INTERFACIAL TENSION REDUCTION OF LIGHT OIL WITH SULFONATE-STRUCTURED SURFACTANTS FOR ENHANCED OIL RECOVERY APPLICATION
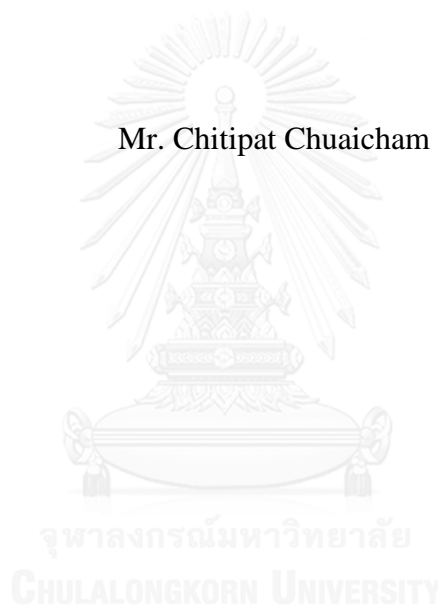
Mr. Chitipat Chuaicham

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Engineering Program in Georesources and Petroleum
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การลดแรงตึงระหว่างผิวของน้ำมันเบาด้วยสารลดแรงตึงผิวที่มีโครงสร้างแบบซัลโฟเนตสำหรับ
การประยุกต์ใช้ในการเพิ่มการผลิตน้ำมัน

นายชิติพัทธ์ เฉื่อยฉ่ำ

Thesis Title	INTERFACIAL TENSION REDUCTION OF LIGHT OIL WITH SULFONATE-STRUCTURED SURFACTANTS FOR ENHANCED OIL RECOVERY APPLICATION
By	Mr. Chitipat Chuaicham
Field of Study	Georesources and Petroleum Engineering
Thesis Advisor	Assistant Professor Kreangkrai Maneeintr, Ph.D.

Accepted by the Faculty of Engineering, Chulalongkorn University in Partial Fulfillment of the Requirements for the Master's Degree

.... Dean of the Faculty of Engineering
(Associate Professor Supot Teachavorasinskun, D.Eng.)

THESIS COMMITTEE

.... Chairman
(Assistant Professor Jirawat Chewaroungroaj, Ph.D.)

.... Thesis Advisor
(Assistant Professor Kreangkrai Maneeintr, Ph.D.)

.... Examiner
(Associate Professor Dawan Wiwattanadate, Ph.D.)

.... External Examiner
(Ake Rittirong, Ph.D.)

ชิติพัทธ์ เฉื่อยฉ่ำ : การลดแรงตึงระหว่างผิวของน้ำมันเบาด้วยสารลดแรงตึงผิวที่มีโครงสร้างแบบ ซัลโฟเนตสำหรับการประยุกต์ใช้ในการเพิ่มการผลิตน้ำมัน (INTERFACIAL TENSION REDUCTION OF LIGHT OIL WITH SULFONATE-STRUCTURED SURFACTANTS FOR ENHANCED OIL RECOVERY APPLICATION) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: ผศ. ดร. เกรียงไกร มณีอินทร์, 90 หน้า.

การเพิ่มประสิทธิภาพการผลิตน้ำมัน โดยเฉพาะอย่างยิ่งกระบวนการอัดฉีดสารลดแรงตึงผิวเป็นวิธีที่มี ประสิทธิภาพในการเพิ่มปริมาณน้ำมันจากกระบวนการผลิต หลักการของกระบวนการดังกล่าวเพื่อเพิ่มปริมาณ การผลิตน้ำมันคือการลดแรงตึงผิวระหว่างน้ำมันดิบกับน้ำโดยการใช้สารลดแรงตึงผิว ในการศึกษาครั้งนี้จะทำ การวัดค่าแรงตึงผิวระหว่างน้ำมันเบาจากแหล่งน้ำมันทางภาคเหนือด้วยสารลดแรงตึงผิวซึ่งมีโครงสร้างแบบ ซัลโฟเนต นอกจากนั้นยังตรวจสอบถึงปัจจัยอื่นซึ่งมีผลต่อค่าแรงตึงผิว เช่น ความดัน อุณหภูมิ ชนิดของสารลด แรงตึงผิว ความเข้มข้นของสารลดแรงตึงผิว ความเข้มข้นของสารละลายเกลือ ไดวาเลนต์ไอออน และการใช้สาร ลดแรงตึงผิวร่วม

ผลการทดลองแสดงว่าความดันมีผลเพียงเล็กน้อยต่อการลดลงของค่าแรงตึงผิวเนื่องจากการทดลองนี้ ทำการศึกษาในสถานะของเหลว สำหรับผลกระทบของความยาวสายโซ่ไฮโดรคาร์บอนของสารลดแรงตึงผิว พบว่าสารลดแรงตึงผิวที่มีความยาวสายโซ่ไฮโดรคาร์บอนใกล้เคียงน้ำมันดิบจะให้ประสิทธิภาพการลดแรงตึง ระหว่างผิวได้ดีกว่า

ความเข้มข้นของสารลดแรงตึงผิวมีบทบาทที่สำคัญในการลดค่าแรงตึงผิว โดยมีผลถึงร้อยละ 98.23 เนื่องจากที่ความเข้มข้นสูงนั้นแสดงถึงการมีจำนวนของสารลดแรงตึงผิวโมเลกุลเดียวมากในสารละลายดังนั้น ค่าแรงตึงผิวจึงลดลง นอกจากนั้นค่าแรงตึงผิวยังลดลงเมื่ออุณหภูมิเพิ่มขึ้นสำหรับทุกชนิดของสารลดแรงตึงผิว

ความเข้มข้นของสารละลายเกลือสามารถลดค่าแรงตึงผิวในทุกช่วงความเข้มข้นของสารลดแรงตึงผิว ไดวาเลนต์ไอออนมีผลกระทบเพียงเล็กน้อยต่อค่าแรงตึงผิว นอกจากนี้สารลดแรงตึงผิวร่วมสามารถใช้เพิ่ม ความสามารถในการละลายของสารลดแรงตึงผิวในสารละลาย อย่างไรก็ตามในการศึกษานี้พบว่าการเพิ่มขึ้นของ ความเข้มข้นของสารลดแรงตึงผิวแสดงผลกระทบเชิงลบต่อการลดค่าแรงตึงผิวเนื่องจากการมีสารลดแรงตึงผิว โมเลกุลเดียวมากเกินไปทำให้เกิดการรวมตัวเป็นไมเซลล์ส่งผลให้เกิดลดลงของสารลดแรงตึงผิวโมเลกุลเดียว บริเวณพื้นที่ผิวระหว่างน้ำมันดิบและน้ำ

ผลการทดลองนี้สามารถใช้เป็นข้อพื้นฐานสำหรับการทำการอัดฉีดสารลดแรงตึงผิวที่แหล่งน้ำมันทาง ภาคเหนือ และใช้เป็นข้อมูลเบื้องต้นสำหรับการทดสอบการอัดฉีดหินตัวอย่างและการศึกษาการจำลอง กระบวนการผลิตน้ำมันเพิ่ม

ภาควิชา   วิศวกรรมเหมืองแร่และปิโตรเลียม   ลายมือชื่อนิสิต _____

สาขาวิชา   วิศวกรรมทรัพยากรธรณีและปิโตรเลียม   ลายมือชื่อ อ.ที่ปรึกษาหลัก _____

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CHITIPAT CHUAICHAM: INTERFACIAL TENSION REDUCTION OF LIGHT OIL WITH SULFONATE-STRUCTURED SURFACTANTS FOR ENHANCED OIL RECOVERY APPLICATION. ADVISOR: ASST. PROF. KREANGKRAI MANEEINTR, Ph.D., 90 pp.

Surfactant flooding is an effective technique for enhance oil recovery. The appropriate surfactant is injected into the production well to reduce oil-water interfacial tension. In this study, the interfacial tension of light oil from the northern oilfield with sulfonate-structure surfactant solutions are measured. In addition, the parameters such as pressure, type of surfactant solution, surfactant concentration, temperature, salinity, divalent and co-surfactant on the interfacial tension are investigated.

The results show the less effect of pressure on interfacial tension reduction because the experiment performs in the liquid phase. For the effect of type of surfactant solution, the surfactant with the similar equivalent alkane-carbon number (EACN) value of crude oil will demonstrate the higher performance in lowing the interfacial tension compared with the others.

Surfactant concentration has an important role in the reduction of interfacial tension accounting to 98.23% because the higher concentration represents to higher in surfactant monomer in solution resulting in lowering interfacial tension. Interfacial tension reduces when the temperature is increased for all surfactant types.

Salinity can also reduce the interfacial tension in all range of surfactant concentration. Divalent ions have less impact on Interfacial tension reduction. In addition, co-surfactant can be used to increase the solubility of surfactant in solution. However, the increasing of surfactant concentration shows the negative effect on interfacial tension reduction in this study because the overwhelming amount of surfactant monomer will stimulate the micelle formation resulting reduce the surfactant monomer at the interface.

The results can be used as the fundamental data for performing surfactant flooding at the northern oilfield and preliminary data for future studies such as core flooding test and enhanced oil recovery (EOR) simulation.

Department:	Mining and Petroleum Engineering	Student's Signature	....
Field of Study:	Georesources and Petroleum Engineering	Advisor's Signature	....
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LIST OF ABBREVIATIONS

CMC	Critical Micelle Concentration
DAS	Drop Analysis System
EACN	Equivalent Alkane Carbon Number
EOR	Enhanced Oil Recovery
GC	Gas Chromatography
IFT	Interfacial Tension
MEA	Monoethanolamine
OOIP	Original Oil In Place
PV	Pore Volume
SDBS	Sodium Dodecyl Benzene Sulfonate
SPM	3-Sulfopropyl Methacrylate
SVBS	Sodium 4-Vinylbenzene Sulfonate
TSS	Toluene 4-Sulfonic Acid Sodium Salt
wt.%	Percent by Weight

NOMENCLATURE

m	Mass
P	Pressure
q	Flow rate per unit cross section area of water
R	Radius of curvature
V	Volume
N_c	Capillary number
C_i	Alkane carbon number of component i,
X_i	Mole fraction of component i

GREEK LETTER

$\gamma_{o/w}$	Interfacial tension between oil and water
μ_o	Oil viscosity
μ_w	Aqueous phase viscosity
ρ	Density
Φ	Porosity of petroleum reservoir

SUBSCRIPTS

i	Component i
o	Oil
w	Water

CHAPTER 1
INTRODUCTION

1.1   Background

More than 85% of the world's energy is supplied by fossil fuel. With US energy demand and consumption forecast, new oil reservoir is needed to serve the rising of oil consumption and to replace the depleted reserve. However, new discoveries are most likely to lie in offshore, deep offshore, or more unwieldy areas. Also, producing unconventional resources would be more expensive than producing from existing fields by enhanced oil recovery (EOR) methods. Thus, EOR is a promising technology to increase oil reserves by recovering residue oil in the reservoir (Sheng, 2011).
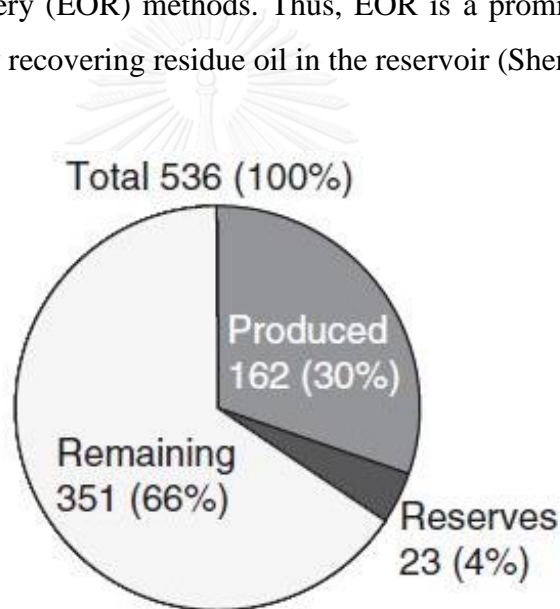
Figure 1.1 US Oil volume distribution in 1993 (Sheng, 2011)

Ordinarily, oil recovery can be classified by its driving mechanisms which are natural drive energy, water and/or gas, and special fluid such as chemical or miscible gasses as primary recovery, secondary recovery and tertiary recovery, respectively. For primary recovery, oil is produced by natural drive energies initially available in the reservoir which are rock and fluid expansion, solution gas, water influx, gas cap and gravity drainage. External fluid or heat is not necessary to be injected into the formation in production but some residual oil is still left over in the reservoir. To recover the

residual oil, secondary recovery can be applied. It requires injection of external fluids, such as water and/or gas to maintain reservoir pressure and volumetric sweep efficiency. Water flooding is one of the widespread method of secondary recovery to improve the oil recovery because of its simple and economical operations (Sheng, 2011).
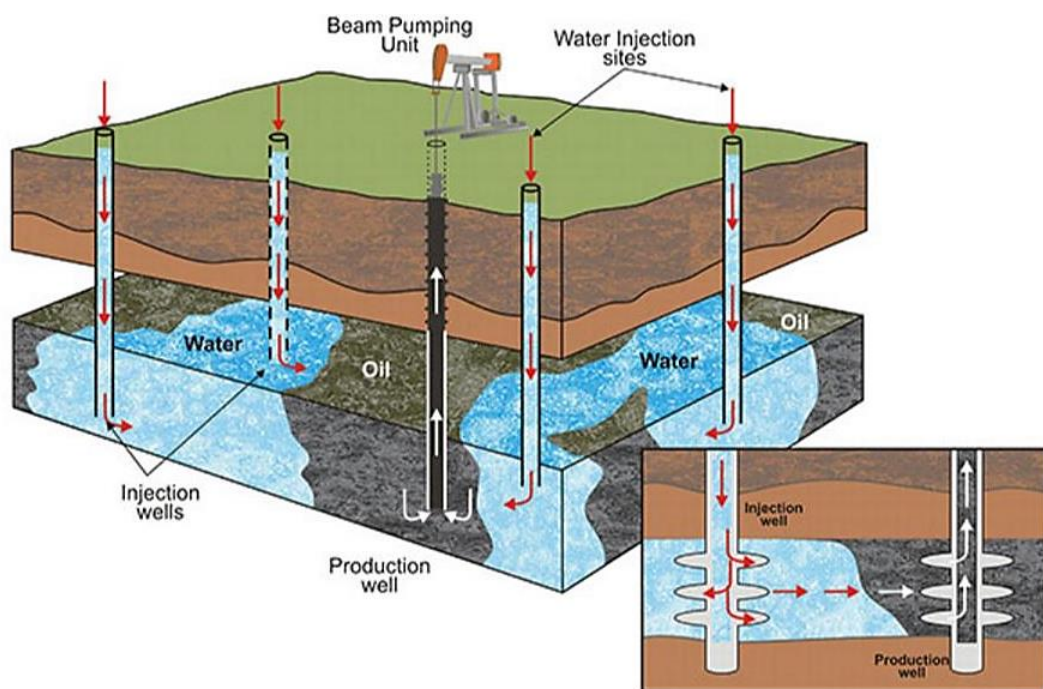
Figure 1.2 Schematic of water flooding (Engineering Terminology, 2014)

However, the problem of water flooding is its low sweep efficiency which associates to the effectiveness of water, displacing agent. The fingering effect is phenomena that register low sweep efficiency in oil recovery particularly in heavy oil reservoirs owing to high mobility (Sedaghat, 2013). Whereby using a special fluid such as chemicals, miscible gases or the injection of thermal energy which refer to tertiary recovery is used to recover the unexploited resources to the extent possible in a technological and economic sense. Consequently, EOR techniques are applied as a tertiary recovery process (Satter, 2015).

Subsequent complete primary recovery, oil is barely delivered a small portion of the initial oil in place (OOIP) even if the secondary recovery, water and gas flooding. Notwithstanding the fact that huge residual oil is forgotten in the reservoir. The remaining oil is an enormous and engaging target for enhanced oil recovery (EOR) techniques in the oil fields (Sofla, 2016)

1.2   Enhanced Oil Recovery Technologies

The enhanced oil recovery process can be classified into four major types which are chemical flooding, gas injection, thermal recovery and others. Figure 1.3 shows a simplified chart of EOR methods carried out in petroleum exploitation projects (Olajire, 2014).
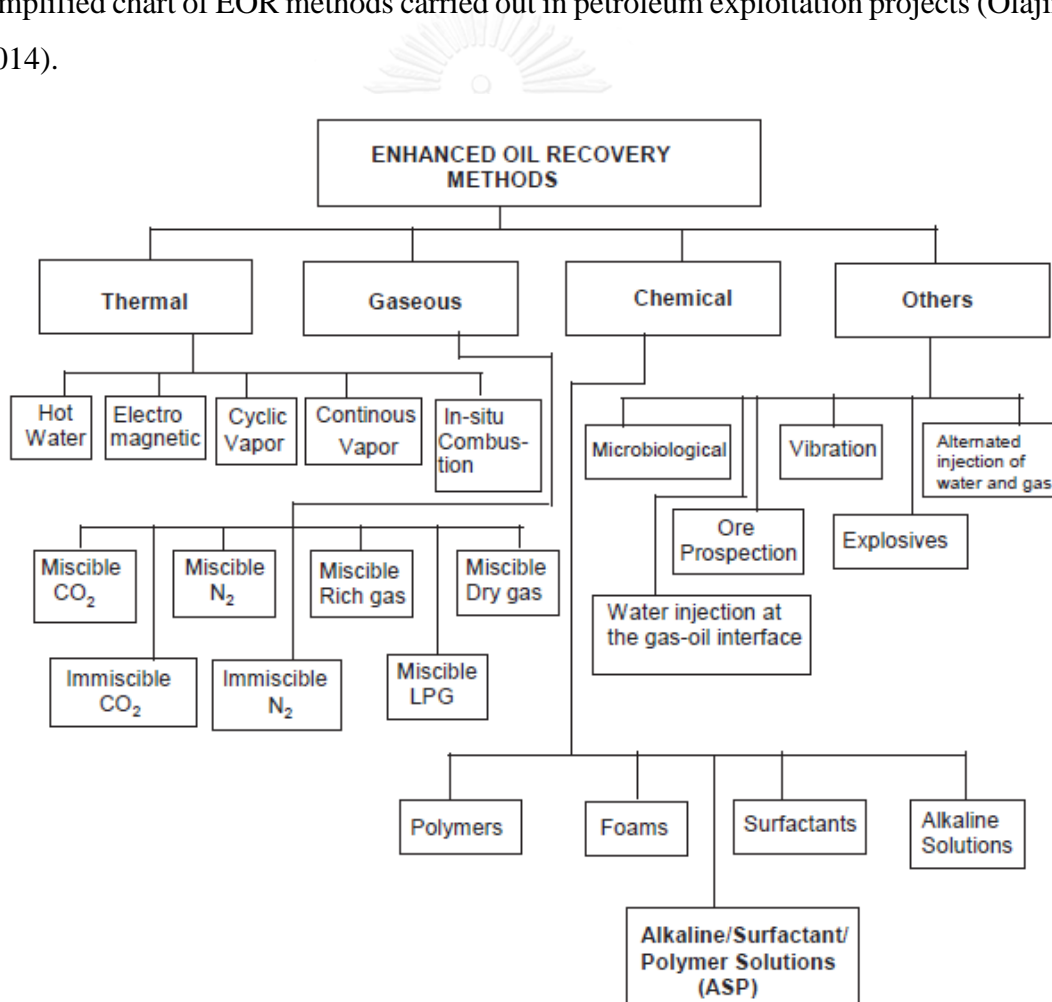
Figure 1.3 Classification of EOR processes (Olajire, 2014)

Thermal Recovery: Its principal mechanism is to decrease the viscosity by contributing heat to heavy oil to improve its mobility in the reservoir which is introduced into the reservoir by steam or oil and combusted by air. Thermal recovery can be applied in both conventional and unconventional reservoirs (Satter, 2015).

- Conventional reservoirs: hot water drive, steam flooding, in-situ combustions, cyclic steam injection (huff-and-puff method)
- Unconventional reservoirs: Steam assisted gravity drive, vapor extraction.

Gas Injection is the method in which gas is injected into reservoir fluids to decrease oil viscosity to enhance oil production. It can be categorized into two types: miscible and immiscible gas injection.

- Miscible: Miscible displacement is a highly efficient method of oil recovery since it alters interfacial tension between fluids and significantly magnifies the microscopic displacement process. Low to medium gravity oil is recovered. It is a popular method of performing the gas injection.
- Immiscible: Inert and flue gas are used for immiscible displacement of oil. This method can be partially miscible depending on pressure and oil composition.

Chemical Injection: Polymer, Surfactant, and alkaline flooding are part of EOR processes. Oil is obtained by adding the chemicals to injected water. Occasionally it is acknowledged as a modifier of water flooding to recover extra volumes of oil (Satter, 2015).

Other: Microbial, acoustic, and electromagnetic. These methods are in an experimental stage with little documentation of any large-scale implementation or their economic feasibility. Though, the microbial enhanced recovery process has been the topic of quite some studies (Satter, 2015).

According to chemical injection EOR, Surface active agents (surfactants) play a major role in the oil industry for chemical stimulation to enhanced oil recovery schemes. Surfactant flooding is one of the methods that manipulate for earning larger oil recovery from reservoirs. Therefore, lessening the quantity of surfactant is economically significant (Barati-Harooni, 2016).

In the northern oilfield or S1, chemical flooding, surfactants is considered to be a suitable method to increase oil production because of low total acid number of oil (0.08 mg KOH/g). Besides, based on the low temperature of the reservoir in S1, there is the low possibility of chemical degradation. This method will be explained later.

1.3   Chemical Flooding

Surfactants are broadly applied in the petroleum production involved several EOR techniques. The efficiency of surfactant flooding depends on the surfactants' ability to diminish the interfacial tension between water and oil. This system effectively increases oil production. Surfactants might produce foam which may lead to an increased oil production by increasing the sweep efficiency and controlling the mobility (Alvarado, 2010; Schramm, 2000).

Surface active agents or surfactants are organic compounds with at least one hydrophilic (water-loving) and a hydrophobic (water-hating) group. Alternatively, they can possess both hydrophilic and hydrophobic which known as an amphiphilic molecule. The hydrophilic group can imparting some water solubility to the surfactant molecule because of ionic or polar in nature,. They can adsorb strongly at the interface between oil/water or air/water to significantly reduce the surface energy at low concentrations (Hiemenz, 1997). The definition of surfactants is often cite to surface active components that have self-assemble at higher concentrations (Laughlin, 1996).

When surfactant is dissolved in a solution, it can locate at the interface so that the hydrophobic group resides near to the oil phase while the hydrophilic group resides adjacent to the water phase which reduces the interface energy of hydrocarbon-water interactions. Therefore, surfactants tend to adsorb strongly at the interface and significantly decrease interfacial tension (Kumar, 2012).

A simple classification of surfactants based on the nature of the hydrophilic groups is commonly used (Ahmadi, 2014).

Table 1.1 Typical Method of Surfactant Classification (Ahmadi, 2014)

Surfactant class	Example
Anionic	Alkyl sulfates and sulfonates
	Petroleum and lignin sulfonates
	Phosphate esters
	Sulfosuccinate esters
	Carboxylates
Nonionic	Alcohol
	Ethoxylated acids
	Alkanolamides
	Ethoxylated amines
	Anime oxides
Cationic	Quaternary ammonium salts
Amphoteric	Carboxybetaines
	Sulfobetaines

According to field data, the northern basin is sandstone rocks whose surface charge is negative. Therefore, the appropriate surfactant for performing enhance oil recovery is anionic surfactant due to the similarity of the prosecution leading to present relatively low adsorption on the rock surface.

Historically, petroleum sulfonates used in EOR processes came as a byproduct of white oil manufacture. In view of limited demand for lube oil stocks, the petroleum sulfonate was in short supply so the synthetic-sulfonates surfactant lead to improvements in EOR surfactants. These sulfonate-surfactant are reported to be more effective in displacing oil. In addition, synthetic sulfonates have better resistance to divalent ions compared to others types of surfactant (Donaldson et al., 1989). Therefore, the suitable surfactant for lowering interfacial tension is sulfonate surfactant.

1.4   Objectives of This Research

1. To measure the interfacial tension of light oil from northern oilfield by using surfactant.

2. To investigate the effect of functional group attached to the structure of surfactant by IFT measurement

3. To assess the effect of parameters such as pressure, temperature, salinity, concentration and types of surfactant on IFT measurement

This study aims to provide the IFT data at different conditions applied for surfactant flooding at the northern oilfield. The results can be used as the fundamental data for future studies such as the core flooding test to find the oil recovery and simulation for EOR.

The outline of this thesis is presented as follow. Chapter 2 presents the theory and literature review describing the fundamental theory of the surfactant, surfactant flooding, and mechanism of oil displace, IFT phenomena, etc. Previous studies related to the research topic are also presented. Chapter 3 mentions about the experiment which is divided into two parts. The first part describes materials and equipment required in this study. The second part explains the experimental procedure with conditions to be examined in the laboratory. Results and discussion will be presented in Chapter 4. The experimental result from the IFT measurement including the effects of parameters on the IFT between crude oil and surfactant solution are described such as pressure, temperature, the concentration of surfactant, salinity and divalent ions. Finally, Chapter 5 will summarize the results from the previous chapter by explaining the effects of each parameter and providing the recommendations for future study.

CHAPTER 2
THEORY AND LITERATURE REVIEW

According to fluid property at northern oilfield, the suitable method for performing chemical flooding of this study is surfactant flooding. The fundamental theory of surfactants, interfacial tension, surfactant in this thesis will be explained in this chapter.

2.1   Interfacial tension

Interfacial tension (IFT) is defined as the force per unit length at the interface between two different two immiscible fluids. In a liquid/vapor system, IFT is called surface tension. IFT appears from inequality in the intermolecular forces acting on molecules at the interface. It can be expressed as a contractile force that attempts to narrow the surface area (Green, 1998; Hiemenz, 1997; Mørk, 2004).

Interfacial tension (IFT) plays an importance role in EOR process. In that there are various parameters influence the IFT behavior between the phases in a reservoir, e.g., type and concentration, a structure of the oil phase (Sheng, 2011; Sharma and Shah, 1989). The surfactant flooding improves oil recovery by lowering the IFT between oil and water phase.

2.2   Surfactant flooding

Surfactant flooding is an EOR method that injects the solution of a surfactant with injection water to remove trapped oil in the reservoir to change fluid properties which are interfacial tension (IFT). When the IFT decreases, the trapped oil will be released and mobile. For the movement of oil through the narrow capillary pores, very low oil/water interfacial tension (IFT) is required. The principle of surfactant flooding is illustrated in Figure 2.1.

RESIDUAL OIL
WATER
ROCK
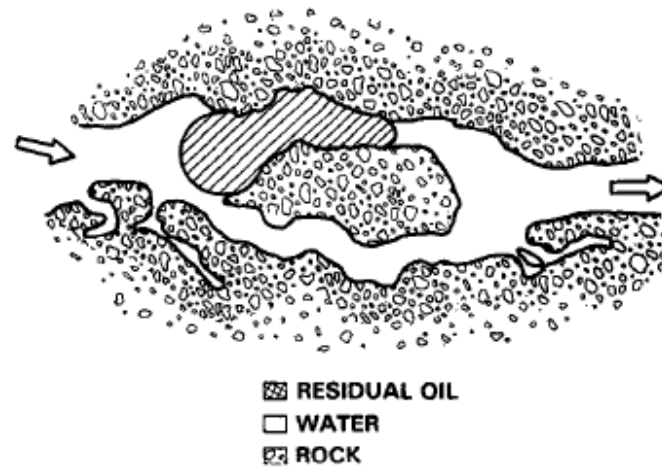
Figure 2.1 The principle of flooding, where residual oil is trapped in the reservoir
(O'Brien et al., 1982)

Typically, surfactant flooding, which is tertiary recovery, is performed as an EOR technique after the application of a water flooding. Figure 2.2 shows a chemical process for enhancing oil recovery.

Region 1 shows the residual oil saturation after water flooding (S_{orw}) which refer to a liquid that remains in the reservoir after performing of water-flooding. After the water-flooding, only an aqueous phase is flowing in Region 1 (Green, 1998; Schramm, 2000). Injected micelle solution such as a surfactant is specified by volume of a primary slug, in the range of 3 to 30% of the flood pattern pore volume (PV). The interfacial tension between the surfactant and oil is very low which enables the gravity forces to displace oil out. The mobilized oil forms an oil bank in front of the micellar slug, as illustrated by Regions 2 and 3 in Figure 2.2 (Green, 1998; Schramm, 2000).

The micellar solution viscosity can be adjusted by adding polymers to improve mobility ratio between the surfactant solution and the oil bank. Both viscosity and capillary forces are altered to enhance oil recovery. Owing to the high cost of surfactants, the volume of the surfactant should not be too large, and a less expensive fluid is used to displace the slug. However, water is not suitable due to low viscosity, which creates undesired mobility effects. To overcome this problem, adding polymers into water is a solving way to improve viscosity of the water, and this solution is

injected after the surfactant solution, as illustrated by Region 4 (Green, 1998; Schramm, 2000).

Flow direction
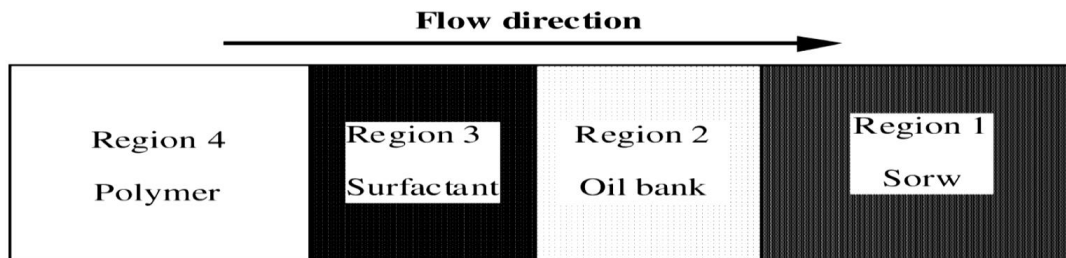
Figure 2.2 Phase position in a chemical flooding process (Schramm, 2000)

When a surfactant is injected into a reservoir, it will accumulate on the interface between oil and water leading to a reduction of IFT which refers to energy to deform the oil droplets. IFT is reduced sufficiently to mobilize oil trapped in the porous media. Figure 2.3 illustrates how the deformed oil drops can flow through narrow pores (Johansen, 2014).
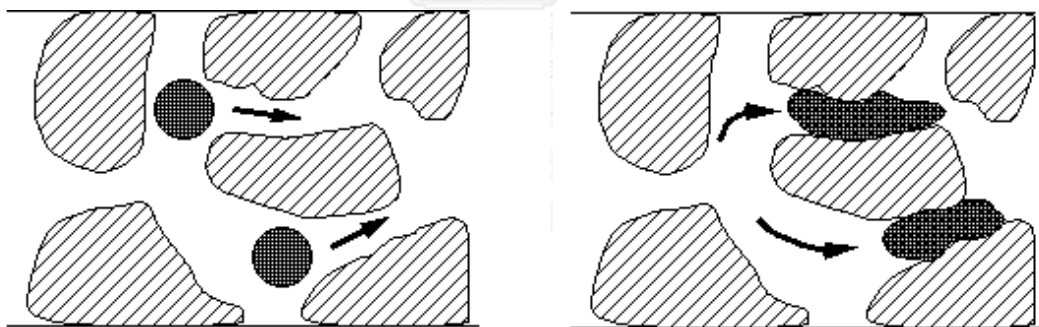
Figure 2.3 The effect of surfactant flooding (Sim Science, 2000)

2.3   Surfactants

Surfactant molecules or amphipathic molecules are lipophilic-lipophobic chemicals that have two different polar portion parts in the structure, which represent to solubility in both polar and nonpolar segment. The chemical agent can also act as a surfactant if it has both lipophilic and lipophobic groups. The surfactant can call water soluble, or water insoluble surfactants depending on the hydrocarbon chain in the

structure. Water soluble surfactant can be called if hydrocarbon chain is less than 12 carbon atom, in contrast, the water-insoluble surfactant has greater 14 carbon atom.
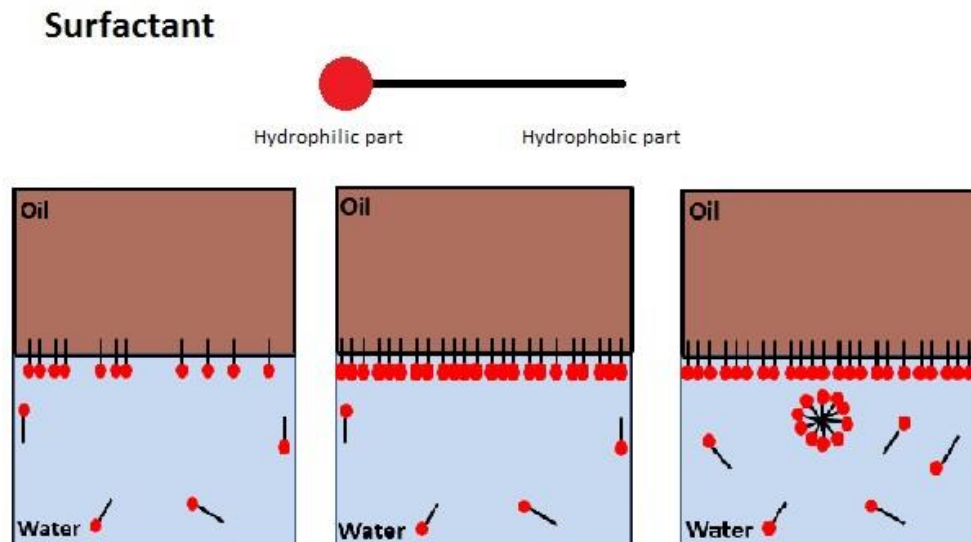
Figure 2.4 Surfactant molecule and surfactant orientation

The surfactant can be classified based on the nature charge on the polar section as cationic, anionic, non-ionic and amphoteric which have a positive charge, negative charge, no charge and both positive and negative charge on polar surface portion as shown in Figure 2.5.
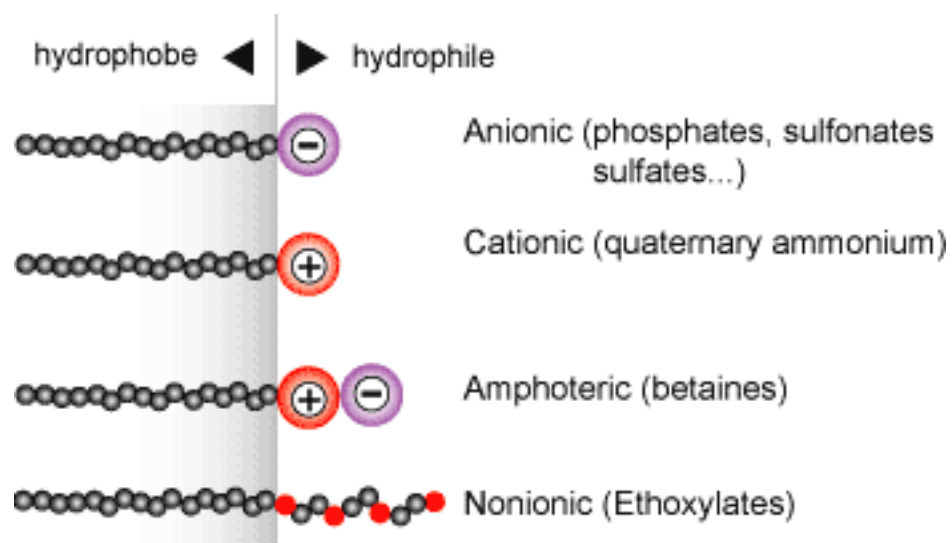
Figure 2.5 The structure of surfactant molecules (UKessays, 2015)

To achieve the reduction in interfacial tension or surface tension efficiently, not only concentration of surfactants but also its structure which affects the orientation at the interface are needed to be considered. Many reservoirs are sandstones which have a negative charge on the rock surface, Therefore the effective surfactant for performing enhance oil recovery is anionic surfactant due to its relatively low absorption on sandstone rock.

2.4   Capillary force and Capillary number

The capillary force is directional forces acting on the liquid meniscus in a capillary when liquid is contacted with a solid surface, e.g., oil in a small pore media. The liquid's Interfacial tension has increased to forces that act on the liquid meniscus which contacts between the capillary wall and liquid. Capillary force has a major role in any system where porous, pore or capillary structures are involved, e.g., a porous media in reservoir rock.

Capillary forces relate to the oil that trapped in pores and cavities in the reservoir. The capillary number which defines as ratio of viscous to capillary forces can be expressed as Equation 2.1 (Donaldson et al., 1989).

$$N_c = \frac{\mu_w \phi q}{\gamma_{o/w}} \qquad (2.1)$$

Where N_c is capillary number

   μ_w is aqueous phase viscosity

   Φ is porosity of petroleum reservoir

   q is flow rate per unit cross section area of water

   $\gamma_{o/w}$ is interfacial tension between oil and water

Conventional water flooding operates close to 10^{-6} of capillary number. Nevertheless, larger of residue oil is still left in the reservoir. To improve oil recovery, the capillary number must be increased to at least 10^{-4}. The capillary can be increased either by rising in aqueous phase viscosity and flow rate or decreasing in the interfacial tension. Viscosity and flow rate cannot be adjusted easily due to a limitation in

variation, so the only parameter that can be modified to achieve the higher capillary number is interfacial tension.
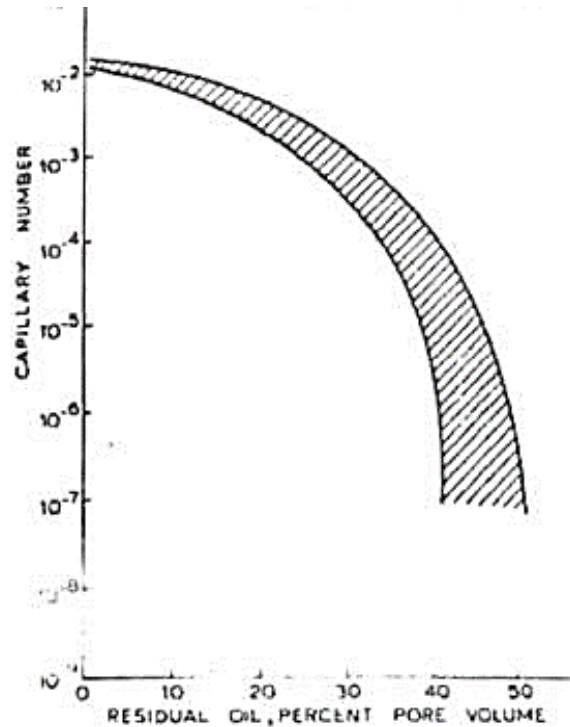
Figure 2.6 A Correlation between capillary number and residual oil saturation
(Donaldson et al., 1989)

2.5   Interfacial phenomena

In the presence of a suitable surfactant, an ultra-low interfacial tension can be achieved at an oil-solution interface. The increase in surfactant concentration shows the IFT reduction trend which illustrates in Figure 2.7. However, the graph is shown that there are two regions of ultra-low interfacial tension in the system around 0.1% and 5%
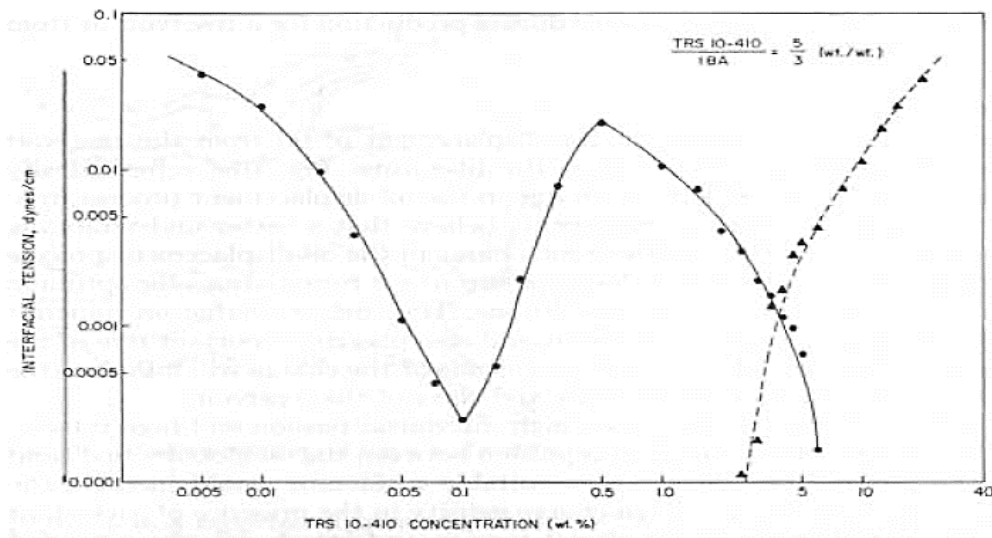
Figure 2.7 Effect of surfactant concentration on the interfacial tension (Donaldson et al., 1989)

To reduce the IFT to the lowest level, a concentration of surfactant that provides the lowest value of IFT is named as Critical Micelle Concentration (CMC) or a concentration where micelles are initially grown. At low surfactant concentration, surfactant molecule shape is a single molecule called as a monomer. The IFT reduces with the increase of surfactant concentration until it reached CMC, the electrostatic force of each monomer which has the same charge reaches the highest point. The new rearrangement to optimize the electrostatic force start from here which result in agglomeration of micelles and loss of active monomer at the interface. The IFT rises with the increase of surfactant concentration. However, at higher concentration, an intermediate phase microemulsion is developed, and it is in equilibrium with excess oil and brine. The IFT begins to decline again.
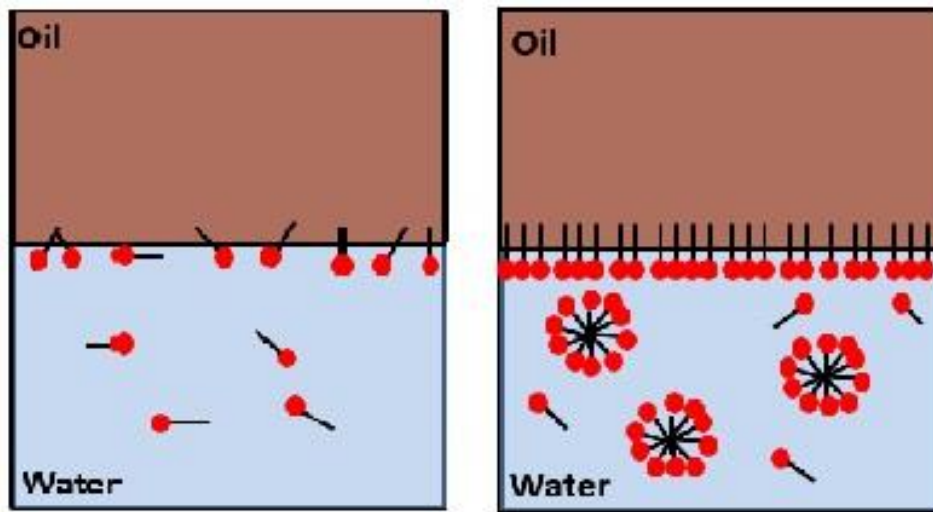
Figure 2.8 Distribution of surfactant molecules in solution at concentrations (a) below and (b) above CMC

2.6   Micelle formation

A micelle is an aggregated surfactant molecule dispersed in a colloid solution. A typical micelle in aqueous solution forms an aggregate with the hydrophilic "head" regions (or lipophobic) contact surrounding solvent, withdrawing the hydrophobic (or lipophilic) single tail regions in the center of the micelle. The distribution of surfactant molecules in solution at concentrations below and above CMC is shown in Figure 2.8.

In surfactant flooding in EOR process, the hydrophilic head interacts with water molecules which are polar-part while the hydrophobic tail which is non-polar part interacts with the oil. Therefore, surfactants can form both oil-in-water which have the tail groups at the center with the heads extending out or water-in-oil emulsions which have the head groups at the center with the tails extending out. Micelles are approximately spherical in shape. Other phases, including shapes such as cubic, hexagonal, and lamellar are also possible as shown in Figure 2.9.

$v/al > 1$

Reversed micelles

← Cubic

Reversed hexagonal

'Water-in-oil'

$v/al \geq 1$

Cubic

$v/al \approx 1$

'Mirror plane'

Lamellar

← Cubic

$1/3 < v/al < 1/2$

Hexagonal

'Oil-in-water'

← Cubic

$v/al < 1/3$

Micelles
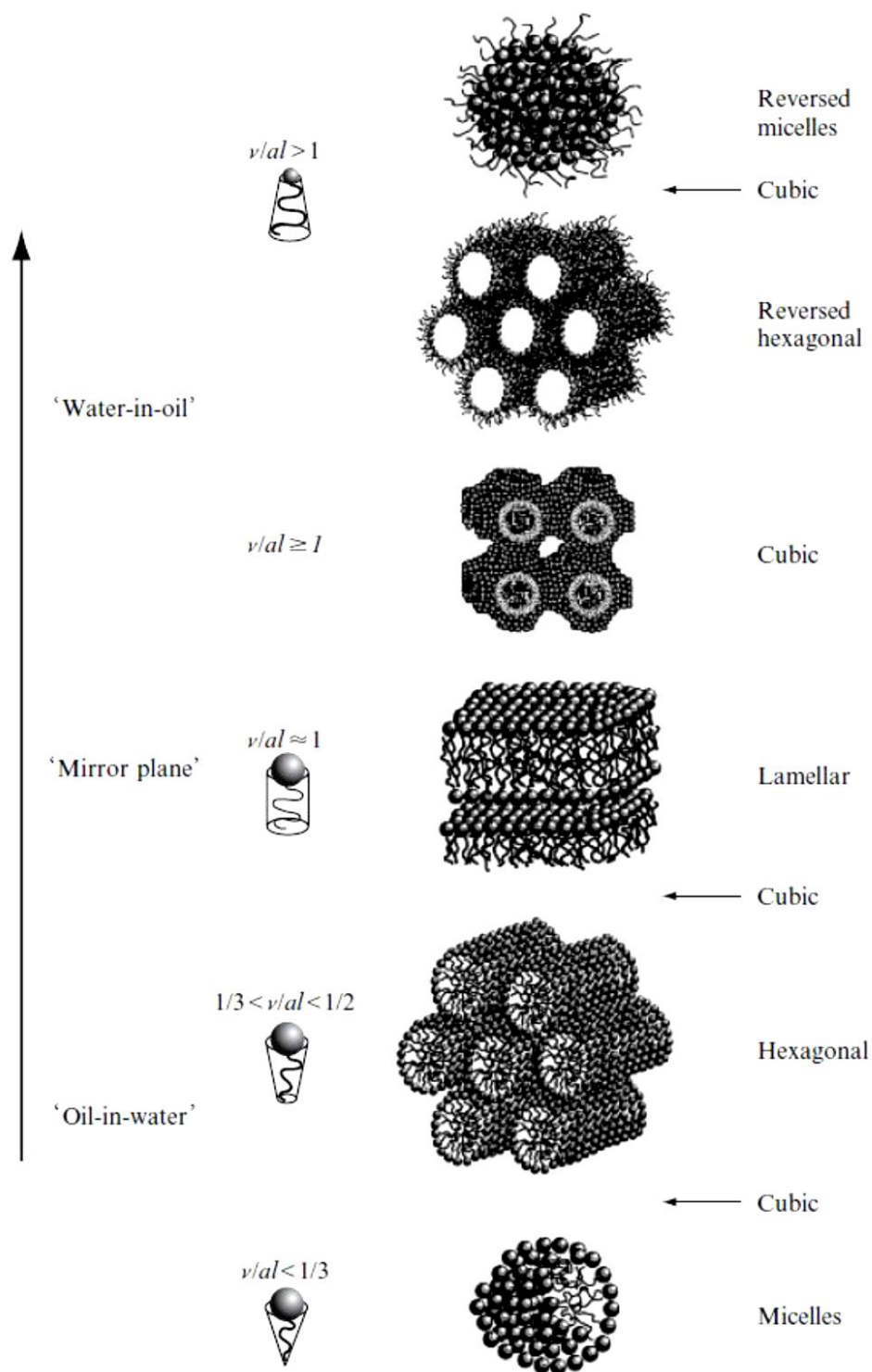
Figure 2.9 Surfactant structures aggregation (Holmberg et al., 2002)

2.7 Equivalent alkane-carbon number (EACN)

The equivalent alkane-carbon number (EACN) concept is the substitution of an alkane or an alkane mixture for a crude oil for phase volume or interfacial studies which has been proposed by Canyias et al. (1976). This concept arises from the observation that the interfacial properties of given crude oil with surfactant can be modeled by the behavior of alkanes in that crude oil. The EACN can be determined from

$$\text{EACN} = \sum_{i=1}^{n} X_i C_i \qquad (2.2)$$

Where C_i is alkane carbon number of component i

X_i is mole fraction of component i

N   is number of components in mixture

2.8 Surfactants used in this study

The anionic surfactants are the most used in EOR process because of surfactant properties, such as decreasing the IFT, their ability to create micelle, are comparatively stable, present low adsorption on reservoir rock and can be produced economically (Green, 1998). The anionic surfactants disperse in water to create an amphiphilic whose has anion and cation which has negatively and positively charged, respectively. Wu (2005) has investigated a series of branched alcohol propoxylate sulfate surfactants for EOR application. The results show that the number of propoxylate groups has a significant influence on the interfacial tension (IFT), the optimal salinity and the adsorption. Optimal salinity and adsorption are shown to decrease as the number of propoxy groups are increased.

Barnes (2008) performed an investigation of anionic surfactants families, internal olefin sulfonates, (IOS), for using in surfactant flooding at high temperatures, (up to 150 °C), and with varying optimal salinities from 1 % to 13 % depending on the carbon number range. The IOS surfactants show little sensitivity to temperature. It is an advantage for reservoirs with temperature gradients. The IOS surfactants exhibit promising over a range of reservoir conditions covering moderate to high temperatures

and from low to high salinity conditions. Both alcohol propoxylate sulfates and IOS have been studied (Flaaten, 2008; Levitt, 2006). They are identified as the promising surfactant candidates for EOR processes. These surfactant candidates are available at low cost and have been tested in different reservoir cores resulting in enhanced oil recovery and low surfactant retention (Levitt, 2006). It was found in Levitt's work that mixing the IOS and the alcohol propoxylate sulfate give the best result.

Furthermore, Bryan (2007) has performed an investigation of alkali surfactants for surfactant flooding of heavy oils. The result shows that an alkali surfactant flooding has a significant potential for non-thermal heavy oil recovery, as the addition of alkali surfactants reduce the IFT between oil and water by such a magnitude that formation of emulsions is possible (Sandersen, 2012).

Sulfonate-structure surfactant, negatively charged on head group, is focused on this study because they are usually applied for widely manufacturing applications. Moreover, it are reported to be more effective in displacing oil and higher resistance to divalent ions compared to others types of surfactant. In this study, there are four types of surfactant which are sodium dodecyl benzene sulfonate, toluene 4-sulfonic acid sodium salt, sodium 4-vinyl benzene sulfonate and 3-sulfopropyl methacrylate.

2.8.1   Sodium dodecyl benzene sulfonate

Sodium dodecyl benzene sulfonate is an anionic surfactant which is common in many laundry detergents. Its formula is $CH_3(CH_2)_{11}C_6H_4SO_3Na$ which has molecular weight 348.48. The molecular structure is represented in Figure 2.10.
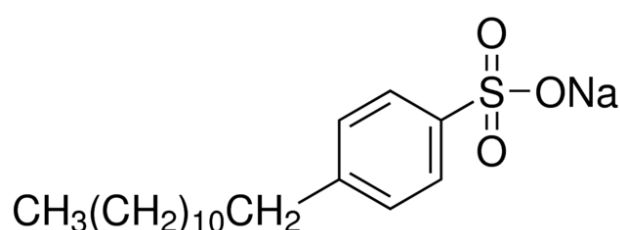
Figure 2.10 Molecular structure of Sodium dodecyl benzene sulfonate (Sigma-aldrich, 2010c)

2.8.2   Toluene 4-sulfonic acid sodium salt

Toluene 4-sulfonic acid sodium salt is an anionic surfactant which has its formula is 4-(CH$_3$)C$_6$H$_4$SO$_3$Na which has molecular weight 194.18. The molecular structure is represented in Figure 2.11.
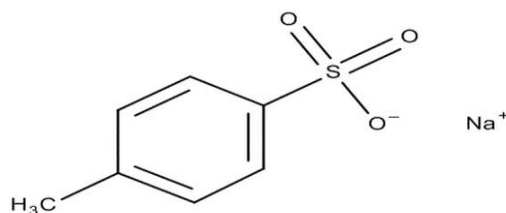
Figure 2.11 Molecular structure of Toluene 4-sulfonic acid sodium salt (Merckmillipore, 2010)

2.8.3   Sodium 4-vinyl benzene sulfonate

Sodium 4-vinyl benzene sulfonate is an anionic surfactant which has its formula of C$_8$H$_7$NaO$_3$S with molecular weight of 206.19. The molecular structure is represented in Figure 2.12.
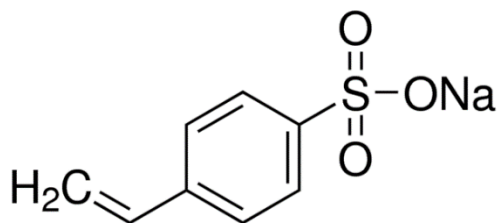
Figure 2.12 Molecular structure of Sodium 4-vinyl benzene sulfonate (Sigma-aldrich, 2010b)

2.8.4   3-Sulfopropyl methacrylate

3-Sulfopropyl methacrylate is an anionic surfactant which has its formula is $H_2C=C(CH_3)CO_2(CH_2)_3SO_3K$ which has molecular weight 246.32. The molecular structure is represented in Figure 2.13.
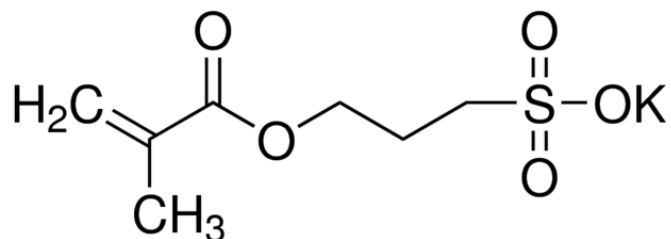
Figure 2.13 Molecular structure of 3-Sulfopropyl methacrylate (Sigma-aldrich, 2010a)

2.9   Literature review

Beneventi et al. (2001) studied role of surfactant structure on surface and foaming properties from measurements of the surface tension of liquid-gas interface. Four different surfactants along with the same hydrophilic but differing only in lengths of the long hydrophobic chain were choosen to observe the surface tension. The results show that the length of the hydrophobic tail has the effect to the surface activity, the increasing in long chain hydrophobic gives a reduction trend of the surface tension.

Zhao (2006) measured Interfacial tension, IFT, between crude oil and decyl methylnaphthalene sulfonate (DMNS) surfactant alkali-free flooding systems. The laboratory results show that DMNS surfactant occupied high efficiency and capacity of decreasing the solution interfacial tension is 31.61 mN m^{-1}. Moreover, sodium chloride (NaCl) results in more effectiveness of surfactant in decreasing interfacial tension and displays the surfactant has a good synergism with presenting of salt. It is also observed that the surfactant can lower the interfacial tension to ultra-low only at a certain range of sodium chloride concentration.

Haiyang (2011) observed the effects of displacement efficiency of surfactant flooding in high salinity by using anionic-nonionic polyoxyethylene alkyl sulfonate surfactants (ANS1 & ANS2). Interfacial tension is an important factor. The low

interfacial tension could be obtained in the surfactant ANS1 concentration beyond 0.2% and ANS2 concentration beyond 0.3%. Moreover, interfacial tension had the trend of first decreasing and then increasing with increasing salinity.

Hutin et al. (2012) studied the effect of the added surfactants on the dynamic interfacial tension behavior of alkaline/diluted heavy crude oil system to obtain a better knowledge of the interacting behavior between EOR of surfactants used in chemical flooding and in-situ surfactants perform in the heavy oil reservoir. The IFT was measured by generated pendant drop and spinning drop tension meters. The addition of Sodium Dodecyl Benzene Sulfonate (SDBS) changed the dynamic IFT behavior of the heavy oil completely as the IFT significantly reduced and finally reached a plateau. It can be attributed the efficiency of SDBS to a synergistic effect between the In-situ surfactant and the combined surfactant that create a mixed interfacial monolayer, which is efficient power in lowering the IFT to ultra-low values.

Ahmadi (2014) evaluated IFT of mulberry leaf-derived surfactant in an oil-aqueous system at 0, 0.05, 0.1, 0.5, 1wt% surfactant. The result shows that increasing of surfactant concentration will reduce IFT value which can be observed at 1 wt.% of a surfactant. It can reduce the interfacial tension from 44 mN/m to 17.9 mN/m, an overall reduction of approximately 60%.

Ko (2014) investigated the relationship between dodecyl alkyl sulfate and specific crude oils by using the gravity drainage flooding test (GDFT) to discover the potential of dodecyl alkyl sulfate to improve oil recovery in porous media. The result revealed that oil production was enhanced by 1.6% after combining only 0.01% of co-surfactant. Besides the phase behavior test, the linear surfactant produced more oil than the branched by 1.3% in the core flooding test.

Youyi (2014) studied the relationship between IFT performance and surfactant structure at difference types of alkyl benzene sulfonate surfactant. The ultralow IFT was obtained at the concentration range of surfactant from 0.05wt% to 0.3wt%. Also, the result indicates that the Length of the carbon chain and branch structure played an important role in alkyl benzene sulfonate reduced IFT.

Marhaendrajana et al. (2015) studied the using Sulfonated Alkyl Ester Surfactant to Reduce Oil-Water Interfacial Tensions for light and heavy oil. They

synthesis sulfonated alkyl ester (SAE) as surfactant which has an ester group as nonionic and sulfonate groups as ionic in one compound. The results show that IFT can be lowered to 10^{-3} mN/m at salinity of 100,000 ppm sodium chloride and surfactant concentration of 0.4 %wt.

Kanokkarn et al. (2017) studied surface tension about diffusivity and foaming properties affected surfactant type and structure. In this study, Methyl ester sulfonate anionic surfactant with different alkyl chain lengths (14-18) was used for IFT measurement to observe the effect of hydrophobic portion. In addition, Polyoxyethylated dodecyl alcohol nonionic surfactant with different head group sizes was investigated the effect of hydrophilic portion. The results were compared with Sodium dodecyl sulfonate. From the experimental results shows that the increasing either alkyl chain length or the size of the hydrophilic head group can affect to a reduction of IFT. The effect of the increase in alkyl chain length was a dominant more than the increase in the size of the hydrophilic head group.

According to Literature reviews, there are many structures of surfactant can be used for lowering the interfacial tension such as short or long chain hydrocarbon, with or without benzene ring which acts as a hydrophobic portion and different functional group size which act as a hydrophilic portion. In addition, the sulfonate-surfactant are reported to be more effective in displacing oil have better resistance to divalent ions compared to others types of surfactant. Therefore, this thesis will study on interfacial tension reduction affected by sulfonate-structured surfactants which have a difference in structure.

CHAPTER 3

EXPERIMENT

3.1 Materials and Equipment

3.1.1 Oil properties

Oil sample used in this experiment is obtained from northern oilfield Thailand. The total acid number is 0.08 mgKOH/g. The oil composition is analyzed by gas chromatography (GC). A gas chromatograph (GC) is an analytical instrument that measures both quantitative and qualitative of components in a sample. The sample solution is fed into the column which helium or nitrogen is introduced as a carrier gas; various components are separated due to interacting with the stationary phase made from the liquid on an inert solid which support on the wall of the column. The quantity of the component is measured by the detector at the exit. To classify the component inside the sample, a known concentration standard sample is injected into the instrument to compare the retention time (appearance time) between standard sample and test sample. Moreover, the concentration is calculated by observing the area under the graph.
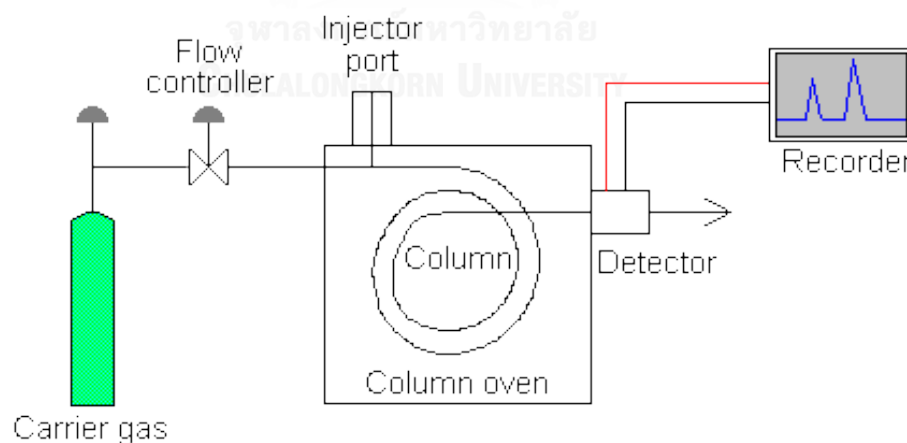
Figure 3.1 Schematic diagram of a gas chromatograph (Hallam, 2010)

The oil composition from C7 to C35+ alkane and the distribution by weight are as shown in Table 3.1

Table 3.1 Composition of oil sample

Component	% mass	Component	% mass
n-C1	0	C18	3.16
n-C2	0	Phytanes	0.37
n-C3	0.54	C19	3.52
i-C4	0.41	C20	3.69
n-C4	1	C21	3.76
i-C5	0	C22	3.43
n-C5	0	C23	3.8
C6	1.14	C24	3.45
C7	2.99	C25	3.72
C8	7.24	C26	3.64
C9	3.49	C27	3.83
C10	2.72	C28	3.05
C11	2.42	C29	3.04
C12	2.32	C30	2.6
C13	3.6	C31	2.24
C14	4.12	C32	1.56
C15	4.32	C33	1.22
C16	3.78	C34	1.16
C17	4.13	C35+	3.51
Pristane	1		

The oil density is measured at 70, 80, and 90°C. Mass and volume of oil are collected independently. Before measurement, the oil sample is heated by heater then mass is measured by the precision weighing machine with 0.00001 g in accuracy, and the oil sample volume is determined by using a syringe. Consequently, the oil density is calculated by using the Equation 3.1

$$\rho = \frac{m}{V}$$ (3.1)

Where ρ is the density of sample

m is the mass of the sample

V is the sample volume

The oil sample density can be shown in Table 3.2.

Table 3.2 Oil sample density

Temperature (°C)	Oil density (g/cm^3)
70	0.85
80	0.85
90	0.84

3.1.2 Brine properties

Brine composition is duplicated according to the produced water composition at northern oilfield analyzed by Intertek Testing Services (Thailand) Ltd. as shown in Table 3.3.

Table 3.3 Produced water composition

Composition ions	Percent by weight
Na^+	36.423
K^+	0.294
Ca^{2+}	0.029
Mg^{2+}	0.176
Sr^{2+}	0.065
Cl^-	58.748
HCO^{3-}	0.57
SO_4^{2-}	2.761
S^-	0.934

The alomost ion compositions in produce water from northern oilfield which has 17,075 ppm in salinity are Na^+ and Cl^- so the simulated brine can be prepared based on principal components in the produced water which are sodium (36.5%) and chloride (58.7%). The only composition of Na^+ and Cl^- which is considered as the main portion of produced water.

Sodium chloride (NaCl) with the purity of 99.9%, which is purchased from Ajax, is dissolved in the de-mineral water to create the salinity approaching the real salinity of produced water. Divalent ions such as calcium and magnesium are ignored in the brine preparation since the quantity of these ions are very small and can be neglected. However, the effect of these divalent ions which has only 4.8 % will be studied further on IFT reduction in the topic of effect of divalent ion on the interfacial tension.

Surfactant solution can be created by mixing the simulated brine with surfactants. To observe the effect of hydro carbon chain length, chemical bonding and benzene ring in structure, four types of surfactants which are Sodium dodecyl-benzene sulfonate ($CH_3(CH_2)_{11}C_6H_4SO_3Na$) purchased from Sigma-Aldrich, technical grade. Toluene 4-sulfonic acid sodium salt ($4-(CH_3)C_6H_4SO_3Na$) purchased from Merckmillipore, technical grade. Sodium 4-vinyl benzene sulfonate ($C_8H_7NaO_3S$)

purchased from Sigma-Aldrich, technical grade. 3-Sulfopropyl methacrylate ($H_2C=C(CH_3)CO_2(CH_2)_3SO_3K$) purchased from Sigma-Aldrich, technical grade are studied.

3.1.3 Equipment for Interfacial Tension Measurement

To measure the IFT between oil and surfactant solution, in this study, the IFT apparatus model 700 from Vinci Company is used. The instrument is shown in Figure 3.1. The rising drop is created at the tie of thin needle immersed in surfactant solution to determine the fluid interfacial properties at the desired conditions. The chamber can contain 25 cm^3 of surfactant solution. The shape of generated rising drop is recognized with an accurately calibrated video lens system. Therefore IFT value is calculated by Drop Analysis System software (DAS). Temperature and pressure condition can be set up to the maximum value of 69 Mpa (10,000 psi) and 453.15 K (180°C), respectively. This IFT apparatus model 700 can measure the IFT in a range of 0.1 to 72 mN/m. The accuracy of this equipment is within 0.01 mN/m. IFT can be automatically calculated by software base on Young-Laplace Equation (Vinci, 2010).

Figure 3.2 The IFT 700 instrument (Vinci, 2010)

3.1.4   Density meter

Density meter, DMA 4500 M model, from the Anton Paar Company, is used for measuring surfactant solution density. The machine can measure in the range of 0 to 3 g/cm^3 with the 10^{-5} decimal precision. Temperature and pressure can be measured up to the maximum value of 95°C and 10 bars, respectively. The approximately one mL surfactant solution is injected into the tube inside the machine at desired condition; then solution density can automatically measure.

Figure 3.3 The DMA 4500 M instrument (Paar, 2016)

3.2   Solution preparation

To prepare the surfactant solution, the surfactant will be dissolved in the simulated brine. At the desired temperature, the surfactant solution is measured by using the density meter.

3.3   Experimental procedure

For IFT measurement, the solution and the crude oil sample will be heated before injecting into the chamber within IFT measurement machine. The surfactant solution is fed into the IFT chamber; then crude oil rising droplet is generated at the desired pressure to measure the IFT. The results are received from the integrated

software provided by the Vinci Company. The acetone and distilled water are required after removing oil and parts containing the surfactant solution. The operating condition parameters for this thesis study are shown in Table 3.4.

Table 3.4 Experimental operating conditions for this study

Parameter	Value
Pressure (psig)	1000, 1,500, and 2,000
Temperature (°C)	70, 80, and 90
Salinity (ppm)	0, 7,500, 10,000 15,000 and 17,500
Surfactant concentration (%)	0, 0.05, 0.1, 0.5 and 1
Type of alkali	1) Sodium dodecyl-benzene sulfonate
	2) Toluene 4-sulfonic acid sodium salt
	3) Sodium 4-vinylbenzenesulfonate
	4) 3-Sulfopropyl methacrylate

3.3.1   Interfacial Tension Measurement

A concise guidance for determining the IFT of crude oil/surfactant solution is to fill the cell with the surfactant solution, set it to the desired pressure, and implement rising oil droplet via the needle, respectively. The designated temperature can be achieved by using the heater which has a NiCr-Ni thermocouple used as the indicator for control the temperature inside both solution and oil sample chamber. The temperature sensor has ±0.1 K in accuracy. Heat loss is limited by the covering jacket for keep the temperature and the pressure constant; then crude oil sample can be slowly injected into the cell. Once the rising droplet is formed, IFT measurement starts and the results are recorded to be further analyzed. The experiment is continuously run until it reaches equilibrium.

3.4   Methodology

Methodology Flowchart of the study can be shown in Figure 3.4

Literature review

Test the composition of the produced water and oil from northern oilfield

Prepare surfactant solution by adding surfactant to simulated brine

Measure the IFT between the solution and oil with the IFT 700 instrument

Observe the effect of co-surfactant and determine the CMC point of the suitable surfactant.

Construct the empirical equation for IFT prediction.

Analyze and discuss the results obtained from the experiment

Repeat the experiment to vary the following parameters

- Pressure
  - 1,000, 1,500, 2,000 psig
- Temperature
  - 70, 80, 90°C
- Salinity
  - 0, 7,500, 10,000 15,000, 17,500 ppm
- Surfactant concentration
  - 0, 0.05, 0.1, 0.5, 1 %
- Type of surfactant
  - 1) Sodium dodecyl-benzene sulfonate
  - 2) Toluene 4-sulfonic acid sodium salt
  - 3) Sodium 4-vinylbenzenesulfonate
  - 4) 3-Sulfopropyl methacrylate

Figure 3.4 Methodology flowchart

CHAPTER 4

RESULTS AND DISCUSSION

In this chapter, the experimental results of the effects of parameters such as pressure, temperature, surfactant concentration, salinity, divalent ions and surfactant with co-surfactant on the IFT between crude oil and simulated brine are shown and discussed. In addition, the correlation between surfactant and IFT is developed and presented.

4.1 Equipment Verification

To ensure the experimental results, the procedure and the equipment have been verified by comparing with the results of Asavaritikrai (2016) and Saengnil (2015). Testing conditions are at 0.05 wt.% of sodium hydroxide, temperature of 90°C and salinity of 750 ppm. Pressures used in the verification are 500, 1000 and 1500 psi. The laboratory results of the verification are shown in Figure 4.1 and Table 4.1.
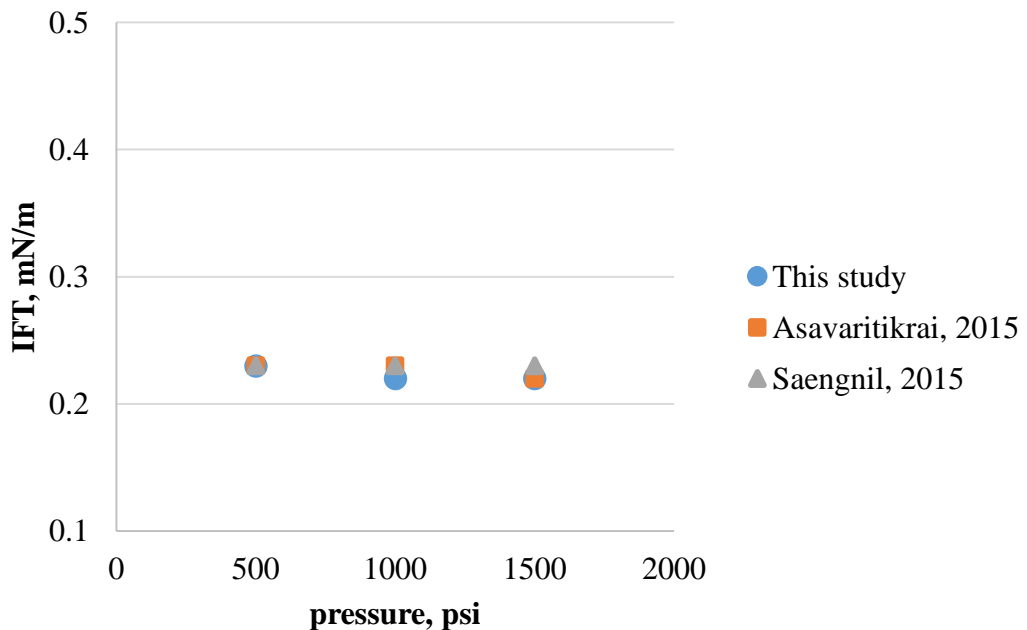
Figure 4.1 Equipment verification result (NaOH concentration = 0.05 wt.%, pressure = 1,000 psi, salinity = 750 ppm)

Table 4.1 Equipment verification result (NaOH concentration = 0.05 wt.%, pressure = 1,000 psi, salinity = 750 ppm)

Pressure (psi)	IFT (mN/m)			% Maximum error
	This study	Asavaritikrai, 2015	Saengnil, 2015	
500	0.23	0.23	0.23	0
1000	0.22	0.23	0.23	4.3
1500	0.22	0.22	0.23	4.3

The IFT result from the study got along well with the results from the previous works with a maximum error of 4.3%. Consequently, it can be concluded that the equipment and procedure valid in order to perform a further study of this research.

4.2 Effect of Pressure on the Interfacial Tension

According to the initial reservoir pressure in northern oilfield of 1500-1700 psi, the pressure used in this study is ranged from 1000 to 2,000 psi in order to cover the wide range of actual operations such as reservoir pressure The results reveal that the change in pressure does not have much effect on the IFT as shown in Figure 4.2 and Table 4.2 as the IFT does not change when pressure changes. The differences are 0.8% and 1.2% when pressures change from 1000 to 1,500 psi and from 1,500 to 2,000 psi, respectively in case of 0.05% surfactant and 80°C. It can be assumed that pressure can be neglected in the application of IFT reduction for surfactant flooding at this oilfield. The effect corresponds to the previous work of Saengnil (2015) and Asavaritikrai (2016) . Therefore, pressure can be neglected in the further study.
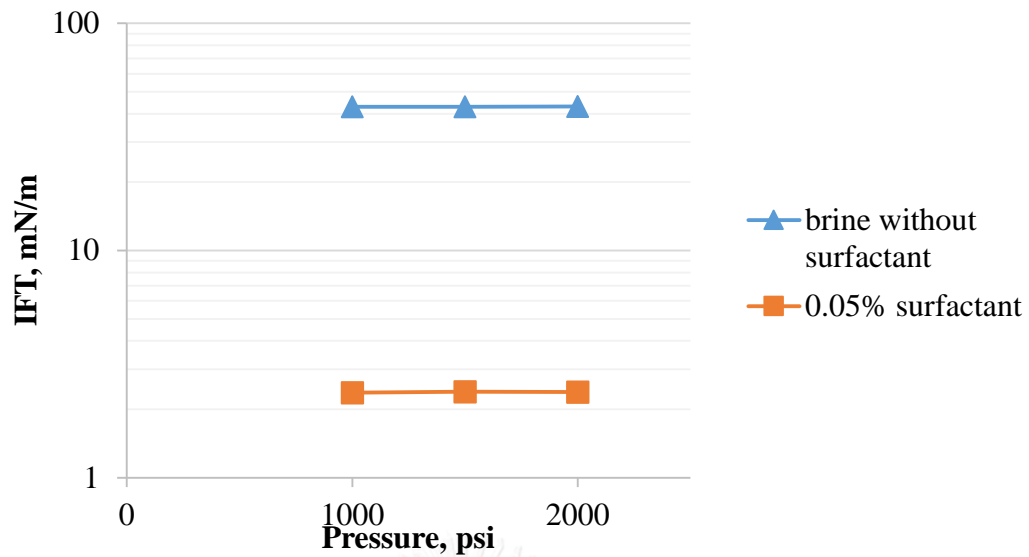
Figure 4.2 Effect of pressure on the IFT (SDBS concentration = 0.05 wt.%,
temperature = 80°C, salinity = 15,000 ppm)

Table 4.2 Effect of pressure on the IFT (SDBS concentration = 0.05 wt.%,
temperature = 80°C, salinity = 15,000 ppm)

Pressure (psi)	IFT (mN/m)	
	Brine without surfactant	0.05% Surfactant
1000	42.97	2.37
1500	42.93	2.35
2000	43.01	2.38

A slight changing in IFT from varying in pressure can be explained by
intermolecular force. Due to the phase of this experiment which is liquid (oil/water)
which has high intermolecular force compared to gas, the changing in pressure does not
affect to IFT. Firoozabadi et al. (1988) studied the IFT in brine and three reservoir oils
system. Their result shows that only one system of reservoir oil, the IFT increased with
increase pressure. On the other hands, the other systems are not much affected by
pressure change. Hassan et al. (1953) concluded that in the range of 1 to 204 atm with
constant temperature, the increasing of pressure shows slightly change on IFT. Thus,
this experimental measurement was operated only at 1,500 psig throughout this study.

4.3 Effect of Type of Surfactant Solution on the Interfacial Tension

There are 4 types of surfactant used in this study, which are sodium dodecyl benzene sulfonate (SDBS), toluene 4-sulfonic acid sodium salt (TSS), sodium 4-vinylbenzene sulfonate (SVBS) and 3-sulfopropyl methacrylate (SPM). The results of all conditions are presented in Table 4.3 to 4.6 based on the types of the surfactant used. The comparison of the results among all surfactant at different concentrations are shown in Figure 4.3 to 4.6

Table 4.3 Results of the IFT of Sodium dodecyl benzene sulfonate solution (in mN/m)

Conc.	Brine	IFT (mN/m)		
(wt.%)	(ppm)	70°C	80°C	90°C
0.05	0	18.61	18.51	18.47
	7500	3.22	3.20	3.15
	10000	2.73	2.70	2.65
	15000	2.45	2.35	2.30
	17500	1.57	1.56	1.54
0.1	0	8.93	8.79	8.75
	7500	2.91	2.81	2.76
	10000	2.17	2.14	2.12
	15000	1.71	1.60	1.54
	17500	1.21	1.17	1.15
0.5	0	6.32	6.29	6.24
	7500	2.08	2.04	1.99
	10000	1.52	1.48	1.42
	15000	1.12	1.05	1.01
	17500	0.97	0.95	0.92
1	0	5.58	5.55	5.49
	7500	1.82	1.75	1.70
	10000	1.39	1.32	1.29
	15000	0.93	0.90	0.87
	17500	0.87	0.84	0.80

Table 4.4 Results of the IFT of Toluene 4-sulfonic acid sodium salt solution

(in mN/m)

Conc. (wt.%)	Brine (ppm)	IFT (mN/m)		
		70°C	80°C	90°C
0.05	0	45.55	44.27	43.26
	7500	44.21	43.40	42.51
	10000	43.71	42.56	41.33
	15000	42.89	41.42	40.88
	17500	41.37	40.85	39.55
0.1	0	44.04	43.36	41.32
	7500	43.19	42.35	40.53
	10000	42.63	41.85	39.44
	15000	41.70	39.76	38.49
	17500	39.83	38.23	37.67
0.5	0	45.28	43.48	41.31
	7500	43.31	42.19	40.65
	10000	42.49	40.35	37.88
	15000	41.27	39.24	36.76
	17500	39.54	38.42	35.31
1	0	40.13	38.17	37.77
	7500	37.31	35.79	34.22
	10000	36.51	34.63	33.87
	15000	35.72	33.69	33.01
	17500	32.61	32.00	31.54

Table 4.5 Results of the IFT of Sodium 4-vinylbenzene sulfonate solution (in mN/m)

Conc. (wt.%)	Brine (ppm)	IFT (mN/m)		
		70°C	80°C	90°C
0.05	0	44.00	43.08	41.73
	7500	43.19	41.71	40.95
	10000	42.58	41.44	40.44
	15000	41.68	40.67	39.12
	17500	40.37	39.71	38.76
0.1	0	43.68	42.70	40.88
	7500	42.32	40.84	38.18
	10000	40.57	39.39	37.33
	15000	39.94	37.82	36.69
	17500	38.73	37.35	35.13
0.5	0	42.31	41.71	39.56
	7500	40.67	38.81	37.09
	10000	39.86	37.51	35.39
	15000	38.72	35.46	34.90
	17500	36.81	35.22	34.70
1	0	40.31	38.46	36.82
	7500	38.46	36.63	35.64
	10000	36.73	35.07	33.73
	15000	35.20	33.23	32.55
	17500	33.94	32.13	30.40

Table 4.6 Results of the IFT of 3-Sulfopropyl methacrylate solution (in mN/m)

Conc. (wt.%)	Brine (ppm)	IFT (mN/m)		
		70°C	80°C	90°C
0.05	0	45.71	44.13	42.72
	7500	44.61	42.90	41.89
	10000	43.82	42.40	41.72
	15000	42.30	41.28	40.61
	17500	41.25	40.22	39.20
0.1	0	45.28	43.58	42.09
	7500	44.35	42.99	41.49
	10000	43.13	41.92	41.09
	15000	41.82	40.45	39.07
	17500	40.77	39.54	38.46
0.5	0	43.12	41.70	40.41
	7500	42.30	41.27	40.66
	10000	41.44	40.01	39.35
	15000	40.07	39.49	38.19
	17500	39.64	38.61	37.49
1	0	41.67	40.47	39.47
	7500	40.87	39.41	38.04
	10000	39.88	38.09	37.11
	15000	38.87	38.51	36.39
	17500	38.04	37.11	35.73

Figure 4.3 Effect of types of surfactant solution on the IFT at 0.05 wt.% surfactant
concentration at salinity = 15,000 ppm

Figure 4.4 Effect of types of surfactant solution on the IFT at 0.1 wt.% surfactant
concentration at salinity = 15,000 ppm

Figure 4.5 Effect of types of surfactant solution on the IFT at 0.5 wt.% surfactant concentration at salinity = 15,000 ppm
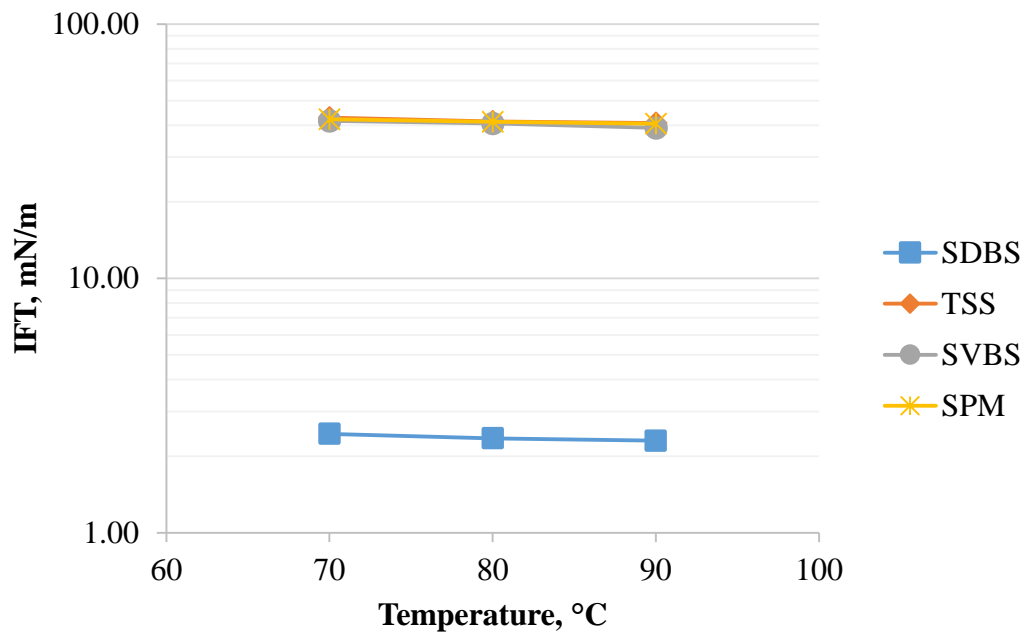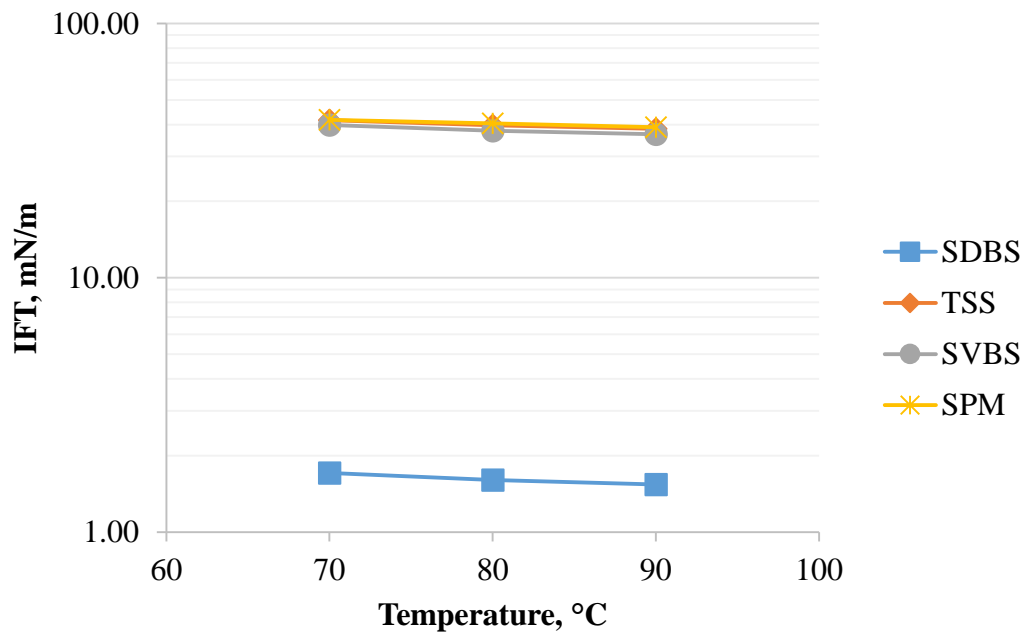

Figure 4.6 Effect of types of surfactant solution on the IFT at 1 wt.% surfactant concentration at salinity = 15,000 ppm
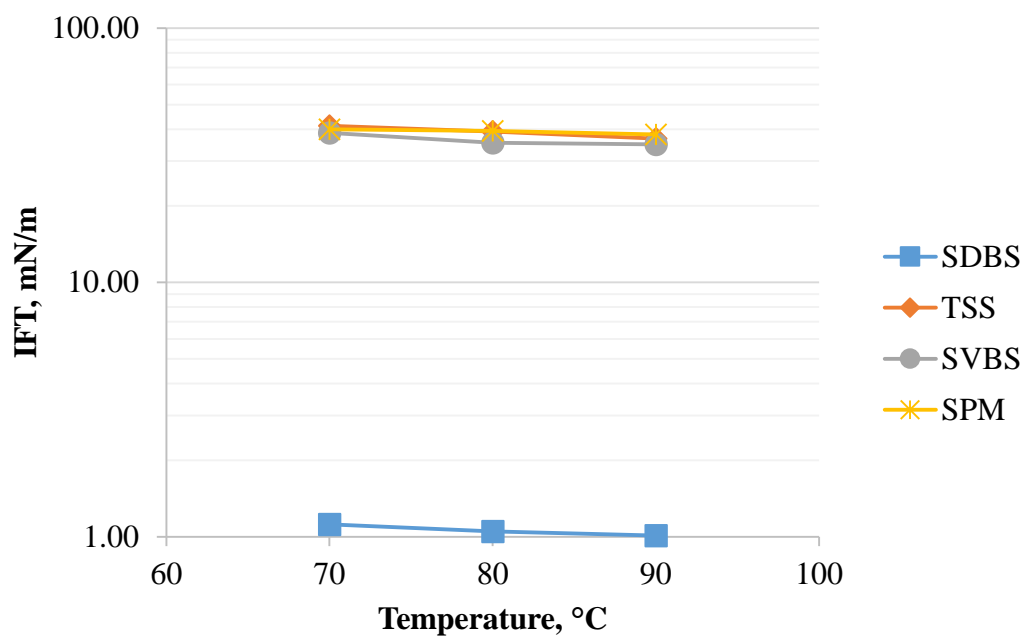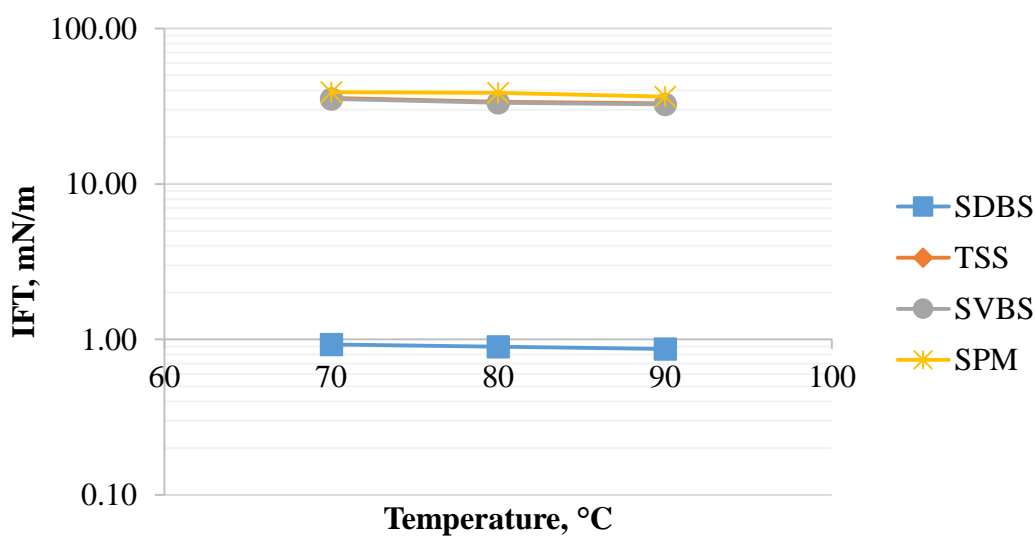
According to the results, sodium dodecylbenzene sulfonate as a surfactant solution gives the lowest IFT compared to other solutions. In the case of sodium dodecyl benzene sulfonate at 0.05 wt.%, IFT is less than 10 mN/m. Increasing in

surfactant concentration, more decreasing in IFT value. At the concentration of 0.5 wt.%, the IFT values are less than 1.00 mN/m. On the other hands, IFT reduction for the other chemicals shows slightly change which still higher than 30 mN/m at 1 wt.%. By using sodium dodecylbenzene sulfonate as a surfactant, the IFT value reduces up to 98.23% while toluene 4-sulfonic acid sodium salt, sodium 4-vinylbenzene sulfonate and 3-sulfopropyl methacrylate, IFT value reduces up to 32.33%, 34.77% and 23.34%, respectively at 90°C, 17,500 ppm in salinity and 1 wt% surfactant concentration.

To observe the effect of hydrocarbon chain lengths attached to the benzene ring of sulfonate surfactant, sodium dodecyl benzene sulfonate and toluene 4-sulfonic acid sodium salt whose have different in hydrocarbon chain lengths were used to measure IFT. The results show that the longer of hydrocarbon chain exhibits the higher in IFT reduction. In order to explain the IFT reduction behavior with sulfonate-surfactant structure, equivalent alkane carbon number or EACN is applied. The equivalent alkane carbon number (EACN) concept is the substitution of an alkane or an alkane mixture for crude oil for phase volume or interfacial studies which have been proposed by Canyias et al. (1976). The suitable surfactant for IFT reduction should have the same EACN in its structure with crude oil. The EACN for all surfactants is shown in Table 4.7.

Table 4.7 EACN of all surfactant and northern oil sample

Surfactant type	EACN
Crude oil	14.8
Sodium dodecyl benzene sulfonate	15
Toluene 4-sulfonic acid sodium salt	1
Sodium 4-vinylbenzene sulfonate	1
3-Sulfopropyl methacrylate	2

From the Table, sodium dodecyl benzene sulfonate presents the similar EACN with crude oil; thus, it shows higher potential to reduce IFT than the others which correspond to the study of the relationship between surfactant structure and IFT performance at difference types of alkyl benzene sulfonate surfactant by Youyi (2014). The results show that the suitable surfactant for surfactant flooding has EACN around 13 -14 which is corresponding to the carbon-chain length in crude oil which has carbon in the range of 16 – 18. It can be concluded that carbon chain length and branch structure have an important role in alkyl benzene sulfonate for IFT reduction (Youyi, 2014).

To observe the chemical bonding effect, the IFT results of sodium dodecyl benzene sulfonate and toluene 4-sulfonic acid sodium salt which have different in chemical bonding to ring structure are compared. IFT reduction shows the similar trend for both cases. Therefore, it can be concluded that there is no dominant effect on chemical bonding because the solubility of water and crude oil can be only effected by the polarity of chemical and solution at the same condition. Moreover, both chemicals have the same hydrocarbon chain length which represents to the same EACN, so it shows the similar results in IFT reduction.

Finally, to understand the effect of the molecular structure of surfactant with and without benzene ring, Sodium 4-vinylbenzenesulfonate which has the benzene ring and 3-Sulfopropyl methacrylate which has no benzene ring in its structure are used to observe the IFT reduction. The results illustrate that the present of the benzene ring in surfactant structure provides positive effect in IFT reduction because benzene ring represented the hydrophobic portion give the increasing solubility of the surfactant in crude oil.

4.4   Effect of Surfactant Concentration on the Interfacial Tension

The surfactant concentration is initially varied from zero to 1.0%wt. for all chemical to observe the amount of IFT reduction and to select the appropriate concentrations for further study. From Figure 4.7 to Figure 4.10 and Table 4.8 to Table 4.11, present the results of all effect of solution concentration of all chemical on IFT reduction ranging from 0 to 1.0 wt.%.
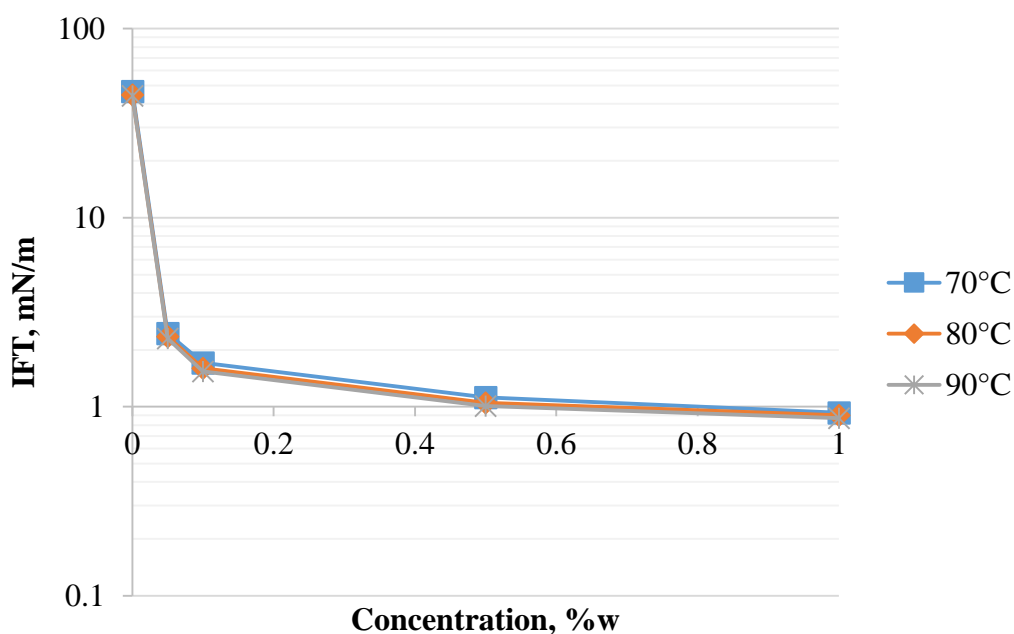
Figure 4.7 Effect of Sodium dodecyl benzene sulfonate's concentration in the wide range on the IFT (salinity = 15,000 ppm)

Table 4.8 Effect of Sodium dodecyl benzene sulfonate's concentration in the wide range on the IFT (salinity = 15,000 ppm)

Conc. of SDBS (wt.%)	0	0.05	0.1	0.5	1.0
IFT at 70°C (mN/m)	46.61	2.45	1.71	1.12	0.93
IFT at 80°C (mN/m)	44.75	2.35	1.60	1.05	0.90
IFT at 90°C (mN/m)	44.23	2.30	1.54	1.01	0.87
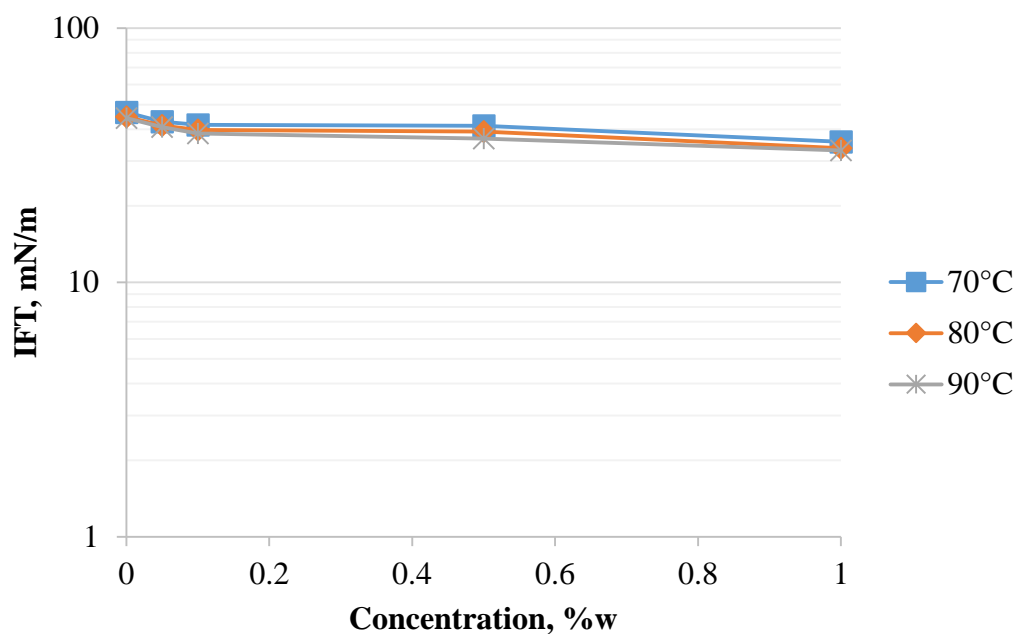
Figure 4.8 Effect of Toluene 4-sulfonic acid sodium salt's concentration in the wide range on the IFT (salinity = 15,000 ppm)

Table 4.9 Effect of Toluene 4-sulfonic acid sodium salt's concentration in the wide range on the IFT (salinity = 15,000 ppm)

Conc. of TSS (wt.%)	0	0.05	0.1	0.5	1.0
IFT at 70°C (mN/m)	46.61	42.89	41.70	41.27	35.72
IFT at 80°C (mN/m)	44.75	41.42	39.76	39.24	33.69
IFT at 90°C (mN/m)	44.23	40.88	38.49	36.76	33.01
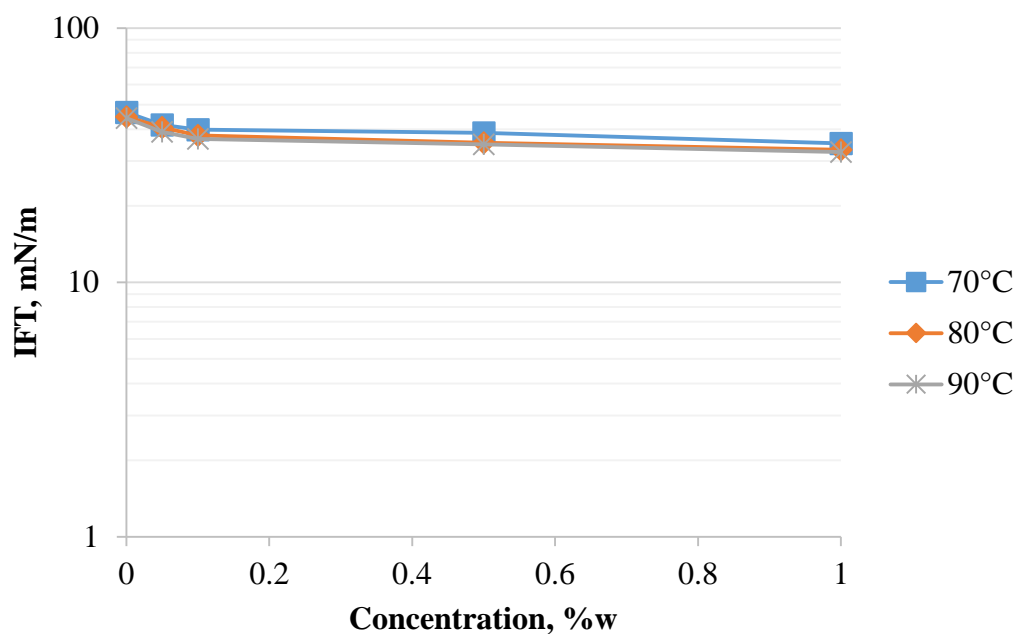
Figure 4.9 Effect of Sodium 4-vinylbenzene sulfonate's concentration in the wide
range on the IFT (salinity = 15,000 ppm)

Table 4.10 Effect of Sodium 4-vinylbenzene sulfonate's concentration in the wide
range on the IFT (salinity = 15,000 ppm)

Conc. of SVBS (wt.%)	0	0.05	0.1	0.5	1.0
IFT at 70°C (mN/m)	46.61	41.68	39.94	38.72	35.20
IFT at 80°C (mN/m)	44.75	40.67	37.82	35.46	33.23
IFT at 90°C (mN/m)	44.23	39.12	36.69	34.90	32.55
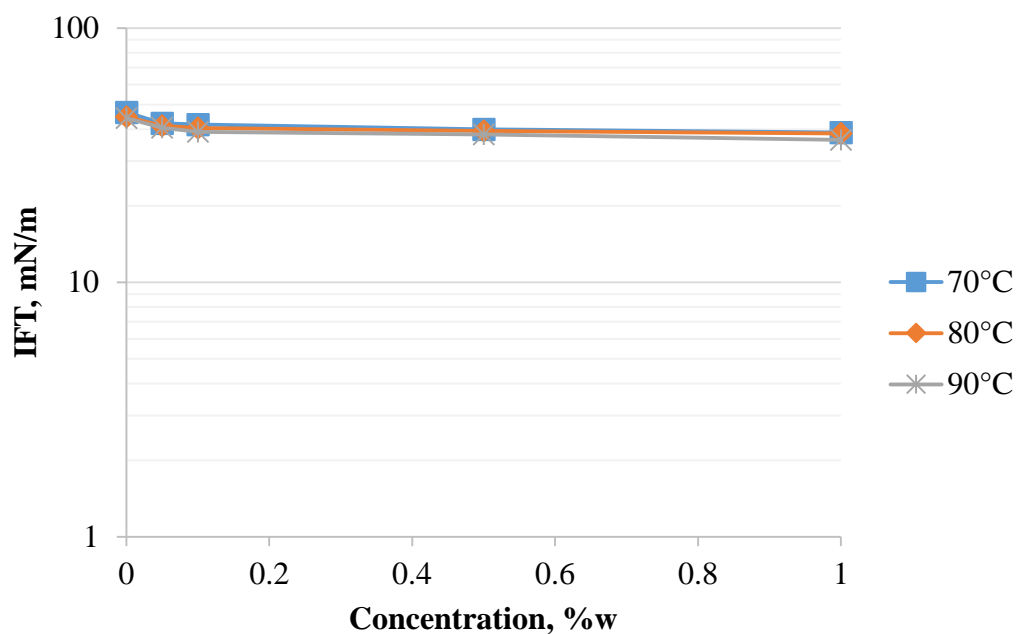
Figure 4.10 Effect of 3-Sulfopropyl methacrylate's concentration in the wide range on the IFT (salinity = 15,000 ppm)

Table 4.11 Effect of 3-Sulfopropyl methacrylate's concentration in the wide range on the IFT (salinity = 15,000 ppm)

Conc. of SPM (wt.%)	0	0.05	0.1	0.5	1.0
IFT at 70°C (mN/m)	46.61	42.30	41.82	40.07	38.87
IFT at 80°C (mN/m)	44.75	41.28	40.45	39.49	38.51
IFT at 90°C (mN/m)	44.23	40.61	39.07	38.19	36.39

The results show that the increase in the surfactant concentration provides the reduction of IFT for all types of surfactant solution. For sodium dodecyl benzene sulfonate solution, the increase in the surfactant concentration can drastically alter the IFT up to 98.23%. It can explain that at higher surfactant concentration, the surfactant monomer can be present at the interface between oil and solution which resulting in decreasing the IFT. IFT starts less than 1 mN/m when the surfactant concentration is

more than 0.5 wt.%. Exceeding this concentration, the IFT is relatively stable because of sufficient amount of the surfactant monomer at the interface.

For the other solutions, the higher concentration can also reduce the IFT but at low efficiency compared to with the sodium dodecyl benzene sulfonate. The IFT is still higher than 30 mN/m when the concentration is at 1 wt.%. Toluene 4-sulfonic acid sodium salt, sodium 4-vinylbenzene sulfonate and 3-sulfopropyl methacrylate can reduce the IFT down to 32.33%, 32.33% and 23.34% at 90°C, 17,500 ppm in salinity and 1.0 wt% surfactant concentration, respectively. It can be explained that those surfactants show less efficient in the IFT reduction because they have no suitable structure for the crude oil which can be observed from equivalent alkane carbon number.

4.5   Effect of Temperature on the Interfacial Tension

Temperature for this study is varied in the range between 70 and 90°C to cover the operating condition in the petroleum oilfield and to see the tendency of IFT reduction. The results are illustrated in Figure 4.11 to Figure 4.14 and Table 4.12. The increase of temperature always gives the declination of the IFT for all types of the surfactant solutions because the increasing in temperature can reduce the free energy of crude oil and water. Therefore, more surfactant monomer can form at the interface leading the declination of IFT. However, the IFT reduction on temperature shows less effect when compare with that of the concentration of surfactant and brine. The percentages of the IFT reduction when increasing temperature range from 3.75 to 6.88%, 0.51 to 1.85%, 0.09 to 1.49% and 0.07 to 1.12% for sodium dodecyl benzene sulfonate, toluene 4-sulfonic acid sodium salt, sodium 4-vinylbenzene sulfonate and 3-sulfopropyl methacrylate, respectively.
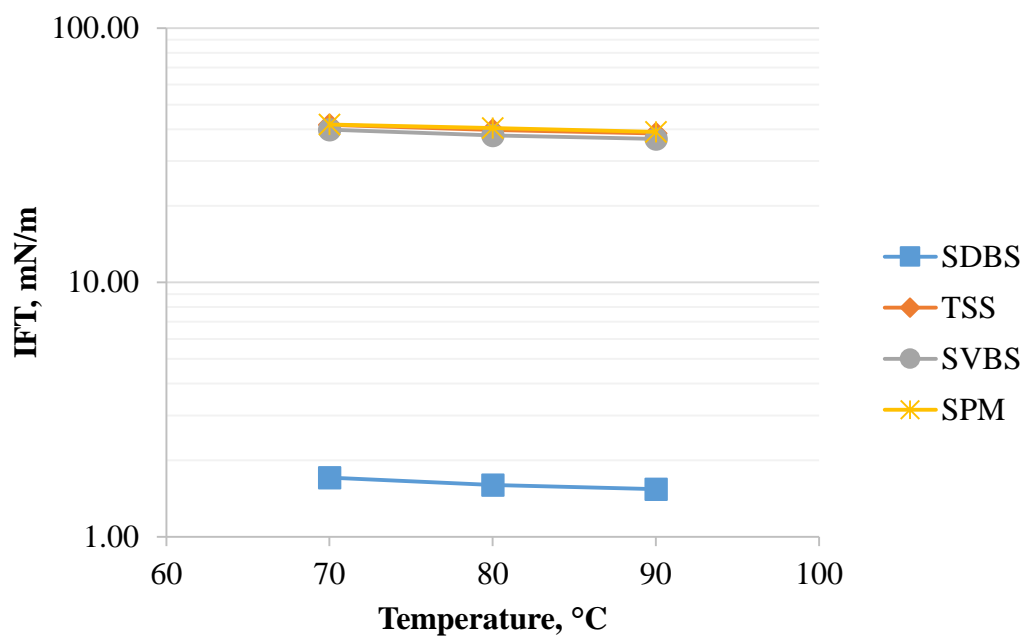
Figure 4.11 Effect of temperature on the IFT (Surfactant concentration = 0.1 wt.%, salinity = 15,000 ppm)

Table 4.12 Effect of temperature on the IFT (Surfactant concentration = 0.1 wt.%, salinity = 15,000 ppm)

IFT (mN/m)	Temperature		
	70°C	80°C	90°C
SDBS solution	1.71	1.60	1.54
TSS solution	41.70	39.76	38.49
SVBS solution	39.94	37.82	36.69
SPM solution	41.82	40.45	39.07
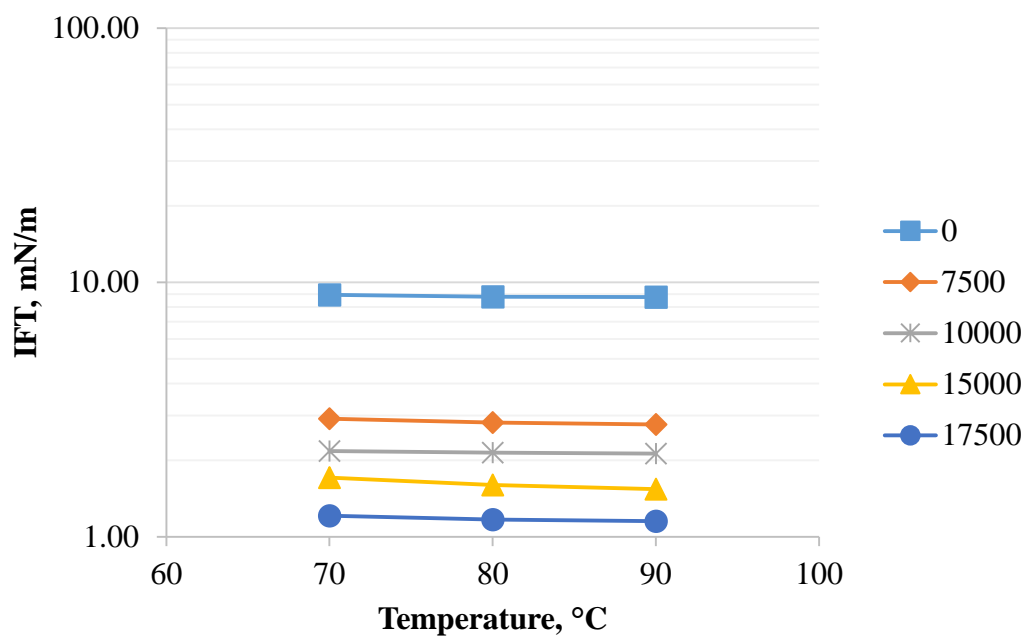
Figure 4.12 Effect of temperature on the IFT with 0.1 wt % Sodium dodecyl benzene

sulfonate solution
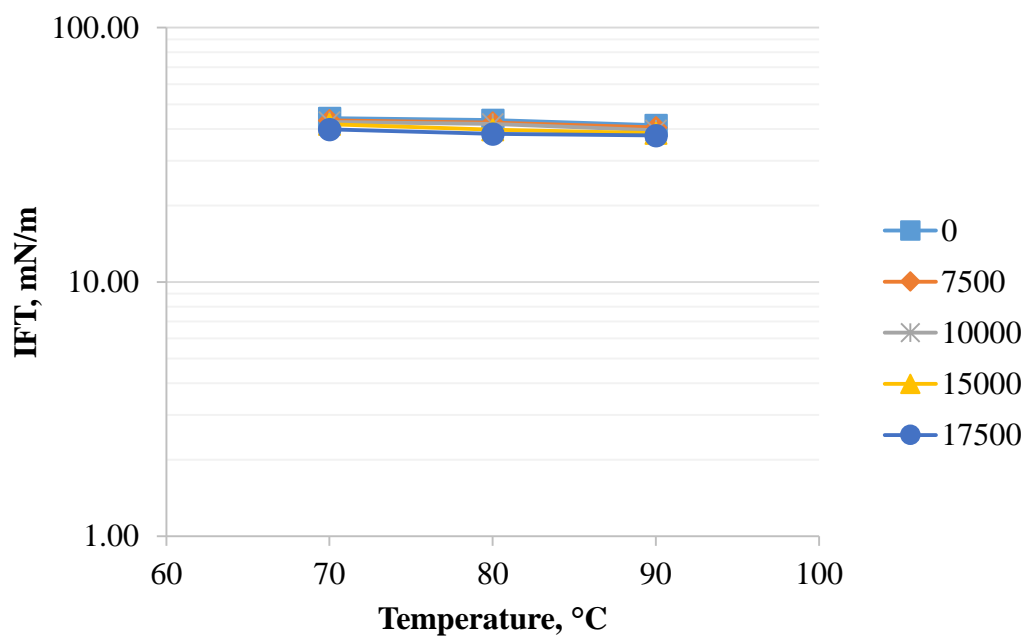
Figure 4.13 Effect of temperature on the IFT with 0.1 wt % Toluene 4-sulfonic acid

sodium salt solution

Figure 4.14 Effect of temperature on the IFT with 0.1 wt % Sodium 4-vinylbenzene
sulfonate solution

Figure 4.15 Effect of temperature on the IFT with 0.1 wt % 3-Sulfopropyl
methacrylate solution

Temperature has slightly effect on the IFT reduction because the temperature range in this study which is 70°C - 90°C is small therefore it shows small change in IFT reduction.

However, theoretical, the higher temperature, the more surfactant can be formed at the interface between oil and water. The results show that the reduction in IFT for sodium dodecyl benzene sulfonate solution is found to be more efficient comparing with the others because it has the most suitable st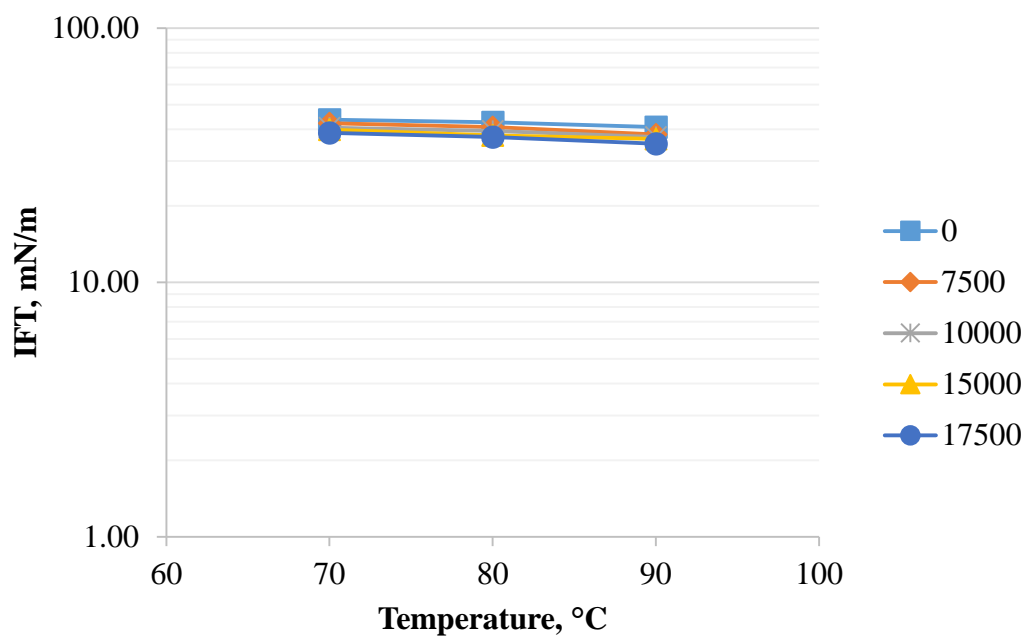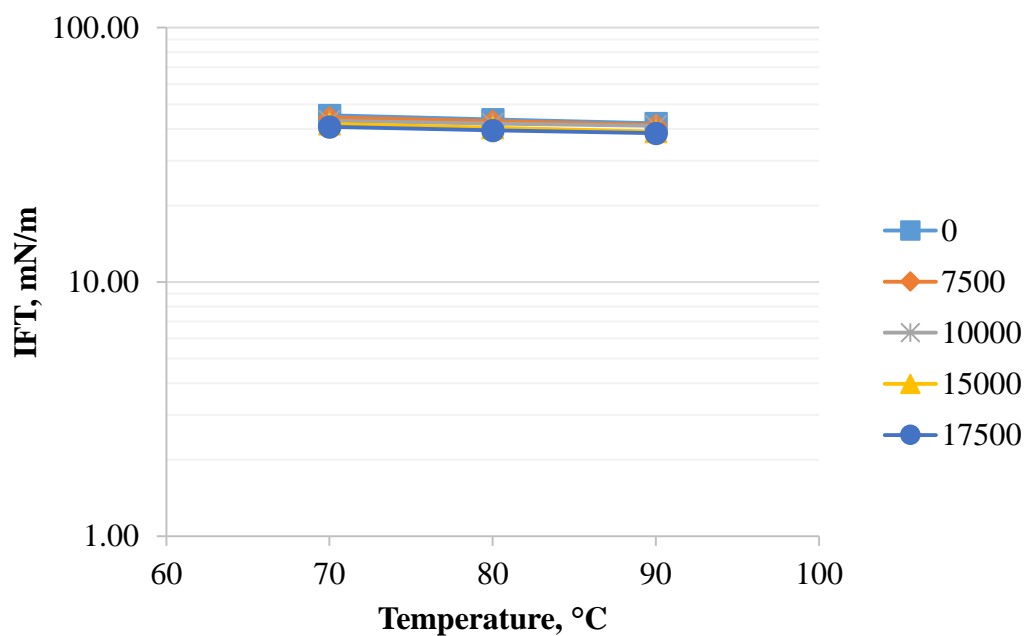ructure when comparing with the oil structure. In addition, this phenomena can be explain by solubility concept. When temperature increase, the solubility will be increased. At high temperature, the solubility of water and surfactant increases leading to the lowering of the IFT between two fluids.

There are many studies that can explain this phenomenon.Wei (2005) reports that the increasing in temperature can reduce the free energy between two immiscible fluids which leading to an increase in the solubility of water in the oil. Therefore, IFT is altered. Okasha et al. (2009) study the intermolecular forces between oil/water interface. They conclude that intermolecular forces are weakened at higher temperature leading to the reduction in IFT. The experimental results show the same trend with the Hjelmeland's study (Hjelmeland et al., 1986).

4.6   Effect of Salinity on the Interfacial Tension

According to Table 3.3 which shows the produced water composition from the oilfield. The main ions in brine are sodium (36.4%) and chloride (58.7%).Therefore, in this study, the brine is prepared by dissolving sodium chloride in the distilled water. A number of salts are simulated base on the concentration of produced water from the northern oilfield and the proportion for each concentration can be found in Appendix A. The salinity is studied at 0, 7,500, 10,000, 15,000 and 17,500 ppm to see the effect on the IFT. The results are shown in Figure 4.16 to Figure 4.19.

Figure 4.16 Effect of salinity on the IFT (SDBS solution, temperature = 80°C)

Figure 4.17 Effect of salinity on the IFT (TSS solution, temperature = 80°C)

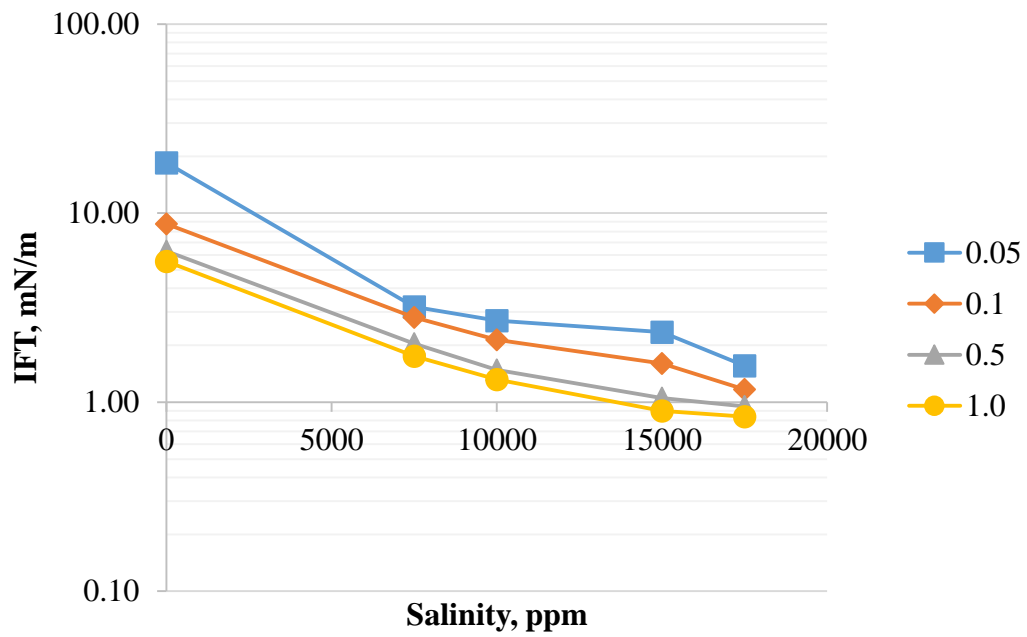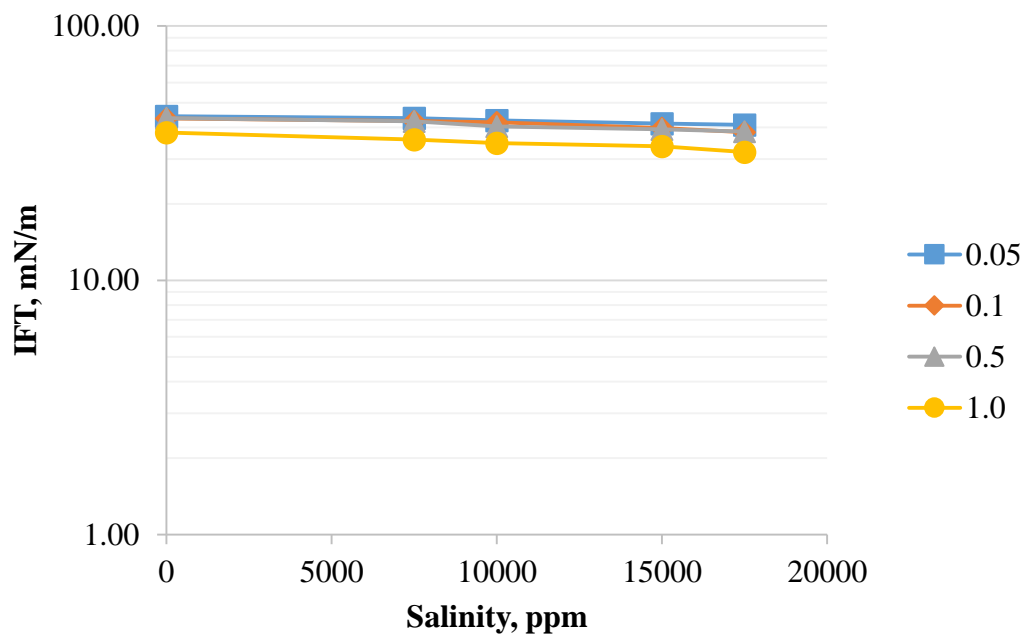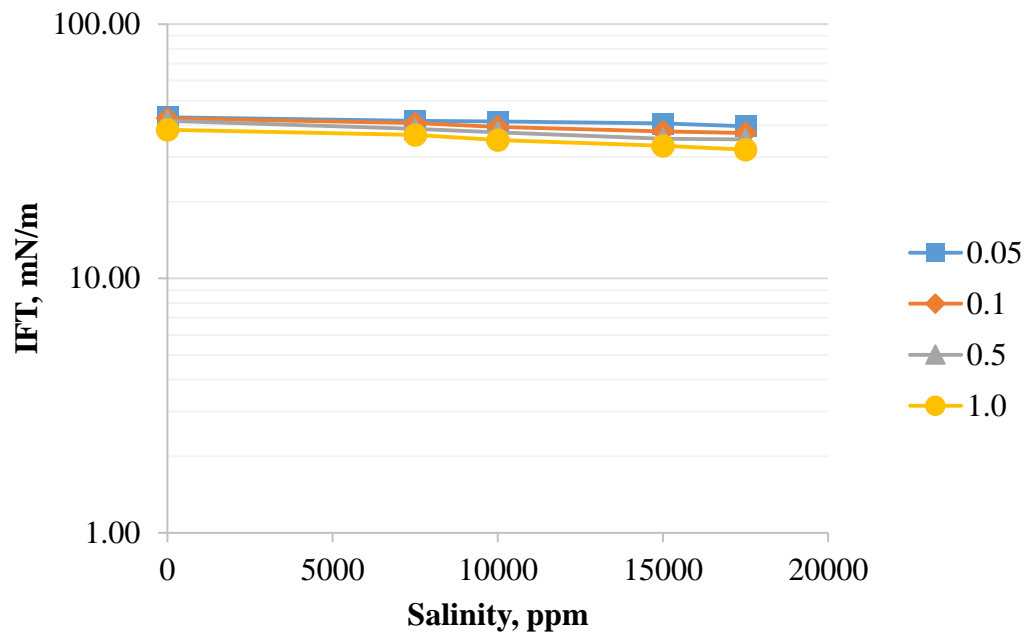Figure 4.18 Effect of salinity on the IFT (SVBS solution, temperature = 80°C)
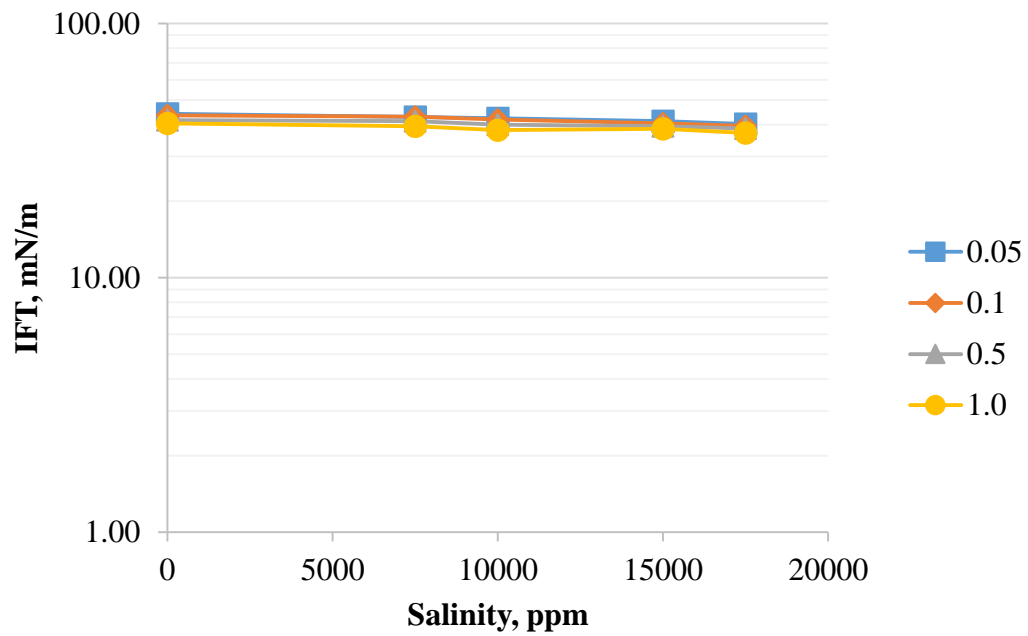
Figure 4.19 Effect of salinity on the IFT (SPM solution, temperature = 80°C)

The results illustrate that the effects of salinity ranging from 0 to 17,500 ppm on the IFT move the same directions in that IFT depends on the salinity of the aqueous phase. The changing in salinity impacts the relative solubility of surfactant in oil and water. Salt ions which have a higher impact than surfactant will push surfactant to the oil/water interface leading to the reduction in IFT. Khaksar Manshad et al. (2016) study the effects of water-soluble ions on interfacial tension between oil and brine in oil reservoirs. They have found that the presence of salt in solution can lower the interfacial tension between oil and water. Lashkarbolooki et al. (2016) investigate the effects of salinity, temperature, pressure, and crude oil type on the dynamic interfacial tensions. The lowering in IFT is presented with increase in salinity

4.7 Effect of Divalent Ions on the Interfacial Tension

Regarding all experiments in the previous sections, it is shown that they do not concern about the effect of divalent ions in brine. Consequently, in this part, the effect of divalent ions on IFT will be investigated. In the previous section, the divalent ions are not concerned because of their low concentration in produced water and can be neglected as shown in Table 3.3, potassium (0.3%), magnesium (0.2%) and sulfate (2.8%). In this study, potassium chloride and magnesium sulfate are added to the solution to simulate the brine solution based on the proportion of ions from produced water of the oilfield. The solution that contains divalent ions is tested at various temperatures for all surfactant types to compare the results with that of the solution without divalent ions. The results as shown in Figure 4.20 to Figure 4.21 and Table 4.13 to Table 4.14.
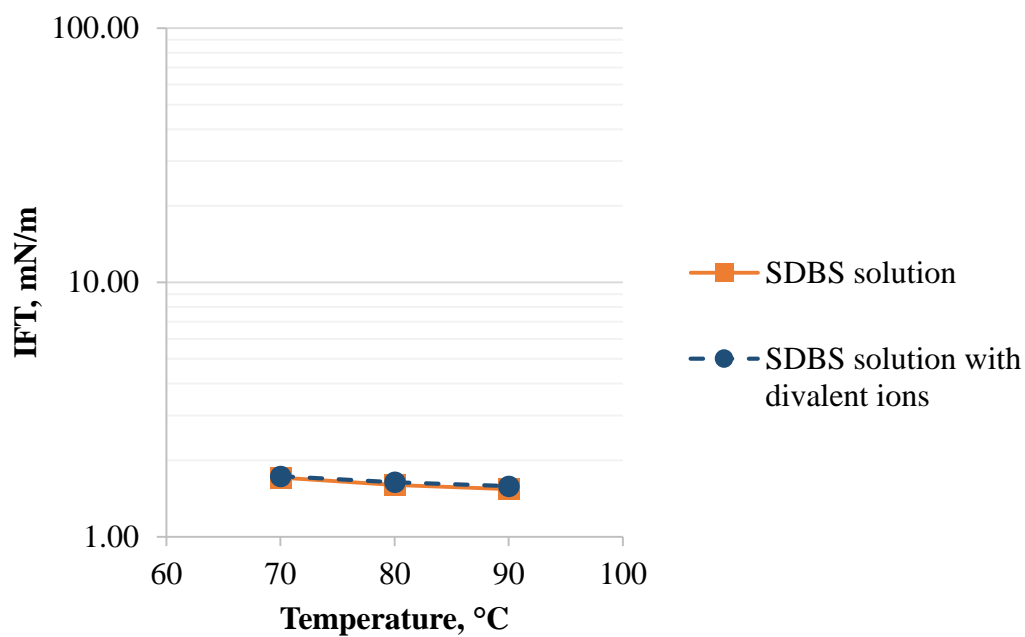
Figure 4.20 Effect of divalent ions on the IFT (SDBS solution = 0.1 wt.%, salinity = 15,000 ppm)

Table 4.13 Effect of divalent ions on the IFT (SDBS solution = 0.1 wt.%, salinity = 15,000 ppm)

IFT (mN/m)	Temperature		
	70°C	80°C	90°C
SDBS solution	1.71	1.60	1.54
SDBS solution with divalent ions	1.73	1.64	1.58
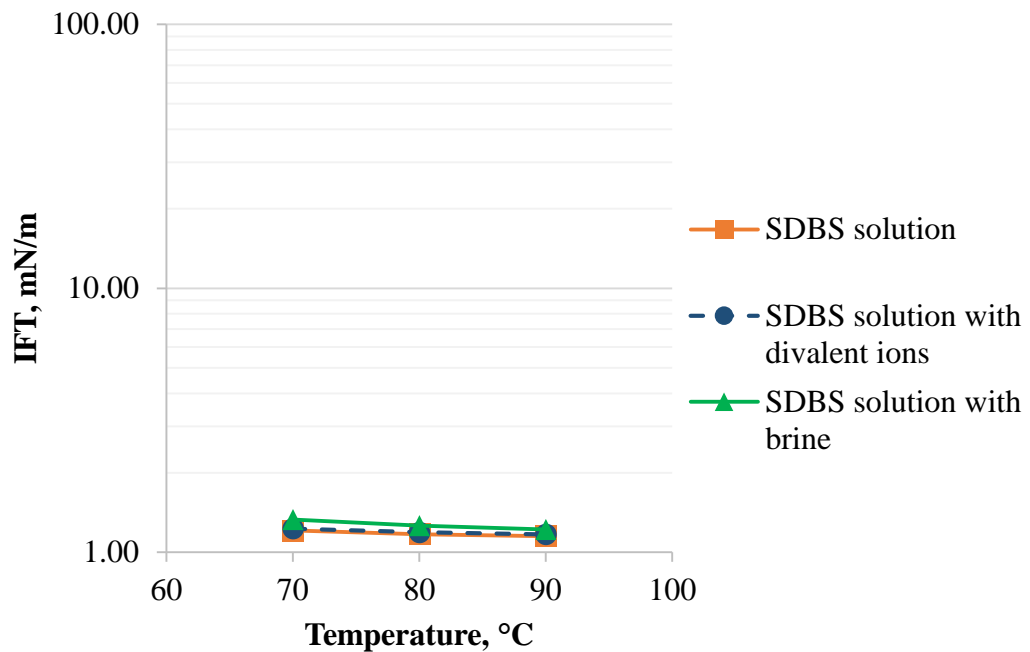
Figure 4.21 Effect of divalent ions on the IFT (SDBS solution = 0.1 wt.%,

salinity = 17,500 ppm)

Table 4.14 Effect of divalent ions on the IFT (SDBS solution = 0.1 wt.%,

salinity = 17,500 ppm)

IFT (mN/m)	Temperature		
	70°C	80°C	90°C
SDBS solution	1.21	1.17	1.15
SDBS solution with divalent ions	1.23	1.19	1.17
SDBS solution with northern brine	1.33	1.26	1.22

From the result shown in Figure 4.20 and Figure 4.21, since the surfactant solutions with and without divalent ions show comparatively similar IFT results. The IFT, therefore, is not affected by the divalent ions for this study because the proportion of divalent ion is considered relatively small amount comparing to the whole solution. However, theoretically, the divalent ion can destroy the ability of the surfactant to lowering the IFT.

4.8   Effect of co-surfactant mixing solution on the Interfacial tension

According to the previous results, it can be clearly seen that the IFT reduce down to 0.80 at the concentration of 1.0 wt.%, 17,500 ppm in salinity and 90°C for the case of sodium dodecyl benzene sulfonate. However, the study is restricted by the solubility of a single surfactant in brine solution because all of them can dissolve less at higher concentration. In order to overcome this problem, co-surfactant is added to increase the solubility of the surfactants so that the critical micelle concentration, the maximum point of IFT reduction, can then be determined.

The study of co-surfactant ability in dissolving more surfactants and reducing IFT can be done by mixing sodium dodecyl benzene sulfonate, SDBS, which is the best surfactant for lowering the IFT in this study and monoethanolamine, MEA, which is a waste product from carbon capture process in petrochemical process as a co-surfactant, at various temperatures. The IFT results are shown in Figure 4.22 and Table 4.15.
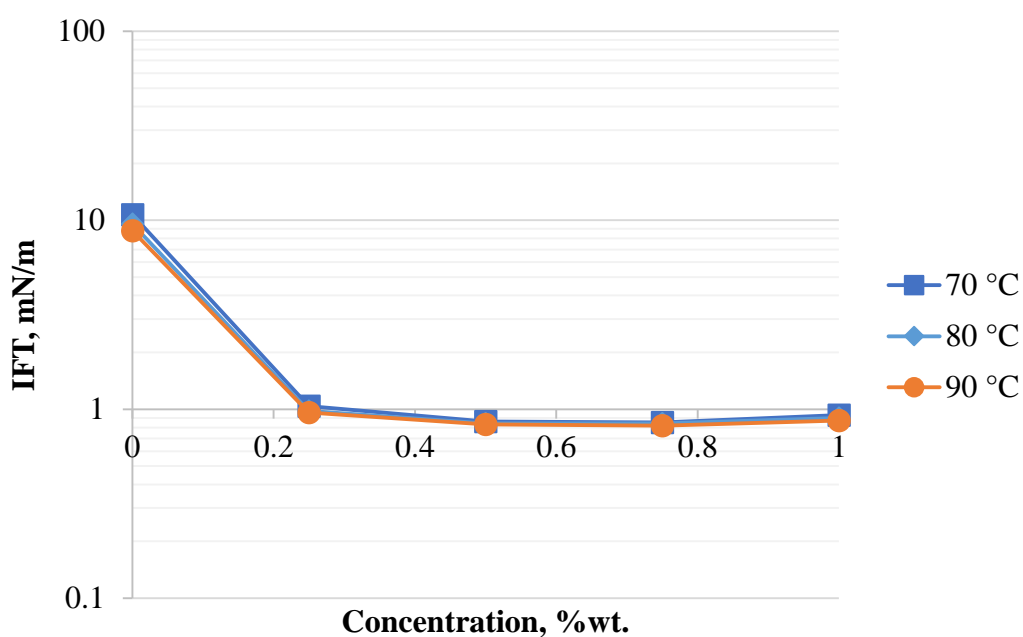
Figure 4.22 Effect of co-surfactant on the IFT (Salinity =15,000 ppm)

Table 4.15 Effect of co-surfactant on the IFT (Salinity =15,000 ppm)

Concentration		IFT (mN/m)		
		Temperature		
SDBS (wt.%)	MEA (wt.%)	70°C	80°C	90°C
1	0	0.93	0.90	0.87
0.75	0.25	0.85	0.84	0.82
0.50	0.50	0.86	0.84	0.83
0.25	0.75	1.04	0.98	0.96
0	1	10.68	9.54	8.81

A monoethanolamine alone can reduce IFT down to 8.81 mN/m at 15,000 ppm, 90°c. Although having the ability to reduce IFT, MEA's performance is incomparable to that of SDBS, which is the general property of MEA that is used to enhance the solubility of main-surfactant in solution.

The restriction of surfactant-brine solubility at high concentration is solved by using co-surfactant MEA, an amine compound, in determining the CMC point. The minimum IFT value can then be defined at this point.

The amount of SDBS added to brine and co-surfactant solution have to gradually increase for evaluating the CMC point, of which result was shown in Figure 4.23 and Table 4.16.
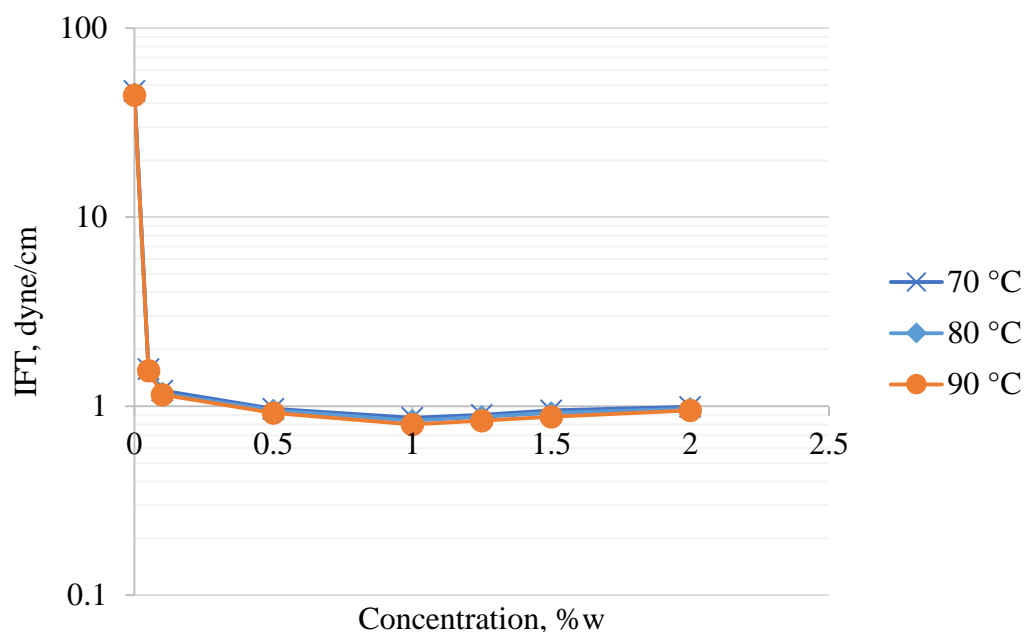
Figure 4.23 Critical micelle concentration for SDBS at 17,500 ppm

Table 4.16 Critical micelle concentration for SDBS at 17,500 ppm

SDBS (wt.%)	MEA (wt.%)	70°C	80°C	90°C
0	0	46.61	44.75	44.23
0.05	0	1.57	1.56	1.54
0.10	0	1.21	1.17	1.15
0.50	0	0.97	0.95	0.92
1	0	0.87	0.84	0.80
1.25	2	0.90	0.88	0.84
1.50	3	0.95	0.92	0.88
2.00	6	0.99	0.97	0.95

The result shown in Table 4.16 was strongly indicated that IFT continuously decreases as the concentration of SDBS increases; however, the IFT returns to increasing trend of the SDBS's concentration higher than 1.0 wt%. This phenomenon can be explained by micelle formation concept, which states that the increasing in surfactant concentration will create more surfactant monomer at the interface, resulting

in the decrement in IFT value. Nevertheless, the overwhelming amount of surfactant monomer will stimulate the micelle formation, negatively impact to the surfactant monomer at interface leading to the increment of IFT value.

In conclusion, the optimum CMC of surfactant that provides the lowest IFT value is at 1.00 wt%

4.9 Correlation

According to the experimental results, the SDBS is the suitable surfactant for surfactant flooding which can reduce IFT down to 0.80 mN/m. In order to predict the IFT value of SDSB as a surfactant for surfactant flooding, the empirical equation is developed base on laboratory results by using nonlinear regression and curve fitting technique. There are three parameters that can affect IFT, temperature, surfactant concentration and salinity. The empirical equation structure can be written as

$$\gamma = aC^b S^c T^d$$

Which γ is Interfacial tension [mN/m]

           C   is Surfactant concentration [wt.%]

           S   is Salinity [ppt]

           T   is Temperature [°c]

To determine coeffecient, a, b, c, d, nonlinear regression and curve fitting technique are used. The results are shown in Table 4.17

Table 4.17 Coefficient value evaluation

Coeffecient	value
A	17.592
B	-0.233
C	-0.782
D	-0.187

The empirical equation can be written as

$$\gamma = \frac{17.592}{C^{0.233}S^{0.782}T^{0.187}}$$

It can be used in a range of surfactant concentration from 0.05 to 1.0 wt%, salinity from 0 to 17,500 ppm, temperature from 70 to 90 °C. The comparison between predicted values and experiment values at vary concentration, salinity and temperature were illustrated in the Figure 4.24. From the results, the developed equation can predict the IFT value of sodium dodecyl benzene sulfonate solution which has the minimum error and maximum error equal to 0.09% and 21.56%, respectively. The experimental results, predicted results and also relative error are shown in Table 4.18 to Table 4.20.

$$\% \text{ Relative error} = \frac{\text{Predicted value} - \text{Experimental value}}{\text{Experimental value}} \times 100$$
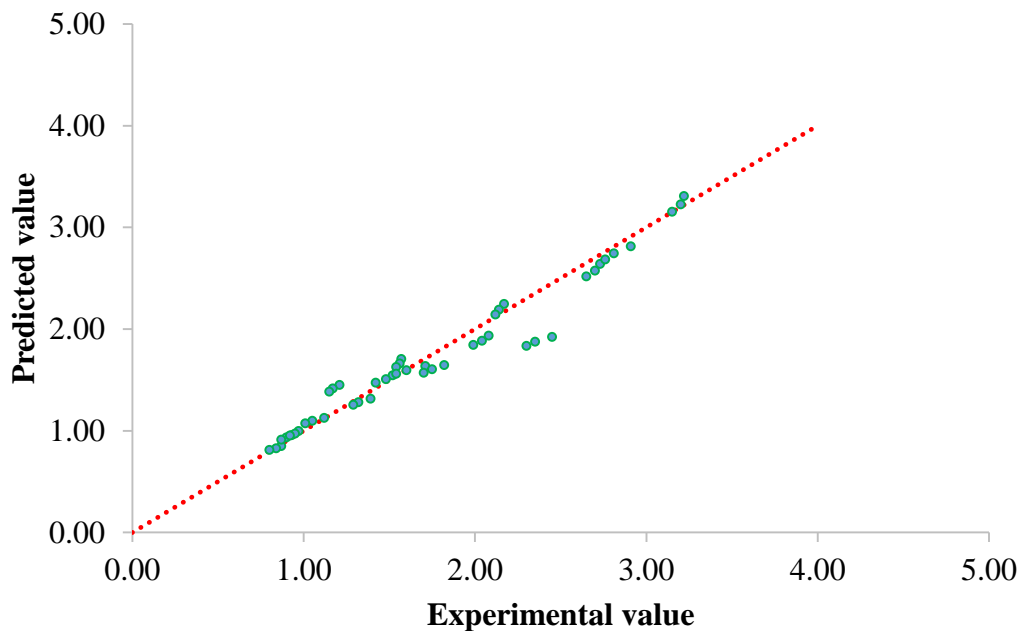
Figure 4.24 The IFT value comparison between predicted values and experiment values

Table 4.18 Comparison between predicted value and experimental value at 70°C

Concentration	Salinity	IFT, mN/m		
%w.	ppm	Predicted value	Experimental value	%Error
0.05	7500	3.30	3.34	2.63
0.05	10000	2.64	2.78	-3.34
0.05	15000	1.92	1.92	-21.56
0.05	17500	1.70	1.60	8.51
0.1	7500	2.81	2.82	-3.37
0.1	10000	2.25	2.35	3.47
0.1	15000	1.64	1.62	-4.37
0.1	17500	1.45	1.35	19.80
0.5	7500	1.93	1.90	-7.09
0.5	10000	1.54	1.58	1.53
0.5	15000	1.12	1.09	0.35
0.5	17500	1.00	0.91	2.71
1.0	7500	1.64	1.60	-9.65
1.0	10000	1.31	1.33	-5.54
1.0	15000	0.96	0.92	2.82
1.0	17500	0.85	0.77	-2.57

Table 4.19 Comparison between calculated value and experimental value at 80°C

Concentration %w.	Salinity ppm	IFT, mN/m		
		Predicted value	Experimental value	%Error
0.05	7500	3.22	3.26	0.72
0.05	10000	2.57	2.71	-4.67
0.05	15000	1.87	1.88	-20.24
0.05	17500	1.66	1.56	6.51
0.1	7500	2.74	2.75	-2.40
0.1	10000	2.19	2.29	2.33
0.1	15000	1.59	1.58	-0.32
0.1	17500	1.41	1.32	20.84
0.5	7500	1.88	1.85	-7.60
0.5	10000	1.51	1.54	1.70
0.5	15000	1.10	1.07	4.40
0.5	17500	0.97	0.89	2.28
1.0	7500	1.60	1.56	-8.36
1.0	10000	1.28	1.30	-2.98
1.0	15000	0.93	0.90	3.63
1.0	17500	0.83	0.75	-1.58

Table 4.20 Comparison between calculated value and experimental value at 90°C

Concentration %w.	Salinity ppm	IFT, mN/m		
		Predicted value	Experimental value	%Error
0.05	7500	3.15	3.18	0.09
0.05	10000	2.52	2.64	-4.99
0.05	15000	1.83	1.83	-20.28
0.05	17500	1.63	1.52	5.54
0.1	7500	2.68	2.68	-2.80
0.1	10000	2.14	2.23	1.05
0.1	15000	1.56	1.54	1.31
0.1	17500	1.38	1.28	20.26
0.5	7500	1.84	1.81	-7.35
0.5	10000	1.47	1.50	3.69
0.5	15000	1.07	1.04	6.17
0.5	17500	0.95	0.87	3.32
1.0	7500	1.57	1.52	-7.72
1.0	10000	1.25	1.27	-2.89
1.0	15000	0.91	0.88	4.87
1.0	17500	0.81	0.73	0.09

CHAPTER 5
CONCLUSION

This chapter concludes all results from the previous chapter. Recommendations are also provided for the future study.

5.1 Conclusions

In this study, the effects of parameters such as pressure, surfactant type, concentration, temperature, salinity, divalent and co-surfactant on the IFT of oil from northern oilfield are investigated. The IFT is measured by the IFT 700 equipment which detects the rising oil drop in the solution.

From the results, surfactant solution can lower IFT down to 98.23%, 32.33 % 34.77% and 23.34% by using sodium dodecyl benzene sulfonate, toluene 4-sulfonic acid sodium salt, sodium 4-vinylbenzene sulfonate and 3-Sulfopropyl methacrylate, respectively.

1. The pressure that used in this study is ranged from 1,000 to 2,000 psi. The results show that pressure has less effect in IFT reduction.

2. The hydrocarbon chain length shows positive effect on IFT reduction. It can explain by equivalent alkane carbon number concept. The suitable surfactant for IFT reduction should have the similar EACN with crude oil.

3. Chemical bonding effect show no effect on IFT reduction because the solubility can be only effected by the polarity of chemical and solution.

4. The presence of benzene ring in surfactant structure exhibits the positive effect on IFT reduction because of increase in hydrophobic portion.

3. The surfactant concentrations used in this study are 0, 0.05, 0.1, 0.5 and 1.0 wt.%. Increasing the surfactant concentration can effectively reduce the IFT.

For sodium dodecyl benzene sulfonate, the IFT reduce down to 0.80 mN/m at the surfactant concentration of 1.0 wt.%, 90°C and 17,500 ppm because of sufficient amount of the surfactant at the oil/water interface. For other solutions, the IFT is still higher than 30.00 mN/m when the concentration of surfactants is at 1 wt.%.

4. Temperature is varied in the range from 70°C to 90°C. According to the results, it can be concluded that an increase in temperature leads to slightly decrease in IFT for all surfactant solutions because of small in temperature change. However, Theoretical, increasing in temperature, more surfactant can form at the interface leading to decreasing in IFT.

5. Increasing salinity always leads to the reduction of the IFT for every type of the solution because changing in salinity impacts the relative solubility of surfactant in oil and water. In addition, salt ions which have higher impact than surfactant will push surfactant to the oil/water interface leading to the reduction in IFT.

6. Divalent ions have less effect on the IFT reduction because amount of divalent ion is considered relatively small comparing to the whole solution. Therefore, it is neglected in this study.

7. Co-surfactant can be used to improve solubility of surfactant in high salinity. In this study; however, the over amount of surfactant monomer shows negatively impact to IFT reduction.

8. The empirical equation is developed in this work can be used to predict the IFT value in that condition.

5.2   Recommendations

The following issues are recommended for the future study

1. Since the salinity used in the current study is high concentration, low salinity can be performed to see the effect on the IFT reduction.

2. IFT measurement of the oil and combination of other chemicals can be performed such as surfactant-polymer, alkaline-surfactant-polymer solution to observe the effectiveness of each combination.

3. After measuring the IFT as fundamental data, core flooding and EOR simulation can be performed to observe the wettability effect and oil production.

4. From the empirical equation, it cannot explain the physical property of parameters which are surfactant concentration, salinity and temperature to IFT reduction phenomena. Therefore, parameter should be studied in future to deepen the understanding in IFT reduction.

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APPENDIX

APPENDIX A
SOLUTION COMPOSITION

The brine used in this study was obtained by dissolving sodium chloride in the distilled water to make its proportion close to that of northern oilfield. The salinity was prepared at 7,500, 10,000, 15,000 and 17,500 ppm. The amount of salt at different salinity can be shown in the Table A.1.

Table A.1 Composition of the simulated brine

Salinity (ppm)	Sodium Chloride (mg/l)
7,500	7.5
10,000	10
15,000	15
17,500	17.5

APPENDIX B

EFFECT OF EACH PARAMETER

The description of effects of each parameter on the IFT is as described in Chapter 4.

Effect of Pressure on the Interfacial Tension
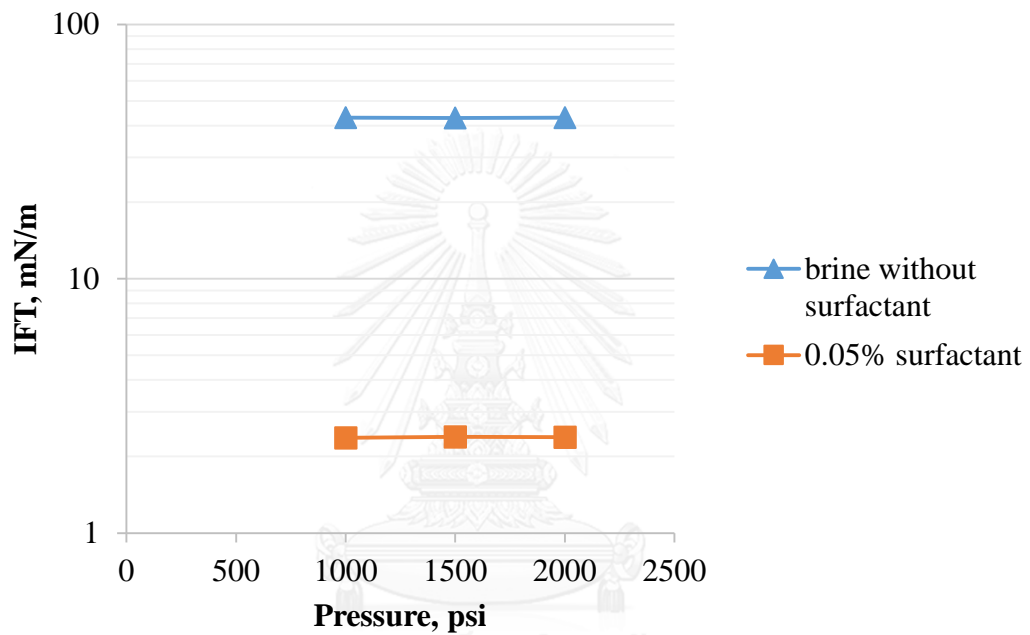
Figure B.1 Effect of pressure on the IFT (Surfactant concentration = 0.05 wt.%, temperature = 80°C, salinity = 15,000 ppm)

Effect of Surfactant type on the Interfacial Tension
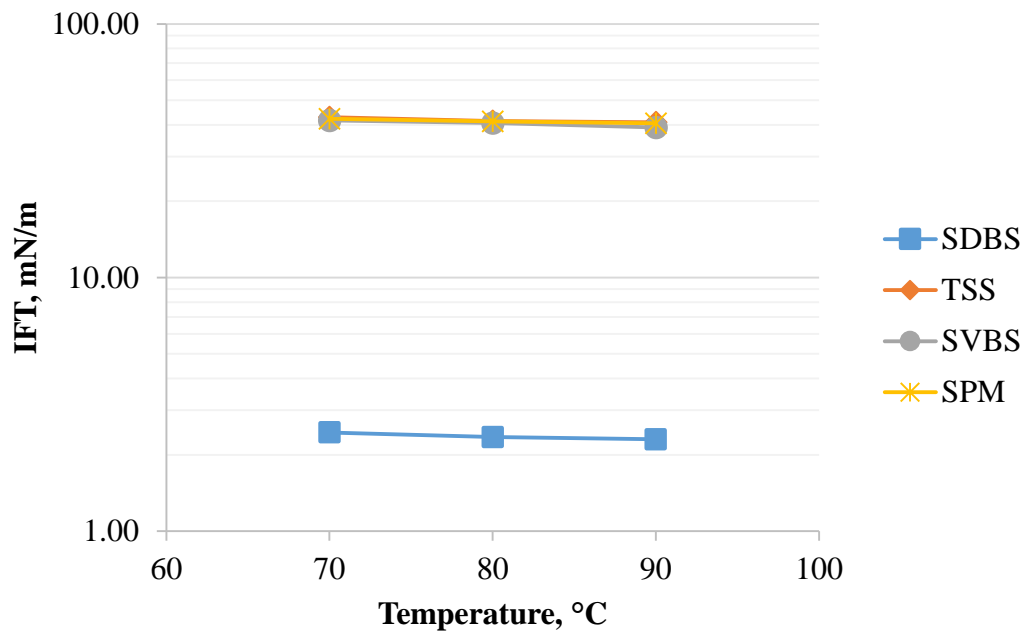
Figure B.2 Effect of type of surfactant solution on the IFT at 0.05 wt.% surfactant
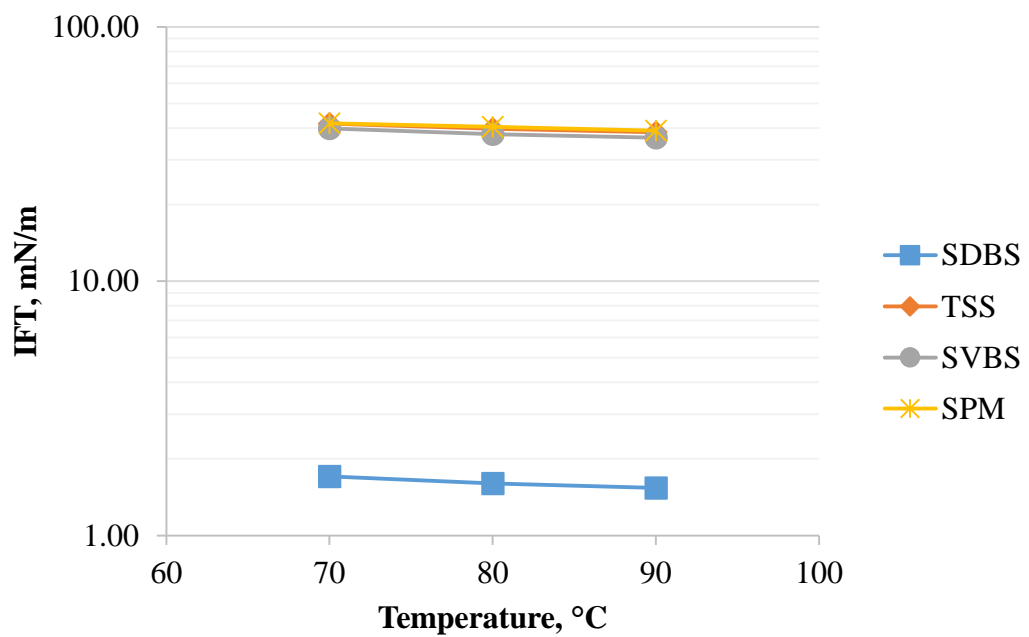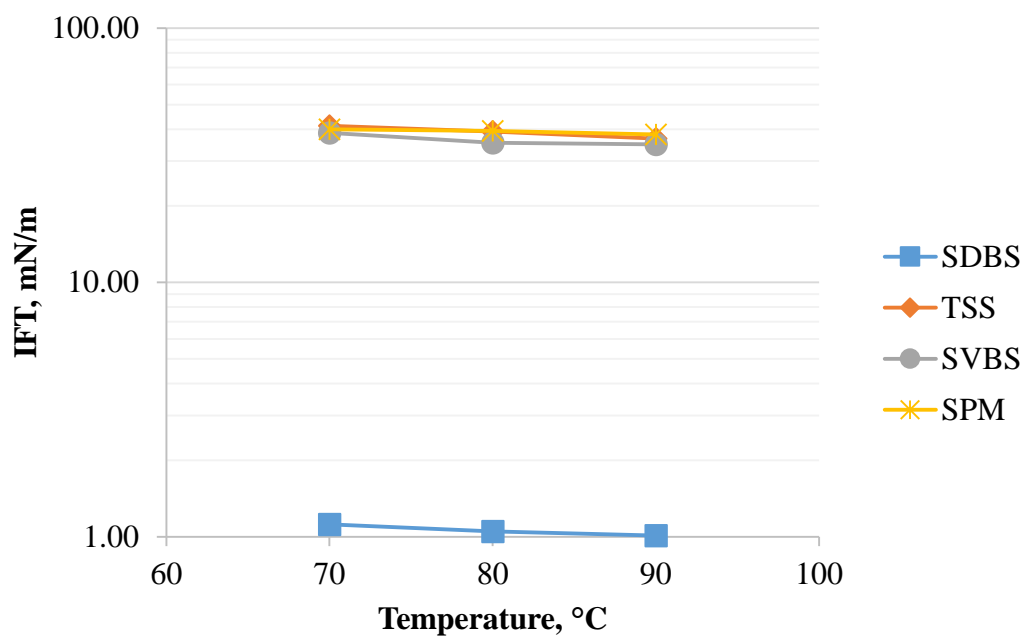
concentration at salinity = 15,000 ppm

Figure B.3 Effect of type of surfactant solution on the IFT at 0.1 wt.% surfactant

concentration at salinity = 15,000 ppm

Figure B.4 Effect of type of surfactant solution on the IFT at 0.5 wt.% surfactant
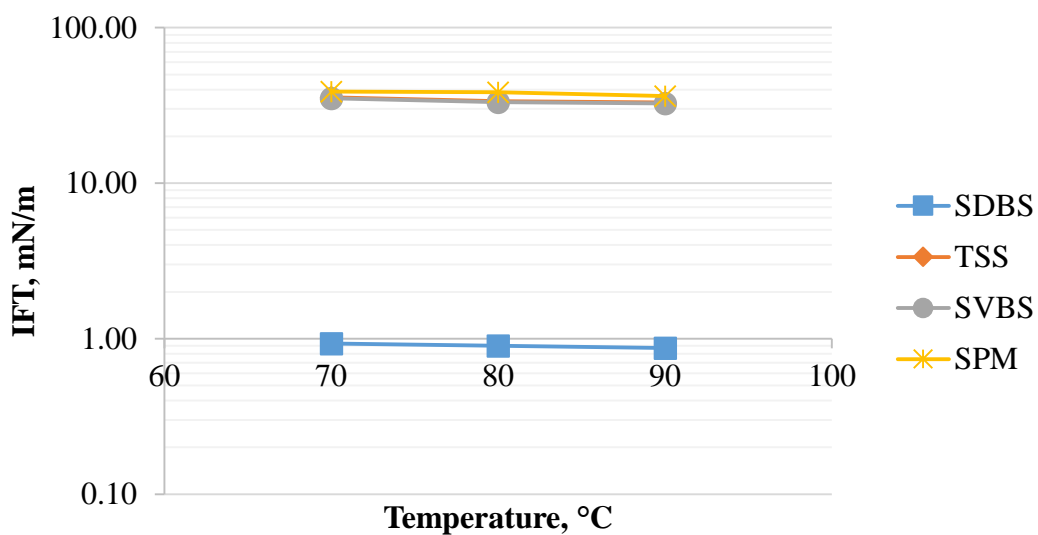concentration at salinity = 15,000 ppm

Figure B.5 Effect of type of surfactant solution on the IFT at 1 wt.% surfactant
concentration at salinity = 15,000 ppm

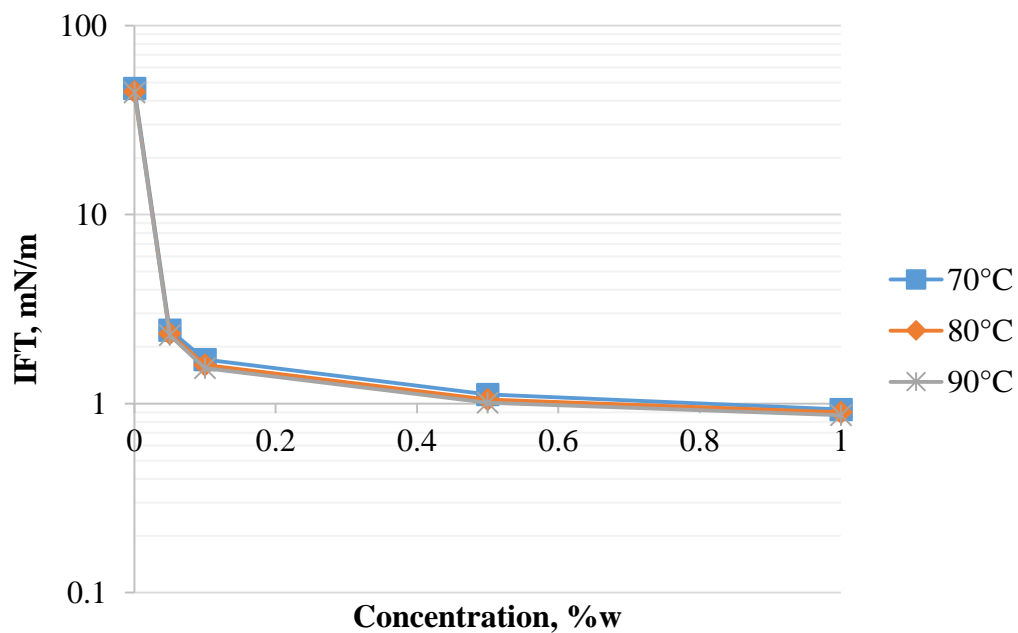**Effect of Surfactant Concentration on the Interfacial Tension**

Figure B.6 Effect of Sodium dodecyl benzene sulfonate's concentration in the wide
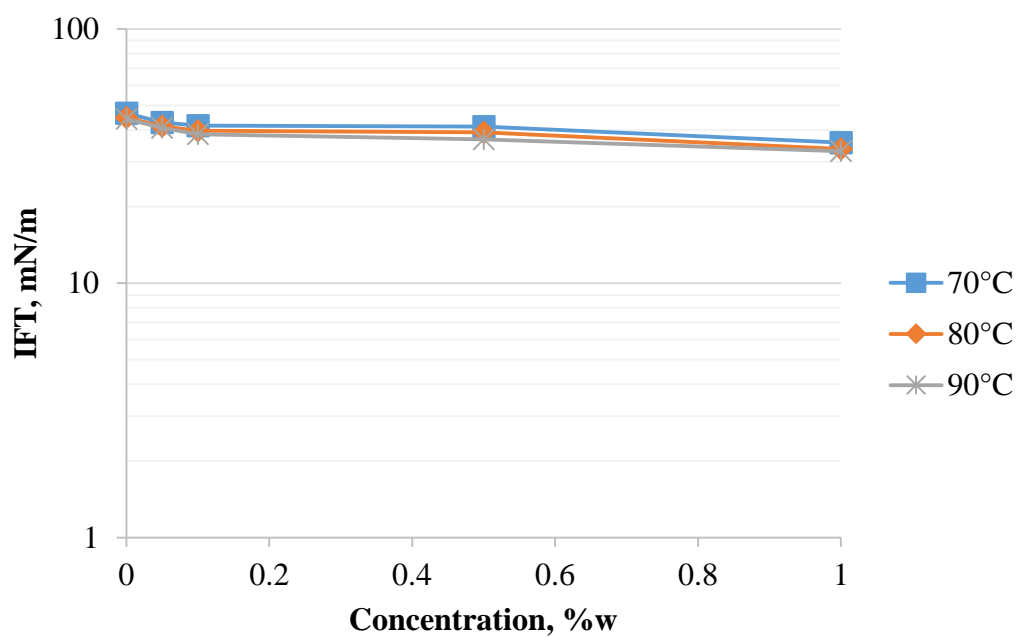range on the IFT (salinity = 15,000 ppm)

Figure B.7 Effect of Toluene 4-sulfonic acid sodium salt's concentration in the wide
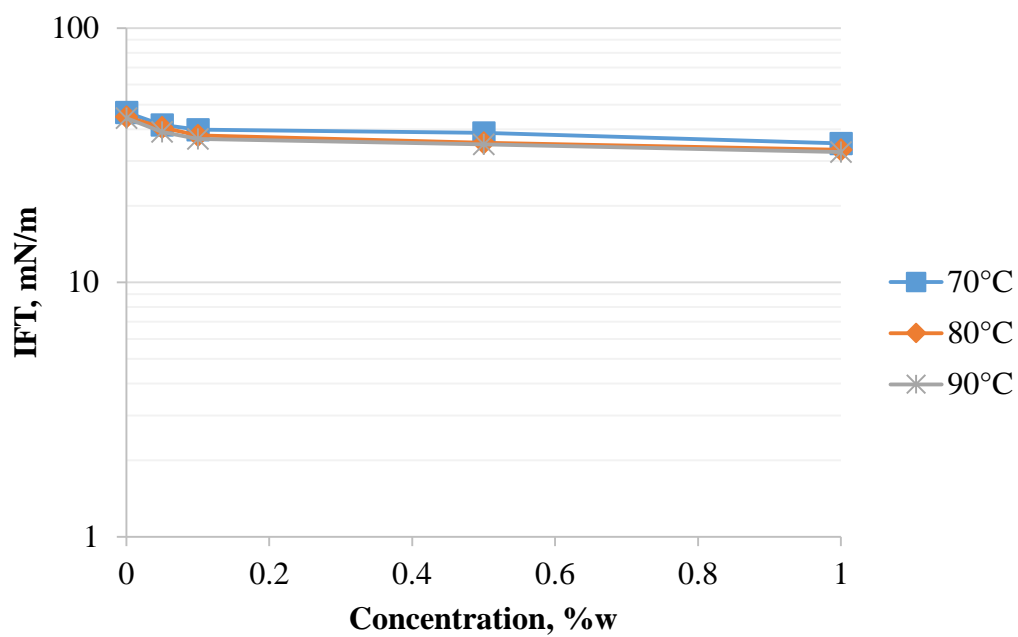range on the IFT (salinity = 15,000 ppm)

Figure B.8 Effect of Sodium 4-vinylbenzene sulfonate's concentration in the wide range on the IFT (salinity = 15,000 ppm)
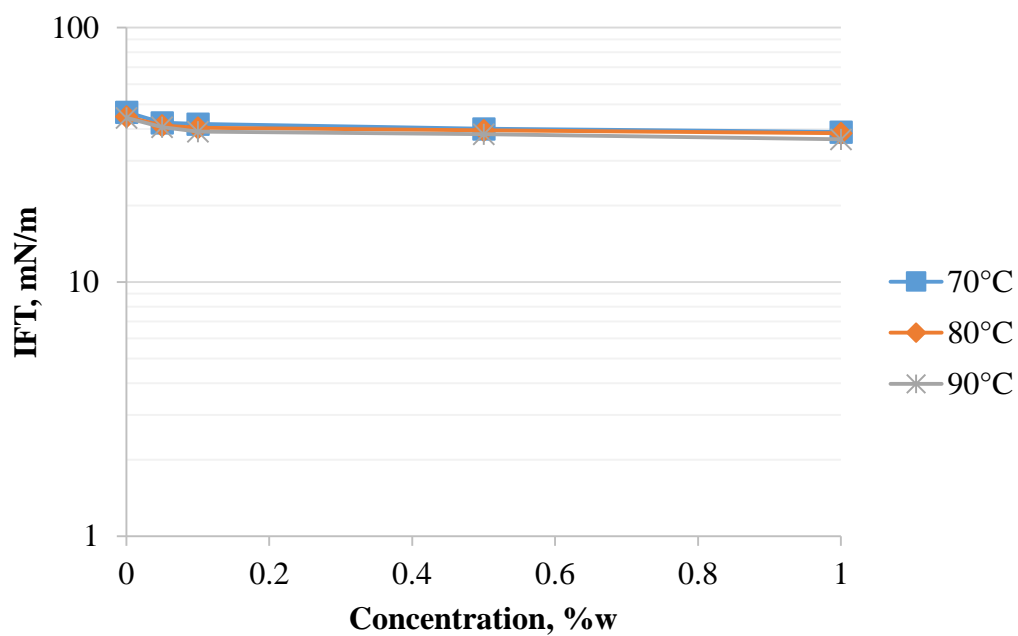

Figure B.9 Effect of 3-Sulfopropyl methacrylate's concentration in the wide range on the IFT (salinity = 15,000 ppm)

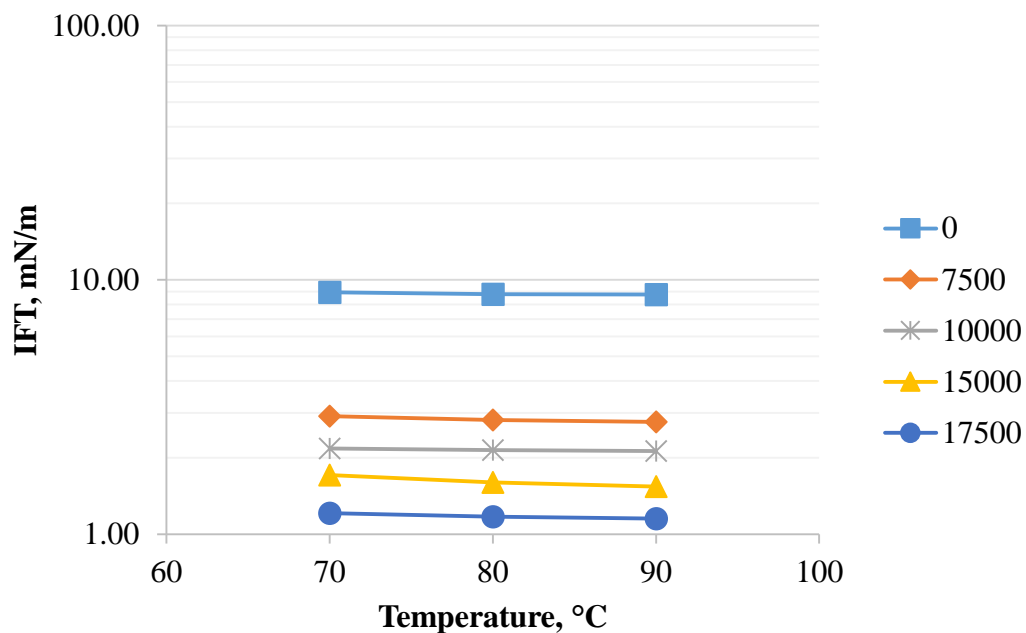**Effect of Temperature on the Interfacial Tension**

Figure B.10 Effect of temperature on the IFT with 0.1 wt % Sodium dodecyl benzene
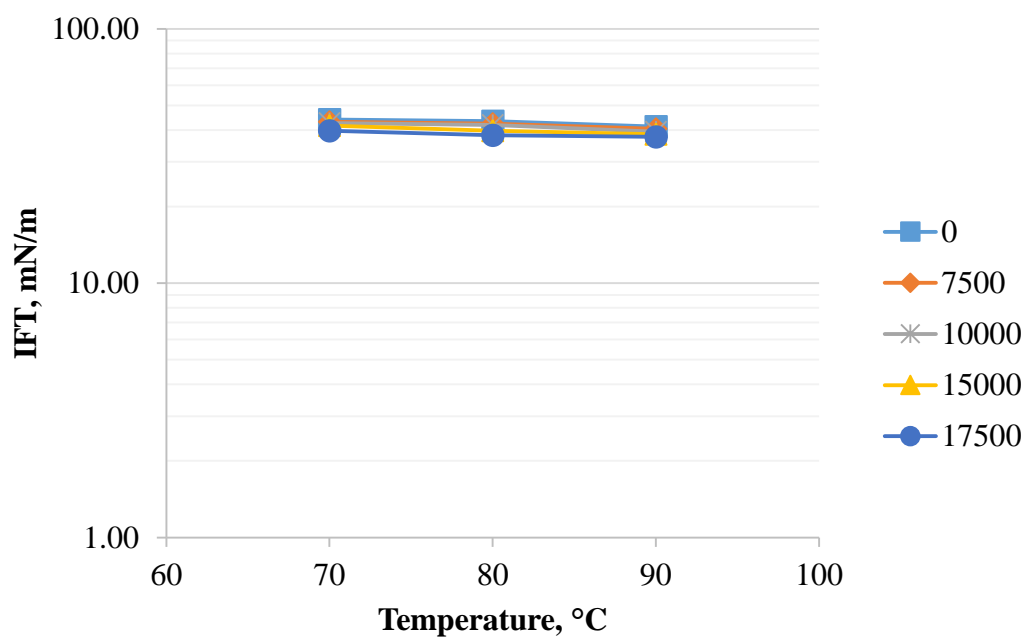
sulfonate solution

Figure B.11 Effect of temperature on the IFT with 0.1 wt % Toluene 4-sulfonic acid
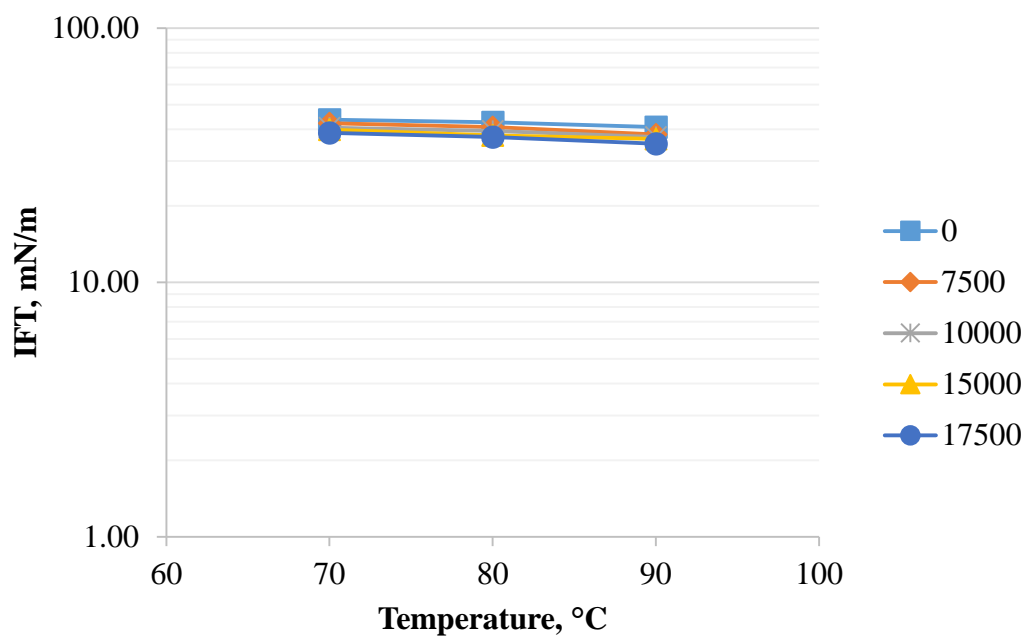
sodium salt solution

Figure B.12 Effect of temperature on the IFT with 0.1 wt % Sodium 4-vinylbenzene
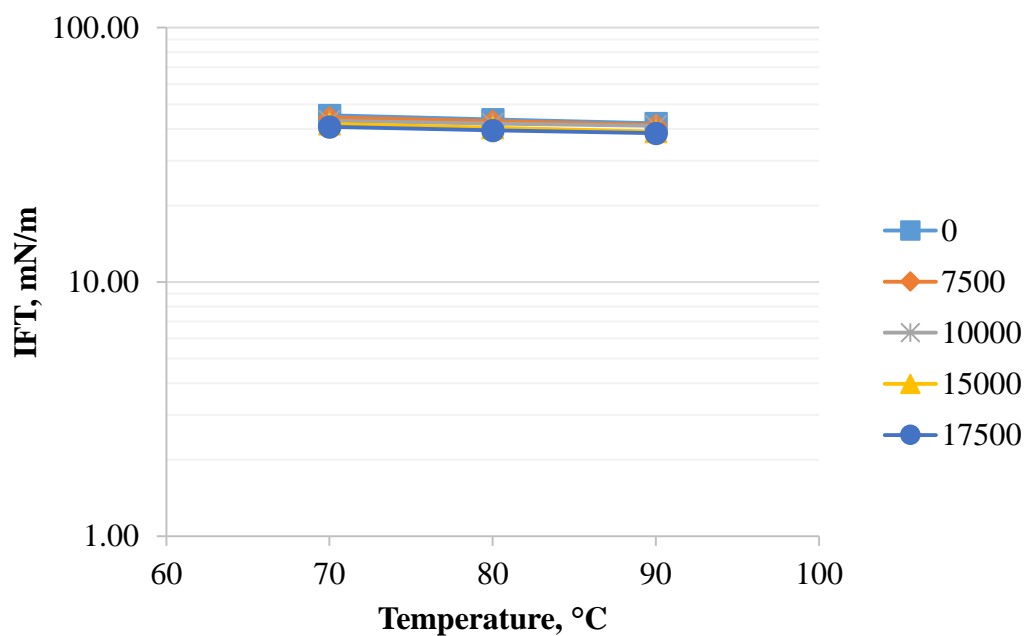
sulfonate solution

Figure B.13 Effect of temperature on the IFT with 0.1 wt % 3-Sulfopropyl

methacrylate solution

Effect of Salinity on the Interfacial Tension

Figure B.14 Effect of salinity on the IFT (SDBS solution, temperature = 80°C)
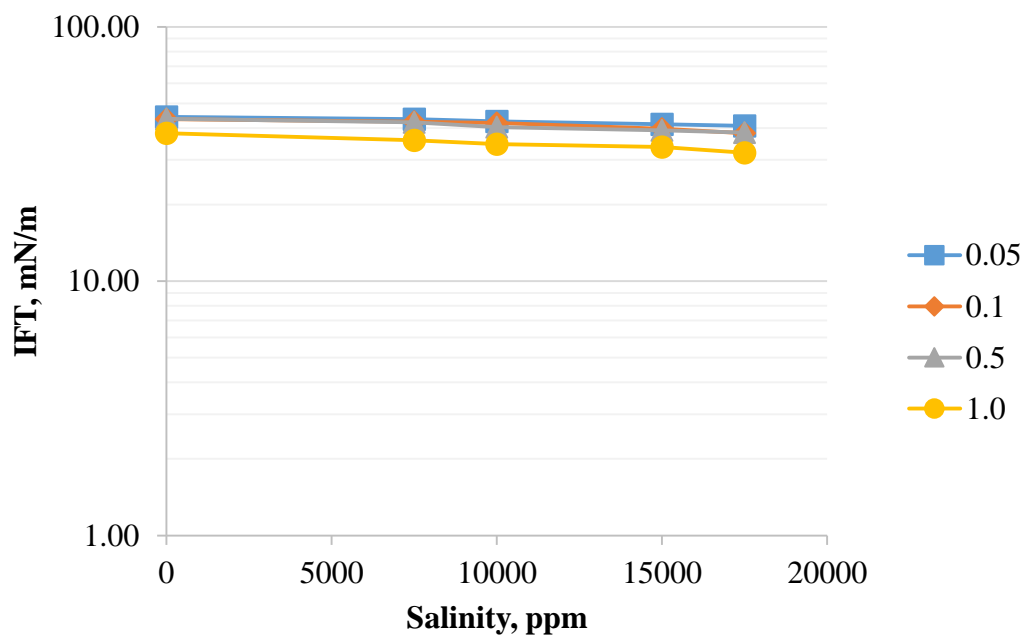
Figure B.15 Effect of salinity on the IFT (TSS solution, temperature = 80°C)

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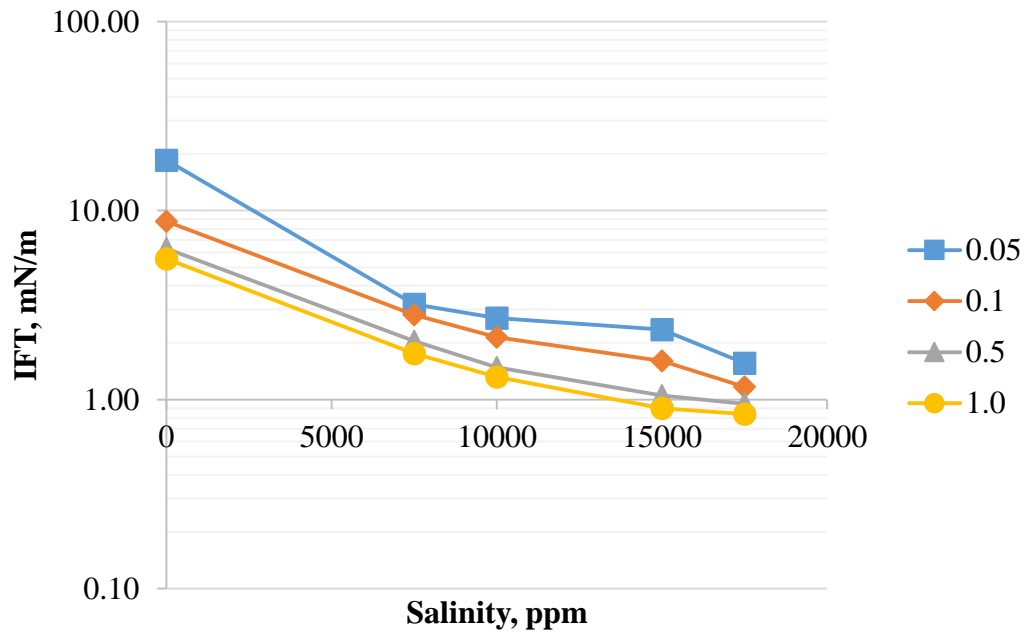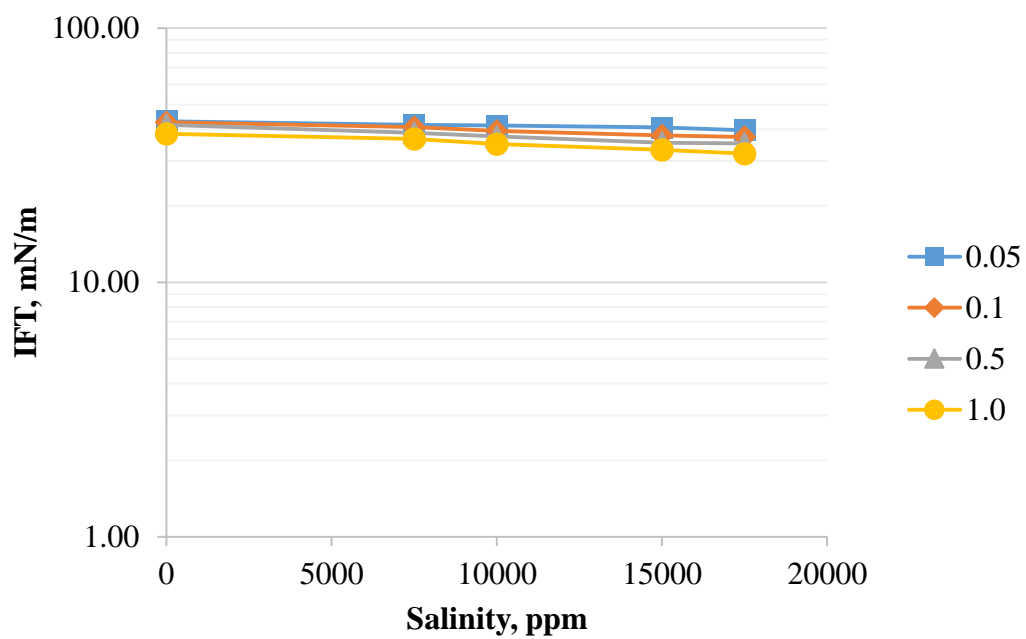Figure B.16 Effect of salinity on the IFT (SVBS solution, temperature = 80°C)
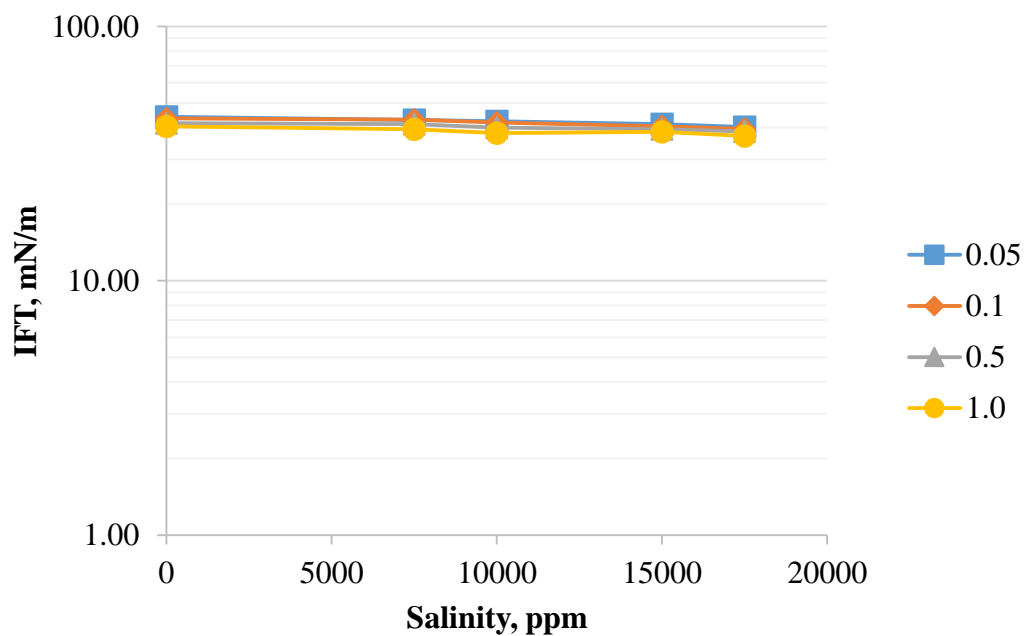
Figure B.17 Effect of salinity on the IFT (SPM solution, temperature = 80°C)

Effect of Divalent on the Interfacial Tension
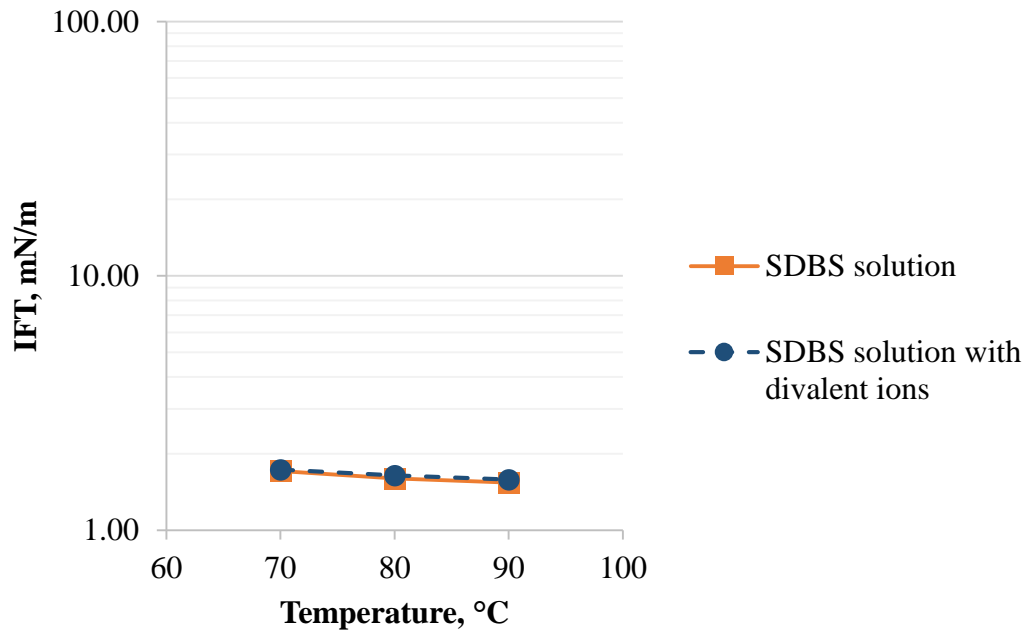
Figure B.18 Effect of divalent ions on the IFT (SDBS solution = 0.1 wt.%,
salinity = 15,000 ppm)
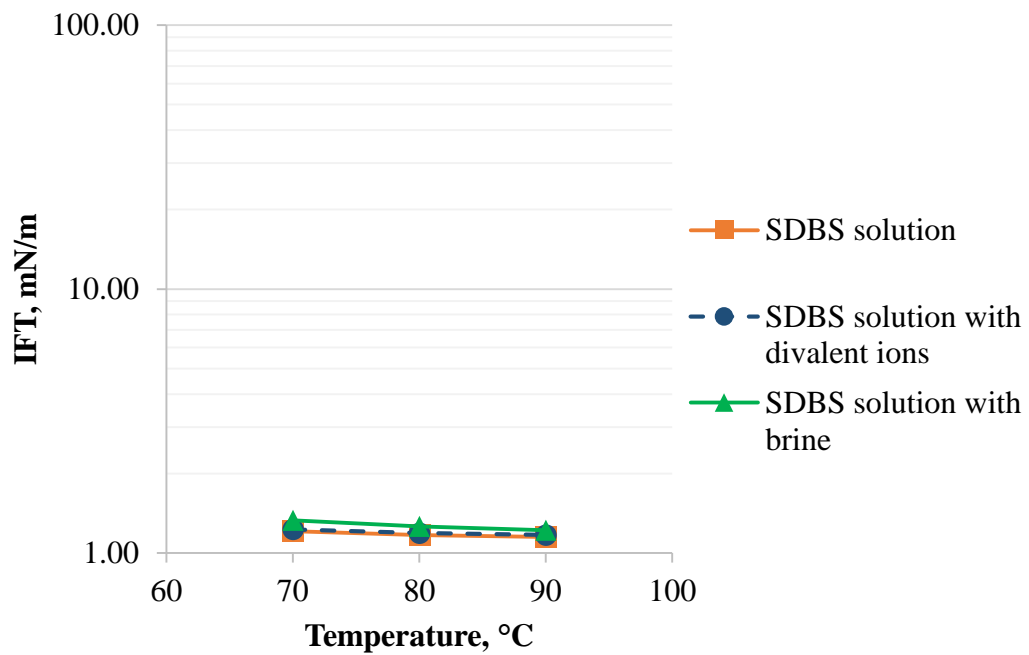
Figure B.19 Effect of divalent ions on the IFT (SDBS solution = 0.1 wt.%,
salinity = 17,500 ppm)

Effect of Co-surfactant on the Interfacial Tension

Figure B.20 Effect of co-surfactant on the IFT (Salinity =15,000 ppm)

Figure B.21 Critical micelle concentration

APPENDIX C

EQUIVALENT ALKANE CARBON NUMBER

The Equivalent alkane carbon number of the northern oil field was calculated shown in Table C.1.

Table C.1 Equivalent alkane carbon number

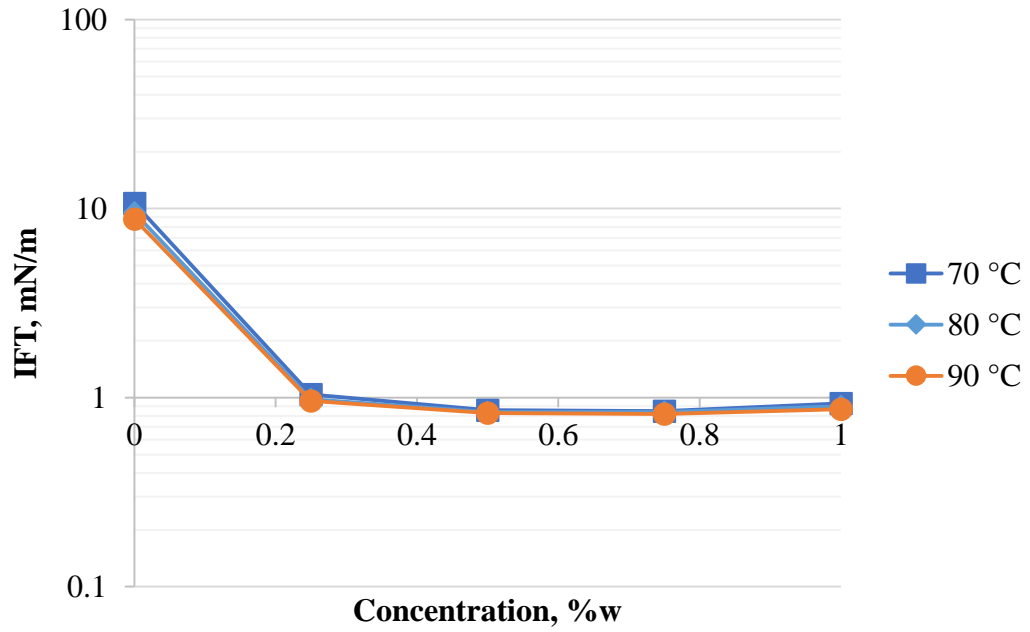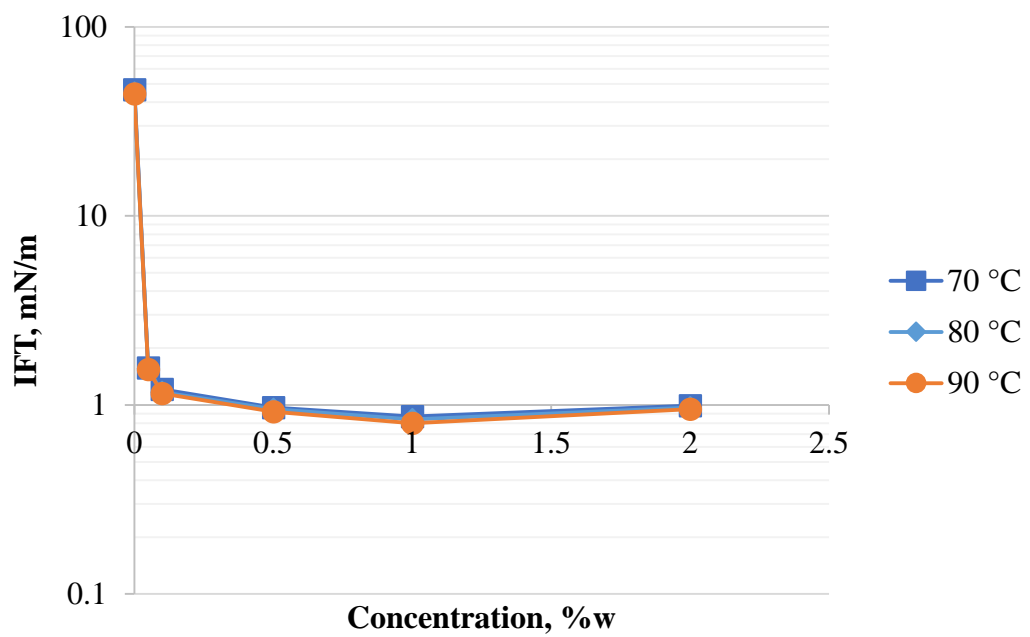| CN	Component	mw	mass	mole	X_i	X_i x CN
1	n-C1	16	0.00	0.00	0.00	0.00
2	n-C2	30	0.00	0.00	0.00	0.00
3	n-C3	44	0.54	0.01	0.03	0.08
4	i-C4	58	0.41	0.01	0.01	0.06
4	n-C4	58	1.00	0.02	0.04	0.14
5	i-C5	72	0.00	0.00	0.00	0.00
5	n-C5	72	0.00	0.00	0.00	0.00
6	C6	86	1.14	0.01	0.03	0.17
7	C7	100	2.99	0.03	0.06	0.44
8	C8	114	7.24	0.06	0.13	1.07
9	C9	128	3.49	0.03	0.06	0.52
10	C10	142	2.72	0.02	0.04	0.40
11	C11	156	2.42	0.02	0.03	0.36
12	C12	170	2.32	0.01	0.03	0.34
13	C13	184	3.60	0.02	0.04	0.53
14	C14	198	4.12	0.02	0.04	0.61
15	C15	212	4.32	0.02	0.04	0.64
16	C16	226	3.78	0.02	0.04	0.56
17	C17	240	4.13	0.02	0.04	0.62
19	Pristane	268	1.00	0.00	0.01	0.15
18	C18	254	3.16	0.01	0.03	0.47
20	Phytanes	282	0.37	0.00	0.00	0.06
19	C19	268	3.52	0.01	0.03	0.52
20	C20	282	3.69	0.01	0.03	0.55
21	C21	296	3.76	0.01	0.03	0.56
22	C22	310	3.43	0.01	0.02	0.51
23	C23	324	3.80	0.01	0.02	0.57
24	C24	338	3.45	0.01	0.02	0.52
25	C25	352	3.72	0.01	0.02	0.56
26	C26	366	3.64	0.01	0.02	0.54
27	C27	380	3.83	0.01	0.02	0.57
28	C28	394	3.05	0.01	0.02	0.46
29	C29	408	3.04	0.01	0.02	0.45
30	C30	422	2.60	0.01	0.01	0.39
31	C31	436	2.24	0.01	0.01	0.33
32	C32	450	1.56	0.00	0.01	0.23
33	C33	464	1.22	0.00	0.01	0.18
34	C34	478	1.16	0.00	0.01	0.17
35	C35+	492	3.51	0.01	0.01	0.52

From $\quad$ EACN $= \sum_{i=1}^{n} X_i C_i$. Thus, EACN $= 14.86$

APPENDIX D
PERCENT DIFFERENCE TABLE

The IFT from various conditions are compared with the base case value to see the direction and the impact of each parameter. The percent difference table can be concluded as shown in Table D.1 to D.6.

The base case solutions are 1) Sodium dodecyl benzene sulfonate solution at 0.1 wt.% 15,000 ppm of salinity, 80°C, 2) Toluene 4-sulfonic acid sodium salt solution at 0.1 wt.% 15,000 ppm of salinity, 80°C, 3) Sodium 4-vinylbenzene sulfonate solution at 0.1 wt.% 15,000 ppm of salinity, 80°C, and 4) 3-Sulfopropyl methacrylate at 0.1 wt.% 15,000 ppm of salinity, 80°C.

Table D.1 Percent difference of pressure effect on the IFT

Pressure (psig)	1,000	1,500	2,000
SDBS solution	0.09	0	0.19

Table D.2 Percent difference of type of surfactant solution effect on the IFT

Type of solution	% Difference
SDBS solution	0
TSS solution	-4,462.81
SVBS solution	-4023.30
SPM solution	-4491.94

Table D.3 Percent difference of surfactant concentration effect on the IFT

Surfactant concentration (wt.%)	0	0.05	0.10	0.50	1.00
SDBS solution	-2,595.78	-43.98	0	48.19	48.80
TSS solution	-12.55	-4.18	0	1.31	15.27
SVBS solution	-18.32	-7.54	0	6.24	12.14
SPM solution	-10.63	-2.05	0	2.37	4.80

Table D.4 Percent difference of temperature effect on the IFT

Temperature (°C)	70	80	90
SDBS solution	-3.01	0	1.20
TSS solution	-4.88	0	3.19
SVBS solution	-5.61	0	2.99
SPM solution	-3.39	0	3.41

Table D.5 Percent difference of salinity effect on the IFT

Salinity (ppm)	0	7,500	10,000	15,000	17,500
SDBS solution	-429.52	-69.28	-28.92	0	29.52
TSS solution	-9.05	-6.51	-5.25	0	3.84
SVBS solution	-12.90	-7.99	-4.15	0	1.24
SPM solution	-7.74	-6.28	-3.63	0	2.25

Table D.6 Percent difference of divalent ion effect on the IFT

Temperature (°C)	70	80	90
SDBS solution	-3.01	0.00	1.20
SDBS solution with divalent ions	-4.22	-1.81	0.60

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CHULALONGKORN UNIVERSITY

VITA

Mr.Chitipat Chuaicham was born on January 4th, 1992 in Phichit, Thailand. He graduated his bachelor degree from King Mongkut's Institute of Technology Ladkrabang in Chemical Engineering in 2013. He studied Master's Degree in Petroleum Engineering at the Department of Mining and Petroleum Engineering, Chulalongkorn University in the academic year 2015.