more in higher temperature. Therefore, the existing of air may cause more surface activity and lower interfacial tension.

(Flock and Gibeau 1986) studied the interfacial tension of n-octane and five different heavy crude oil from Alberta reservoir (Wainwright B crude oil from the Waineright area, Epping crude oil from the Lloydminster area, Shell crude oil from the three Creeks site) at different temperature. Brine used in this experiment are double distilled de-ionized, heavy water and water from Battle River. It can be concluded that there are three kinds of crude oil that the interfacial tension reduces when the temperature increases. However there is some crude oil that the interfacial tension increases when the temperature increases.

CHAPTER 3

THEORY

This chapter summarized the main theories about the alkaline flooding. In addition, the content includes the effect of various factors on interfacial tension.

3.1 Alkaline flooding

After the primary recovery, some parts of oil are left in the formation because of unfavorable conditions for oil production such as pressure depletion, oil wettability on rock surface etc. Secondary recovery (water flooding or gas injection) maintains pressure for oil to flow which is higher than capillary pressure. However, some rocks have unfavorable wettability which can occur from the interaction between different charges. Therefore using secondary recovery is not enough to release the attached oil on rock surface. Alkaline flooding has ability to change wettability to more favorable condition by reducing the interfacial tension to have less capillary pressure.

Alkaline flooding has been first used in 1917 by Squires. The alkaline solution was injected into formation to react with the acid in oil and generate in-situ surfactant. Therefore, oil in formation can be displaced easier due to lower interfacial tension. Moreover, alkaline flooding is simple comparing to other chemical flooding and inexpensive. However the alkaline flooding has some limitation such as the minimum amount of acid in oil etc. The experiment from laboratory is used to observe the response of alkaline flooding in a practical way.

Alkaline flooding is one of the EOR methods using injected water or brine that contains alkaline solution such as sodium hydroxide, sodium orthosilicate or sodium carbonate. The mechanism of alkaline flooding can be explained that alkaline will form in-situ surfactant by the reaction between alkaline solution and acid compound in oil. This surfactant would increase the oil recovery by reducing the interfacial tension between oil and brine solution (Abadli 2012).

There are many types of alkaline solution. Sodium hydroxide (NaOH) is one of the most commonly used as alkaline solutions because it can perform least interfacial tension among other alkaline solution. Sodium hydroxide is strong base; therefore it can completely react itself with acid in oil. The other alkaline substance can also reduce the interfacial tension but the performance is depend on how strong the base is.

The important factor that helps alkaline flooding to be successful is acid in oil; therefore acid number is one of the factors that we need to consider. The minimum acid oil number that would active the alkaline flooding is about 0.5 or higher. The optimum concentration of alkaline solution reduces the interfacial tension to the lowest value. The interfacial tension reduction would create the emulsification which is oil in water emulsion. This emulsion would improve sweep efficiency by reducing the mobility of water in displacement process. When the interfacial tension reduces, the capillary number is increased as a result of higher displacement efficiency.

Changing in wettability can be occurred from alkaline solution. At the beginning, the oil migration would make the rock surface wettability from water wet to oil wet which come from oil deposition on rock surface (unfavorable condition). Alkaline solution can generate in situ surfactant and reduce the interfacial tension between oil and aqueous phase in order to release oil from rock surface.

The alkaline reagents tend to move the oil by changing the pH value of brine or aqueous phase to be more basic. The interaction between alkaline and acid compound in the oil generates the in-situ surfactant at the contact of oil-brine interface. After that, the crude oil is recovered by displacing of brine solution. Alkaline typically applies to the reservoirs that have high amount of acid component in the oil (Abadli 2012).

The disadvantage of alkaline flooding is the alkaline consumption that would decrease the quantity of alkaline solution. Some types of minerals in the formation can consume the alkaline substance; therefore this is one of the limitations to use alkaline.

Furthermore, alkaline flooding is not suitable for carbonate rock reservoir because carbonate rock contain calcium ion which can react with alkaline reagent and form hydroxide precipitation which obstructs the flow path in the reservoir (Abadli 2012).

The main advantages of using alkaline flooding are the interfacial tension reduction and decreasing the surfactant adsorption in AS or ASP flooding which can save the cost of surfactant in order to do flooding (Abadli 2012). Furthermore, these alkaline are cheap and easily available.

Alkaline flooding can also called caustic flooding. The ionization of alkaline compound increases the pH of the oil-brine system. For example, sodium hydroxide can be ionized to generate OH^- (Sheng 2011)

$$NaOH \rightarrow Na^+ + OH^-$$

Sodium carbonate can ionized to

$$Na_2CO_3 \rightarrow 2Na + CO_3^{2-}$$

Followed by the hydrolysis reaction

$$CO_3^{2-} + H_2O \rightarrow HCO_3^- + OH^-$$

The pH values of various typical alkaline are shown in Figure 3.1. For example, the pH of sodium hydroxide solutions reduces from 13.2 to 12.5 when there is an incremental salinity from 0 to 1% of sodium chloride. The pH of sodium carbonate solution has less effect on the salinity (Labrid 1991).

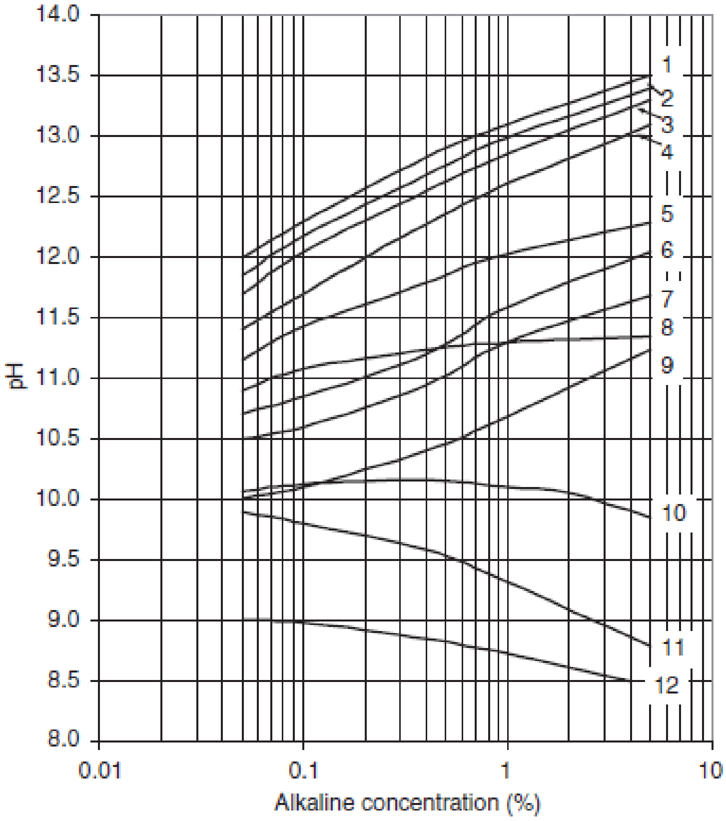


Figure 3.1: pH value of alkaline solution at different concentration at 25 °C: 1 sodium hydroxide, 2 sodium orthosilicate, 3 sodium metasilicate, 4 sodium silicate pentahydrate, 5 sodium phosphate, 6 sodium silicate$[(Na_2O)(SiO_2)_n], n = 2$, 7 sodium silicate$[(Na_2O)(SiO_2)_n], n = 2.4$, 8 sodium carbonate, 9 sodium silicate$[(Na_2O)(SiO_2)_n], n = 3.22$, 10 sodium pyrophosphate, 11 sodium tripolyphosphate, 12 sodium bicarbonate. (Labrid 1991)

To decrease IFT effectively, it has been investigated that among typical alkaline, it has a little different in IFT reduction. The IFT can reduce to minimum value at the small value interval of alkaline concentrations, normally 0.05 to 0.1wt% with a minimum IFT of 0.01 mN/m (Green and Willhite 1998).

Recovery Mechanisms of Alkaline

There are three mechanisms in alkaline flooding

- Emulsification and Entrainment-This phenomenon occurs when there are fine emulsion and can travel through the pore without trapping between porous media.
- Wettability Alteration-This phenomenon can alter the wettability of rock surface to more favor condition in order to reduce the capillary force holding the oil in the porous media and reduce the residual oil saturation further.
- Emulsification and Entrapment -This phenomenon can improve sweep efficiency because the large emulsions block flow path and change flow path to other direction which has residual oil left.

There are many variables to consider in order to apply alkaline flooding such as pH value, temperature, mineralogy of formation and composition of mixed water.

3.2 Reaction of Alkaline with Crude Oil

1. In-situ soap generation

For alkaline flooding, the surfactant or soap is created under the ground by sponification reaction between alkaline solution and acid components or saponifiable components in crude oil (naphthenic acids). Acid number is a number for demonstrated sufficient quantity of acid component in the oil in order to create surfactant. By definition, Acid number is the amount of potassium hydroxide (KOH) to neutralize the acid in oil in term of mg KOH/g oil (Abadli, 2012). The soap or surfactant creation is described by the partitioning acid in crude oil (HA_o) to water which depending on the solubility as

$$HA_o \leftrightarrow HA_w$$

$$K_D = \frac{[HA_w]}{[HA_o]}$$

HA_W- the concentration of acid in water, K_D- the partition coefficient of acid

HA are defined as a single acid species and the subscript o and w denote oleic and aqueous phases, respectively.

As shown in Figure 3.2, when the time passes, the acid components will isolate itself in the brine solution or aqueous phase to create soluble anionic surfactant (A-) which is soap by using hydrolysis reaction (Abadli 2012).

$$HA_w + OH^- \leftrightarrow H_2O + A^-$$

The above reaction illustrates how alkaline is consumed to create soap because alkaline uses hydrogen to create soap (Abadli 2012).

$$HA_w \leftrightarrow H^+ + A^-$$

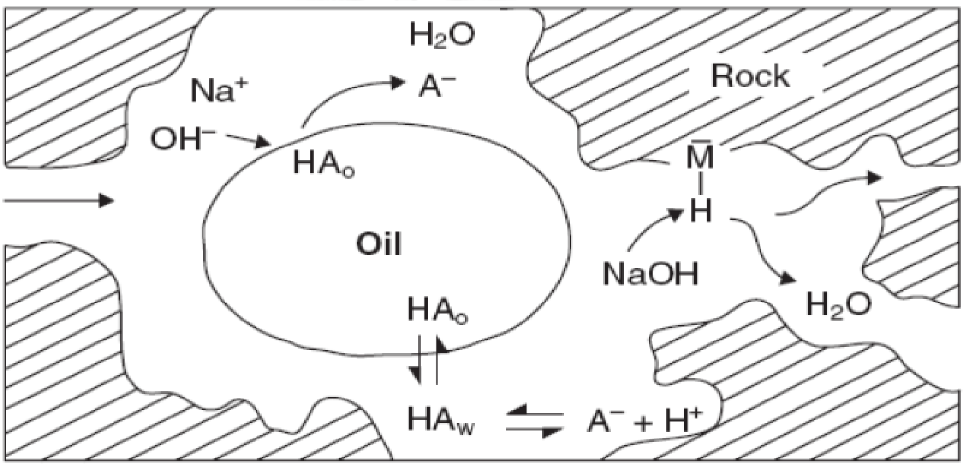


Figure 3.2 Alkaline Flooding Process (Abadli 2012)

The acid dissociation constant

$$K_A = \frac{[H^+][A^-]}{[HA_w]}$$

Where bracket is defined as molar concentration.

The overall hydrolysis and extraction are given by

$$HA_o + NaOH \leftrightarrow NaA + H_2O$$

This brine solution pH has a strongly effect on this reaction occurring at the water/oil interface. A fraction of organic acids in oil are ionized with the addition of an alkaline, while others remained electronically neutral. The generation of acid soaps is from the hydrogen bonding interaction between the ionized and neutral acids (Abadli 2012).

2. Emulsification

The IFT between oil-brine interfaces has an important effect to emulsification. The emulsion can generate easily at low IFT. The stability of an emulsion mainly depends on the film of the water/oil interface (Sheng 2011).

The emulsification is not completely reversible. When the dynamic IFT reaches ultralow, emulsification can occur. Even when dynamic IFT goes up, emulsified oil droplets do not easily coalesce. In alkaline flooding, emulsification is instant, and emulsions are very stable. From this emulsification point of view, the dynamic minimum IFT plays an important role in enhanced oil recovery. From the low IFT point of view, we may think we should use equilibrium IFT because reservoir flow is a slow process. However, the coreflooding results from the laboratory show that when the minimum dynamic IFT reaches 10^{-3} mN/m level and the equilibrium IFT is at 10^{-1} mN/m; the ASP incremental oil recovery factors are similar to those when the equilibrium IFT is 10^{-3} mN/m. One explanation is that once the residual oil droplets become mobile owing to the instantaneous minimum IFT, they coalesce to form a continuous oil bank. This continuous oil bank can be moved even when the IFT becomes high later. Then for this mechanism to work, the oil droplets must be able to coalesce before the IFT becomes high. It can be seen that it will be more difficult for such a mechanism to function in field conditions rather than in laboratory corefloods (Huang and Yu 2002).

3.3 Acid Number

A measure of the potential of a crude oil to form surfactants is given by the acid number (sometimes called total acid number, or TAN). This is the mass of potassium hydroxide (KOH) in milligrams that is required to neutralize one gram of crude oil. Usually, acid number determined by nonaqueous phase titration is used to estimate the soap amount (Buckley and Fan 2005). However, short chain acids, which also react with alkali, may not behave like surfactant because they are too hydrophilic. Also, phenolics and porphyrins in crude oil will consume alkali and will not change the interfacial properties as much as surfactant. Asphaltene and/or resin may have carboxylate functional groups but not be extracted into the aqueous phase. Total acid number determined by nonaqueous phase titration could not distinguish the acids that can generate natural soap and those that can consume alkali without producing surfactant (Sheng 2011).

Figure 3.3 shows that even if the acid number of the oil is zero, oil/water IFT could be reduced by adding alkalis in the water. The organic acid is removed from the oil sample (with zero acid number). The figure shows that at an equal alkaline concentration, different alkalis give different IFTs. These different IFTs are not caused by different values of pH only, because at equal alkaline concentration, the pH value of sodium orthosilicate is higher than those of sodium carbonate and sodium bicarbonate. However, the IFT for sodium orthosilicate is higher. It is implied that some other factors could also reduce IFT, or the acid number measured does not reflect all the factors that contribute to IFT reduction (Li 2007).

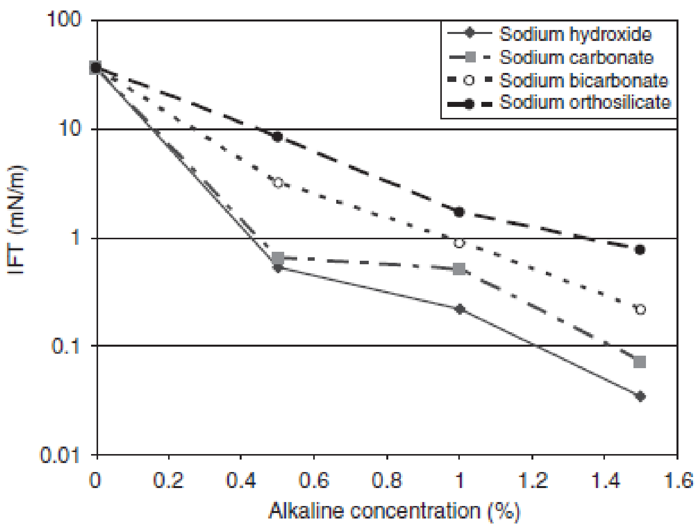


Figure 3.3 Oil–water IFT at different alkaline concentrations with zero acid number in the oil. (Li 2007)

CHAPTER 4

EXPERIMENTS

In this study, there are two experiments that have been performed in order to measure fluid property measurement, interfacial tension measurement.

4.1 Fluid properties

Oil from north of Thailand is used to determine interfacial tension. Sodium hydroxide and sodium carbonate are used as alkaline chemical substance. Brine and produced water are used as the aqueous solution.

4.1.1 Oil Composition

The gas chromatography (GC) has been used to analyze the oil composition. This method is one of chemical analysis methods that use to investigate the complex compound sample. The concept of this method is to flow the fluid through the narrow tube which is known as column which consists of different type of mediums (mobile phase). The oil sample fluid would flow pass in the gas stream at different rate depending on their various chemical and physical properties and their interaction with a specific column filling (stationary phase). When the oil fluid passes through the end of column, it would be detected and identified. The stationary phase in the column would help to separate the different components, causing each one to exit the column at different time.

The oil composition has various types of hydrocarbon from C7 to C35+.

Table 4.1 Oil Sample Composition (Intertek 2015a)

Composition	Percent by weight
C7	0.05
C8	0.68
C9	0.93
C10	1.00
C11	1.45
C12	1.84
C13	3.06
C14	3.52
C15	4.86
C16	3.87
C17	4.71
C19H40	2.44
C18	3.49
C20H42	0.82
C19	3.89
C20	4.41
C21	4.81
C22	4.48
C23	4.97
C24	4.26
C25	4.42
C26	4.33
C27	4.56
C28	3.58
C29	3.97
C30	3.72
C31	3.27
C32	2.87
C33	3.64
C34	1.70
C35+	4.40

4.1.2 Oil Density

The oil density is measured at different temperature. The mass and volume of oil are measured separately. The oil sample would be boiled to reach the desired temperature and then measure weight by precision scale meter and measure volume by using syringe. The oil density can be calculated by dividing mass by volume.

$$\rho = \frac{m}{V}$$

Where ρ is density,

m is mass, and

V is volume.

Table 4.2 Oil Density

Temperature (^oC)	Oil Density (g/cm^3)
70	0.850
80	0.849
90	0.848

4.1.3 Brine Properties

Brine composition would be designed based on produced water that comes out from the reservoir to the surface. The produced water compositions are in the followed table.

Table 4.3 Produced Water Composition (Intertek 2015b)

Chemical Ion	Concentration (ppm)
Sodium, Na	270
Calcium, Ca	6.67
Magnesium, Mg	2.28
Barium, Ba	0.46
Chloride, Cl	21.2
Sulfate, SO_4	4.43
Carbonate, CO_3	58.5
Bicarbonate, HCO_3	588
Hydroxide, OH	0

From the composition table, there are four main chemical compositions which are sodium (28.4 %), chloride (2.2 %), carbonate (6.1 %), Bicarbonate (61.8 %). The divalent ion such as calcium and magnesium have small amount, therefore we would neglect them in brine composition.

4.2 Interfacial tension Measurement

4.2.1 Apparatus

The interfacial tension meter 700 (IFT 700) is used for determination of interfacial tension between liquid-gas and liquid-liquid interfaces at reservoir condition.

The IFT 700 can perform experiment at high pressure up to 10000 psi and high temperature up to 200 ^{o}C conditions. Basically, a drop is created from a calibrated capillary into a bulk fluid in a cell at reservoir conditions, Then, using rising pendent drop method, a camera connected to a computer records the shape of the drop and provides the IFT value.

Figure 4.1 IFT 700

4.2.2 Procedure

At the beginning, brine would be prepared at different salinity and alkaline concentration. Then, the IFT 700 is set up in order to start measure the interfacial tension. Acetone and distilled water would be used as cleaning fluid to clean the equipment components such as chamber, needle, pipe system, and pump. Then, all the components of IFT 700 would be combined and check the vertical setup.

The alkaline solution (bulk fluid) and oil (drop fluid) is fed into the pump in order to start the experiment. There are two pumps separately for oil and alkaline solution. Then, temperature would be set at the computer monitor at the desired value. This condition is kept for 20 minutes to reach equilibrium. The oil sample would be injected through the needle in order to form the droplet. Then pressure is set as the desired value.

The drop and bulk densities are inserted in the software. The camera is adjusted to the clear resolution. Then, The IFT 700 would be run measurement and recorded the results.

The measurements of this research are varied 4 groups of parameters which are temperature, pressure, alkaline concentration and salinity. The alkaline solution is prepared at different concentrations for 4 values which are 0.00 %wt, 0.025 %wt, 0.05 %wt and 0.075 %wt. There are two types of alkaline in this research which are sodium hydroxide and sodium carbonate. The salinity would be varies in all alkaline solution. The salinities in this research are 0 ppm, 500 ppm, 750 ppm and 1000 ppm. For the temperature, alkaline solution is testing for 3 values which are 70 C, 80 C, and 90 C. Finally, pressure is also studies at different values which are 500 psi, 1000 psi, 1500 psi.

Table 4.4 The operating condition in experiment

Alkaline	Alkaline Concentration	Salinity	Temperature	Pressure
Sodium Hydroxide	0.00 %wt	0 ppm	70 C	500 psi
Sodium Carbonate	0.025 % wt	500 ppm	80 C	1000 psi
	0.05 %wt	750 ppm	90 C	1500 psi
	0.075 %wt	1000 ppm		

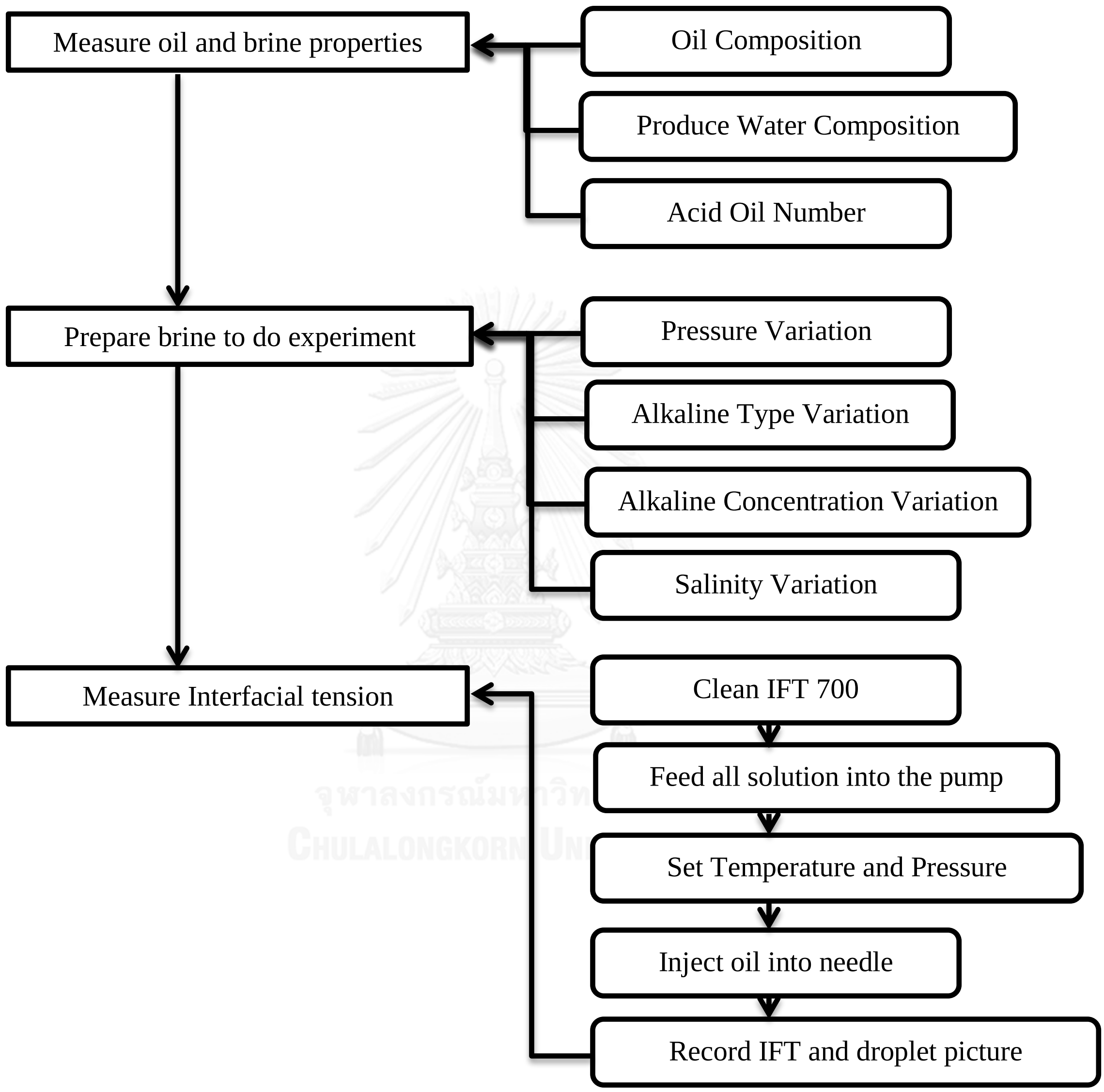


Figure 4.2 Methodology Flow Chart

CHAPTER 5

RESULTS AND DISCUSSION

The experiment results are presented and discussed for the effects of various parameters in this chapter such as effect of pressure, types of alkaline solution, effect of alkaline concentration, effect of temperature, effect of salinity and effect of divalent ion.

5.1 The effect of pressure on the interfacial tension

The pressure used in this research ranges from 500 to 1500 psi because this range of pressure would cover the pressure in Fang Oilfield. The results are shown in Figure 5.1 and Table 5.1. From the results, it is obvious that pressure has less effect on the interfacial tension reduction because the system that we studied is liquid phase system.

From figure 5.1, the values of interfacial tension do not change significantly. The percent change of interfacial tension when the pressure change is small. The distilled water, sodium hydroxide solution and sodium carbonate solution have the percent different around 0.62%, 0% and 2.72% , respectively when the pressure changes. From the result, it can be concluded that pressure has less effect on the interfacial tension because the liquid phase has more attractive force between molecules than gas phase. From previous studies, the interfacial tension would have just slightly changed with pressure at constant temperature in the range pressure of 1 to 204 atm. (Hassan, Nielsen et al. 1953). Therefore, the experiment would be used the same pressure at 1000 psi for other cases.

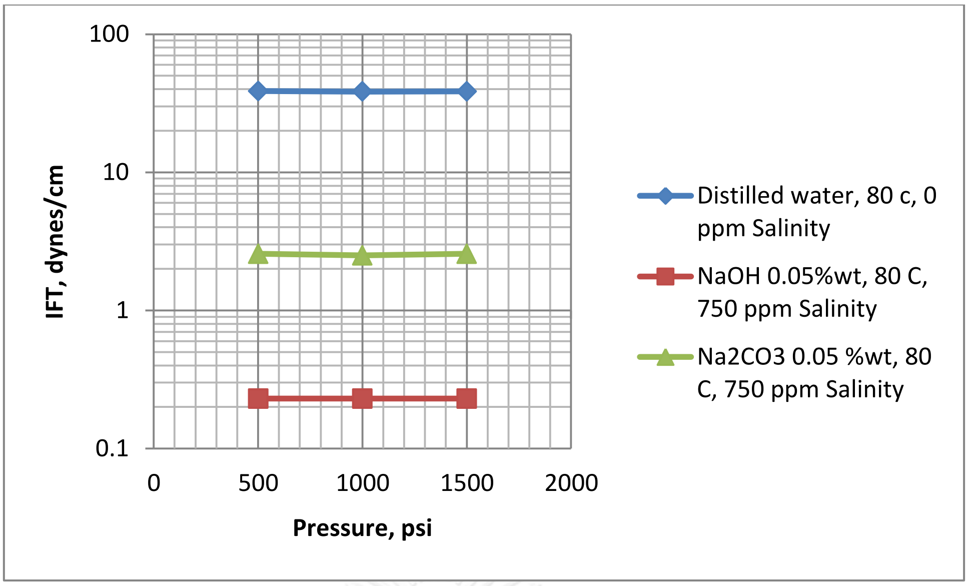


Figure 5.1 Effect of pressure on interfacial tension reduction

Table 5.1 Effect of pressure on interfacial tension reduction (dynes/cm)

Distilled Water	Pressure, psi	500	1000	1500
	IFT, dynes/cm	38.43	38.67	38.5
NaOH 0.05 %wt and 750 ppm	Pressure, psi	500	1000	1500
	IFT, dynes/cm	0.23	0.23	0.23
Na_2CO_3 0.05 %wt and 750 ppm	Pressure, psi	500	1000	1500
	IFT, dynes/cm	2.57	2.50	2.57

5.2 The effect of type of alkaline solution on the interfacial tension

The experiment is performed by using two different types of alkaline solutions which are sodium hydroxide (NaOH) and sodium carbonate (Na_2CO_3) and the results are compared to distilled water.

The sodium hydroxide has higher effect than sodium carbonate. At the same value of alkaline concentration, the interfacial tension tested with sodium hydroxide is lower that from sodium carbonate because sodium hydroxide is stronger base. Sodium hydroxide can completely dissociate and react with acid in oil, while sodium carbonate can partially dissociate in aqueous phase.

$$Na_2CO_3 \rightarrow 2Na^+ + CO_3^{2+}$$

$$CO_3^{2+} + H_2O \rightarrow HCO_3^- + OH^-$$

The comparison of three solutions which are sodium hydroxide solution, sodium carbonate solution and distilled water at 0.075 %wt and 750 ppm salinity as demonstrated in Figure 5.2 and Table 5.2-5.4. The water solution has the highest interfacial tension. The percent different of the interfacial tension between distilled water and sodium hydroxide solution is about 99%. The percent different of the interfacial tension between distilled water and sodium carbonate is about 89-92%.

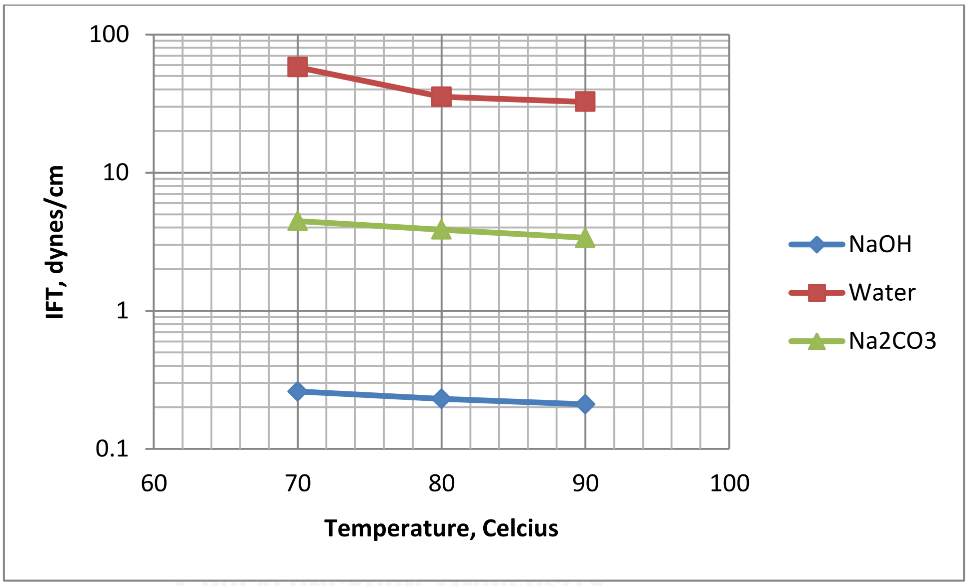


Figure 5.2 The effect of different types of alkaline (NaOH 0.05 %wt+750 ppm and Na_2CO_3 + 750 ppm)

Table 5.2 The interfacial tension of distilled water (dynes/cm)

	Salnity, ppm	70 °C	80 °C	90 °C
Water without Alkaline	0	58.65	38.67	32.50
	500	57.97	36.57	31.38
	750	58.00	35.37	32.53
	1000	57.87	35.30	32.40

Table 5.3 The interfacial tension of NaOH solution (dynes/cm)

	Salinity, ppm	70 °C	80 °C	90 °C
NaOH 0.025%wt	0	16.30	15.46	13.65
	500	15.70	11.36	9.14
	750	14.33	10.39	8.19
	1000	13.42	8.85	6.26
	Salinity, ppm	70 °C	80 °C	90 °C
NaOH 0.05 %wt	0	0.67	0.40	0.36
	500	0.34	0.33	0.32
	750	0.26	0.23	0.21
	1000	0.24	0.23	0.21
	Salinity, ppm	70 °C	80 °C	90 °C
NaOH 0.075 %wt	0	0.29	0.28	0.23
	500	0.25	0.24	0.23
	750	0.22	0.20	0.20
	1000	0.22	0.18	0.18

Table 5.4 The interfacial tension of Na_2CO_3 solution (dynes/cm)

	Salinity, ppm	70 °C	80 °C	90 °C
Na_2CO_3 0.025 %wt	0	28.94	23.41	21.26
	500	26.66	22.16	20.03
	750	25.73	21.71	19.08
	1000	24.19	18.24	16.1
	Salinity, ppm	70 °C	80 °C	90 °C
Na_2CO_3 0.05 %wt	0	8.42	6.37	5.52
	500	7.61	5.47	4.87
	750	4.46	3.87	3.37
	1000	2.54	2.50	2.01
	Salinity, ppm	70 °C	80 °C	90 °C
Na_2CO_3 0.075 %wt	0	3.82	3.22	2.91
	500	3.12	1.8	0.96
	750	2.81	1.52	0.80
	1000	1.50	1.18	0.60

The creation of in situ surfactant is occurred from the reaction between acid compounds in oil and alkaline solution. This reaction is known as saponification reaction. The in situ-surfactant would reduce the interfacial tension between oil and aqueous by using the polar (hydrophilic part) and non-polar (hydrophobic part) head of in-situ surfactant connecting between two phases.

The oil phase is dissolved by non-polar part or hydrophobic, while the aqueous is dissolved by polar part or hydrophobic part. From the graph, the interfacial tension would be high when the alkaline concentration is low because the creation of in-situ surfactant is low. When the alkaline concentration is higher, the interfacial tension tends to be lower because the creation of in-situ surfactant is high.

5.3 The effect of alkaline concentration on the interfacial tension

The studies of alkaline concentrations on the interfacial tension in this experiment are prepared from 2 alkaline solutions which are sodium hydroxide and sodium carbonate and the concentration of this study is varied from 0 to 0.075 %wt for all types of alkaline solution as shown in Figure 5.3 and 5.4 and Table 5.3 and 5.4.

In all cases, the interfacial tension tends to reduce, while the alkaline concentration is increasing. The reaction between alkaline substance and acid compound in oil has higher rate when the alkaline concentration is higher. The in-situ surfactant can be easily form and move to the interface between oil and aqueous phase.

At low alkaline concentration from 0 to 0.05 %wt (pH in range of 11.75 to 12 for sodium hydroxide solution and 10.75 to 11 for sodium carbonate from Figure 3.1), the interfacial tension greatly reduces. When the alkaline concentration is more than 0.05 %wt (pH above 12 for sodium hydroxide solution and 11 for sodium carbonate from Figure 3.1) , the interfacial tension becomes relatively stable because the in-situ surfactant is more difficult to occupy in the interface between oil and aqueous phase. The interfacial tension has small reduction with the alkaline concentration.

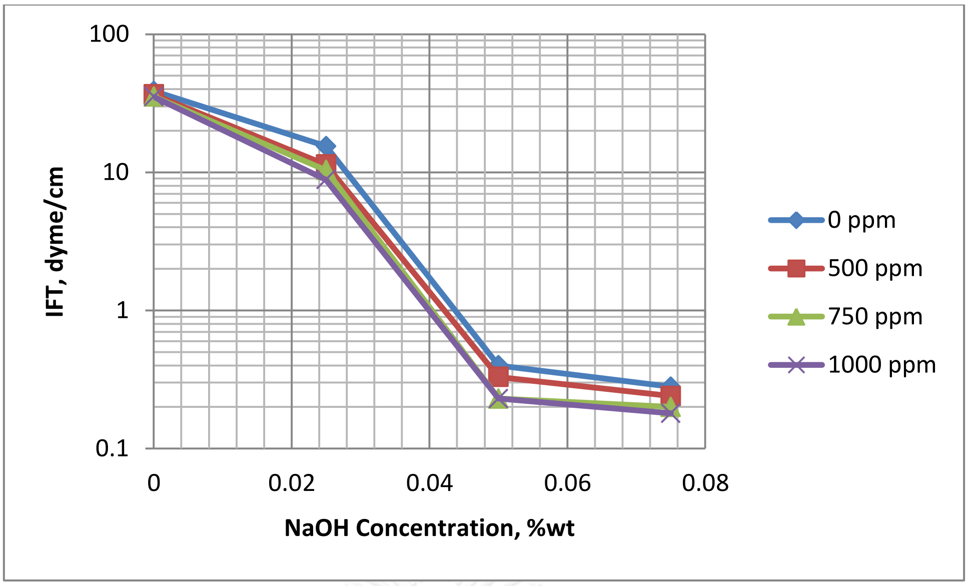


Figure 5.3 Effect of alkaline concentration of NaOH solution at 80 ^{o}C

The interfacial tension of strong base alkaline can be reduced grater when the solution has more salinity. Figure 5.3 demonstrated that the solution which has lower salinity has smaller step in order to reduce the interfacial tension from concentration from 0 to 0.05 %wt (pH in range of 11.75 to 12 for sodium hydroxide solution from Figure 3.1). The interfacial tension decreases from 37 down to 0.2 dynes/cm. When the concentration of alkaline reaches 0.05 to 0.075 %wt (pH in range of 12 to 12.25 for sodium hydroxide solution from Figure 3.1); the interfacial tension tends to be stable at around 0.2 dynes/cm.

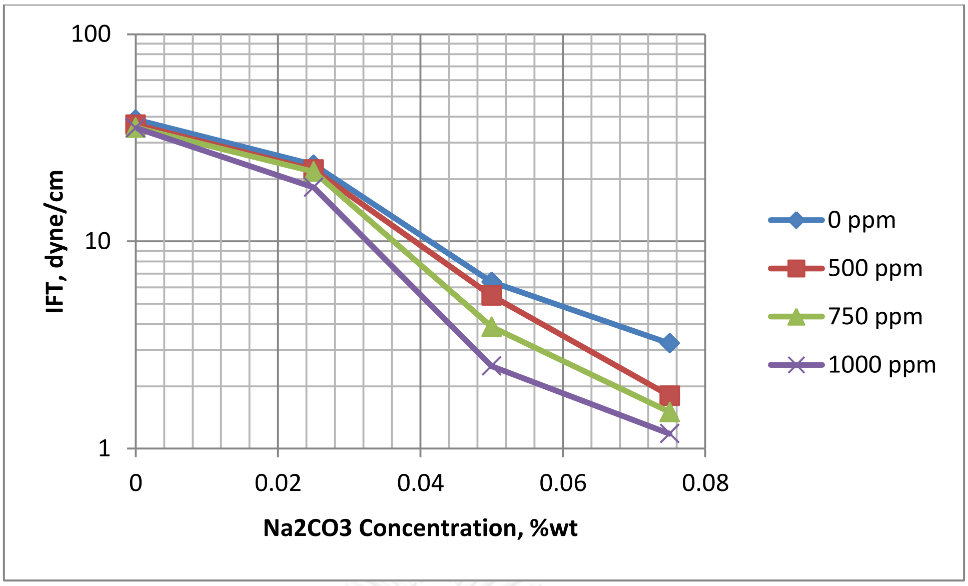


Figure 5.4 Efect of alkaine concentration of Na_2CO_3 solution at 80 ^oC

The results of the effect of alkaline concentration comparing to distilled water is presented in Figure 5.4 and Table 5.3 and 5.4. From the figure, it is clear that the interfacial tension reduction of weak base has less performance. Weak base cannot dissociate itself completely; therefore the generation of in-situ surfactant is lower than in the strong base alkaline solution.

5.4 The effect of temperature on the interfacial tension

The studied temperature in this experiment is on the range from 70 to 90 ^oC which is the conditions corresponding to the Fang oilfield condition. The experimental results are shown in Figure 5.5, 5.6 and 5.7.

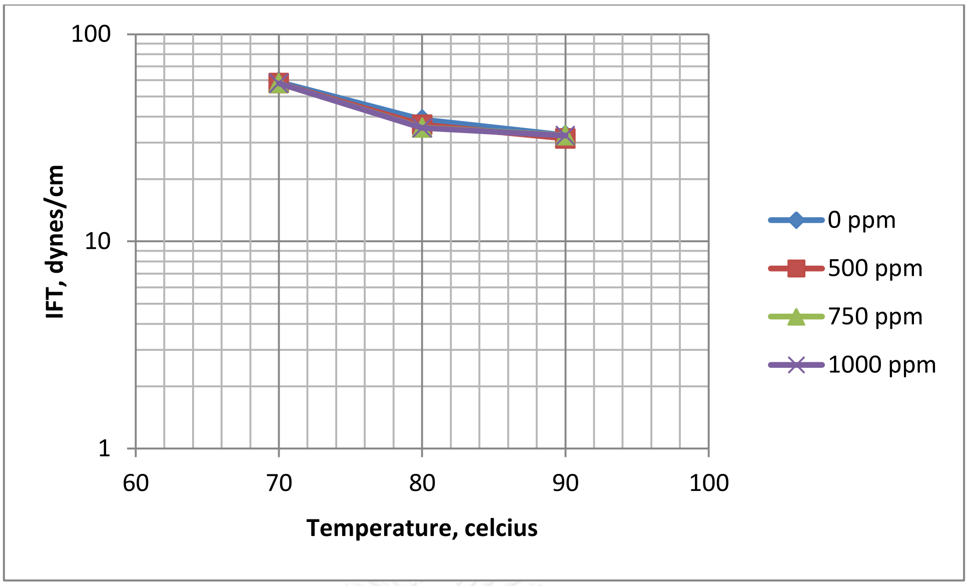


Figure 5.5 Effect of temperature of solution without alkaline substance

At zero alkaline concentration as shown in Figure 5.5, when the temperature increases, the interfacial tension decreases because of some in-situ surfactant generated by the sodium hydrogen carbonate and acid compound in oil sample. Sodium hydrogen carbonate can dissolve in water and act as mildly base in aqueous solution. One more reason is surface active agent inside oil gain more kinetic energy when the temperature increase and then react in order to generate in-situ surfactant. Therefore, the interfacial tension tends to reduce. The percent different in the case of 750 ppm at 70^o and 80^o is 39 percent while the percent different in the case of 750 ppm at 80^o and 90^o is 8 percent.

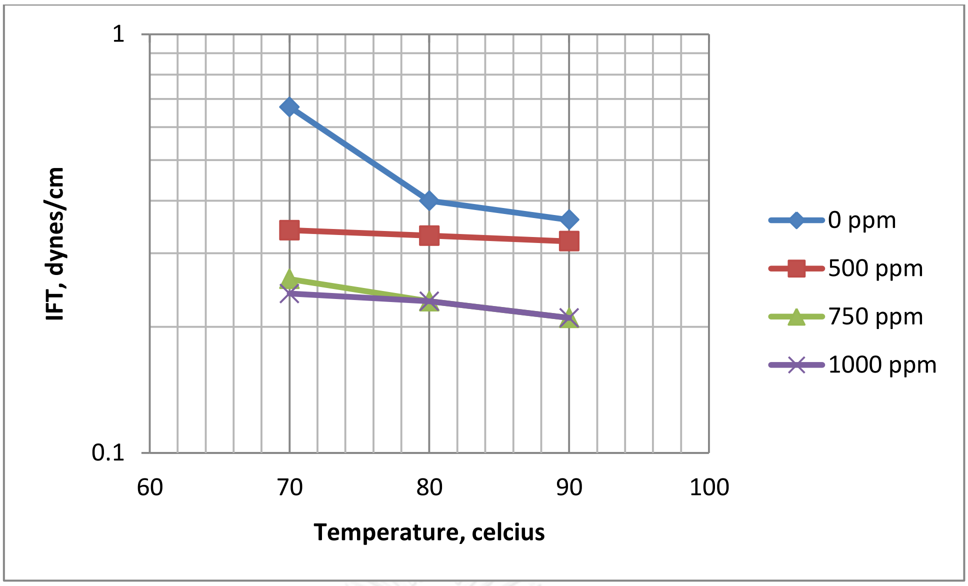


Figure 5.6 Effect of temperature of NaOH solution

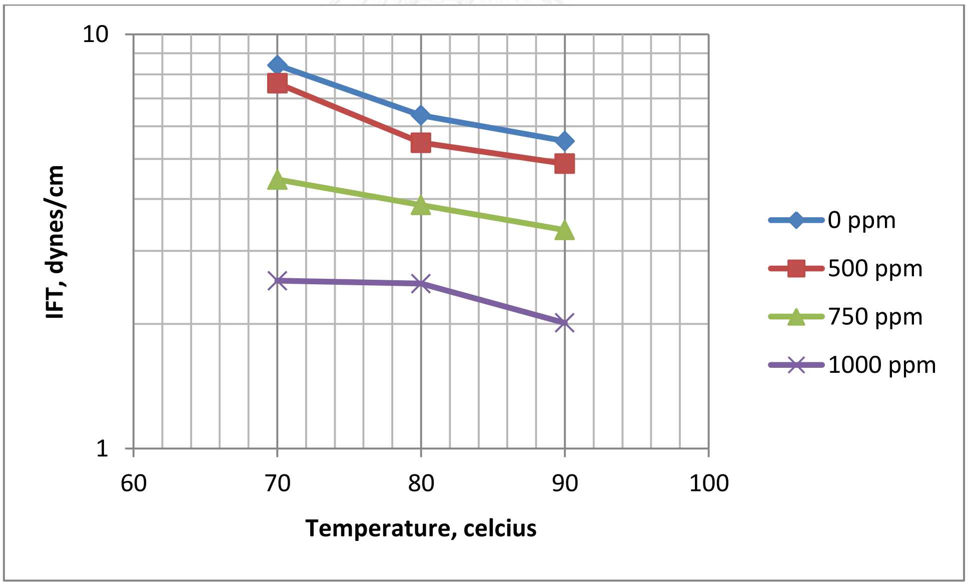


Figure 5.7 Effect of temperature of Na_2CO_3 solution

From Figure 5.6, when the temperature increases with sodium hydroxide solution, the interfacial tension reduces. This result gets along well with the result from Taha and Abdul-Jalil (2009). The reduction in the interfacial tension is caused by the weakening of intermolecular force between oil-brine interfaces and the kinetic energy at higher temperature that help the in-situ surfactant to occupy in the monolayer between oil and aqueous phase. The percent different is high because of lower intermolecular force when the temperature is increasing from 70 to 80 ^{o}C. At higher temperature, the percent different would be lower because there is less and less space for in-situ surfactant to occupy in the monolayer between oil and aqueous phase. The percent different in the case of 750 ppm at 70^{o} and 80^{o} is 11 percent while the percent different in the case of 750 ppm at 80^{o} and 90^{o} is 9 percent. The effect of temperature to strong base is in the same way as the weak base alkaline solution. The result is shown in Figure 5.7. Increment of temperature may help the weak base alkaline to dissociate more than at low temperature and help the reaction generated in situ surfactant to be better. The percent different in the case of 750 ppm at 70^{o} and 80^{o} is 13 percent while the percent different in the case of 750 ppm at 80^{o} and 90^{o} is 13 percent.

The temperature has an opposite effects to the interfacial tension. When the temperature increases, the reaction between acid compound and alkaline solution tend to be increase, thus making more in-situ surfactant. The energy from increment of temperature would increase the kinetic energy and move the acid compound and alkaline substance to have more saponification reaction at the oil and aqueous interface.

5.5 The effect of salinity on the interfacial tension

The brine solution for this study has different salinities. Sodium chloride and Sodium bicarbonate are used to prepared brine solution. The ratio between sodium chloride and sodium bicarbonate is controlled to be the same as the composition of produced water because the result can be apply in the real data from Fang oilfield. The studied range of salinity is on 0 to 1000 ppm.

Salinity has a relationship to the interfacial tension. The typical ions that found in the aqueous phase are sodium and bicarbonate. The test report that has been shown in Chapter 3 is one of the evidences that can confirm the majority of ions are sodium and bicarbonate. These ions tend to balance ion between oil and aqueous phase and push in situ surfactant to the interface between oil and aqueous phase. The in-situ surfactant molecule has two parts which are hydrophobic part and hydrophilic part.

The hydrophobic parts dissolve in oil phase, while the hydrophilic parts dissolve in aqueous phase. When there is more in-situ surfactant at the interface between oil and aqueous phase, the interfacial tension tends to be reduced.

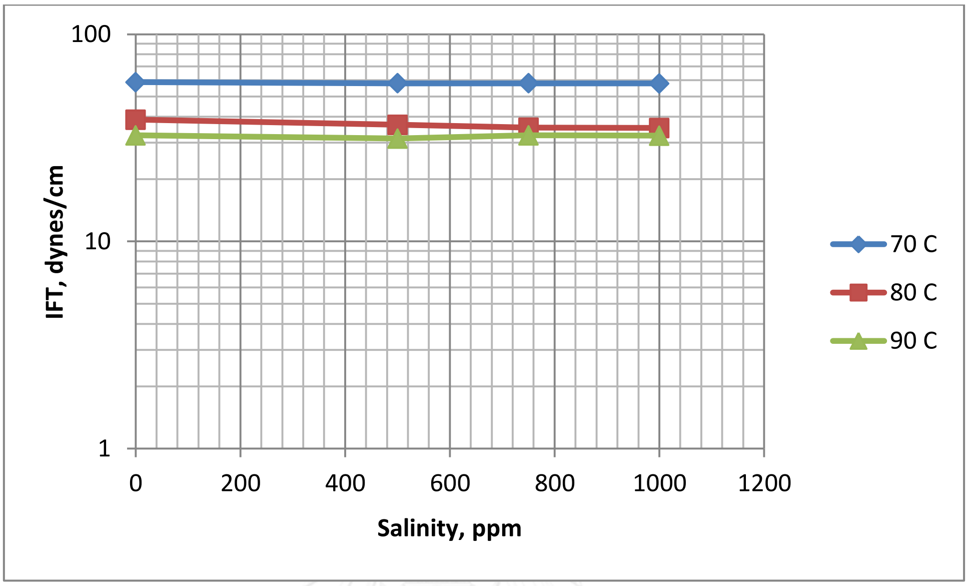


Figure 5.8 Effect of salinity of solution without alkaline substance

From Figure 5.8, at zero alkaline concentration, the interfacial tension is comparatively constant with small fluctuation because there is a small amount of in-situ surfactant generated. The interfacial tension can be fluctuated because the sodium hydrogen carbonate can act as mildly base and react with acid in oil to generate in-situ surfactant. Therefore, incremental of salinity has less significant on driving in-situ surfactant to the interface between oil and aqueous phase due to less amount of in situ surfactant.

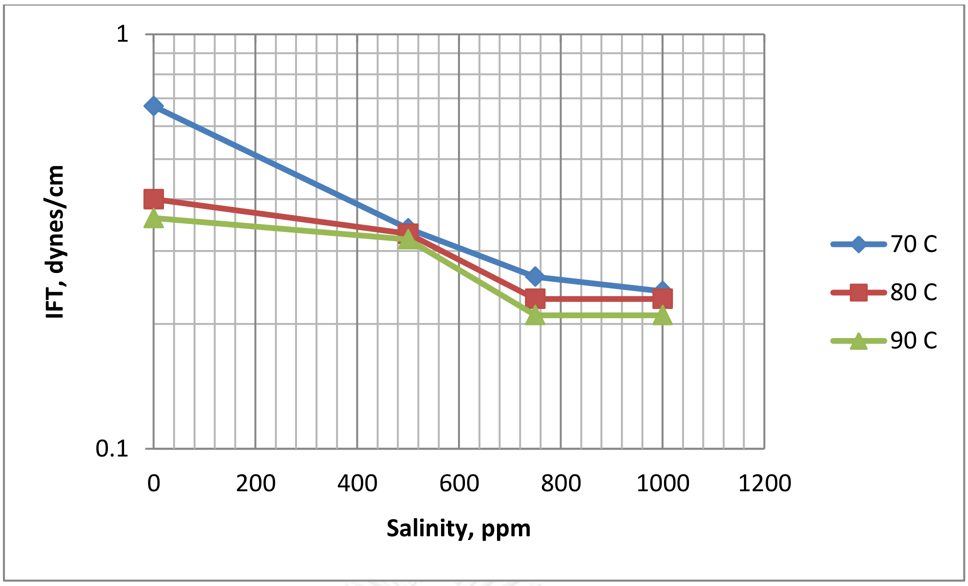


Figure 5.9 Effect of salinity of NaOH solution

The effect of salinity on each alkaline concentration is shown in Figure 5.9. When there is more salinity in the aqueous phase, the interfacial tension becomes lower. Although the low concentration of alkaline can generate low quantity of in-situ surfactant, high salinity can help to drive less amount of in-situ surfactant to the interface between oil and aqueous phase. When the salinity is greater than 800 ppm, the in-situ surfactant cannot be packed further in the monolayer. Therefore, there is no more space for more in-situ surfactant to occupy in the monolayer.

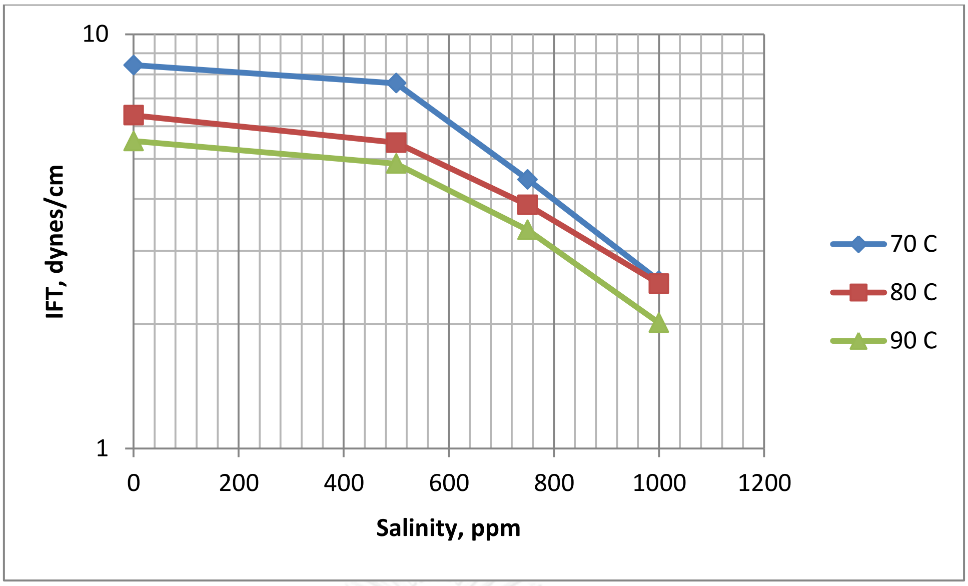


Figure 5.10 Effect of salinity of Na_2CO_3 solution

The effect of salinity to strong base and weak base alkaline are in the same manner but the effect of salinity in strong base alkaline has more effect than in weak base alkaline as shown in Figure 5.10. At the same salinity, monolayer generated by weak base can still be inserted in-situ surfactant while the monolayer generated by strong base cannot be further inserted the in-situ surfactant in monolayer packing because there is some space left in the packing of monolayer of weak base greater than in the monolayer of strong base. The strong base alkaline can completely dissociate itself and react with the acid compound in oil, while the weak base alkaline partially dissociate itself and react with the acid compound in oil. Therefore, the amount of in-situ surfactant generated from strong base alkaline can be push to interface greater than the in-situ surfactant from weak base alkaline.

5.6 The effect of divalent ion on the interfacial tension

One of the limitations that could affect to the in situ surfactant generated in the reservoir is the divalent ion in the ionic environments of oil reservoirs. Their sensitivity to the presence of divalent ions is studied in this section. The interactions were investigated by implementing experiments that has different salinity in alkaline solution. The salts that have been used in this experiment are sodium chloride, calcium chloride and magnesium chloride. Calcium and magnesium are represented as the divalent ion in this experiment. The amount of magnesium and calcium is the same ratio as the produced water from Fang oilfield. The divalent ion would react with in situ surfactant and precipitate the insoluble soap. When the insoluble soap is generated, the in situ surfactant concentration reduces. Therefore there is less amount of in-situ surfactant at the interface between oil and aqueous phase. The interfacial tension tends to increase.

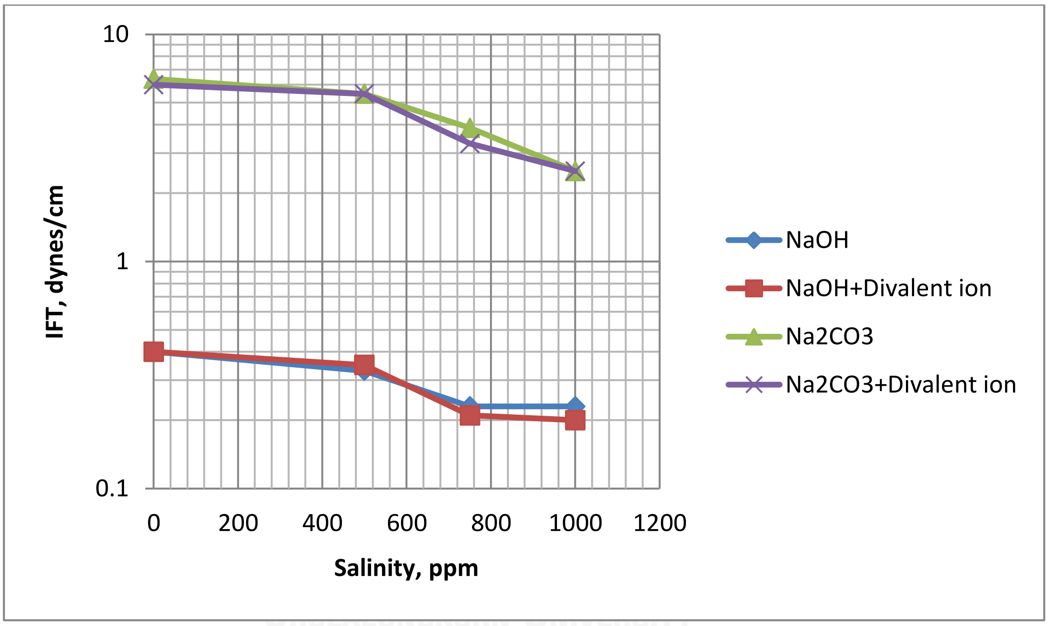


Figure 5.11 Effect of divalent ion on IFT

From Figure 5.11, the plots between alkaline solution without divalent ion and with divalent ion are nearly on the same value. However the divalent ion has the negative effect to the interfacial tension, the amount of divalent ion in alkaline solutions have a little amount which is less than one percent of the total salinity. Furthermore, the fluid contact between oil and alkaline solution is less during the measurement; therefore the divalent ion cannot be much affected to the in-situ surfactant. Therefore, the divalent ion would not have much effect on the interfacial tension in this case.

CHAPTER 6

CONCLUSIONS AND RECOMMENDATION

This chapter summarizes the experimental results from the previous chapters. The effects of all parameters on interfacial tension are concluded. In addition, some recommendation of future study is mentioned.

6.1 Conclusions

The interfacial tension measurement in this experiment uses the rising drop method. The benefit of this experiment is to indicate the suitable range of the conditions that can help to reduce the interfacial tension.

The results from this study show that the alkaline solution can reduce the interfacial tension down to 0.2 dynes/cm for sodium hydroxide solution and 0.6 dynes/cm for sodium carbonate solution; however, there are various parameters that can affect the value of interfacial tension during alkaline flooding. The conclusions of the effects from each design parameter on alkaline flooding process are noted as followed.

1. The pressure covers the range from 500 psi to 1500 psi. Pressure has less effect on the interfacial tension reduction in alkaline flooding. The interfacial tension is comparatively constant while the pressure changes. Therefore, we can assume to neglect the effect of pressure for alkaline flooding in Fang oilfield.
2. Although the two alkaline solutions have the same effect to reduce the interfacial tension, sodium hydroxide has higher performance than sodium carbonate. At range of 0.025 to 0.050 %wt alkaline concentration, sodium hydroxide can reduce the interfacial tension down to 0.23 dynes/cm while sodium carbonate can reduce the interfacial tension down to 4 dynes/cm.
3. Alkaline concentration has effect on the interfacial tension reduction. it can be reduced by increasing alkaline concentration. Sodium hydroxide at 0.05 %wt can greatly reduce interfacial

tension from 43 dynes/cm (distilled water) down to 0.3 dynes/cm. For higher concentration, sodium hydroxide cannot reduce much the interfacial tension. Sodium hydroxide at 0.075 %wt just reduces the interfacial tension down to only 0.2 dynes/cm which is not much different from the interfacial tension from sodium hydroxide at 0.05 %wt. In the same way, sodium carbonate at 0.05 %wt can greatly reduce interfacial tension down to around 5 dynes/cm. At higher concentration of sodium carbonate can reduce interfacial tension just only down to 2 dynes/cm.

4. Salinity can affect the interfacial tension only when there is alkaline in the solution. The solution without alkaline is not affect to the interfacial tension while the salinity has been changed. The more salinity is, the greater interfacial tension can be reduced.
5. When the temperature changes, the interfacial tension also change. Temperature has an opposite effect on the interfacial tension. Temperature can reduce the interfacial tension while it is increasing. Although temperature can greatly decrease the interfacial tension in distilled water, temperature can just reduce some of the interfacial tension in alkaline solution. The interfacial tension of oil and alkaline solution is already low by in situ surfactant; therefore temperature would have less effect.
6. In this study, divalent ion has small effect on the interfacial tension value.

7. The condition that can minimize the interfacial tension to lowest value are as followed:

- Pressure in range of 500 to 1500 psi

- Sodium hydroxide can play a better role than sodium bicarbonate on the interfacial tension reduction.

- The compatible concentration of sodium hydroxide and sodium bicarbonate are 0.05 %wt and 0.075 %wt respectively.

- The temperature is 90 degree Celsius.

- The salinity is 1000 ppm.

6.2 Recommendation

The following issues are recommended for future study.

1. This pendent drop method can measure the interfacial tension of other types of chemical flooding in order to study the effect on the interfacial tension reduction.
2. This interfacial tension value can be used to apply alkaline flooding in Fang oilfield in order to reduce the interfacial tension.
3. This interfacial tension result can use for further study such as core flooding and simulation in the future.
4. In order to get more precise value of the interfacial tension, we can repeat the measurement for some experiment that has error in the interfacial tension value.

REFERENCES

Abadli, F. (2012). Simulation Study of Enhanced Oil Reovery by ASP (Alkaline, Surfatant and Polymer) Flooding for Norne Field C-segment. . Department of Petroleum Engineering and Aplied Geophysics, Norwegian University of Science and Technology. **Master's Thesis in Reservoir Engineering**.

Buckley, J. and T. Fan (2005). Crude Oil/Brine Interfacial tension. The Society of Core Analysts Symposium. Toronto, Society of Petrophysicists and Well Log Analysts.**:** 175-185.

Cooke, C., et al. (1974). Oil Recovery by Alkaline Waterflooding. SPE-AIME Symposium on Improved Oil Recovery. Tulsa, Okla, American Institute of mining, Metallurgical and Petroleum Engineers lnc.**:** 1365-1374.

Flock, D. L. and J. P. Gibeau (1986). The effect of temperature on the interfacial tension of heavy crude oils using the Pendent Drop apparatus. JCPT Heavy Oil, University of Alberta.

Green, D. W. and G. Willhite (1998). Enhanced OIl Recovery. USA, The Sciety of Petroleum Engineers Inc.

Hassan, M. E., et al. (1953). "Effect of Pressure and Temperature on Oil-Water Interfacial tension for aSeries of Hydrocarbons." JPT: 299-306.

Hjelmeland, O. S. and L. E. Larrondo (1983). Experimental Investigation of the Effects of Temperature, Pressure, and Crude Oil Composition on Interfacial tension Properties. SPE Reservoir Engineering, SPE annual Technical Conference and Exhibition. San Francisco Society of Petroleum Engineers.

Huang, Y. and D. Yu (2002). Mechanisms and pricipals of physicochemical flow. Mechanisms and pricipals of physicochemical flow.

Intertek (2015a). Report No: MTP/9593/2015, Intertek Testing Service (Thailand) Ltd.

Intertek (2015b). Report No: MTP/5654/2015, Intertek Testing Service (Thailand) Ltd.

Labrid, J. (1991). The use of alkaline agents in enhanced oil recovery process. Basic Concepts in Enhanced Oil Recovery Processes**:** 123-155.

Li, H. (2007). "Advanced in Alkaline-Surfactant-Polymer Flooding and Pilot Tests." Science Press.

Sarkar, S. (2012). Evaluation of Alkaline, Surfactant and Polymer Flooding for Enhanced Oil Recovery in the Norne E-segment Based on Applied Reservoir Simulation. . Department of Petroleum Engineerin and Applied Geophysics., Norwegian University of Science and Technology. **Master's Thesis in Reservoir Engineering**.

Sheng, J. J. (2011). Modern Chemical Enhanced Oil Recovery. Burlington, USA, Elsevier lnc.

Taha, M. and A. Abdul-Jalil (2009). Effect of Brine Salinity on Interfacial tension in Arab Carbonate Reservoir, Saudi Arabia. SPE International Middle East oil and gas show Bahrain, Society of Petroleum Engineers**:** 1-9.

Wang, W. and A. Gupta (1995). Investigation of the Effect of Temperature and Pressure on Wettability Using Modified Pendent Drop Method. SPE Annual Technical Conference and Exhibition Dallas, Society of Petroleum Engineers 117-226.

APPENDIX

APPENDIX A

Solution Preparation

Solution Preparation

In order to prepare brine solution, sodium chloride and sodium bicarbonate has been used create the simulated brine composition corresponding to the produced water composition. Sodium chloride and sodium bicarbonate would dissociate themselves and generate sodium ion, chloride ion, carbonate ion and bicarbonate ion. Then we prepare the brine composition at different salinity from 0 ppm to 1000 ppm. This range of salinity covers the formation brine salinity which can be used in practical situation.

	NaCl (mg/l)	$NaHCO_3$ (mg/l)
0 ppm	0	0
500 ppm	21.74	478.26
750 ppm	32.61	717.39
1000 ppm	43.48	956.52

APPENDIX B

Interfacial tension Measurement

In order to measure IFT of oil brine system interface, the pendent drop instrument is applied by using rising drop method. The oil is injected through the needle to form a tiny oil drop on the top of the needle which is surrounding in the aqueous phase. The experiment procedures were followed:

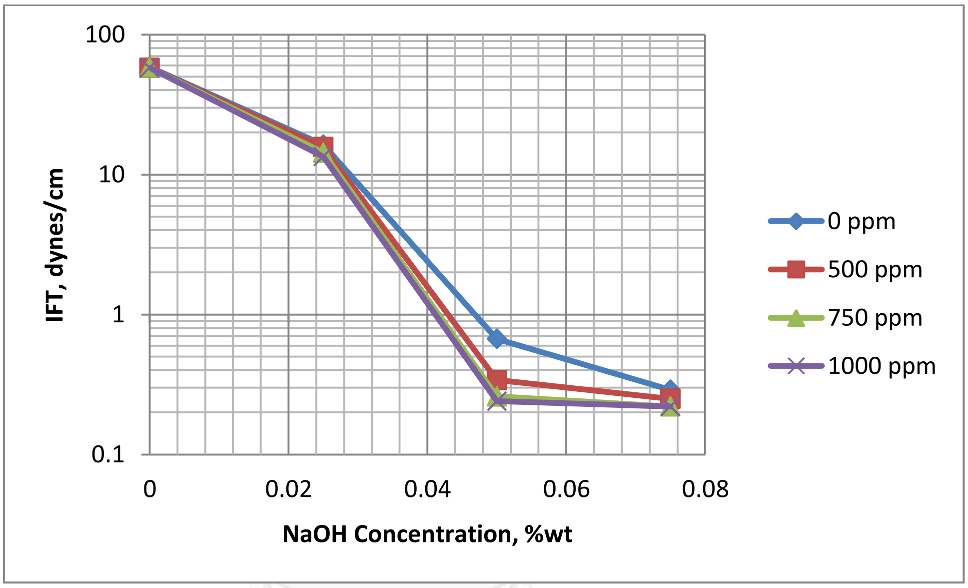
1. Clean all parts of the instrument which contact the fluid (oil or solution) by using acetone to flow and wash the contamination.
2. Set up the instrument to be in the vertical direction.
3. Set up the computer software and video camera to ready for IFT measurement.
4. Select the temperature that uses to vary.
5. Pump the synthetic brine and set up the pressure by using hand pump.
6. Gradually pump the oil drop to the top of the needle inside the cell.
7. If the pressure is not stable, using hand pump to pump more brine into the cell in order to increase pressure or release the brine out in order to reduce pressure.
8. Record the image and IFT data.

APPENDIX C

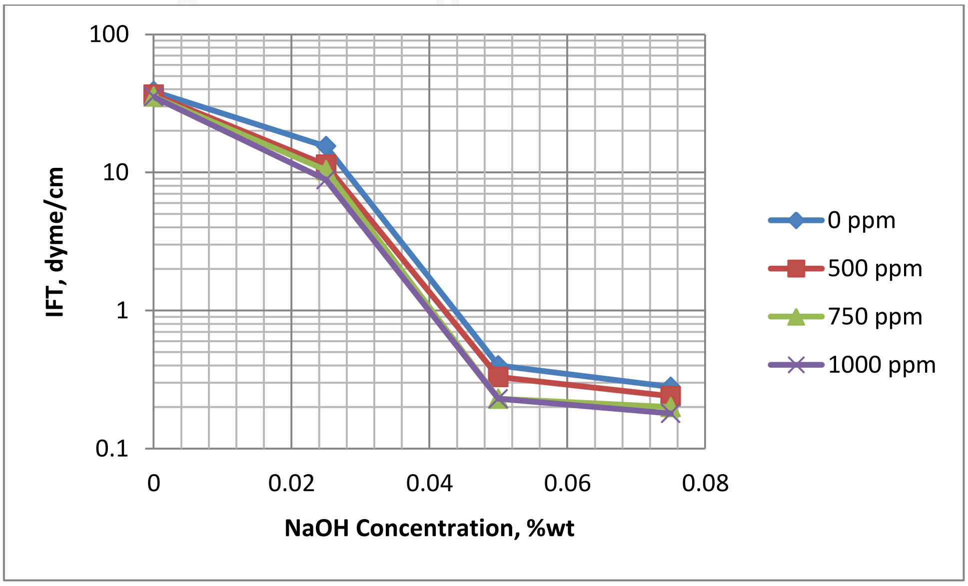
The Effect of Each Parameter

The description of each parameter that effect to the interfacial tension is the same as in the chapter 4.

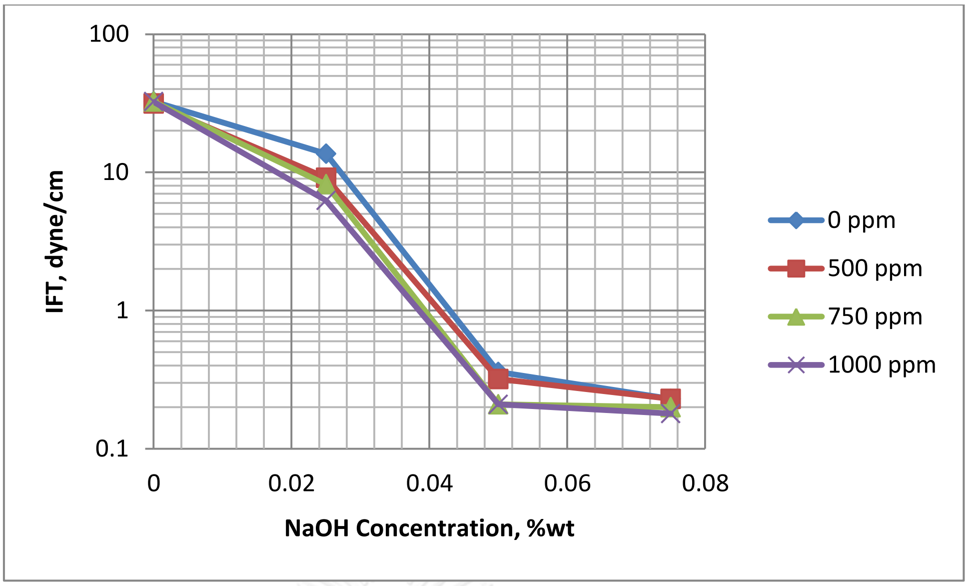
The Effect of Alkaline Concentration on IFT



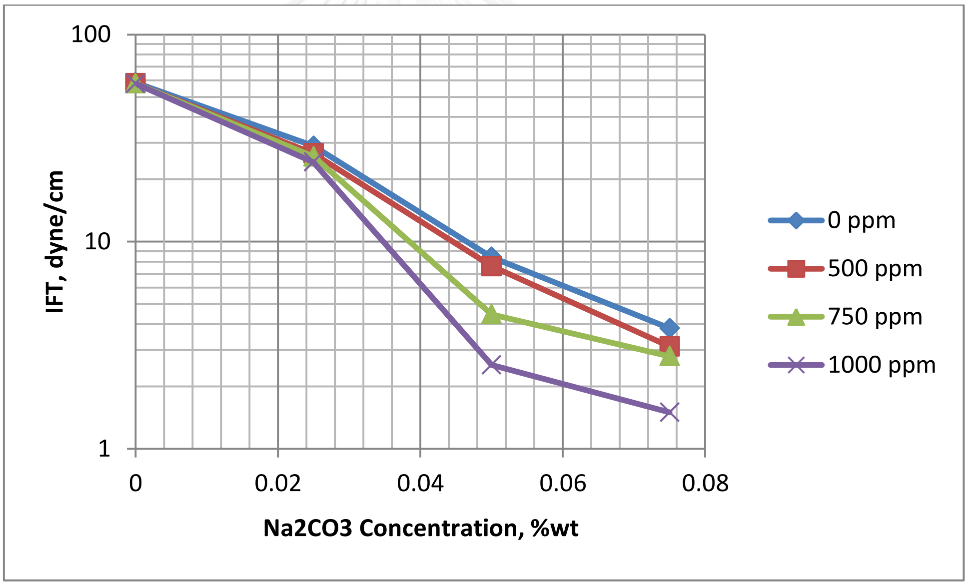
70 ^{o}C NaOH



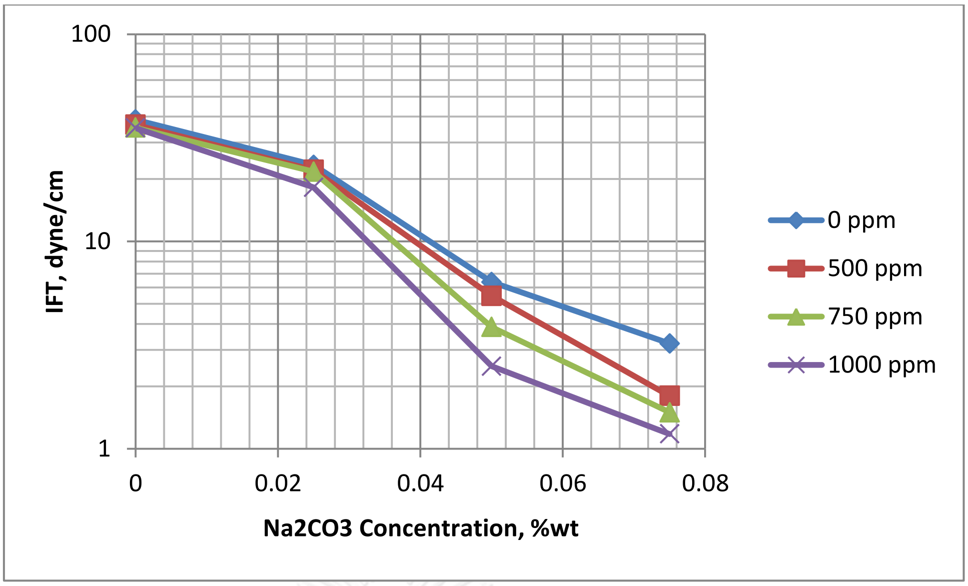
80 ^{o}C NaOH



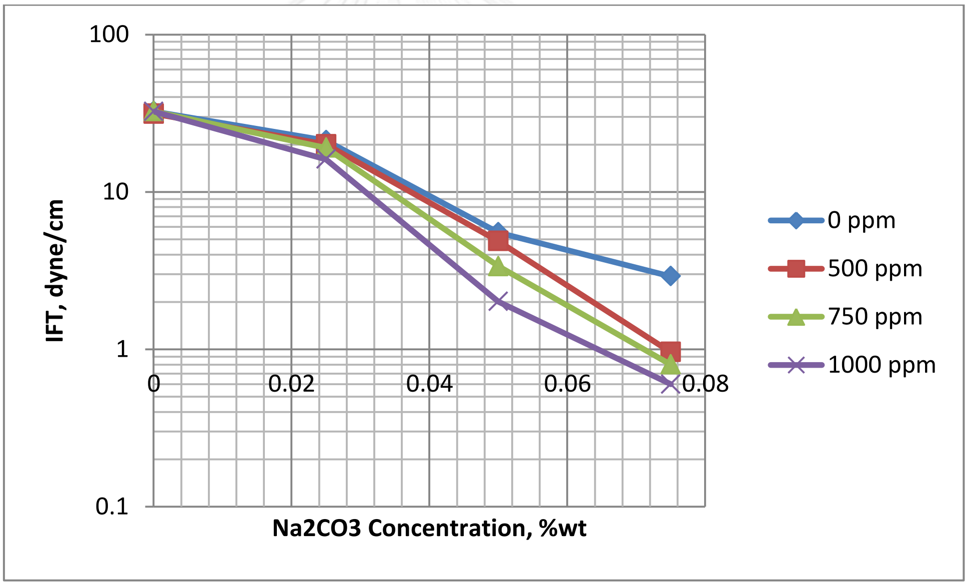
90 ^{o}C NaOH



70 ^{o}C Na_2CO_3

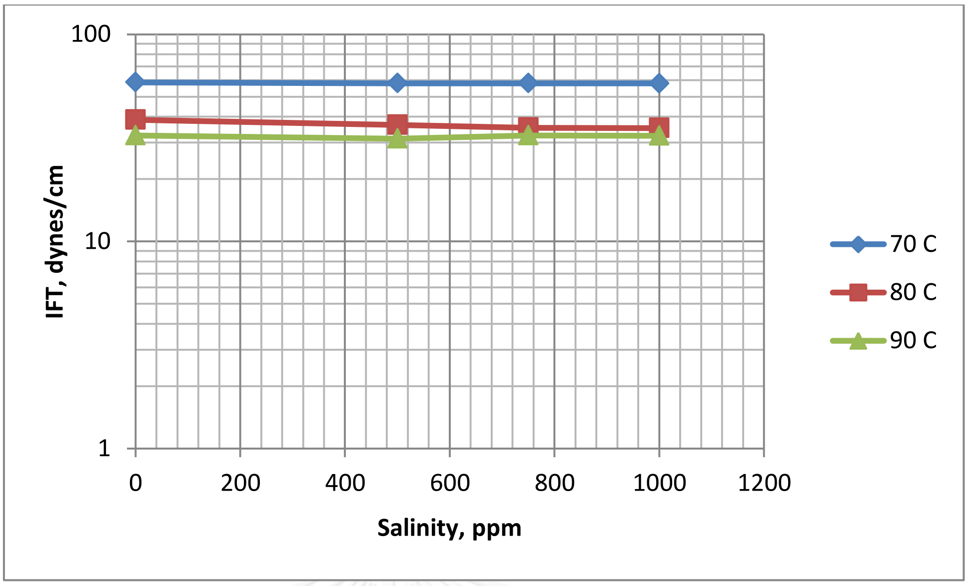


80 ^{o}C Na_2CO_3

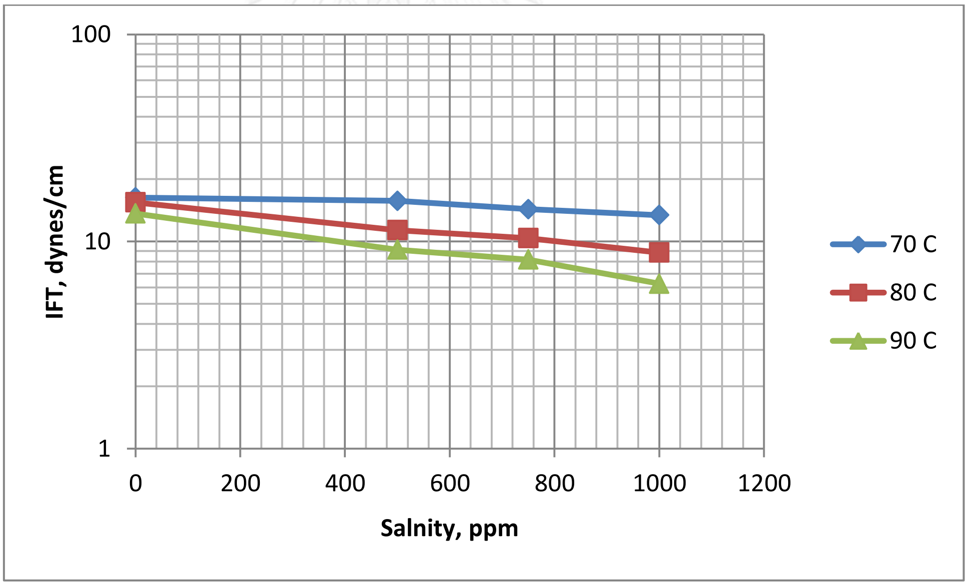


90 ^{o}C Na_2CO_3

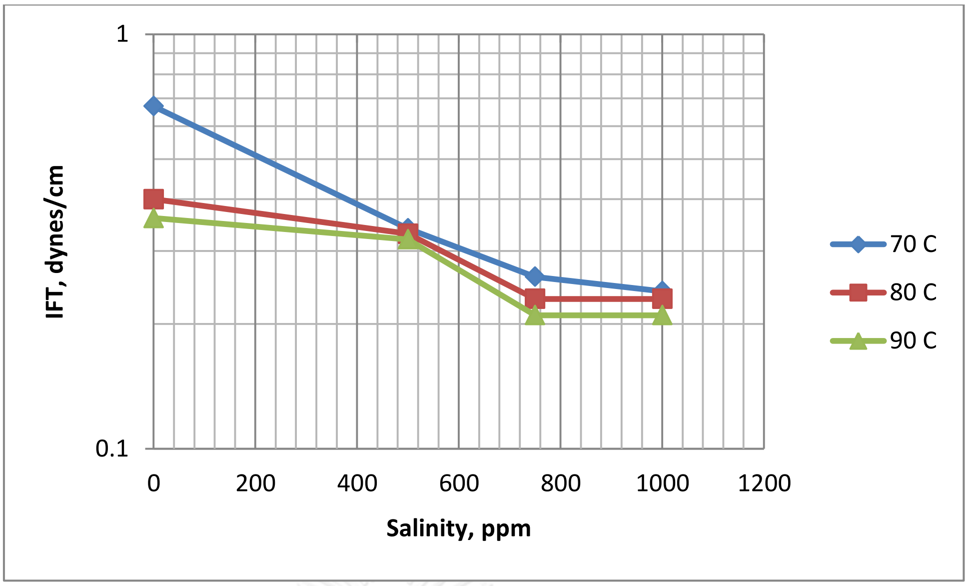
The effect of salinity on the interfacial tension



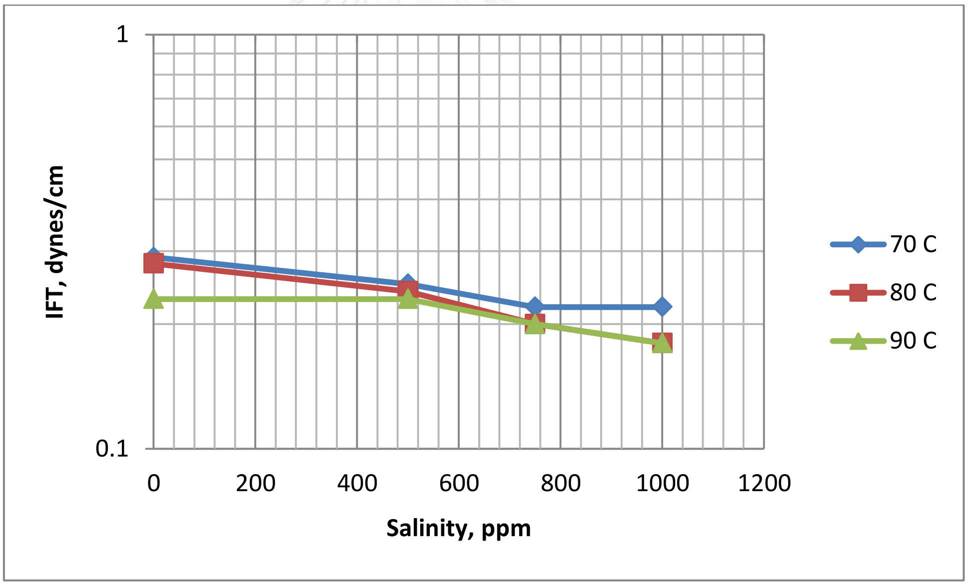
NaOH 0% wt



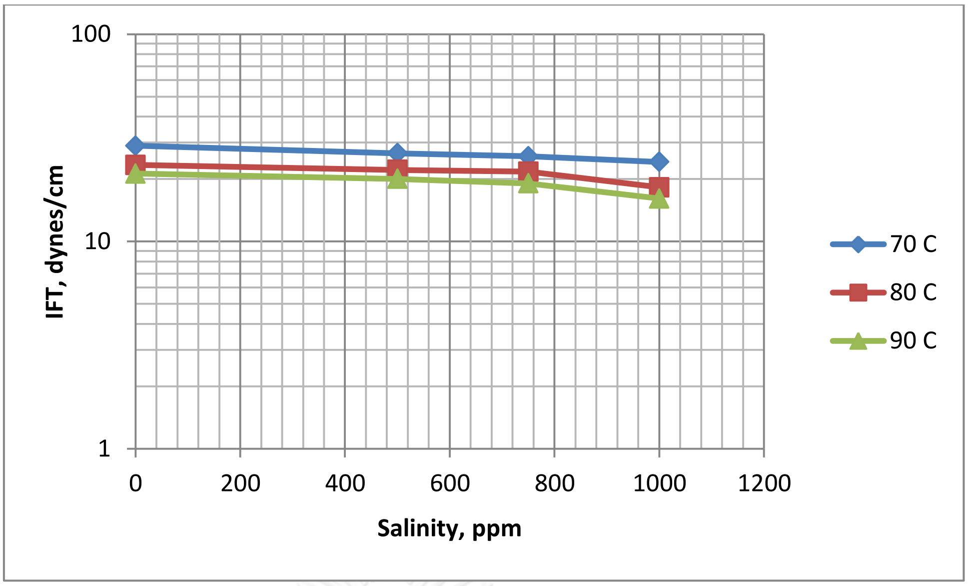
NaOH 0.025 % wt



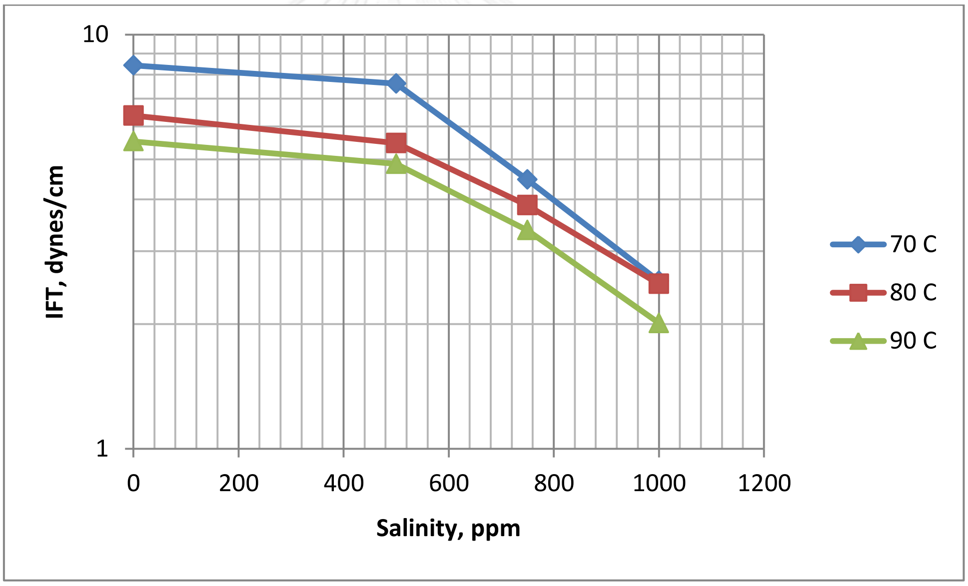
NaOH 0.05 %wt



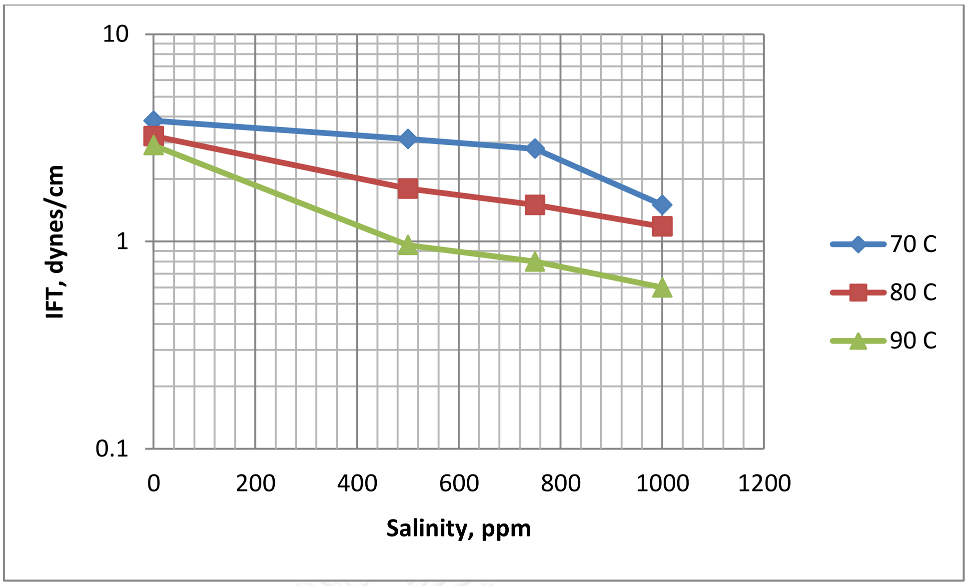
NaOH 0.075 %wt



Na_2CO_3 0.025 %wt

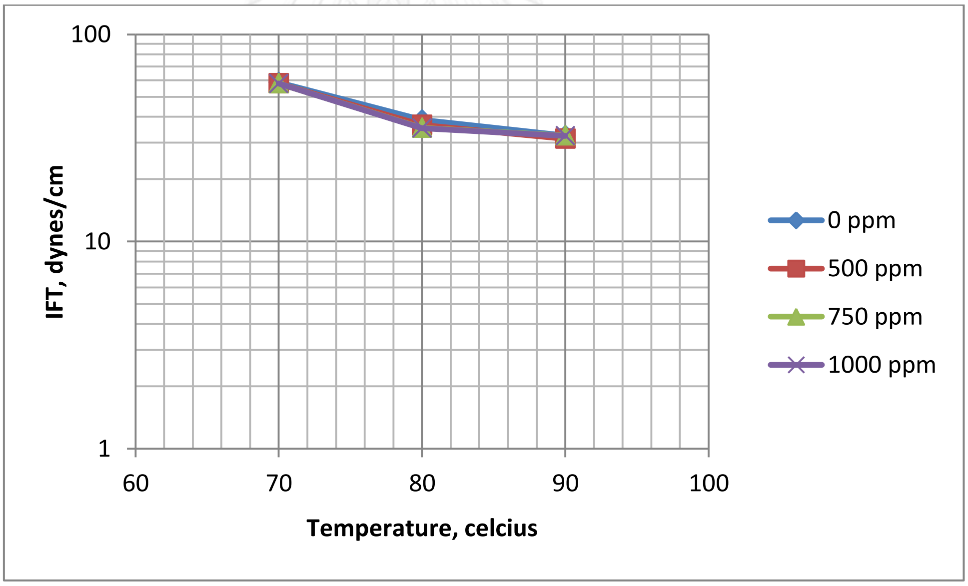


Na_2CO_3 0.05 %wt

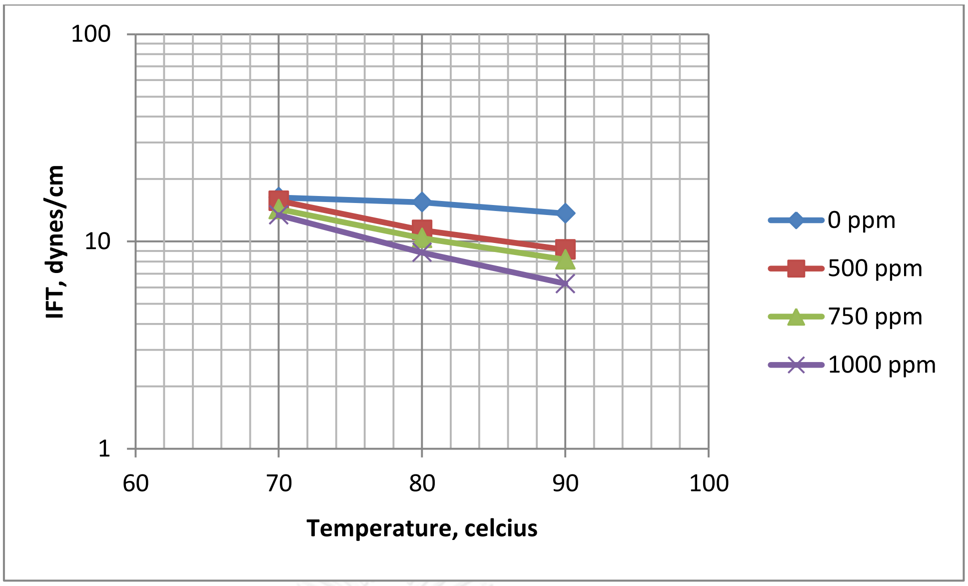


Na_2CO_3 0.075 %wt

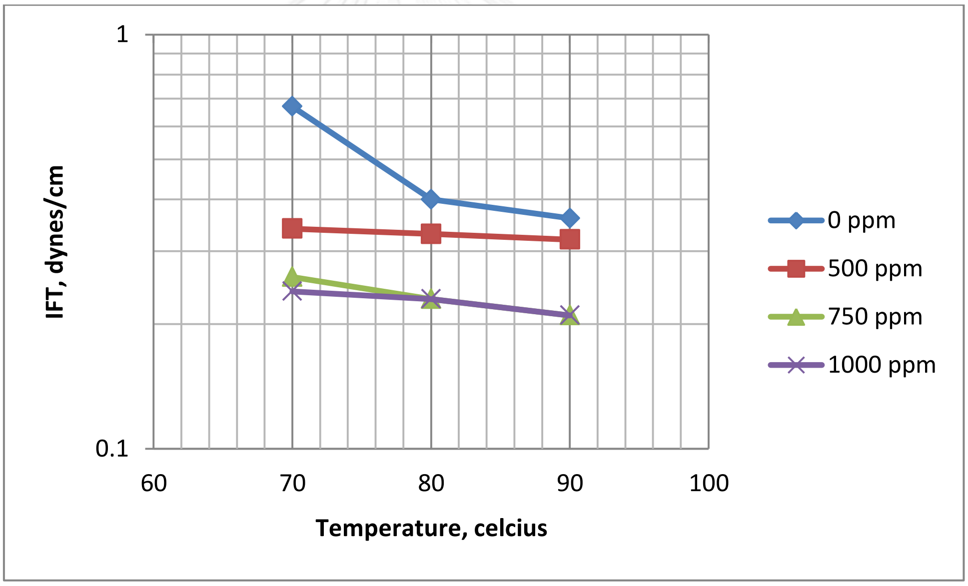
The effect of temperature on the interfacial tension



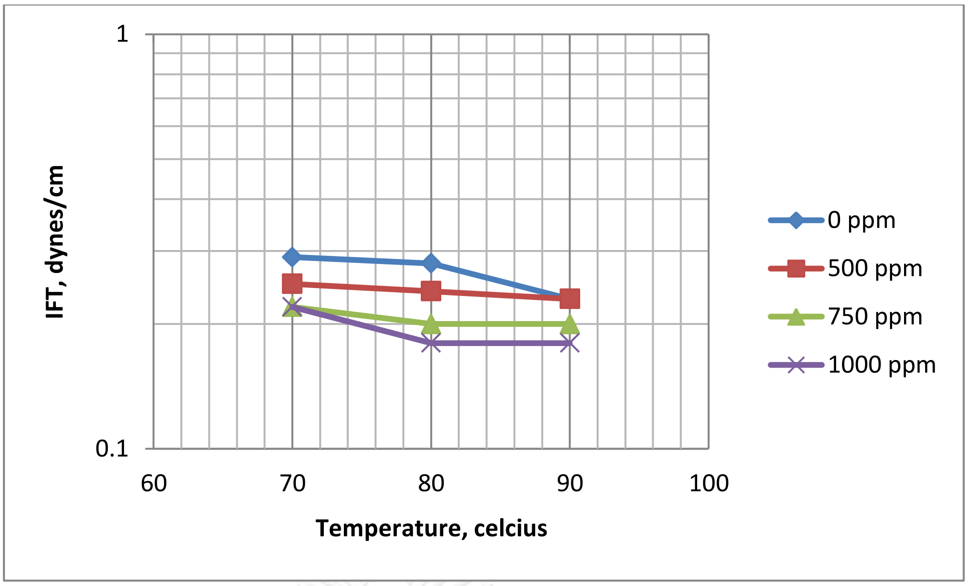
NaOH 0%wt



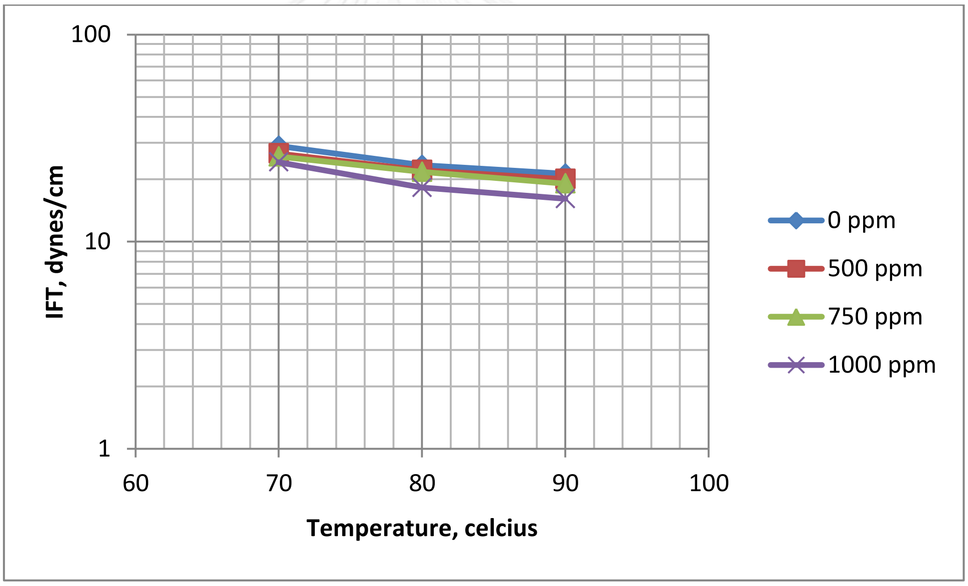
NaOH 0.025 %wt



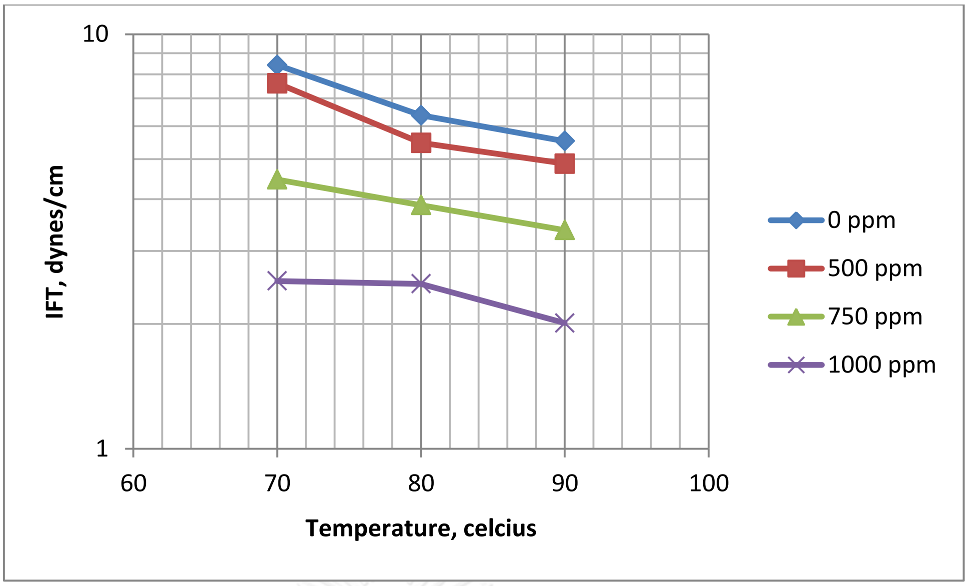
NaOH 0.05 %wt



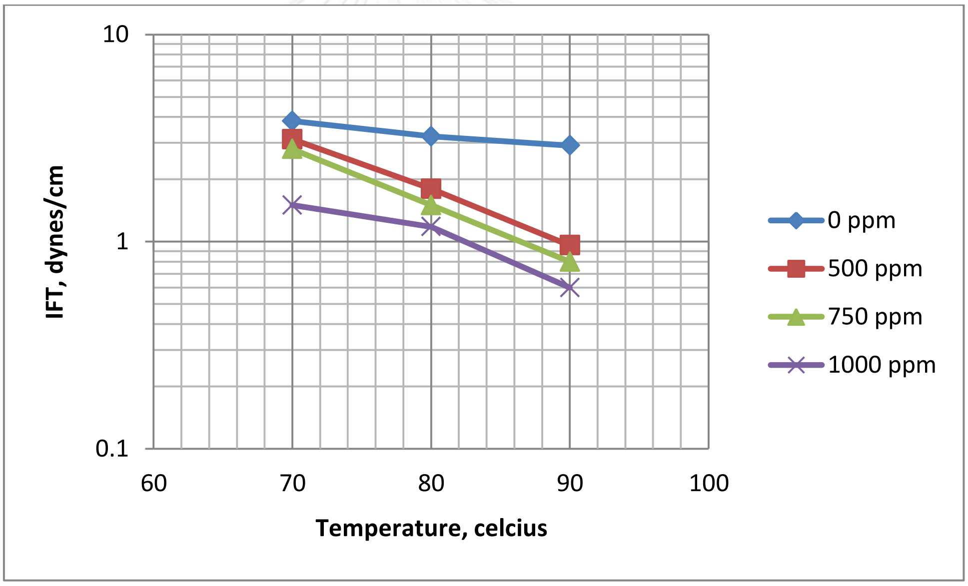
NaOH 0.075 %wt



Na_2CO_3 0.025 %wt

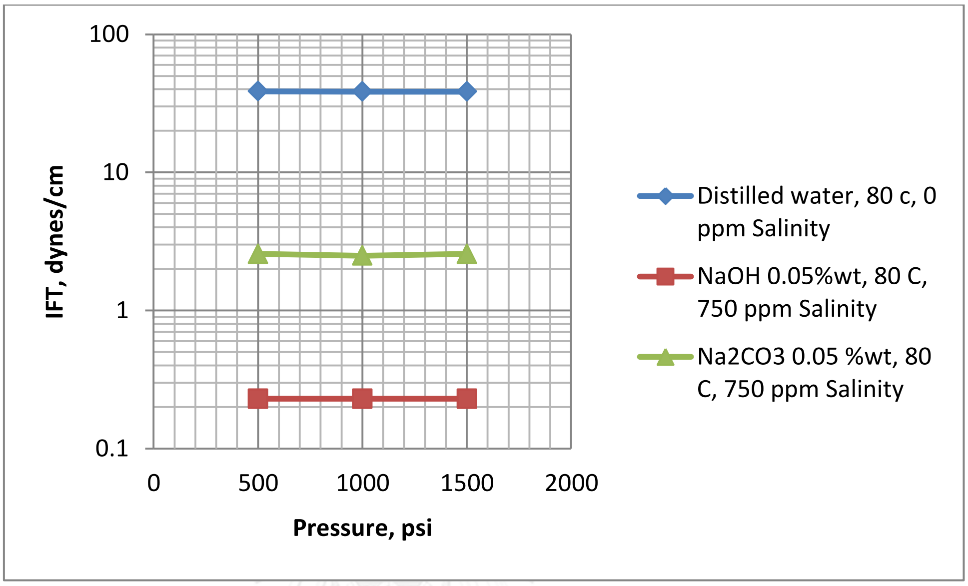


Na_2CO_3 0.05 %wt



Na_2CO_3 0.075 %wt

The effect of pressure on the interfacial tension



Pressure Effect

APPENDIX D

Oil and Solution Density Measurement

The oil density measurement is performed by using the syringe to suck the oil volume at desired temperature at 10 cubic centimeters. The syringe would be weighted by digital weighting apparatus.

Finally the volume would be divided by weight in order to determine the oil density.

For alkaline solution density measurement, the density meter is used to determine the alkaline solution density. The alkaline solution is injected into the density meter and then the density value would be detected automatically in digital number.

APPENDIX E

The Percent Different Table

The percent different table is concluded as below :

The base case solution are distilled water at at 750 ppm 80 ^oC, NaOH at 0.05 %wt 750 ppm 80 ^oC and Na_2CO_3 at 0.05 %wt 750 ppm 80 ^oC.

Percent Different of Temperature Effect on IFT

Temperature	70 ^oC	80 ^oC	90 ^oC
Distilled Water	39.01	0	8.02
NaOH	11.53	0	8.69
Na2CO3	13.22	0	12.91

The effect of temperature on the interfacial tension has more effect in range of temperature 70 to 80 ^oC and then the effect of temperature would be lower in range of temperature 80 to 90 ^oC.

Percent Different of Salinity Effect on IFT

Salinity	0 ppm	500 ppm	750 ppm	1000 ppm
Distilled Water	8.53	3.28	0	5.80
NaOH	42.50	30.30	0	0
Na2CO3	39.24	29.25	0	35.40

The interfacial tension tend to reduce when the salinity increase.

Percent Different of Pressure Effect on IFT

Pressure	500 psi	1000 psi	1500 psi
Distilled Water	0.62	0	0.18
NaOH	0	0	0
Na2CO3	2.72	0	2.72

The effect of pressure on the interfacial tension is small.

Percent Different of Alkaline Types Effect on IFT

Alkaline Type	%
Distilled Water	0
NaOH	99.34
Na_2CO_3	89.05

Sodium hydroxide solution can reduce the interfacial tension to the lowest value of the interfacial tension, while sodium carbonate has less performance on the interfacial tension reduction.

Percent Different of Alkaline Concentration Effect on IFT

Alklaine conc	0 %wt	0.025 %wt	0.05 %wt	0.075 %wt
NaOH	99.34	97.78	0	13.04
Na2CO3	93.09	61.24	0	61.24

The sodium hydroxide concentration can reduce the interfacial tension to the lowest value at lower alkaline concentration than the sodium carbonate concentration.

VITA

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