Phase Behavior of Alkaline Surfactant Polymer in Hard Water

by

Noor Shakila binti Abd Rahman

Dissertation submitted in partial fulfillment of

the requirements for the

Bachelor of Engineering (Hons)

(Petroleum Engineering)

MAY 2013

Universiti Teknologi PETRONAS

Bandar Seri Iskandar

31750 Tronoh

Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

Phase Behavior of Alkaline Surfactant Polymer Flooding in Hard Water

by

Noor Shakila Binti Abd Rahman

A project dissertation submitted to the

Petroleum Engineering Programme

Universiti Teknologi PETRONAS

In partial fulfillment of the requirement for the

BACHELOR OF ENGINEERING (Hons)

(PETROLEUM ENGINEERING)

Approved by,

(Iskandar Bin Dzulkarnain)

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

May 2013

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgement, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

NOOR SHAKILA BINTI ABD RAHMAN

ACKNOWLEDGMENTS

First and foremost, I thank God Almighty for giving me strength and healthiness to complete this project. Many sincere thanks to my great supervisor **Mr. Iskandar bin Dzulkarnain** for his constant support and guidance for the accomplishment of this work. I am deeply thankful to him for the opportunity, resources and the freedom to do my project. I also would like to express my gratitude to **Mr. Shahrul, Mr. Saiful, Mr Shaharuddin** and **Ms. Siti Fatimah** for their kind concern guiding me with the equipment and materials throughout this period. Not to be forgotten, thank you to all faculty members of the **Geoscience and Petroleum Engineering Department** also **Chemical Engineering Department** for the knowledge that they imparted and their constant encouragement and constructive feedback. I am indebted to **Universiti Teknologi PETRONAS** for providing me with an enriching atmosphere to learn and grow both as an engineer and a person.

Thanks to all of my colleagues and friends with whom I had the opportunity to learn, share and enjoy. It has been a great pleasure. A final word of gratitude is reserved for my family who has always provided me with their unending support and love.

ABSTRACT

The needs and increasing price of the oil time by time has become the motivation to have more research on the oil recovery in this recent day such as Alkaline Surfactant Polymer (ASP) which is categorized as tertiary recovery or enhanced oil recovery (EOR). The ASP flooding was developed in the early 1980's as a lower-cost alternative to micellar/surfactant polymer flooding.

The process of this flooding consists of injecting a slug mixture of alkali-surfactant-polymer, followed by the injection of additional polymer and then chase water. The combination of these three chemicals in the slug is more effective than injection of individual components. Despite the effectiveness of combining these three chemicals, the ASP flooding will form precipitation as a reaction to the formation water which has high content of divalent ions such as ferum and magnesium in offshore formation water (hard water) compared to the onshore formation water.

The precipitation formed will reduce the permeability thus decrease the production. Hence, in order to prevent the form of precipitation or scale, an optimum concentration of ASP and salinity of the hard water will be studied experimentally. The experiment will be conducted by varying the salinity of hard water also the concentration of the alkali, surfactant and polymer to identify the formulation that will gives no precipitation and the Winsor Type III microemulsion. This optimum ASP formulation will give higher oil recovery as the reaction of alkali and acid in the crude oil will create in-situ surfactant which will reduce the interfacial tension (IFT) and polymer will act as thickening agent to improve the sweep efficiency.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

NOMENCLATURES AND ABBREVIATIONS

ASP	Alkaline Surfactant Polymer
DW	Distilled Water
EOR	Enhanced Oil Recovery
IFT	Interfacial Tension
$NaB(OH)_4$	Sodium Metaborate
NaCl	Sodium Chloride
OOIP	Original Oil in Place
PAM	Polyacrylamide
SDS	Sodium Dodecyl Sulfate
Wt%	Weight percentage

CHAPTER 1

INTRODUCTION

1.1 Background

The demand for crude oil around the world and the increasing price of oil has boosted the motivation to do more research on oil recoveries. The recoveries are divided into three which are primary recovery (natural drives), secondary recovery (artificial lift) and tertiary recovery (enhanced oil recovery). The primary recovery will give average recovery about 12-15% of original-oil-in-place (OOIP) which may be less for heavy oil and more for lighter oil. The secondary recovery will provide outsource energy to the reservoir by water or injection which then will recovers an additional 15 to 20% of OOIP over the primary recovery whereas the enhanced oil recovery (tertiary recovery) will recover additional 10 to 15% of OOIP over the secondary recovery (Blaine Hawkins, 2004).

In real cases, most of oil reservoirs do not have uniform porosities and permeabilities. When water or other fluids were injected in the reservoir with high pressure, the fluids will move into the path of least resistance which is the one with low pressure that will be known as the producing well. The high permeability zones and fractures give the least resistance to flow, most of the injected fluid will follows this path and hence most of the oil remaining in the lower permeability zone is by-passed.

After the primary and secondary processes have been utilized, there is significant amount of oil remaining in the reservoir. Hence, there are many researches had been done for the past few years to find ways to recover the remaining oil using enhance oil recovery method which also known as the tertiary recovery. Many EOR techniques were tried worldwide such as thermal (steam flooding, cyclic steam simulation, in-situ combustion), gas flooding which can be divided into miscible (CO_2 flooding, cyclic CO_2 stimulation, N_2 flooding, N_2- CO_2) and immiscible (air injection), also chemical flooding. This paper will discuss further on chemical flooding which is estimated that several hundred chemical EOR field trials have been conducted over the past 50 years with many occurring during 1970's and 1980'. There were several flooding systems have been reported such as polymer, polymer/alkaline, surfactant/polymer and alkaline/surfactant/polymer (ASP) flooding systems.

The ASP process was developed in the early 1980's as a low-cost alternative to micellar/surfactant polymer flooding. The process of this flooding consists of injecting a slug mixture of alkali-surfactant-polymer, followed by the injection of additional polymer and then chase water. The combination of these three chemicals in the slug is more effective than injection of individual components.ASP flooding is simple in concept, but very complicated in design and application. It requires much laboratory testing and research and sometimes a proper formulation of alkali-surfactant-polymer mixture cannot be designed to achieve good displacement in a particular reservoir.

In selecting chemicals for an ASP flood (or any chemical EOR flood for that matter), it is necessary to consider availability, quantities required, cost, performance, and logistics. All of these factors are critical due to the large quantities usually required to flood one field, which can run into hundreds of millions of pounds. Therefore in order to minimize costs, it is critical that (Corp, 2011):

- There be chemical manufacturing plants large enough to accommodate the capacity needed and in close proximity to the field being flooded to reduce transportation costs
- Chemical cost is low enough to make the sizable investment in chemicals profitable in the long term.

1.2 Problem Statement

The significant amount of oil left in the reservoir after the first and secondary recovery has initiated the studies on the tertiary recovery known as Enhanced Oil Recovery (EOR) and this paper is focusing on the chemical EOR. Several chemical flooding has been studied and applied around the world and the latest is Alkaline Surfactant Polymer (ASP) flooding. The ASP flooding has been done successfully in China for onshore field and very few ASP flooding done in offshore which it have not being done in Malaysia due to some restriction.

The high content of divalent ions such as ferum and magnesium in offshore formation water compared to the onshore formation water will form precipitation as a reaction by the Alkaline Surfactant Polymer flooding. The precipitation formed will reduce the permeability thus decrease the production. To prevent the form of precipitation, an optimum concentration of ASP and salinity of the hard water need to be studied experimentally.

1.3 Objectives

- To study the optimum concentration of the mixture of chemical for Alkaline Surfactant Polymer
- To investigate the optimum salinity of the hard brine that will give no precipitation in reaction with ASP
- To propose that Alkaline Surfactant Polymer flooding can tolerate with the formation water from offshore reservoir or hard water

1.4 Scope of Study

The scope of study of this proposal is to study and analyze the phase behavior for each of the chemical which are alkaline, surfactant and polymer also to investigate the effect of these chemicals on microemulsion. The phase behavior analyzed will be used to estimate the optimum salinity of hard brine and optimum concentration for each of chemicals used in the Alkaline Surfactant Polymer (ASP) flooding. This optimum formulation of ASP will react with the formation water (synthetic hard water) and result no precipitation.

1.5 Relevancy of Project

In Malaysia, all field is located offshore which may contain high ferum and magnesium ions in the formation water, hence, it is relevant to have further study on the phase behavior of ASP in hard water. Furthermore, there is no ASP flooding has ever implemented yet in Malaysia so it will good to have investigation on this.

1.6 Feasibility of the Project within the Scope and Time Frame

This project will be divided into two parts which are FYP1 and FYP2. During FYP1, the author will do the reading and researching part of the literature review of the project to improve the knowledge on the project assigned. Author will analyze and construct the experiment procedure that will be done also the chemical and apparatus needed. For FYP2, the author will conduct all experiments needed to satisfy the objectives mention before. The result will then analyze for conclusion and recommendation for future work.

CHAPTER 2

LITERATURE REVIEW

2.1 Chemical Enhanced Oil Recovery (EOR)

The chemical EOR techniques have developed as an economical and viable alternative for increasing the oil recovery after the primary and secondary recovery. This success though relies heavily on a thorough understanding and fine-tuning of the chemical interactions between the injected chemicals, the fluids in the reservoir itself and the rock. These interactions will eventually determine the optimal injection and production scenarios and ultimately the total increment of oil recovery (Fadili, Kristensen, & Moreno, 2009). There few main recovery mechanisms of chemical EOR which are (Petrofed, 15-16 April 2010):

- Reduction in interfacial tension between oil and brine
- Solubilization of released oil
- Change in the wettability towards more water wet
- Reducing mobility contrast between crude oil and displacing fluid

EOR methods such as chemical flooding, miscible flooding, and thermal recovery involve altering the mobility ratio and/or the IFT between the oil and water. Recovery efficiency was found to be reliant on the capillary number, which defined as:

$$N_C = \mu v / \gamma Ø$$

The viscous force is defined as the flow velocity, fluid viscosity, and the flow path length. Capillary forces vary with the fluid 1FT and the pore geometry of the medium.

Taber defined the capillary number in terms of the pressure drop, the flow length, and the interfacial tension.

$$N_C = \Delta p / L\gamma$$

According to Taber, as this ratio increased to a value of 5 psi/ft/dyne/cm [0.2 kPa/m/N/m] the residual oil saturation (ROS) was reduced significantly. By decreasing the IFT using surfactants, or by altering the field geometry that can decrease the path length, the capillary number could be increased. Melrose and Brandner indicated that as the capillary number rose to a value of 10^{-4}, the microscopic displacement efficiency to both oil and water, increased (Jr., Ertekin, & Stahl, 1985).

Chemical EOR methods focus mainly on improving the sweep efficiency by correcting reservoir heterogeneity or controlling fluid mobility using alkali, or they focus on increasing displacement efficiency by reducing residual-oil saturation (Baojun Bai, 2008). There are several types of chemical EOR such as alkaline flooding, surfactant flooding, polymer flooding, alkaline surfactant flooding and alkaline surfactant polymer flooding.

2.2 Alkaline Flooding

The process of alkaline flooding in oil and gas industry was first considered in the late 1920's (Konopnicki & Zambrano, 1984). Alkaline flooding is one of the enhanced oil recovery method in which an alkaline chemical such as sodium hydroxide, sodium orthosilicate or sodium carbonate is added to the injected water. This alkaline chemical will reacts with acidic components in crude oil and forms in-situ surfactant. This surfactant will increase oil recovery by reducing the interfacial tension between the displacing fluid and the displaced fluid. The application of alkaline flooding has four mechanisms which are (Abadli, 2012):

- Emulsification and entrainment
- Wettability reversal (oil-wet to water-wet)
- Wettability reversal (water-wet to oil-wet)
- Emulsification and entrapment.

Most of the researchers stated that the lowest IFT occurs at very low alkali concentrations. On the other hand, the alkali consumption in the reservoir demands injection of higher alkali concentrations which has can be solved by combining adding the surfactant which is more hydrophilic than the in-situ generated soap (Delshad, Han, Veedu, & Pope, 2011). The use of alkali also reduces the adsorption of anionic surfactant on sandstones and corrosion also a problem associated with the alkali process (Guo, Zitha, Faber, & Buijse, 2012). However, the alkaline flooding is not recommended for carbonate reservoirs due to the profusion of calcium and the mixture between the alkaline chemical and the calcium ions can produce hydroxide precipitation that may damage the formation (Abadli, 2012).

2.2.1 Field application of alkaline flooding

An alkaline flooding system has been designed for application in the Main Zone reservoir of the Joughin Unit in the Torrance Field. The flood encompasses the major portion of the Unit (Section B) and consists of twelve inverted nine-spot patterns with a caustic injection rate of 38,000 bpd (6042 m^3/d). A 30% pore volume pre-flush injection of softened fresh water began on June 30, 1981 to reduce the divalent ion content and salinity of the reservoir. A 16% pore volume caustic slug consisting of 1.2% sodium orthosilicate began in early-1985. Caustic injection required approximately two years (Konopnicki & Zambrano, 1984).

2.3 Surfactant Flooding

The structure of surfactant is divided into two which are hydrophilic and lipophilic. The hydrophilic head group and a lipophilic tail together contains surfactant molecule. The head refers to the solubilizing group – the lyophilic or hydrophilic group in aqueous systems and the tail refers to the lyophobic or hydrophobic group in water. The whole molecule is called an amphiphile telling a dual-nature which makes the surfactant reside at the interface between the aqueous and organic phases, lowering the interfacial tension (Abadli, 2012).

Surfactants are classified to some specific types in terms of ionic nature of surfactants such as:

- Anionic surfactants are defined due to negative charge on the head group. This type of chemicals have some specifications such as stability, reducing IFT, low adsorption character. That is why they can be considered effective chemical EOR components. Some examples can be shown as anionic surfactants like carboxyl (RCOO-M+) and sulfonate (RS03-M+).
- Cationic surfactants have positive charge compared to anionic surfactants. Addition of cationic surfactants to polymer flooding will increase efficiency by changing the wettability. Due to neutral charge on the head group some surfactant types are called nonionic. For salinity stability analyses nonionic surfactants are highly used.
- Amphoteric class consists of two or more of the other classes. The composition of these surfactants can be mixture of anionic, cationic and others.

Surfactant agents are introduced into the reservoir in order to get moveable trapped oil droplets and to increase oil recovery by lowering the interfacial tension between oil and water. The coalescence of these drops leads to an increment in oil saturation. As the oil bank start to flow, it will mobilize and carry all residual oil in front. Eventually, the ultimate residual oil is determined by interfacial tension between oil and surfactant solution behind the oil collection.

There are few weaknesses of surfactant which are precipitation, phase trapping and adsorption. The adsorption is related to the economics of surfactant flooding, where more surfactant need to be injected into the reservoir to counter back the surfactant loss. The surfactant injection is feasible when oil prices are relatively high and if the residual oil saturation after water-flooding is high because they are expensive (Aida, 2010).

2.3.1 Field application of surfactant flooding

A low concentration surfactant flooding has been implemented in the Bothamsall Field in July 1983 which was discovered in 1958. According to (Cooper, Southworth, Walsh, & Morgan, 1985), between July 1983 and September 1984, an injection of a 0.25 PV surfactant slug has took place in the central injection well of an inverted four-spot pattern followed by brine water drive of controlled salinity. The total production of the wells during this injection period averaged 270b/d and it was significantly less than originally anticipated.

2.4 Polymer Flooding

Polymer flooding is one type of enhanced oil recovery method that uses polymer solutions to increase oil recovery by increasing the viscosity of the displacing water to decrease the water/oil mobility ratio. During polymer flooding, a water-soluble polymer is added to the injected water in order to increase water viscosity. Depending on the type of polymer used, the effective permeability to water can be reduced in the swept zones to different values. It is believed that polymer flooding cannot reduce the residual oil saturation (S_{or}), but it is still an efficient way to reach the S_{or} more quickly or/and more economically. Adding a water-soluble polymer to the water-flood allows the water to move through more of the reservoir rock, resulting in a larger percentage of oil recovery. In the process, the volumetric sweep is improved, and the oil is more effectively produced. There are three potential ways in which polymer flooding makes the oil recovery process more efficient (Abadli, 2012):

- Through the effects of polymers on fractional flow.
- By decreasing the water/oil mobility ratio.
- By diverting injected water from zones that have been swept.

The most important aspect for polymer flooding are reservoir temperature and chemical properties of the formation water because at high temperature or with high salinity in reservoir water, the polymer cannot be kept stabile, and polymer concentration will lose most of its viscosity. There are mainly two types of polymers which might be effective in reduction of mobility ratio:

i. *Polyacrylamides*- a condensation polymers and the performance depend on the molecular weight and degree of hydrolysis. When partially hydrolyzed, some of the acryl amide is replaced by or converted into acrylic acid. This tends to increase the viscosity of fresh water but reduces the viscosity of hard waters.
ii. *Biopolymers*- A biopolymers are derived from a fermentation process. It has a smaller molecular weight than polyacrylamide. Its molecular structure gives the

molecule great-stiffness, a characteristic that gives the biopolymer excellent viscosifying power in high salinity water. However, they have less viscosifying power than polyacrylamide in fresh waters. They have good viscosifying power in high salinity water and good resistance to shear degradation.

Polymer flooding will improves only volumetric sweep efficiency. Micro-emulsion/polymer flooding produces significant incremental oil but is not economical because of high chemical costs (Gao, Li, & Li, 1995). The polymer also can form a ‘bridge’ between two oil droplets and decrease the emulsion stability; however, polymer can also enhance the emulsion stability via electrostatic and steric stabilization (Nguyen & Sadeghi, 2012).

2.4.1 Field application for polymer flooding

Polymer flooding is implemented in Daqing field with about 220,000 B/D incremental oil production from polymer flooding and 12% OOIP incremental recovery as of 2005. Over 2000 wells is injecting polymer at Daqing with typical slug size of 0.6 PV. Most well patterns are 5-spot about 30-50% of injected polymer is produced and maximum produced polymer concentration is approximately 2/3 of injected (Pope, 2007).

2.5 Alkaline Surfactant Polymer Flooding

ASP has been implemented in onshore field of Karamay oil field in China and La Salina Field, Lake Maracaibo is the first offshore application of the ASP technology in the world.(Hernandez et al., 2001) The ASP technology emphasizes alkali flooding technology to recover the trapped oil because the cost of alkali is considerably lower that the surfactant (Gao, et al., 1995).

The key features of the ASP model are (Mohammadi, Delshad, & Pope, 2008):

i. In-situ generation of soap by reaction with the acid in crude oil
ii. Phase behavior as a function of soap and surfactant concentrations
iii. Interfacial tension reduction as a function of soap and surfactant concentrations
iv. Reduction of surfactant adsorption with increasing pH
v. Ion exchange reactions with clays in the rock
vi. Aqueous chemical reactions

vii. Dissolution/precipitation reactions

2.5.1 ASP in general

The surfactants injected will alter the IFT between the oil and water. According to the nature of surfactants injected, a significant portion of these surfactants may adsorb on the rock material. However, some portion of these surfactants will mix into the connate water and/or aquifer water from the injection stream. Along with the injected water, some portion of this connate or aquifer water will eventually be produced and may form stable water-in-oil (W/O) emulsions. It is also well-known that emulsion stability is quite transient with just the right conditions for emulsion formation or water may exist as a liquid phase along with hydrocarbons. There is uncertainty not just emulsion formation during production but also concerning the extent to which the viscosity of the fluids increase as a result of emulsion formation (Kalra, Venkatraman, Raney, & Dindoruk, 2012).

ASP is a modification on the alkaline flooding process by adding surfactant to the chemical mixture to raise the optimum salinity where middle phase emulsion or micro-emulsion forms and to compensate for the shortage of in-situ generated soap in low acid content oil. For a successful displacement of trapped oil by chemical flooding, chemical slug should achieve the following aspect (Bataweel & Nasr-El-Din, 2012):

i. Achieve and maintain the ultra-low IFT during the displacement process
ii. Improve mobility control for microscopic and macroscopic displacement
iii. Compatibility of mixture and formation brine to prevent surfactant precipitation or separation in presence of divalent cations
iv. Low surfactant adsorption at the reservoir rock
v. Compatibility between surfactant and polymer to minimize separation, complexation and retention

IFTs are directly related to the interfacial tension properties that ultimately dictate oil recovery efficiency. Ultra-low IFTs are the result of surfactant arrangement at the oil: water interface. The type and concentration of alkali and surfactant dictate the level of interfacial tension reduction and, therefore, the oil recovery by the IFT mechanism. Mobility control is also a primary oil recovery mechanism of the ASP technology and is developed through polymer inclusion (Wanli et al., 2000). The salinity at which given surfactant achieves lowest IFT is referred to as its optimum salinity. Mixtures of surfactant with different optimum salinities are known to exhibit a combined optimum salinity that obeys a concentration-dependent mixing rule (Stoll et al., 2011).

2.5.2 Microemulsion Phase Behavior

Phase-Behavior experiment were used as the primary screening method to identify surfactant formulations qualitatively and the promising candidates were validated by interfacial tension (IFT) measurements (between the surfactant solution and oil) at different salinities to identify the lowest IFT formulation. To be able to clearly read the interface between aqueous phase and microemulsion phase, as well as between microemulsion phase and oil, the oil ratio (the ratio of oil volume of total liquid volume) should be close to 50%, and the total surfactant concentration should be at least 0.5% (Zhang, Ravikiran, Freiberg, & Thomas, 2012).

Emulsion according to (Romero, 2009) is a dispersion of two immiscible liquids, in this case is oil and water that has two important functions which are: (1) to decrease the interfacial tension between oil and water and (2) to stabilized the dispersed phase against coalescence once it is formed. Based on Winsor Ratio concept indicated by (Buijse, Tandon, Jain, Handgraaf, & Fraaije, 2012), an optimum WR is equal to 1 based on the formula and figure below:

$$WR = \frac{E_{Tail\text{-}Oil}}{E_{Head\text{-}Brine}}$$

Figure 1 Winsor Ratio concept (from Buijse, Tandon, Jain, Handgraaf, & Fraaije, 2012)

Winsor also stated that, there are three types of phase equilibrium in microemulsion phase behavior which are Type I, Type II and Type III. Type I is an oil-in-water microemulsion with an excess brine phase, Type II is a water-in-oil microemulsion with an excess oil phase whereas Type III provides low interfacial tensions, especially where equal volumes of water and oil are solubilized in the microemulsion. (Sahni, 2009) report that, the salinity at which the transition occurs between Type I and Type III is referred to as lower critical salinity, whereas the transition that occurs between Type III and Type II is referred to upper critical salinity.

There is a method to describe and graphically represent the oil and water solubilized in microemulsion by (HEALY, REED, & STENMARK, 1976). At first, they should measure the volumes of oil (V_o) and water (V_w) the microemulsion contained, and then normalize these volumes to the total volume of pure surfactant (V_s) to obtain water solubilization ratio values (V_o/V_s and V_w/V_s, respectively) for each salinity the will tested. These ratios then will be plotted according to the salinity tested, and form solubilization curves which will produce an intersection point of oil and water solubilization ratio. This intersection is defined as the optimal solubilization ratio and optimal salinity.

An empirical correlation between solubilization ratios and interfacial tension was first published by Healy and Reed but Huh later on developed a theoretical relationship. A simplified equation for IFT is as follows:

$$\gamma = \frac{C}{\sigma^2}$$

A typical value of C=0.3 dynes/cm. Solubilization ratio (σ) is defined as the volume of oil or water divided by the volume of pure surfactant (Yang, 2010).

The Figure 2 shows the three type of microemulsion form (brownish) with reaction of varying salinity of brine and concentration of alkali. The black phase represents crude oil and the clear phase is the brine (Regtien, 2010). The intersection between the water solubilization ratio and oil solubilization ratio indicate the optimum salinity and concentration.

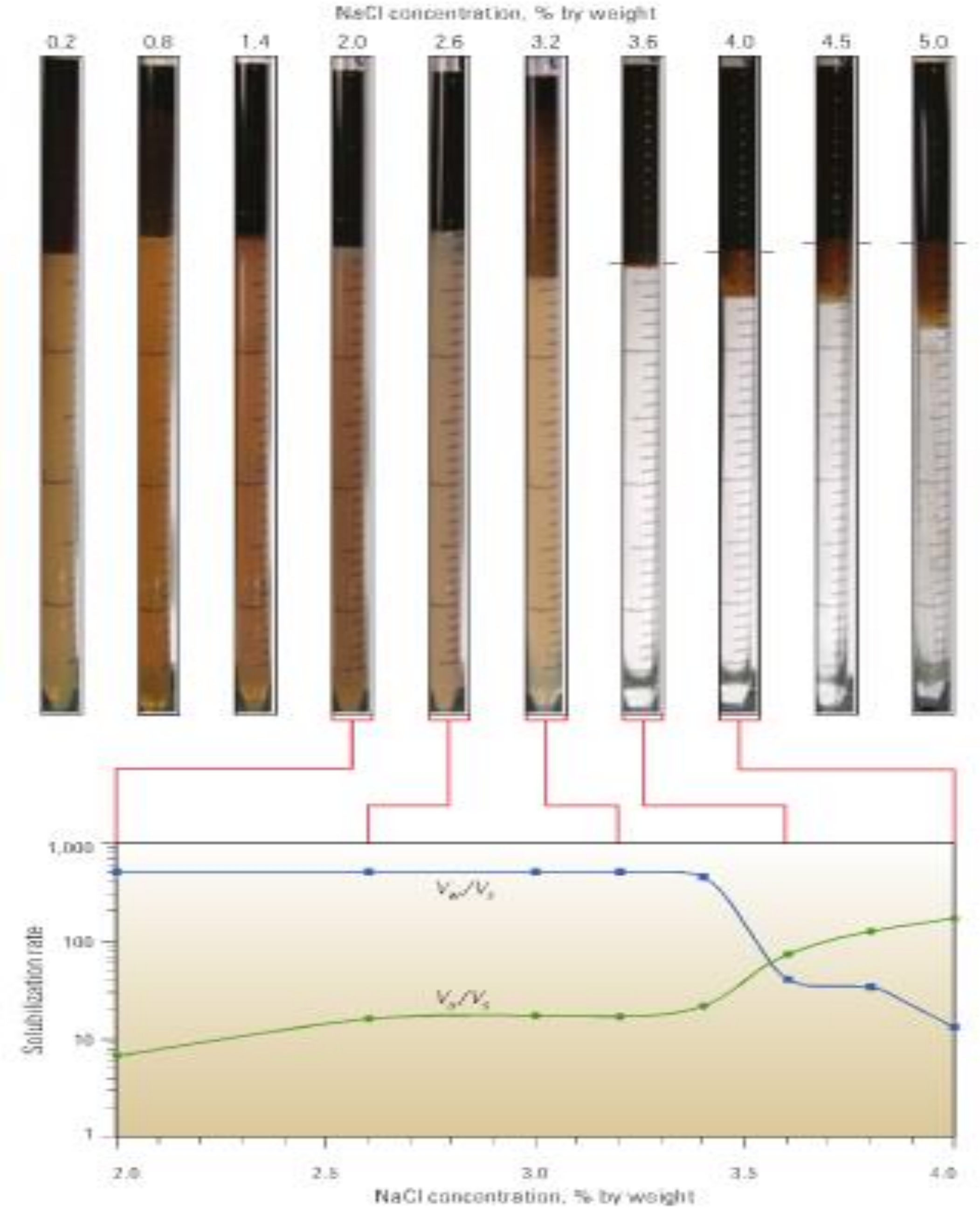


Figure 2 Microemulsion phase of different salinity and concentration of alkali (From Regtien, 2010)

2.5.3 ASP flooding in hard water

There are some modification is made to solve the scale formation in the hard water. In order to prevent scaling during ASP flooding, divalent cations need to be captured by addition agents that form water-soluble complexes with metal ions in the brine. Precipitation of mostly calcium carbonate at high pH precludes the use of seawater or produced water with high hardness in ASP without some treatment: water softening or desalination is necessary. Onshore, fresh water may be supplied without major technical problems, though it adds to the capital and operating costs whereas in offshore, the challenge of supplying fresh water is far more formidable (Karazincir et al., 2011).

According to (Flaaten, Nguyen, Pope, & Zhang, 2008) , sodium metaborate [$NaB(OH)_4$] as a weaker alkali may avoid the scale formation caused by the strong alkali as it is more tolerance towards the hard ions. Sodium metaborate has an advantage that the borate ions will form soluble complexes with dissolved calcium ions and minimize the formation of precipitate (Sahni, 2009). By replacing inorganic alkali to organic alkali and mixed with similar chemical used in the ASP flooding, it will give more tolerance for high salinity and high divalent cations concentrations (Berger & Lee, 2006).

Another research done by (Ibrahim, Alta???ee, Elraies, & Saaid, 2013) introduces a new in-situ precipitation inhibitor that able to improves the performance of the Alkaline Surfactant Polymer (ASP) flooding. The precipitation inhibitor known as sodium acrylate proved an excellent performance in preventing the formation of magnesium and calcium precipitate at 80^oC and the solution remained clear for 45 days. It also reduced the interfacial tension to 0.04mN/m and can be used in hard brines without softening the injection water.

2.5.4 Field application of ASP flooding

The field test started on September 24, 1994 in Western part of central Saertu, Daqing oil field with an increment of 21.4% OOIP oil recovery and reduction of water cut from 92% to 48.6%. The ASP flooding then was conducted in West part of north 1 zone of Daqing Oilfield in 1997 to investigate the displacement effectiveness. The program includes 6 injected wells and 12 production wells. It shows a good result where the water cut is reduced to 54.4% from 95% and lasted for 1 year. The recovery factor obtained is increased by 21%. There are 2 other fields implementing ASP flooding which are West Xing 2 area of Daqing Oilfield (September, 28 1996) and Xing-2 central area of Daqing Oilfield (April 2004) where both result 22% OOIP incremental of oil recovery according to (Shutang & Qiang, 2010).

CHAPTER 3

METHODOLOGY

3.1 Research Methodology

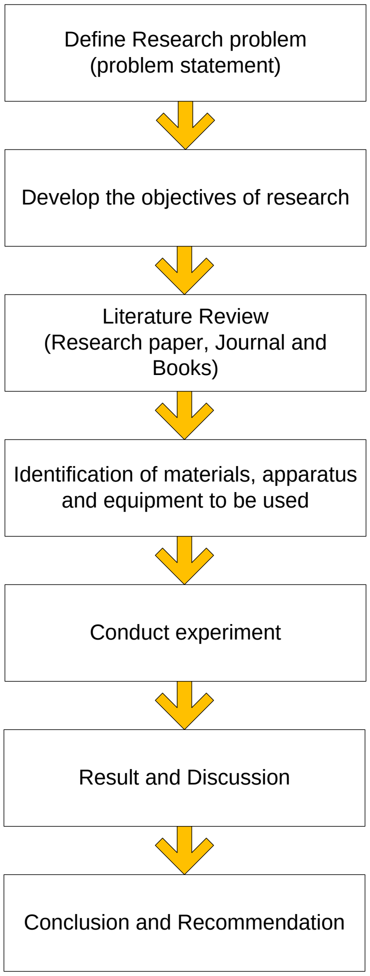


Figure 3 Research methodology

3.2 Project Activities (Experimental Description)

3.2.1 Tools and Materials

This section describes the list of experimental equipment and materials that is used in the preparation of the experiments done. The materials include 0.4 and 0.8wt% Sodium Metaborate [$NaB(OH)_4$], 0.4 and 0.8wt% Sodium Dodecyl Sulfate (SDS), 0.4 and 0.8wt% Polyacrylamide (PAM), Sodium Chloride (NaCl), Calcium Chloride (CaCl), Magnesium Chloride (MgCl), Distilled water and Dulang crude oil. The lists of experimental equipment are as follows:

Vials

The aqueous compatibility experiment was conducted using 10mL vials. The vials were used to observe the reaction of solution prepared whether there is formation of precipitate or not.

Weighing scale

The weighing scale is used to measure the weight of materials for aqueous compatibility and microemulsion phase behavior experiments.

Dropper

Dropper is an apparatus that is used in the viscosity test to drop the solution on a plate to measure the viscosity.

Pipette

A pipette with sucker used for pipetting the desired volume of aqueous solution. This apparatus could accurately dispense 5mL of fluid volume.

Measuring cylinder

A few 10mL measuring cylinders is used in the microemulsion phase behavior experiment. This graduated measuring cylinder is chosen in order to make it easy and accurate in measuring the height of water, oil and microemulsion formed as the measurement will be used in Chun Huh equation for calculating the solubilization ratio.

Convection oven

The convection oven is set to a desired temperature to incubate the aqueous compatibility and microemulsion phase behavior experiments.

Stirrer

A stirrer with magnetic stirrer is used to mix and make the stock solution that will be used in both experiments; aqueous compatibility and microemulsion phase behavior experiments.

Spinning drop tensiometer

Spinning drop tensiometer is used to measure the interfacial tension (IFT) between the solution and crude oil. The rotating horizontal tube is filled with solution (denser liquid) and drop of crude oil is injected in it to form a shape of length is 3 times the width.

Viscometer

The Brookfield viscometer is used to measure the viscosity of the solution. This equipment has 6 spindles that will give 6 readings of viscosity. The viscosity with the highest percentage will be taken as the actual viscosity of that solution.

The sections is continued with the procedure of the experiments that will be done which are aqueous compatibility, microemulsion phase behavior, IFT measurement using spinning drop method and viscosity measurement experiments. The procedures are as follows:

3.2.2 Aqueous Compatibility Test

Table 1 Experiment 1 (Aqueous Compatibility Test)

<table>
<tr><td>Experiment Title</td><td colspan="2">Aqueous Compatibility Test</td></tr>
<tr><td>Objective</td><td colspan="2">To find the optimum salinity of aqueous solution using Sodium Metaborate [$NaB(OH)_4$], Sodium Dodecyl Sulfate (SDS), and hard water (contain sodium, magnesium and calcium ion) to avoid precipitation of micro white particle</td></tr>
<tr><td>Theory</td><td colspan="2">The experiment was conducted to evaluate the aqueous solubility limitations by mixing alkaline stock, surfactant stock, and hard water solution over a range of salinities. With increasing in salinity, the aqueous solution tends to become cloudy or phase separation occurs because aqueous solubility decreases with salinity.</td></tr>
<tr><td rowspan="2">Methodology</td><td>Equipment/Apparatus</td><td>10 mL vials, graduated cylinder, weighing scale, convection oven</td></tr>
<tr><td>Material/Chemical</td><td>Sodium Metaborate, Sodium Dodecyl Sulfate, Sodium Chloride, Magnesium Chloride, Calcium Chloride, Distilled water, hard water of different salinity.</td></tr>
<tr><td>Hazard Identification</td><td colspan="2">All the chemicals involved are volatile. Inhalation can cause irritation to the lungs and will cause irritation to the skin.</td></tr>
<tr><td>Experiment procedure</td><td colspan="2">Preparation
• Alkali and Surfactant stock: a stock solution contains of alkali or surfactant and distilled water, mixed together until diluted.</td></tr>
</table>

- The concentration of the stock solution is varied and can be calculated using this formula:

$$\frac{2g\ of\ solute}{x\ g\ of\ solute} = \frac{1000\ mL}{y\ mL}$$

**y=volume of solution needed

x=amount of solute to dilute in y mL of solution

- Hard water: Prepared by mixing sodium chloride, magnesium chloride and calcium chloride in distilled water by using above formula.

Sample testing

- Solution containing alkali stock and hard water in wide range of salinities was dispensed in 10mL vials to check the compatibility of the components.
- Once all components were added into vials, vials were gently shaken and set inside the convection oven at the temperature of 50°C.
- After sufficient time to reach equilibrium (for this experiment 24 hours), the vials were checked visually and the salinity where cloudiness or phase separation occurred were recorded.
- The step is repeated to test solution containing alkali stock, surfactant stock and hard water.

Data Recording

($[NaB(OH)_4]$ + Hard water)

Solution	Precipitation	Cloudiness
a% $[NaB(OH)_4]$ + x ppm hard water		
b% $[NaB(OH)_4]$ + y ppm hard water		

([NaB(OH)4] + SDS + Hard water)

Solution	Precipitation	Cloudiness
a% $[NaB(OH)_4]$ + a% SDS + x ppm		

	hard water		
	b% [$NaB(OH)_4$] + b% SDS + y ppm hard water		
Expected Results	**Calculation**	$\frac{2g\ of\ solute}{x\ g\ of\ solute} = \frac{1000\ mL}{y\ mL}$	
	Data interpretation : Data recorded will be interpreted by observing if there is phase separation and cloudy solution or not.		
Conclusion	Aqueous solubility should be form a single and clear phase at the optimal salinity. Through this experiment, the optimal salinity of hard water will be determined and will be used in the microemulsion phase behavior test.		

3.2.3 Microemulsion Phase Behavior

Table 2 Experiment 2 (Microemulsion Phase Behavior)

Experiment Title	**Microemulsion Phase Behavior**
Objective	To check the performance of alkali, surfactant and hard water formulation with the specific crude oil
Theory	At low salinities, two phases which are lower phase micro-emulsion and pure excess oil are formed. The oil is normally on top of the micro emulsion because it has a lower density. It is called a Winsor type I, or type II (-). When the salinity is very high, a two phase solution is also formed with an upper phase micro-emulsion being in contact with excess brine. The density of the micro-emulsion is lower than the density of brine hence the reason for being the upper phase. The upper phase microemulsion is also named type II (+) or Winsor type II. At some optimum salinity somewhere between low and high salinity,

	a three phase solution is formed, where the middle phase is a micro-emulsion containing all the surfactant in the system in contact with excess oil and brine. The oil with the lowest density is on top while pure excess brine with the largest density is at the bottom of the micro-emulsion. The middle phase micro-emulsion is also named type III, or Winsor type III. Due to the presence of all the surfactant of the mixture in the type III micro-emulsion, its presence with oil will create a low interfacial tension which will enable easy displacement of the oil.	
Methodology	**Equipment/Apparatus**	**10mL measuring cylinder, convection oven**
	Material/Chemical	**Alkali stock, surfactant stock, hard water, crude oil and distilled water**
Hazard Identification	All the chemicals involved are volatile. Inhalation can cause irritation to the lungs and will cause irritation to the skin.	
Experiment procedure	Preparation: • Alkali and Surfactant stock: a stock solution contains of alkali or surfactant and distilled water, mixed together until diluted. • The concentration of the stock solution is varied and can be calculated using this formula: $\frac{2g\ of\ solute}{x\ g\ of\ solute} = \frac{1000\ mL}{y\ mL}$ **y=volume of solution needed x=amount of solute to dilute in y mL of solution • Hard water: Prepared by mixing sodium chloride, magnesium chloride and calcium chloride in distilled water by using above formula.	
	1. Procedure: • Injected components into the 10mL measuring cylinder consisted of alkali stock, surfactant stock,	

<table>
<tr>
<td rowspan="2"></td>
<td colspan="2">hard water and crude oil

First, hard water were added, followed by sodium alkali stock and surfactant stock. The order of addition is critical because the surfactant performance can be altered if surfactant stock contacts concentrated sodium carbonate
After injecting the aqueous components, the crude oil was added last
Solution were mix gently and thoroughly and were sealed to prevent reaction with oxygen
The measuring cylinder were placed in a convection oven at temperature of 50^oC
</td>
</tr>
<tr>
<td colspan="2">Data recorded:
<table>
<tr><td>Solution</td><td>a% [$NaB(OH)_4$] + a% SDS + x ppm hard water</td><td>b% [$NaB(OH)_4$] + b% SDS + x ppm hard water</td></tr>
<tr><td>Volume of oil</td><td></td><td></td></tr>
<tr><td>Volume of water</td><td></td><td></td></tr>
<tr><td>Volume of microemulsion</td><td></td><td></td></tr>
</table>

Solubilization ratio was observed over range of concentration of alkali, surfactant and polymer. All information was recorded.</td>
</tr>
<tr>
<td>Expected Results</td>
<td>Calculation</td>
<td>1. Solubilization ratio plot

Oil solubilization ratio: volume of oil solubilized divided by the volume of active surfactant in the microemulsion phase. The volume of oil is estimated by the interval between initial aqueous level and top interface level
</td>
</tr>
</table>

		- Water solubilization ratio: interval between initial aqueous level and bottom interface level $\sigma_o = \frac{V_o}{V_s}$ $\sigma_w = \frac{V_w}{V_s}$
	Data interpretation : - The trend of microemulsion phase behavior experiment was obtained through generating solubilization ratio of oil/water	
Conclusion	Optimal salinity is the intersection where oil solubilization and water solubilization curves are crossed	

3.2.4 Interfacial Tension (IFT) measurement

Table 3 IFT measurement

Experiment Title	**Interfacial Tension (IFT) measurement using spinning drop method**	
Objective	To make correlation between dynamic IFT and retention of emulsion	
Theory	The experiment was conducted to measure the dynamic Interfacial Tension (IFT) between crude oil and the solution prepared	
Methodology	**Equipment/Apparatus**	20mL vials, syringes, Spinning Drop Machine
	Material/Chemical	Crude oil, mixture of hard water (Sodium Chloride, Magnesium Chloride and Calcium Chloride), alkali (Sodium Metaborate) and surfactant (Sodium Dodecyl Sulfate), ethanol, distilled water Chloride, Calcium Chloride, Distilled water, hard water of different salinity.

<table>
<tr>
<td>Hazard Identification</td>
<td>All the chemicals involved are volatile. Inhalation can cause irritation to the lungs and will cause irritation to the skin.</td>
</tr>
<tr>
<td rowspan="3">Experiment procedure</td>
<td>Preparation

Alkali and Surfactant stock: a stock solution contains of alkali or surfactant and distilled water, mixed together until diluted.
The concentration of the stock solution is varied and can be calculated using this formula:

$$\frac{2g\ of\ solute}{x\ g\ of\ solute} = \frac{1000\ mL}{y\ mL}$$

**y=volume of solution needed
x=amount of solute to dilute in y mL of solution
Hard water: Prepared by mixing sodium chloride, magnesium chloride and calcium chloride in distilled water by using above formula.

</td>
</tr>
<tr>
<td>Sample testing

The density and Refractive Index (RI) of each aqueous solution containing hard water, alkali and surfactant also crude oil is measured.
The equipment is set up correctly where the solution is in the tube and crude oil will be injected in to form a pill-like shaped. The length of the shape should be 3 times of its width.
The measurement is run using full shape (drop type) and Profile Fit (L-Y / VG) with speed of 1200 (1/min) at start.
The drop will be calibrated and calculate for the dynamic IFT to get the average.

</td>
</tr>
<tr>
<td>Data Recording
<table>
<tr><th>Solution</th><th>Run</th><th>IFT (mN/m)</th></tr>
<tr><td rowspan="2">a% [NaB(OH)$_4$] + a% SDS + x ppm hard water</td><td>1</td><td></td></tr>
<tr><td>2</td><td></td></tr>
</table>
</td>
</tr>
</table>

		3
Expected Results	**Calculation**	$\frac{2g\ of\ solute}{x\ g\ of\ solute} = \frac{1000\ mL}{y\ mL}$
	Data interpretation : 100 readings will be recorded take the average value. The IFT recorded will be plotted to investigate the performance of each solution prepared and compare with the solubilization ratio calculated in the previous experiment.	
Conclusion	The Interfacial Tension (IFT) recorded should be a low value to indicate the effectiveness of the solution prepared.	

3.2.5 Viscosity measurement

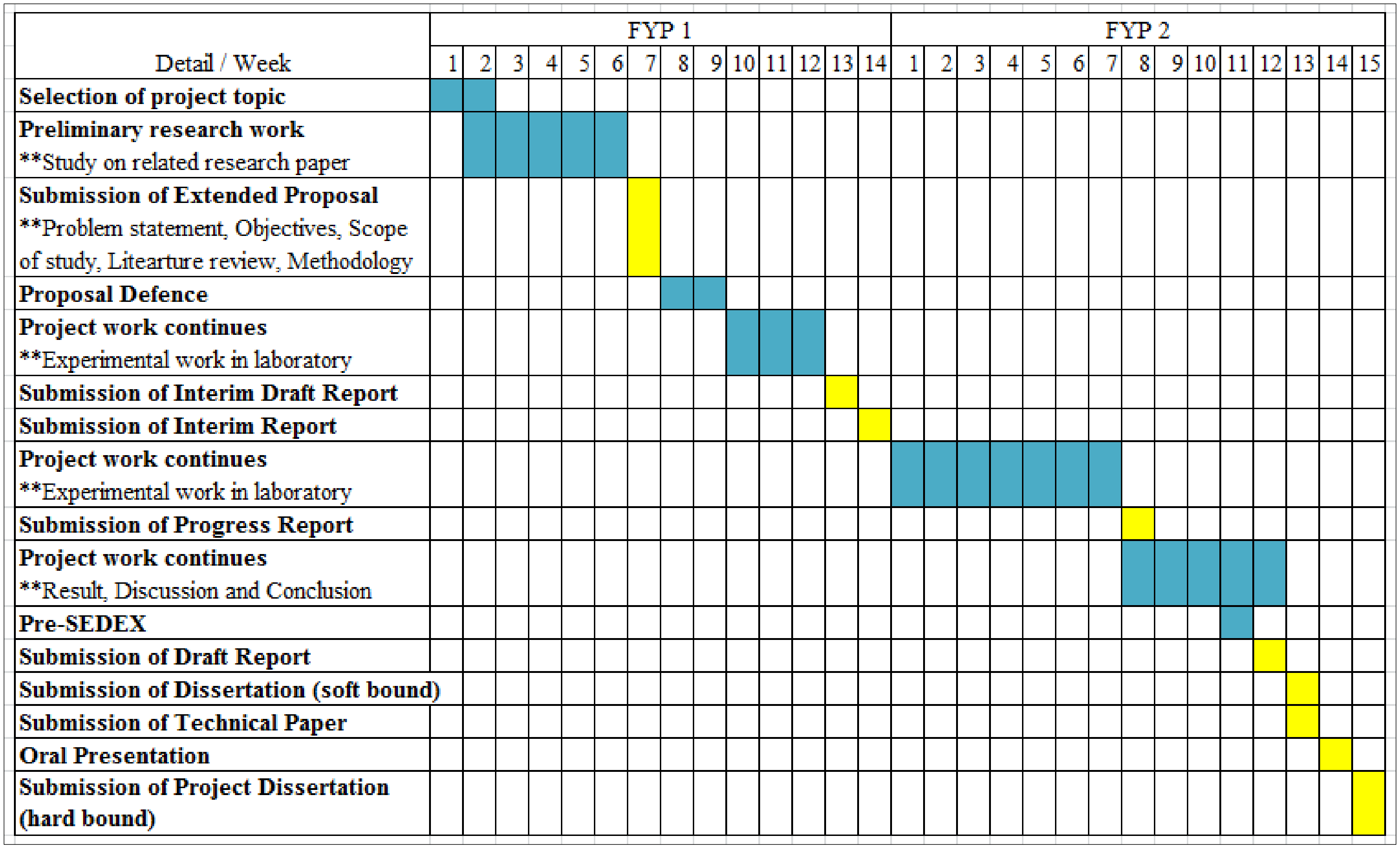
Table 4 Viscosity measurement

Experiment Title	**Viscosity measurement**	
Objective	To study the effect of hard water to the performance of polymer	
Theory	The experiment was conducted to measure the viscosity of mixture of hard water and polymer, brine and polymer also distilled water and polymer and to compare the performance of polymer in different solution	
Methodology	**Equipment/Apparatus**	20mL vials, dropper, Brookfield viscometer
	Material/Chemical	Crude oil, mixture of hard water and PAM, brine and PAM, distilled water and PAM
Hazard Identification	All the chemicals involved are volatile. Inhalation can cause irritation to the lungs and will cause irritation to the skin.	
Experiment	Preparation	

<table>
<tr><td rowspan="3">procedure</td><td>Polymer stock: a stock solution contains of polymer and distilled water, mixed together until diluted.
The concentration of the stock solution is varied and can be calculated using this formula:
$$\frac{2g\ of\ solute}{x\ g\ of\ solute} = \frac{1000\ mL}{y\ mL}$$
**y=volume of solution needed
x=amount of solute to dilute in y mL of solution
Hard water: Prepared by mixing sodium chloride, magnesium chloride and calcium chloride in distilled water by using above formula.</td></tr>
<tr><td>Sample testing
The viscometer was set up correctly using 100 rpm, temperature of 50^{o}C and centipoise (cp) for the shear viscosity unit.
Each solution will be tested for 6 different spindle</td></tr>
<tr><td>Data Recording<table><tr><th>Solution</th><th>Spindle</th><th>Viscosity (cp)</th></tr><tr><td rowspan="3">a% PAM + x ppm hard water</td><td>1</td><td></td></tr><tr><td>2</td><td></td></tr><tr><td>3</td><td></td></tr></table></td></tr>
<tr><td rowspan="2">Expected Results</td><td>Calculation $$\frac{2g\ of\ solute}{x\ g\ of\ solute} = \frac{1000\ mL}{y\ mL}$$</td></tr>
<tr><td>Data interpretation :
Each spindle will give a reading of shear viscosity and percentage. The highest percentage among 6 spindles will be taken as actual shear viscosity.</td></tr>
<tr><td>Conclusion</td><td>The shear viscosity of the solution should be higher than the viscosity of crude oil in order to improve the sweep efficiency of ASP flooding.</td></tr>
</table>

3.3 Gantt Chart

Table 5 FYP Gantt chart and Key Milestone

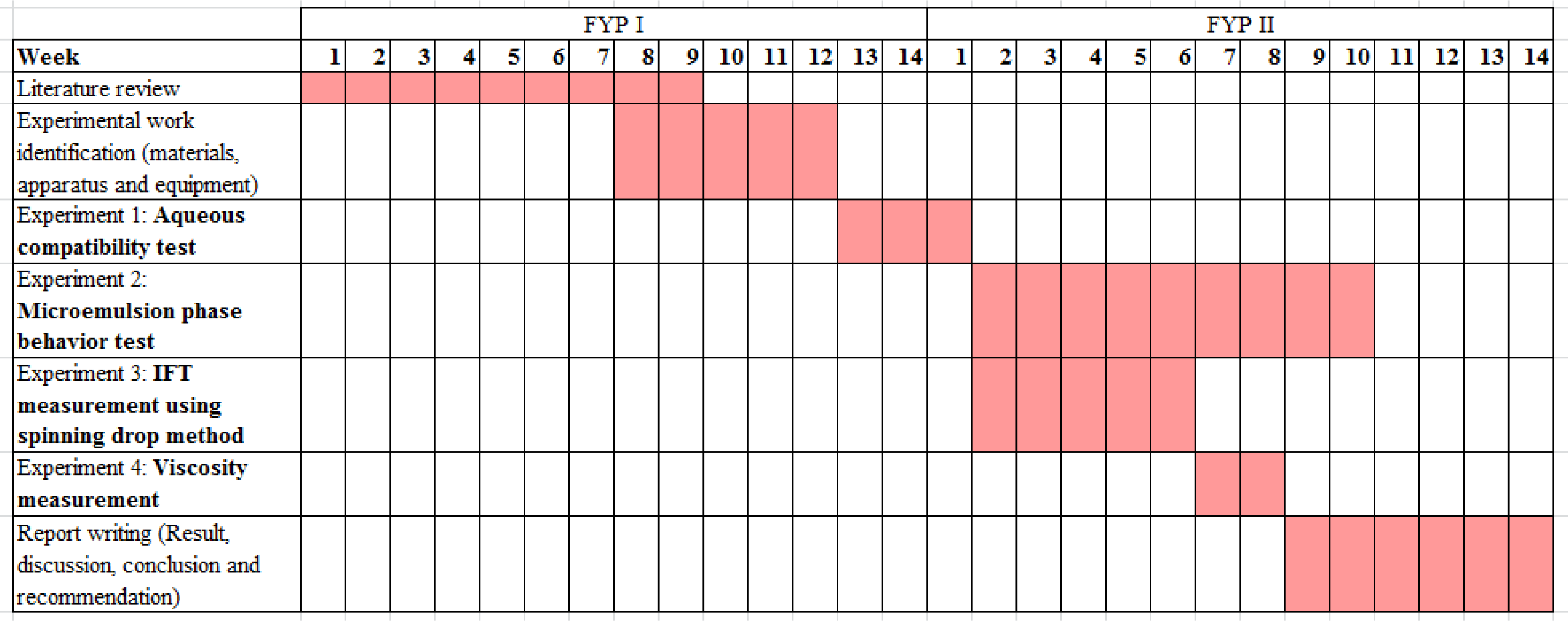


Detail / Week	FYP 1														FYP 2														
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Selection of project topic	🟦	🟦																											
Preliminary research work **Study on related research paper		🟦	🟦	🟦	🟦	🟦																							
Submission of Extended Proposal **Problem statement, Objectives, Scope of study, Litearture review, Methodology							🟨																						
Proposal Defence								🟦	🟦																				
Project work continues **Experimental work in laboratory										🟦	🟦	🟦																	
Submission of Interim Draft Report													🟨																
Submission of Interim Report														🟨															
Project work continues **Experimental work in laboratory															🟦	🟦	🟦	🟦	🟦	🟦	🟦								
Submission of Progress Report																						🟨							
Project work continues **Result, Discussion and Conclusion																						🟦	🟦	🟦	🟦	🟦			
Pre-SEDEX																									🟦				
Submission of Draft Report																										🟨			
Submission of Dissertation (soft bound)																											🟨		
Submission of Technical Paper																											🟨		
Oral Presentation																												🟨	
Submission of Project Dissertation (hard bound)																													🟨

🟦 Process

🟨 Key Milestones

Table 6 Project Gantt chart



	FYP I														FYP II													
Week	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**
Literature review	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥																			
Experimental work identification (materials, apparatus and equipment)								🟥	🟥	🟥	🟥	🟥																
Experiment 1: **Aqueous compatibility test**													🟥	🟥	🟥													
Experiment 2: **Microemulsion phase behavior test**																🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥				
Experiment 3: **IFT measurement using spinning drop method**																🟥	🟥	🟥	🟥	🟥								
Experiment 4: **Viscosity measurement**																					🟥	🟥						
Report writing (Result, discussion, conclusion and recommendation)																							🟥	🟥	🟥	🟥	🟥	🟥

CHAPTER 4

RESULT AND DISCUSSION

4.1 Aqueous solubility test

The hard water used varies in salinity where each will contain different amount of sodium chloride, magnesium chloride and calcium chloride in it. The weight percentage (wt%) of these element differentiate the level of salinity of each hard water. In Malaysia water, the salinity recorded is around 27800ppm. A study has been done to investigate the effect of salinity towards alkali, also alkali and surfactant. The hard water contains hard ions such as magnesium and calcium ions which will react with the sodium metaborate to form precipitation.

Table 7 Alkali-Hard water Test

		Salinity	Precipitation
1a	0.2% $NaB(OH)_4$	27800	Yes
1b	0.5% $NaB(OH)_4$		Yes
1c	1.0% $NaB(OH)_4$		Yes
2a	0.2% $NaB(OH)_4$	23800	No
2b	0.5% $NaB(OH)_4$		Yes
2c	1.0% $NaB(OH)_4$		Yes
3a	0.2% $NaB(OH)_4$	21400	No
3b	0.5% $NaB(OH)_4$		No
3c	1.0% $NaB(OH)_4$		No

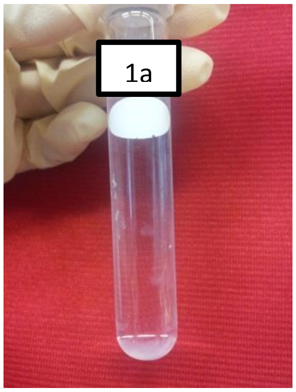
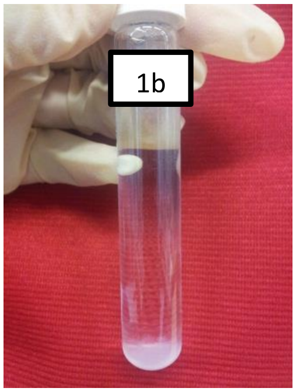
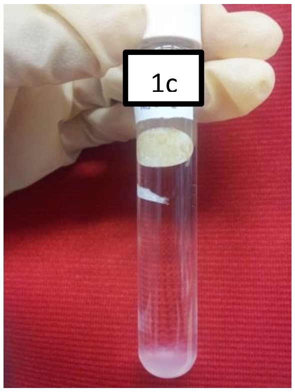
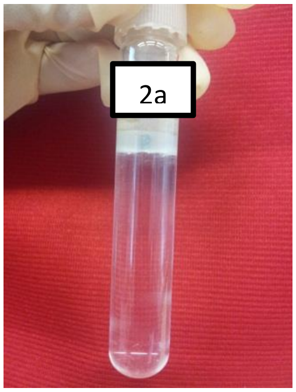
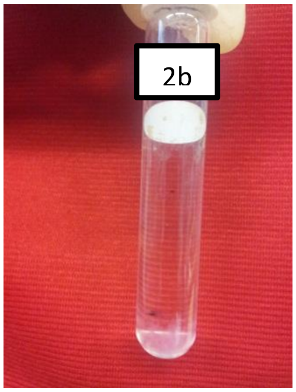
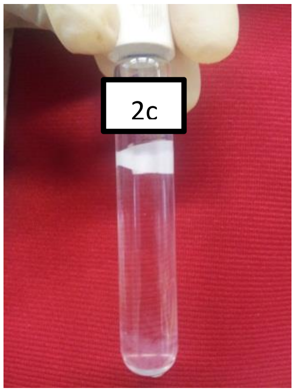
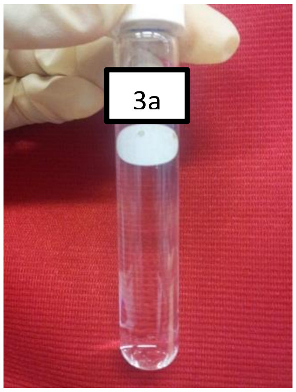
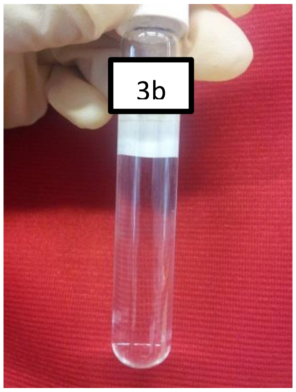
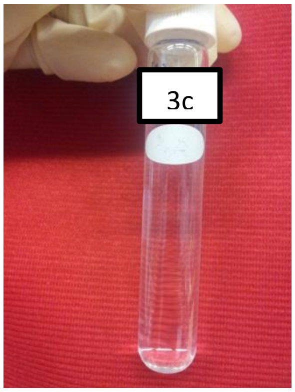
<table>
<tr><td colspan="3">27800 ppm</td></tr>
<tr>
<td> </td>
<td> </td>
<td> </td>
</tr>
<tr><td colspan="3">23800 ppm</td></tr>
<tr>
<td> </td>
<td> </td>
<td> </td>
</tr>
<tr><td colspan="3">21400 ppm</td></tr>
<tr>
<td> </td>
<td> </td>
<td> </td>
</tr>
</table>

Figure 4 Alkali-Hard water Sample

Table 8 Alkali-Surfactant-Hard water Test

		Salinity	Precipitation
1a	0.2% $NaB(OH)_4$ + 0.2% SDS	27800	Yes
1b	0.5% $NaB(OH)_4$ + 0.2% SDS		Yes
1c	1.0% $NaB(OH)_4$ + 0.2% SDS		Yes
2a	0.2% $NaB(OH)_4$ + 0.5% SDS	23800	Yes
2b	0.5% $NaB(OH)_4$ + 0.5% SDS		Yes
2c	1.0% $NaB(OH)_4$ + 0.5% SDS		No
3a	0.2% $NaB(OH)_4$ + 1.0% SDS	21400	No
3b	0.5% $NaB(OH)_4$ + 1.0% SDS		No
3c	1.0% $NaB(OH)_4$ + 1.0% SDS		No

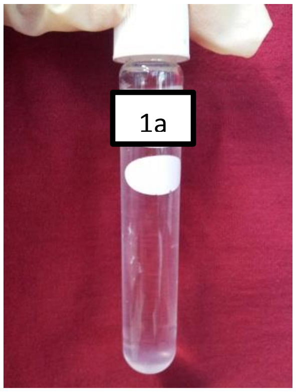
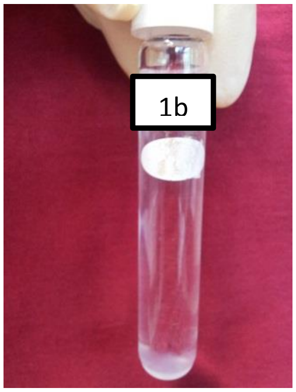
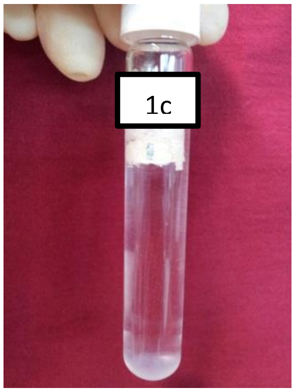
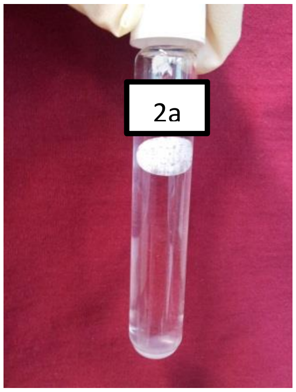
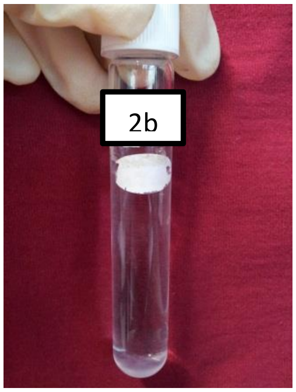
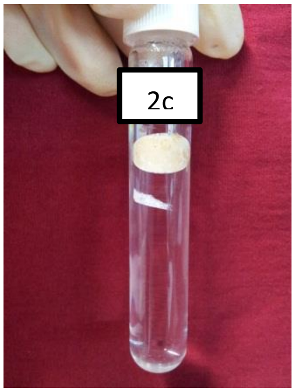
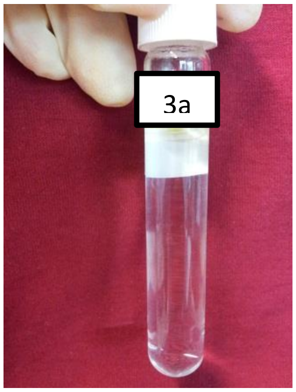
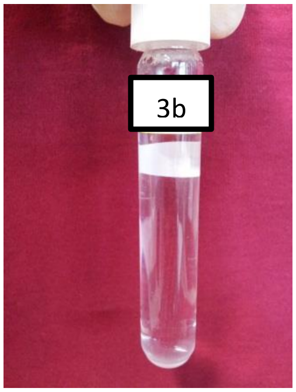
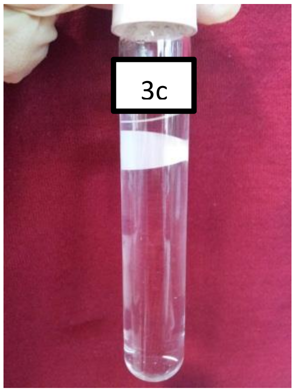
<table>
<tr><td colspan="3">27800 ppm</td></tr>
<tr>
<td> </td>
<td> </td>
<td> </td>
</tr>
<tr><td colspan="3">23800 ppm</td></tr>
<tr>
<td> </td>
<td> </td>
<td> </td>
</tr>
<tr><td colspan="3">21400 ppm</td></tr>
<tr>
<td> </td>
<td> </td>
<td> </td>
</tr>
</table>

Figure 5 Alkali-Surfactant-Hard water Sample

(Yang, 2010) report that with an increasing in salinity, the aqueous solution tends to become cloudy or phase separation occurs because aqueous solubility decreases with salinity. The phase separation mentioned is formation of precipitation in the solution. From the observation throughout the experiment, it shows that as the salinity decrease, the amount of precipitation (in the form of suspension) decrease which is tally with theory by (Yang, 2010). Figure 5 shows that salinity of 21400ppm which consists of 20000ppm sodium chloride, 1000ppm of magnesium chloride and 400ppm of calcium chloride gave no precipitation in the mixture of $NaB(OH)_4$ and SDS, hence, it will be used as base case to identify the optimum salinity using microemulsion phase behavior test.

The salinity tested ranged from 11400ppm to 26400ppm which is presented in Table 8 below. Each of the salinity is tested with different formulation of alkali (sodium metaborate) and surfactant (sodium dodecyl sulfate). According to the observation from result of microemulsion phase behavior test, it shows three different layers of mixture. The three different layers indicated by distinct color of mixture which the uppermost is black, followed by brown and colorless/clear which are oil, microemulsion and brine respectively.

Table 9 Salinity tested in Microemulsion Phase Behavior test

Salinity (ppm)	Formulation (ppm)
11400	10000 NaCl + 1000 MgCl + 400 CaCl
16400	15000 NaCl + 1000 MgCl + 400 CaCl
21400	20000 NaCl + 1000 MgCl + 400 CaCl
26400	25000 NaCl + 1000 MgCl + 400 CaCl

4.2 Microemulsion Phase Behavior Test

The interaction between sodium metaborate with the acid in the crude will form microemulsion, in this case brown in color which will combine with the surfactant added and reduce the interfacial tension (IFT). The observation has been made after 24, 72 and 120 hours. Based on research done by (Yang, 2010), the optimal salinity of hard water is defined by the intersection of oil solubilization ratio and water solubilization ratio. The oil/ water solubilization is calculated based on the ratio of volume of oil/water and volume of surfactant.

The water and oil solubilization ratio after 120 hours is plotted in a graph to identify the intersection point of these plots which indicates the optimum salinity of hard water. Table 9 summarized the oil and water solubilization ratio for each formulation.

Table 10 Microemulsion Phase Behavior test (after 120 hours)

			Height (cm)			Solubilization ratio	
	NaCl (wt%)	Sample	Water	Microemulsion	Oil	Water	Oil
0.4% $NaB(OH)_4$ + 0.4% SDS	1.0	1a	4.8	0.6	4.6	12.000	11.500
	1.5	2a	4.6	0.8	4.6	11.500	11.500
	2.0	3a	4.6	1.0	4.4	11.500	11.000
	2.5	4a	4.6	1.0	4.4	11.500	11.000
0.4% $NaB(OH)_4$ + 0.8% SDS	1.0	1b	4.6	1.0	4.4	5.750	5.500
	1.5	2b	4.2	1.4	4.4	5.250	5.500
	2.0	3b	3.6	2.0	4.4	4.500	5.500
	2.5	4b	4.2	1.4	4.4	5.250	5.500
0.8% $NaB(OH)_4$ + 0.4% SDS	1.0	1c	4.8	0.6	4.6	12.000	11.500
	1.5	2c	4.8	0.6	4.6	12.000	11.500
	2.0	3c	4.6	1.0	4.4	11.500	11.000
	2.5	4c	3.8	1.8	4.4	9.500	11.000
0.8% $NaB(OH)_4$ + 0.8% SDS	1.0	1d	4.6	1.0	4.4	5.750	5.500
	1.5	2d	4.6	0.8	4.6	5.750	5.750
	2.0	3d	4.2	1.4	4.4	5.250	5.500
	2.5	4d	4.4	1.0	4.6	5.500	5.750

Figure 6, 7, 8 and 9 shows the formulation of different salinity of hard water with 0.4% of $NaB(OH)_4$ and 0.4% of SDS, 0.4% of $NaB(OH)_4$ and 0.8% of SDS, 0.8% of $NaB(OH)_4$ and 0.4% of SDS also 0.8% of $NaB(OH)_4$ and 0.8% of SDS respectively. The intersection point between oil solubilization ratio and water solubilization ratio for all samples indicates the optimum salinity of hard water to be used with respective formulation.

The optimum salinity for formulation of 0.4% of NaB(OH)4 and 0.4% of SDS, 0.4% of NaB(OH)4 and 0.8% of SDS, also 0.8% of NaB(OH)4 and 0.8% of SDS is 16400ppm whereas the optimum salinity for formulation 0.8% of NaB(OH)4 and 0.4% of SDS is 21400ppm (2.0 wt% NaCl).

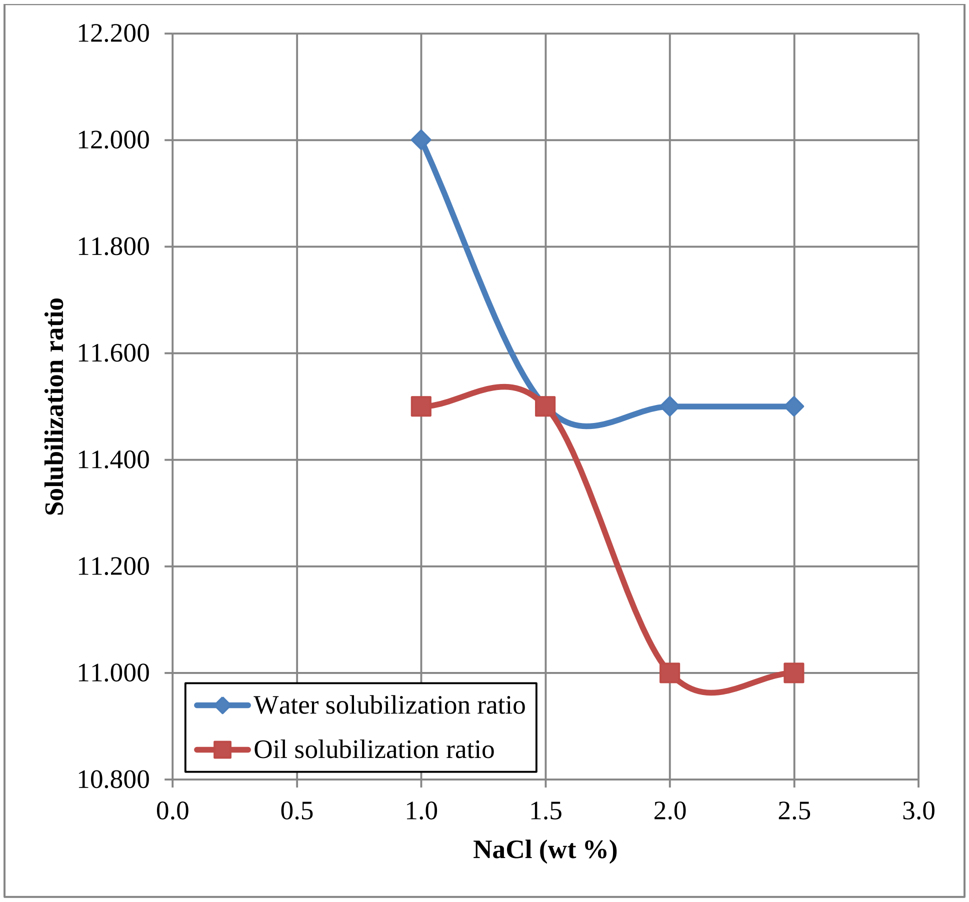


Figure 6 Solubilization ratio plot of 0.4% $NaB(OH)_4$ and 0.4% SDS after 120 hours

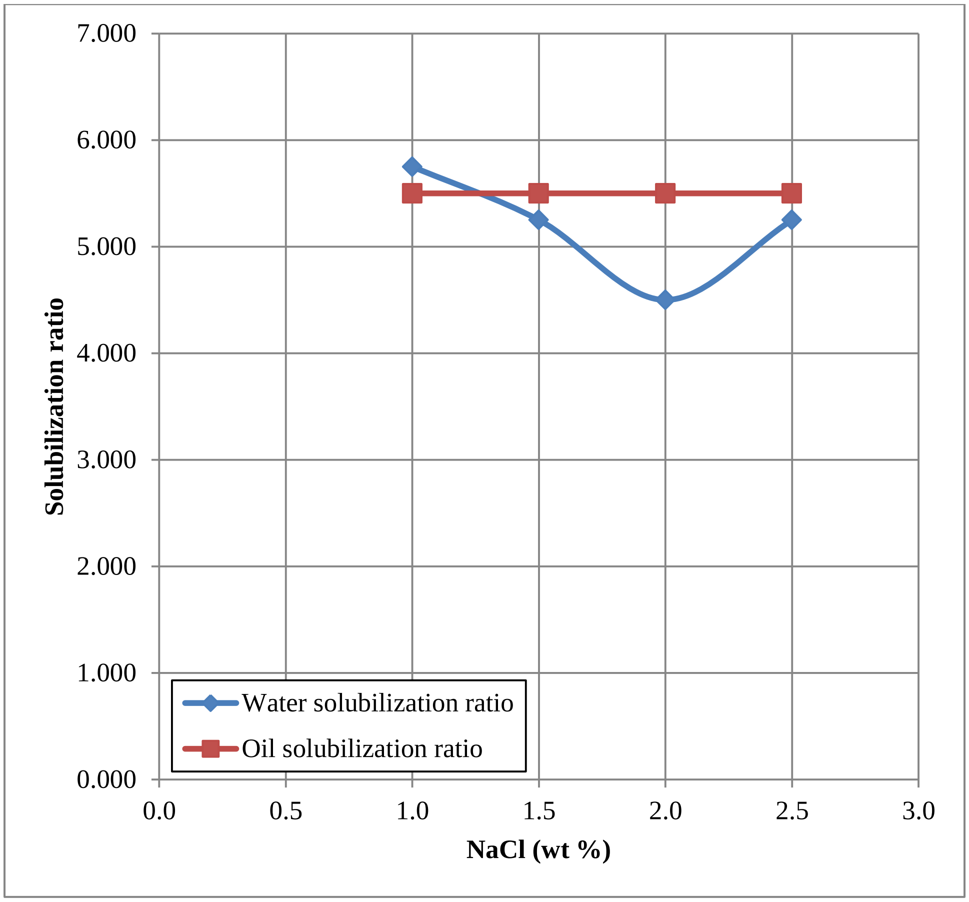


Figure 7 Solubilization ratio plot of 0.4% NaB(OH)$_4$ and 0.8% SDS after 120 hours

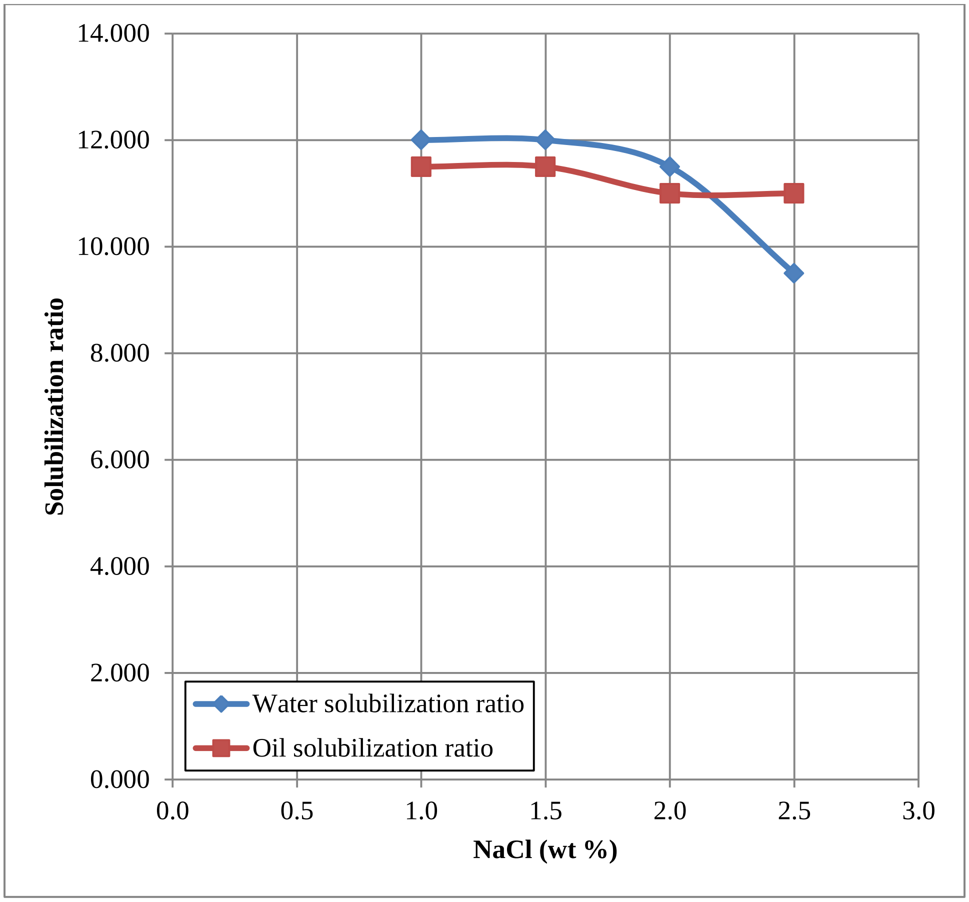


Figure 8 Solubilization ratio plot of 0.8% NaB(OH)$_4$ and 0.4% SDS after 120 hours

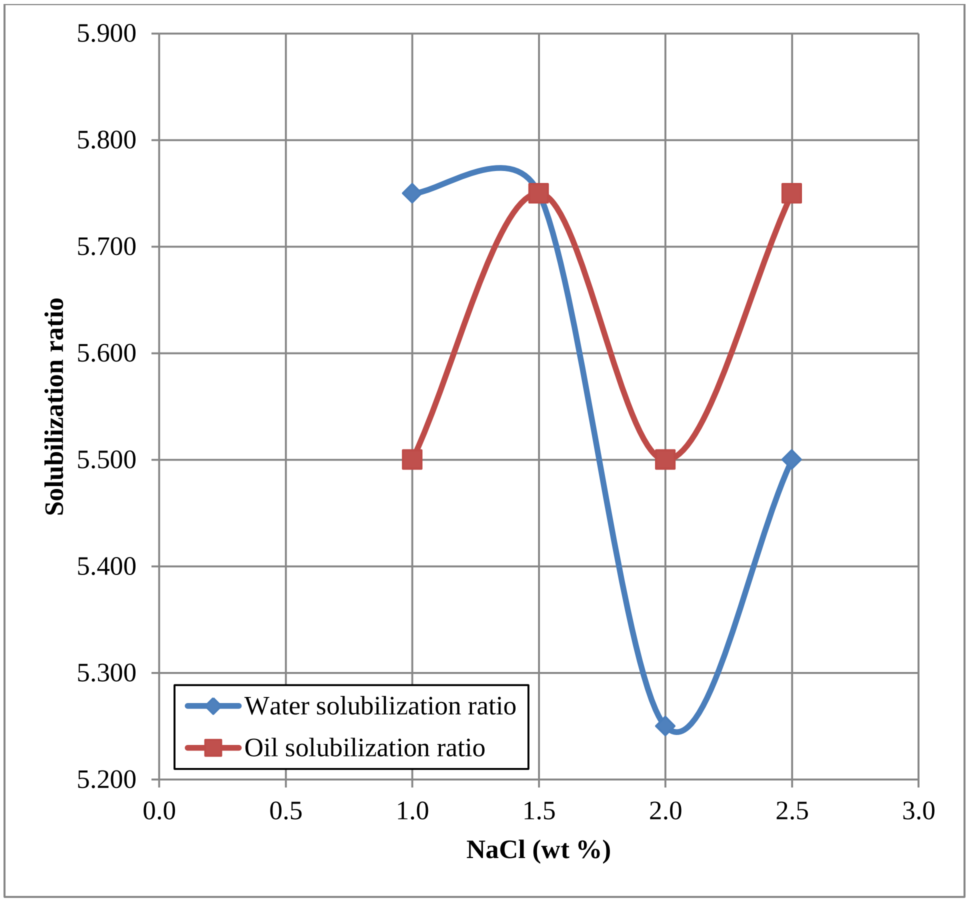


Figure 9 Solubilization ratio plot of 0.8% NaB(OH)$_4$ and 0.8% SDS after 120 hours

Height of oil, water and microemulsion is recorded and plotted in a graph to see the different height of microemulsion formed by a specific formulation of NaB(OH)4 and SDS and different salinity of hard water after 24, 72 and 120 hours as summarized in Table 10. According to (Glover, 1979), microemulsion retention is shown to increase linearly with salinity at low salt concentrations and depart from linearity with higher retentions above a critical salinity.

Effects of salinity and surfactant concentration on microemulsion phase behavior have a significant impact on relative magnitudes of retention attributed to adsorption vs. entrapment of immiscible microemulsion phases (Glover, 1979). However, the retention result shown in Table 11, does not really represent as what has mentioned by (Glover, 1979) due to small range concentration of surfactant used. Most samples become more stabilized after 72 hours where the height of microemulsion does not change in the following 48 hours of observation.

Figure 10 shows result based on formulation of 0.4% of $NaB(OH)_4$ and 0.4% of SDS where the highest microemulsion formed after 120 hours of 1.0 cm are with salinity of 2.0% and 2.5% NaCl which are 21400 and 26400ppm respectively. Sample from formulation of 0.8% of $NaB(OH)_{4,}$ 0.4% of SDS in Figure 11 shows the highest microemulsion after 120 hours is 2.0 cm with salinity of 21400ppm (2.0 wt% NaCl). The highest microemulsion formed after 120 hours for formulation of 0.8% of $NaB(OH)_{4,}$ 0.4% of SDS with 26400ppm hard water (2.5 wt% NaCl) is 1.8cm whereas for formulation of 0.8% of $NaB(OH)_{4,}$ 0.8% of SDS with salinity of 21400ppm the microemulsion is 1.4cm showed in Figure 12 and 13 respectively.

The small amount of microemulsion formed for all formulation indicates that the less reaction between alkali used and crude oil. This happen because of sodium metaborate is a weak alkali which has been mentioned by (Flaaten, Nguyen, Pope, & Zhang, 2008). Table 11 summarized the height of microemulsion reduction for each formulation after 24, 72 and 120 hours.

Table 11 The height of microemulsion after 24, 72 and 120 hours for each sample

			24 hours			72 hours			120 hours		
			Volume (cm)			Volume (cm)			Volume (cm)		
	NaCl (wt%)	Sample	Water	Microemulsion	Oil	Water	Microemulsion	Oil	Water	Microemulsion	Oil
0.4% NaB(OH)$_4$ + 0.4% SDS	1.0	1a	4.4	1.2	4.4	4.8	0.6	4.6	4.8	0.6	4.6
	1.5	2a	4.4	1.0	4.6	4.6	0.8	4.6	4.6	0.8	4.6
	2.0	3a	4.2	1.4	4.4	4.6	1.0	4.4	4.6	1.0	4.4
	2.5	4a	4.6	1.0	4.4	4.6	1.0	4.4	4.6	1.0	4.4
0.4% NaB(OH)$_4$ + 0.8% SDS	1.0	1b	4.6	1.0	4.4	4.6	1.0	4.4	4.6	1.0	4.4
	1.5	2b	4.0	1.6	4.4	4.2	1.4	4.4	4.2	1.4	4.4
	2.0	3b	3.2	2.4	4.4	3.4	2.2	4.4	3.6	2.0	4.4
	2.5	4b	4.0	1.6	4.4	4.2	1.4	4.4	4.2	1.4	4.4
0.8% NaB(OH)$_4$ + 0.4% SDS	1.0	1c	4.8	0.8	4.4	4.8	0.6	4.6	4.8	0.6	4.6
	1.5	2c	4.6	1.0	4.4	4.6	0.8	4.6	4.8	0.6	4.6
	2.0	3c	4.4	1.2	4.4	4.6	1.0	4.4	4.6	1.0	4.4
	2.5	4c	3.6	2.0	4.4	3.8	1.8	4.4	3.8	1.8	4.4
0.8% NaB(OH)$_4$ + 0.8% SDS	1.0	1d	3.8	1.8	4.4	4.2	1.4	4.4	4.6	1.0	4.4
	1.5	2d	4.6	0.8	4.6	4.6	0.8	4.6	4.6	0.8	4.6
	2.0	3d	3.8	1.8	4.4	4.2	1.4	4.4	4.2	1.4	4.4
	2.5	4d	4.2	1.4	4.4	4.4	1.0	4.6	4.4	1.0	4.6

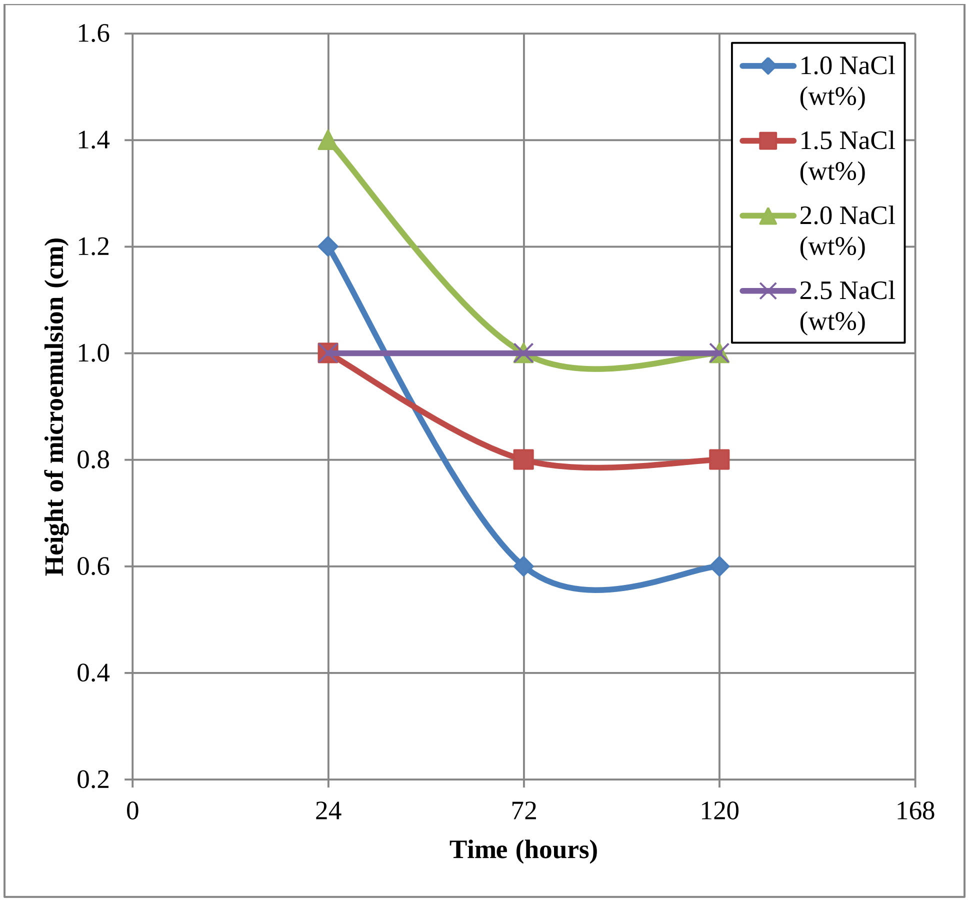


Figure 10 Microemulsion retention test using 0.4% $NaB(OH)_4$ + 0.4% SDS after 24, 72 and 120 hours

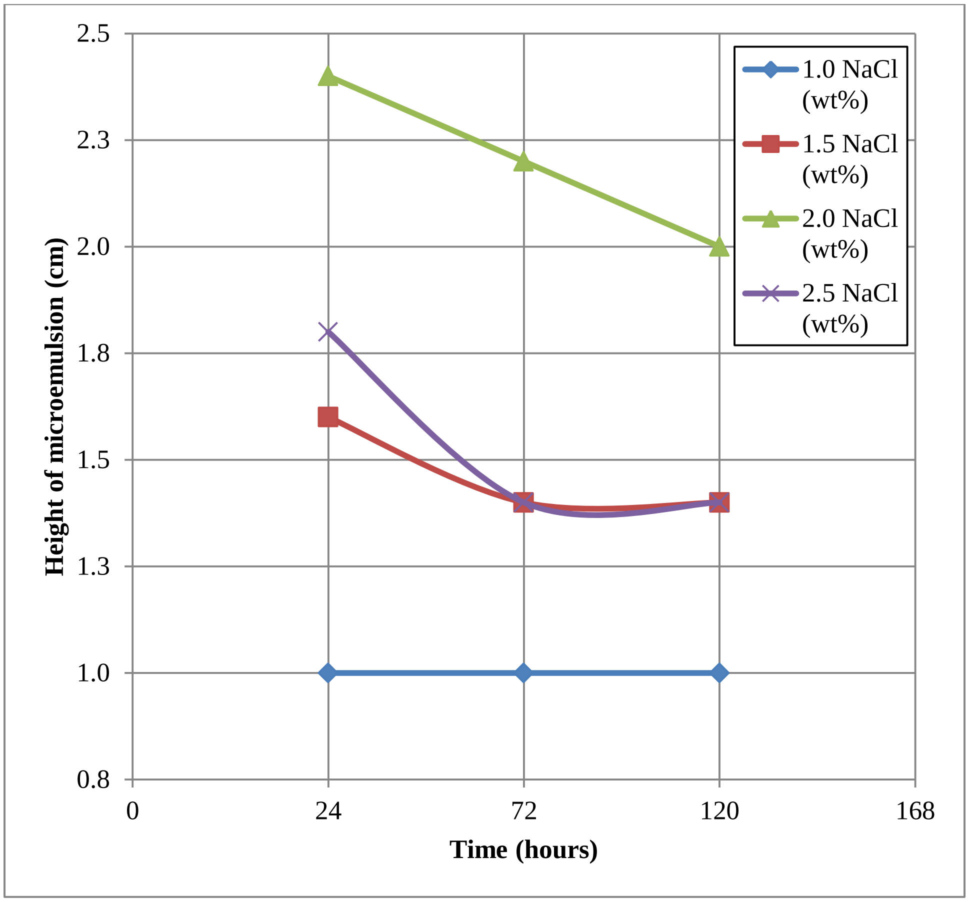


Figure 11 Microemulsion retention test using 0.4% $NaB(OH)_4$ + 0.8% SDS after 24, 72 and 120 hours

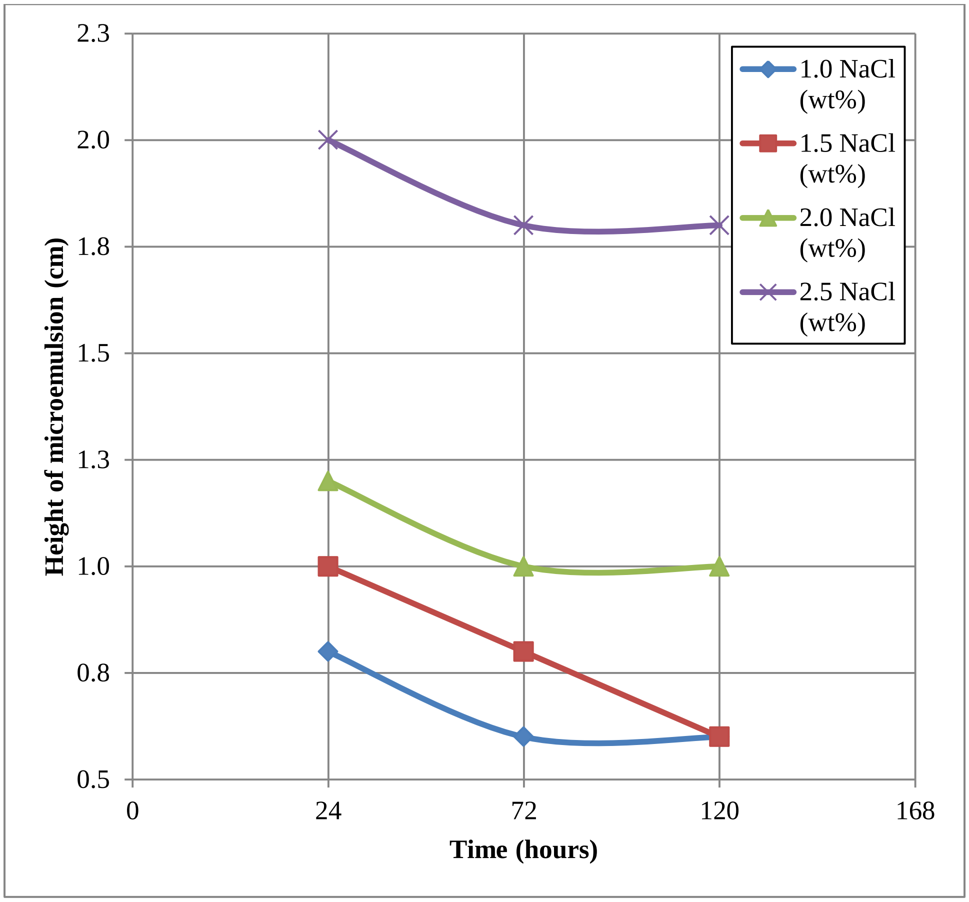


Figure 12 Microemulsion retention test using 0.8% $NaB(OH)_4$ + 0.4% SDS after 24, 72 and 120 hours

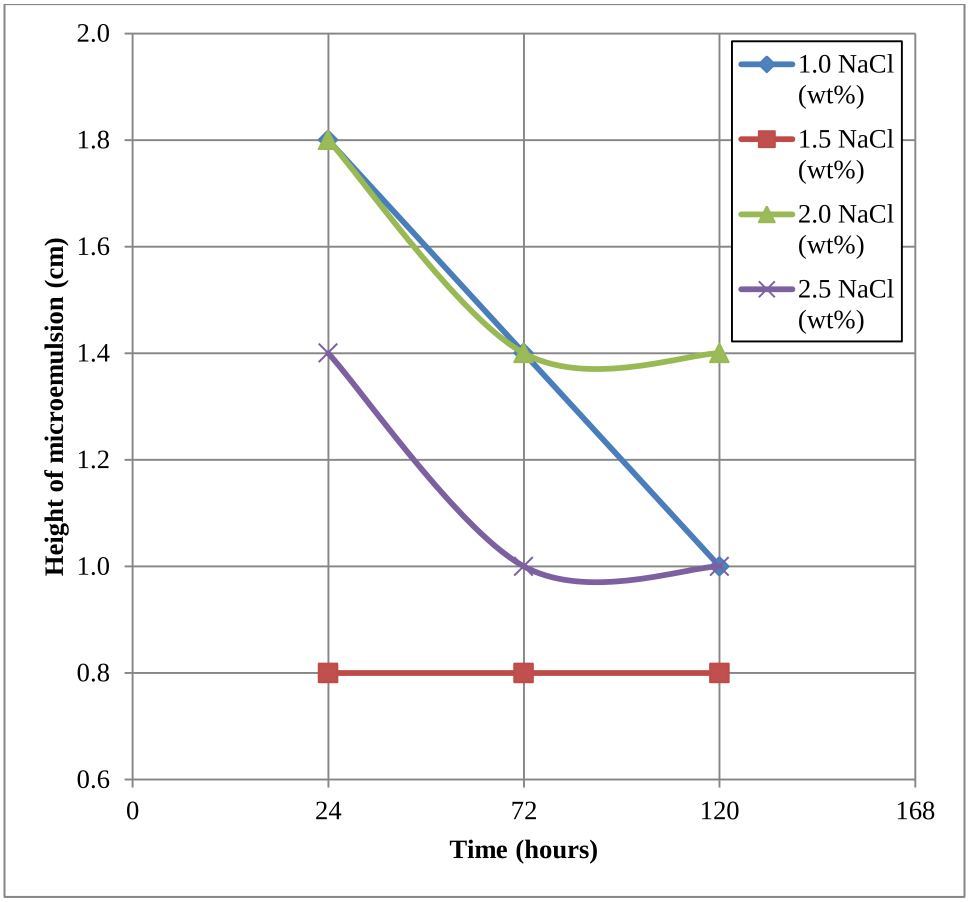


Figure 13 Microemulsion retention test using 0.8% $NaB(OH)_4$ + 0.8% SDS after 24, 72 and 120 hours

Table 12 Microemulsion Retention Test (24, 72 and 120 hours)

			Height (cm)		
	NaCl (wt%)	Sample	24 hours	72 hours	120 hours
0.4% NaB(OH)$_4$ + 0.4% SDS	1.0	1a	1.2	0.6	0.6
	1.5	2a	1.0	0.8	0.8
	2.0	3a	1.4	1.0	1.0
	2.5	4a	1.0	1.0	1.0
0.4% NaB(OH)$_4$ + 0.8% SDS	1.0	1b	1.0	1.0	1.0
	1.5	2b	1.6	1.4	1.4
	2.0	3b	2.4	2.2	2.0
	2.5	4b	1.8	1.4	1.4
0.8% NaB(OH)$_4$ + 0.4% SDS	1.0	1c	0.8	0.6	0.6
	1.5	2c	1.0	0.8	0.6
	2.0	3c	1.2	1.0	1.0
	2.5	4c	2.0	1.8	1.8
0.8% NaB(OH)$_4$ + 0.8% SDS	1.0	1d	1.8	1.4	1.0
	1.5	2d	0.8	0.8	0.8
	2.0	3d	1.8	1.4	1.4
	2.5	4d	1.4	1.0	1.0

(Sahni, 2009) has described briefly the three types of phase equilibrium in microemulsion phase behavior based on Winsor theory. According to Winsor, the three types are Type I, Type II and Type III. Type I is an oil-in-water microemulsion with an excess brine phase, Type II is a water-in-oil microemulsion with an excess oil phase whereas Type III provides low interfacial tensions, especially where equal volumes of water and oil are solubilized in the microemulsion.

Throughout the experiment, only Type III microemulsion phase behavior had been recognized. At the early stage of the experiment, the solution is mixed well with the crude oil and as the observation continues, the mixture has separated into three different layers consist of brine (at the bottom), microemulsion (at the middle) and oil (at the top) which described it as Type III microemulsion phase behavior.

4.3 Spinning Drop method

Based on Chun Huh equation, the value of interfacial tension (IFT) for each sample is calculated. The IFT calculated from the Microemulsion Phase Behavior experiment (Day 1) is compared to the IFT measured by the Spinning Drop machine. Even though IFT measured by spinning drop method is fluctuated but it is more reliable compared to the IFT calculated from Chun Huh equation as the microemulsion phase behavior experiment should has been done using borosilicate pipette instead of graduated measuring cylinder in order to have better solubilization ratio. The percentage error is calculated by the formula below:

$$Error\ (\%) = \frac{IFT\ (Spinning\ drop\ method) - IFT\ (Chun\ Huh)}{IFT\ (Spinning\ drop\ method)} \times 100\%$$

The high difference values of IFT are caused by parallax error in while measuring the height of oil, microemulsion and water for solubilization ratio calculation and also poor familiarization of equipment (Spinning drop tensiometer). The shape obtained is not perfect as it does not follow the requirement of the height is 3 times the width. According to (Flaaten, Nguyen, Pope, & Zhang, 2008), the increments of hard water salinity will decrease the IFT of the microemulsion interface. However, due to some error in handling the equipment, IFT for 26400ppm (2.5 wt% NaCl) salinity hard water cannot be measured and the result for other salinity does not appeared the same as reported by (Flaaten, Nguyen, Pope, & Zhang, 2008). The result is summarized in Table 12 below and plotted in Figure 14, 15, 16 and 17.

Table 13 Differences of IFT value calculated using Chun Huh equation and Spinning Drop method

	NaCl (wt%)	Spinning drop (mN/m)	Chun Huh	Error (%)
0.4% $NaB(OH)_4$ + 0.4% SDS	1.0	1.815	0.0023	99.88
	1.5	1.176	0.0023	99.81
	2.0	2.225	0.0025	99.89
0.4% $NaB(OH)_4$ + 0.8% SDS	1.0	0.741	0.0099	98.66
	1.5	1.513	0.0099	99.34
	2.0	0.478	0.0099	97.93
0.8% $NaB(OH)_4$ + 0.4% SDS	1.0	1.146	0.0023	99.80
	1.5	0.755	0.0023	99.70
	2.0	1.452	0.0025	99.83
0.8% $NaB(OH)_4$ + 0.8% SDS	1.0	1.752	0.0099	99.43
	1.5	0.714	0.0091	98.73
	2.0	0.485	0.0099	97.96

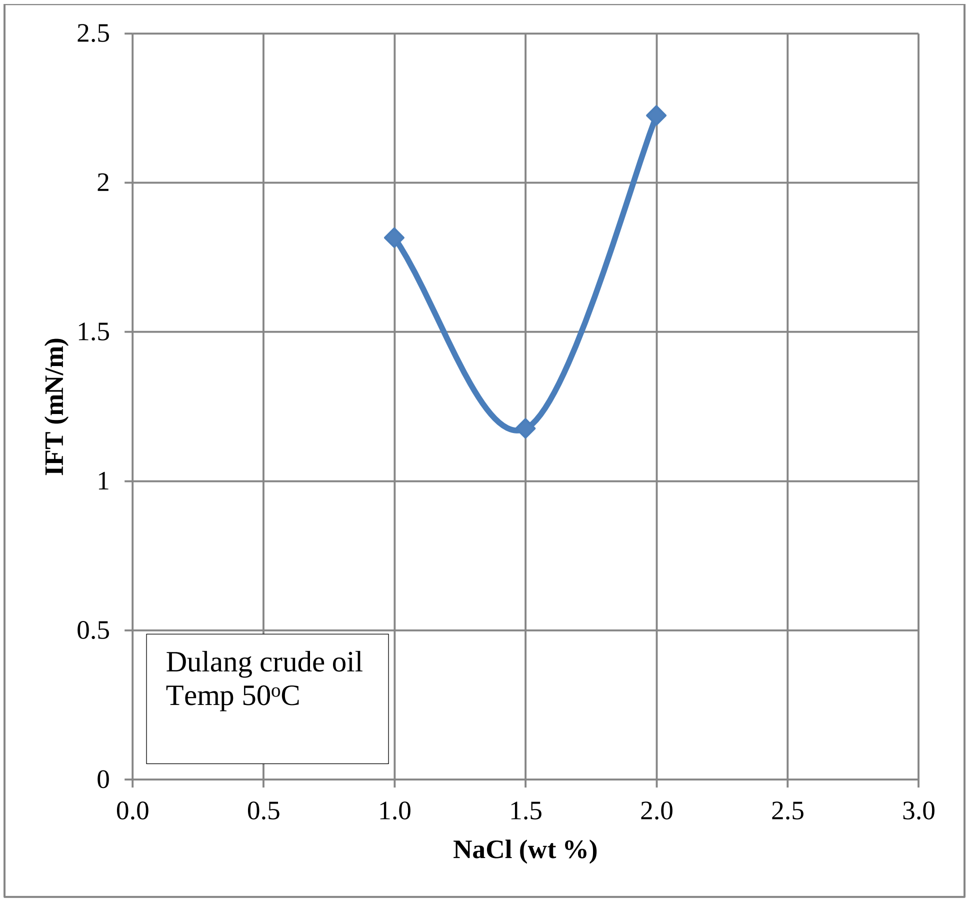


Figure 14 IFT measurement using Spinning Drop machine using 0.4% $NaB(OH)_4$ + 0.4% SDS

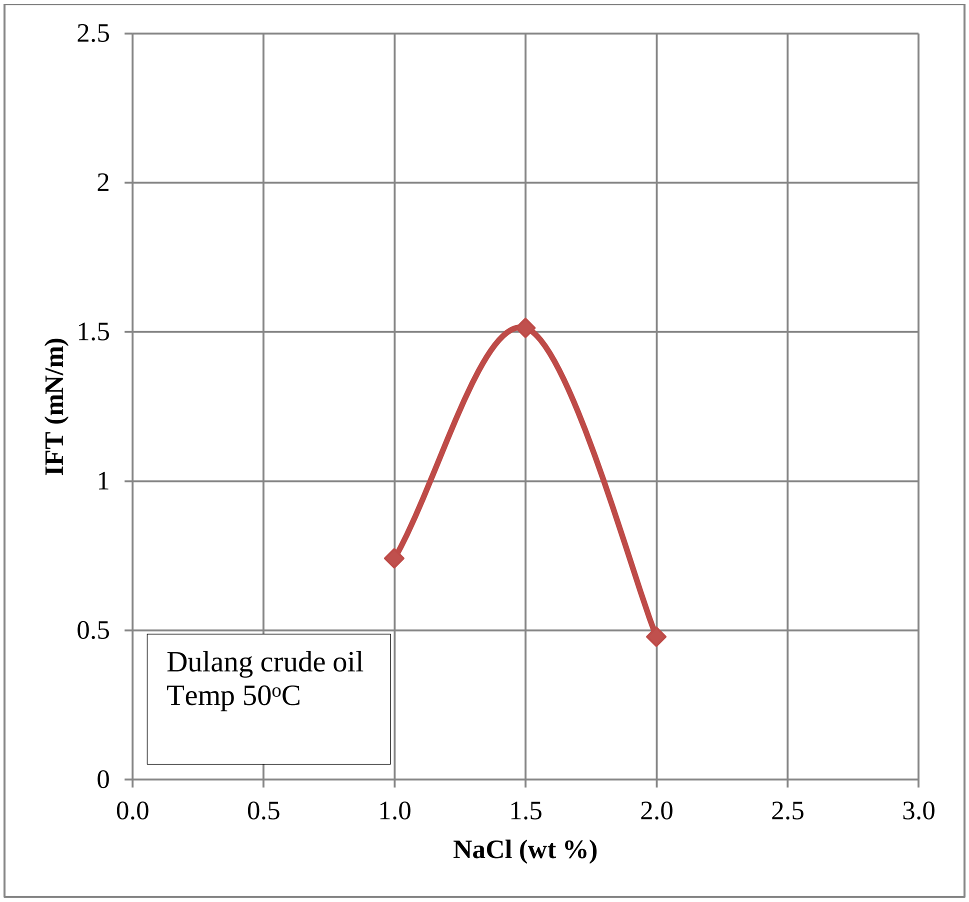


Figure 15 IFT measurement using Spinning Drop machine using 0.4% $NaB(OH)_4$ + 0.8% SDS

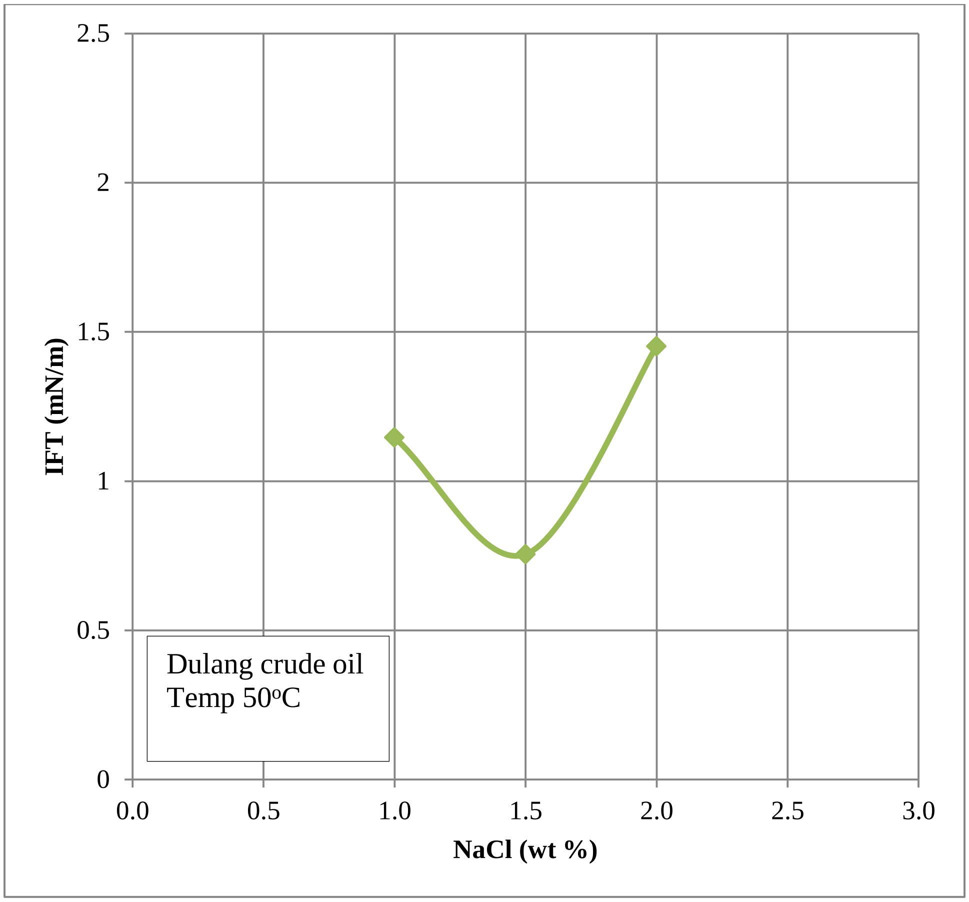


Figure 16 IFT measurement using Spinning Drop machine using 0.8% $NaB(OH)_4$ + 0.4% SDS

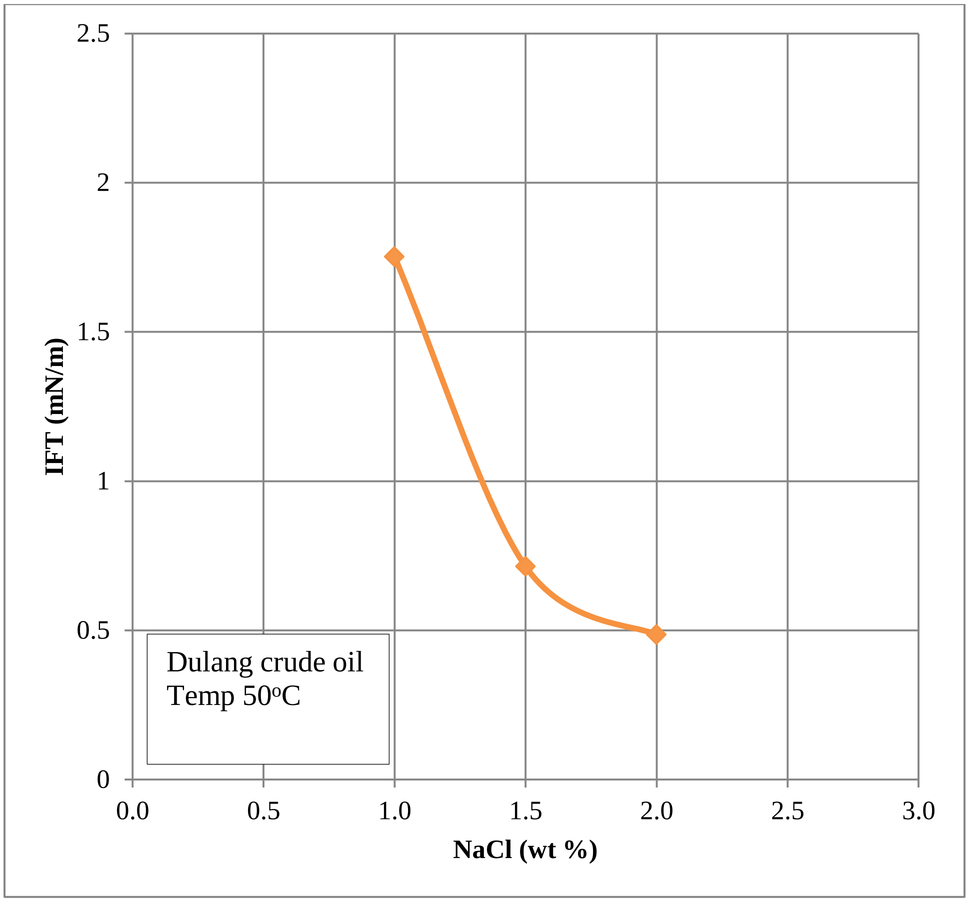


Figure 17 **IFT measurement using Spinning Drop machine using 0.8% $NaB(OH)_4$ + 0.8% SDS**

4.4 Viscosity measurement

Figure 18 and 19 are the plot of viscosity measurement using 0.4% Polyacrylamide at 100 and 1000rpm and 0.8% Polyacrylamide at 100 and 1000rpm respectively. The viscosity measured for 1000rpm is more stable compared to the one tested with 100rpm. According to (Abadli, 2012), *Polyacrylamides* (type of polymer used in the experiment) is a condensation polymers and the performance depend on the molecular weight and degree of hydrolysis. (Nasr-El-Din, 1991) mentioned that, when partially hydrolyzed, some of the acryl amide is replaced by or converted into acrylic acid which will increase the viscosity of fresh water but the viscosity of hard water will be reduced.

As the concentration of the sodium ions in solution is increased, the repulsive forces within the polymer chain decrease, due to charge screening effects, and the chain coils up. This causes the hydraulic radius of the chain to decrease and the degree of polymer chain entanglement to reduce (Nasr-El-Din, 1991). The viscosity measured using 100 and 1000rpm shows the reduction of viscosity as the salinity increased which is parallel to what has been reported by (Abadli, 2012). For mixture of polymer and brine water (only Sodium Chloride and distilled water), most of the result shows slightly higher viscosity reading compared to mixture of polymer and hard water due to strong interactions between the polymer chain and any cations present in the solvent especially divalent cations as mentioned by .

However, the result is differ to what (Abadli, 2012) has reported where the viscosity for mixture of polymer and distilled water is lower than mixture of polymer and hard water. Viscosity measured using 100rpm (333 s^{-1}) is higher compared to 1000rpm (3333 s^{-1}) rotation. This shows that the higher shear rate used cause the viscosity to drop due to the mechanical shear degradation that able to break the polymer chain and reduce the polymer performance to sweep the oil in ASP flooding (Nasr-El-Din, 1991).

The solution with 0.8% PAM gives higher viscosity reading compared to solution with 0.4% PAM and can be taken as the concentration that can improve the sweep efficiency for the tertiary recovery as (Flaaten, Nguyen, Pope, & Zhang, 2008) has mentioned, the increment in viscosity is needed to offset the increase in the aqueous relative permeability that occurs when IFT is reduced.

Table 14 Viscosity measurement using Brookfield viscometer for different NaCl (wt %) concentration of polyacrylamide

100rpm			1000rpm		
PAM (wt %)	NaCl (wt %)	Viscosity (cp)	PAM (wt %)	NaCl (wt %)	Viscosity (cp)
0.4	0.50	2.99	0.4	0.50	0.67
	1.00	2.39		1.00	0.42
	1.50	2.35		1.50	0.31
	2.00	2.33		2.00	0.32
	2.50	2.19		2.50	0.25
	2.78	0.84		2.78	0.61
	DW	2.55		DW	0.38
0.8	0.50	3.67	0.8	0.50	0.86
	1.00	1.35		1.00	0.41
	1.50	1.29		1.50	0.36
	2.00	1.14		2.00	0.71
	2.50	0.98		2.50	0.22
	2.78	1.39		2.78	0.46
	DW	1.13		DW	0.24

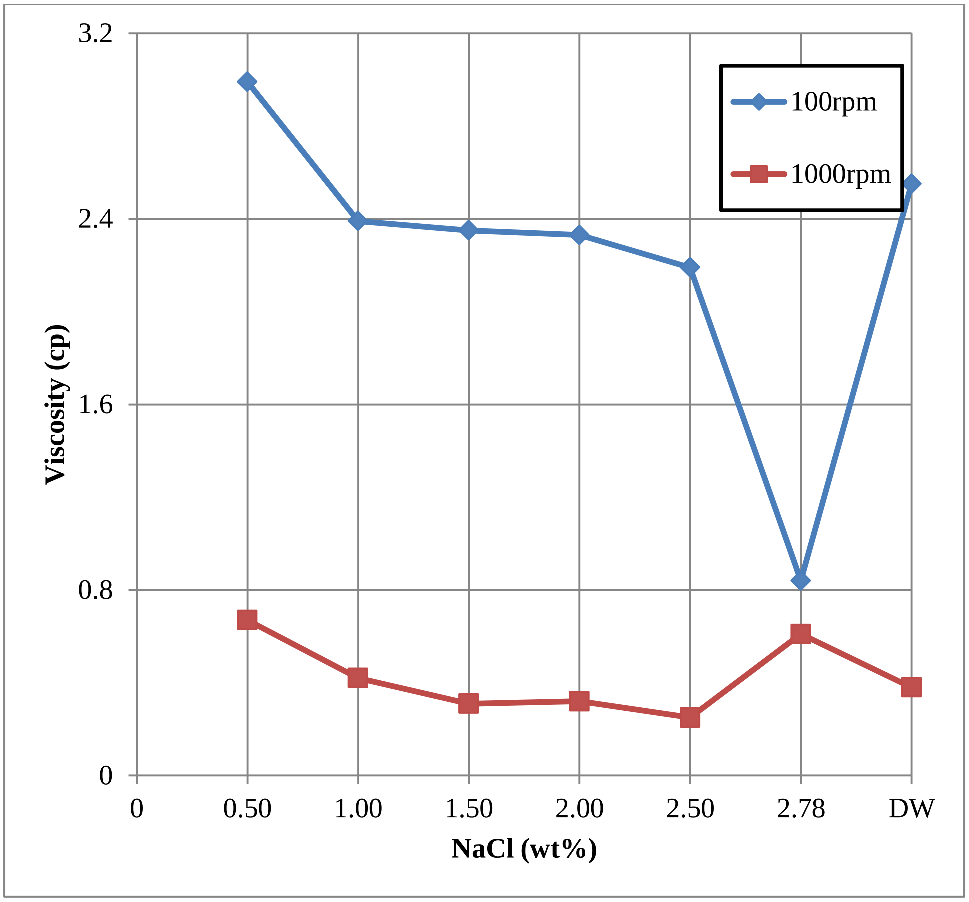


Figure 18 Viscosity measurement using 0.4% Polyacrylamide at 100 and 1000rpm

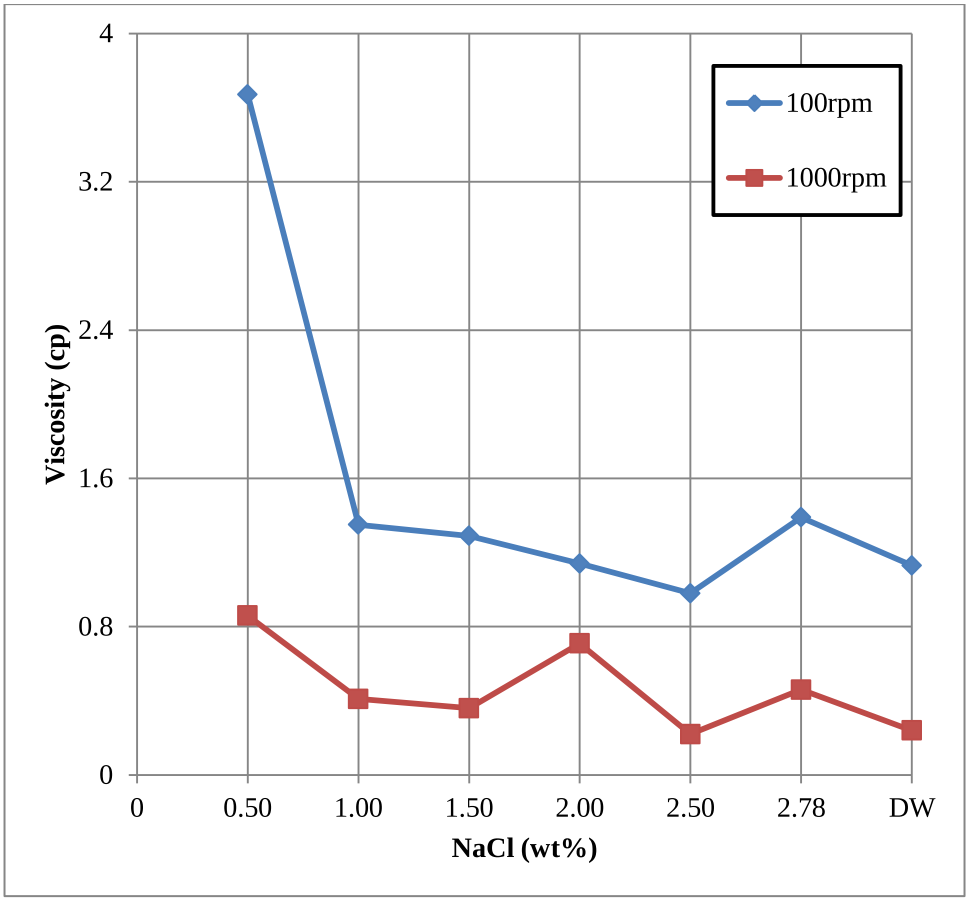


Figure 19 Viscosity measurement using 0.8% Polyacrylamide at 100 and 1000rpm

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

The project entitled Phase Behavior of Alkaline Surfactant Polymer (ASP) in Hard Water has able to achieved the two objectives which are to study the optimum concentration of the mixture of chemical for ASP and to propose that ASP flooding can tolerate with the formation water from offshore reservoir or hard water within the time frame. The study on literature review on the research paper and project work done by others has helped the author to gain a lot of information and familiarized her on the mechanisms of ASP flooding.

Based on the experiment conducted (aqueous compatibility test, microemulsion phase behavior), the optimum salinity of the hard water for each formulation can be determined. The optimum salinity for formulation of 0.4% of $NaB(OH)_4$ and 0.4% of SDS, 0.4% of $NaB(OH)_4$ and 0.8% of SDS, also 0.8% of $NaB(OH)_4$ and 0.8% of SDS is 16400ppm whereas the optimum salinity for formulation 0.8% of $NaB(OH)_4$ and 0.4% of SDS is 21400ppm (2.0 wt% NaCl). Since all the formulation is merely using the same concentration of $NaB(OH)_4$ and SDS, 16400ppm (1.5 wt% of NaCl) is said to be the optimum salinity of the hard water.

The optimum concentration of $NaB(OH)_4$ and SDS are 0.4% and 0.8% respectively. It is because; this formulation gives the highest microemulsion after 120 hours observation where the higher volume of microemulsion indicates that more oil is carried along and produced. It also concludes that the sodium metaborate is a weak alkali and sodium dodecyl sulfate is a poor surfactant as it gives small volume of microemulsion for all samples. The optimum concentration of polyacrylamide that can be used to improve the sweep efficiency is 0.8% as the viscosity measurement is higher compared to 0.4% concentration.

Hence, the objectives of this project have been achieved where the optimum salinity of hard water that gives no precipitation also the right concentration of alkali, surfactant and polymer has been identified. Since the interfacial tension is lowered, the ASP is proposed to be successful in hard water.

5.2 Recommendation for Future Work

The study of Phase Behavior of Alkaline Surfactant Polymer in Hard Water should be done with the real reservoir temperature of 70 to 80°C. For this work, it is not possible to have the analysis for the real reservoir condition as most of the equipment available limit to temperature of 50°C. The student also should be equipped with complete resource in order to have a better analysis. The materials provided should be in better quality so that student can make comparison between the good and low quality materials used in the analysis. For future work, the project can be improved by adding materials that can sustain the microemulsion formed such as alcohol and consider on the precipitation inhibitor to allow high salinity (similar to the reservoir condition) hard water to be used in the analysis. The successfulness of this project also can be proved by including the core flooding experiment.

REFERENCES

Abadli, F. N. U. o. S. a. T., Faculty of Engineering Science and Technology, Department of Petroleum Engineering and Applied Geophysics). (2012). *Simulation Study of Enhanced Oil Recovery by ASP (Alkaline, Surfactant and Polymer) Flooding for Norne Field C-segment.* Norwegian University of Science and Technology.

Aida, L., Lindomar, Spari, Henok. (2010). Surfactant Flooding of the Norne Field E-segment (E. i. Team, Trans.) (pp. 21): Norwegian University of Science and Technology.

Baojun Bai, S. (2008). EOR/ IOR.

Bataweel, M. A., & Nasr-El-Din, H. A. (2012). *ASP vs. SP Flooding in High Salinity/Hardness and Temperature in Sandstone Cores*. Paper presented at the SPE EOR Conference at Oil and Gas West Asia, Muscat, Oman. http://www.onepetro.org/mslib/app/Preview.do?paperNumber=SPE-155679-MS&societyCode=SPE

Berger, P. D., & Lee, C. H. (2006). *Improved ASP Process Using Organic Alkali*. Paper presented at the SPE/DOE Symposium on Improved Oil Recovery, Tulsa, Oklahoma, USA. http://www.onepetro.org/mslib/app/Preview.do?paperNumber=SPE-99581-MS&societyCode=SPE

Blaine Hawkins, A. S. (2004, 2nd March). [Enhanced Oil Recovery Water Usage].

Buijse, M. A., Tandon, K., Jain, S., Handgraaf, J.-W., & Fraaije, J. (2012). *Surfactant Optimization for EOR using Advanced Chemical Computational Methods*. Paper presented at the SPE Improved Oil Recovery Symposium, Tulsa, Oklahoma, USA. http://www.onepetro.org/mslib/app/Preview.do?paperNumber=SPE-154212-MS&societyCode=SPE

Cooper, M. N., Southworth, R. A., Walsh, D. M., & Morgan, J. C. (1985). *FIELD EXPERIENCE IN THE BOTHAMSALL SURFACTANT FLOOD PROJECT*. Paper presented at the Offshore Europe, Aberdeen, United Kingdom. http://www.onepetro.org/mslib/app/Preview.do?paperNumber=00013990&societyCode=SPE

Delshad, M., Han, C., Veedu, F. K., & Pope, G. A. (2011). *A Simplified Model for Simulations of Alkaline-Surfactant-Polymer Floods*. Paper presented at the SPE Reservoir Simulation Symposium, The Woodlands, Texas, USA. http://www.onepetro.org/mslib/app/Preview.do?paperNumber=SPE-142105-MS&societyCode=SPE

Fadili, A., Kristensen, M. R., & Moreno, J. (2009). *Smart Integrated Chemical EOR Simulation*. Paper presented at the International Petroleum Technology Conference, Doha, Qatar. http://www.onepetro.org/mslib/app/Preview.do?paperNumber=IPTC-13762-MS&societyCode=IPTC

Flaaten, A., Nguyen, Q. P., Pope, G. A., & Zhang, J. (2008). *A Systematic Laboratory Approach to Low-Cost, High-Performance Chemical Flooding*. Paper presented at the SPE/DOE Symposium on Improved Oil Recovery, Tulsa, Oklahoma, USA. http://www.onepetro.org/mslib/app/Preview.do?paperNumber=SPE-113469-MS&societyCode=SPE

Gao, S., Li, H., & Li, H. (1995). LABORATORY INVESTIGATION OF COMBINATION OF ALKALINE-SURFACTANT-POLYMER FOR DAQING EOR. *SPE Reservoir Engineering, 10*(3), 194-197. doi: 10.2118/27631-pa

Glover, C.J., Exxon Production Research; Puerto, M.C., Exxon Production Research Co.; Maerker, J.M., Exxon Production Research Co.; Sandvik, E.L., Exxon Production Research Co. (1979). *Surfactant Phase Behavior and Retention in Porous Media.* http://www.onepetro.org/mslib/servlet/onepetropreview?id=00007053

Guo, H., Zitha, P. L. J., Faber, R., & Buijse, M. (2012). A Novel Alkaline/Surfactant/Foam Enhanced Oil Recovery Process. *SPE Journal, 17*(4), pp. 1186-1195. doi: 10.2118/145043-pa

HEALY, R. N., REED, R. L., & STENMARK, D. G. (1976). Multiphase Microemulsion Systems. *Society of Petroleum Engineers Journal, 16*(3), 147-160. doi: 10.2118/5565-pa

Hernandez, C., Chacon, L. J., Anselmi, L., Baldonedo, A., Qi, J., Dowling, P. C., & Pitts, M. J. (2001). *ASP System Design for an Offshore Application in the La Salina Field, Lake Maracaibo*. Paper presented at the SPE Latin American and Caribbean Petroleum Engineering Conference, Buenos Aires, Argentina. http://www.onepetro.org/mslib/app/Preview.do?paperNumber=00069544&societyCode=SPE

Ibrahim, A., Alta???ee, A., Elraies, K., & Saaid, I. (2013). *An Experimental Study on Chemical Flooding Using In-Situ Precipitation Inhibitor*. Paper presented at the 18th Middle East Oil & Gas Show and Conference (MEOS), Bahrain International Exhibition Centre, Manama, Bahrain. http://www.onepetro.org/mslib/app/Preview.do?paperNumber=SPE-164226-MS&societyCode=SPE

Jr., R. A. F., Ertekin, T., & Stahl, C. D. (1985). Effect of Capillary Number and Its Constituents on Two-Phase Relative Permeability Curves. *Journal of Petroleum Technology, 37*(2), 249-260. doi: 10.2118/12170-pa

Kalra, A., Venkatraman, A., Raney, K. H., & Dindoruk, B. (2012). Prediction and Experimental Measurements of Water-in-Oil Emulsion Viscosities During Alkaline/Surfactant Injections. *Oil and Gas Facilities, 1*(3), pp. 34-43. doi: 10.2118/143992-pa

Karazincir, O., Thach, S., Wei, W., Prukop, G., Malik, T., & Dwarakanath, V. (2011). *Scale Formation Prevention During ASP Flooding*. Paper presented at the SPE International Symposium on Oilfield Chemistry, The Woodlands, Texas, USA. http://www.onepetro.org/mslib/app/Preview.do?paperNumber=SPE-141410-MS&societyCode=SPE

Konopnicki, D. T., & Zambrano, L. G. (1984). *Application of the Alkaline Flooding Process in the Torrance Field*. Paper presented at the SPE Enhanced Oil Recovery Symposium, Tulsa, Oklahoma. http://www.onepetro.org/mslib/app/Preview.do?paperNumber=00012701&societyCode=SPE

Mohammadi, H., Delshad, M., & Pope, G. A. (2008). *Mechanistic Modeling of Alkaline/Surfactant/Polymer Floods*. Paper presented at the SPE/DOE Symposium on Improved Oil Recovery, Tulsa, Oklahoma, USA. http://www.onepetro.org/mslib/app/Preview.do?paperNumber=SPE-110212-MS&societyCode=SPE

Nasr-El-Din, H.A., Hawkins, B.F., Green, K.A. (1991). *Viscosity Behavior of Alkaline, Surfactant, Polyacrylamide Solutions Used for Enhanced Oil Recovery*. Paper presented at the SPE Symposium on Oilfield Chemistry, Anaheim, California. http://www.onepetro.org/mslib/servlet/onepetropreview?id=00021028

Nguyen, D. T., & Sadeghi, N. (2012). *Stable Emulsion and Demulsification in Chemical EOR Flooding: Challenges and Best Practices*. Paper presented at the SPE EOR Conference at Oil and Gas West Asia, Muscat, Oman. http://www.onepetro.org/mslib/app/Preview.do?paperNumber=SPE-154044-MS&societyCode=SPE

Petrofed. (15-16 April 2010). Method to Maximize Recovery from Mature Fields, from http://petrofed.winwinhosting.net/upload/15-16_April_10/Day%202/Session%205/2_TRMISRA.pdf

Pope, G. A. (Producer). (2007). Overview of Chemical EOR. Retrieved from http://www.uwyo.edu/eori/_files/misc_download/overview%20of%20chemical%20eor.pdf

Regtien, J. (2010). Enhanced Oil Recovery (pp. 31). Retrieved from http://content.yudu.com/A1rqhi/Winter2010/resources/32.htm

Romero, M. I. (2009). *Flow of Emulsions in Porous Media*.

Sahni, V. M. (2009). *Experimental Evaluation of Co-solvents in Development of High Performance Alkali/Surfactant/Polymer Formulations for Enhanced Oil Recovery.* Master of Science in Engineering, The University of Texas at Austin.

Shutang, G., & Qiang, G. (2010). *Recent Progress and Evaluation of ASP Flooding for EOR in Daqing Oil Field*. Paper presented at the SPE EOR Conference at Oil & Gas West Asia, Muscat, Oman. http://www.onepetro.org/mslib/app/Preview.do?paperNumber=SPE-127714-MS&societyCode=SPE

Stoll, W. M., Shureqi, H. a., Finol, J., Al-Harthy, S. A. A., Oyemade, S. N., Kruijf, A. d., . . . Faber, M. J. (2011). Alkaline/Surfactant/Polymer Flood: From the Laboratory to the Field. *SPE Reservoir Evaluation & Engineering, 14*(6), pp. 702-712. doi: 10.2118/129164-pa

Wanli, K., Yi, L., Baoyan, Q., Guangzhi, L., Zhenyu, Y., & Jichun, H. (2000). Interactions between alkali/surfactant/polymer and their effects on emulsion stability. *Colloids and Surfaces A: Physicochemical and Engineering Aspects, 175*(1–2), 243-247. doi: http://dx.doi.org/10.1016/S0927-7757(00)00461-1

Yang, H. T. (2010). *Development of Improved ASP Formulations for Reactive and Non-reactive Crude Oils.* Master of Science in Engineering, The University of Texas Austin.

Zhang, J., Ravikiran, R., Freiberg, D., & Thomas, C. P. (2012). *ASP Formulation Design for Heavy Oil*. Paper presented at the SPE Improved Oil Recovery Symposium, Tulsa, Oklahoma, USA. http://www.onepetro.org/mslib/app/Preview.do?paperNumber=SPE-153570-MS&societyCode=SPE

APPENDICES

Table 15 Spinning Drop result for 11400ppm

Run	11400ppm			
	2a (0.4% $NaB(OH)_4$ + 0.4% SDS)	2b (0.4% $NaB(OH)_4$ + 0.8% SDS)	2c (0.8% $NaB(OH)_4$ + 0.4% SDS)	2d (0.8% $NaB(OH)_4$ + 0.8% SDS)
1	1.758	0.749	1.16	1.719
2	1.799	0.691	1.129	1.751
3	1.825	0.748	1.129	1.711
4	1.801	0.753	1.134	1.712
5	1.79	0.734	1.132	1.756
6	1.788	0.718	1.134	1.771
7	1.825	0.705	1.132	1.766
8	1.747	0.719	1.132	1.765
9	1.83	0.736	1.129	1.754
10	1.819	0.718	1.161	1.753
11	1.756	0.736	1.143	1.756
12	1.829	0.734	1.129	1.754
13	1.76	0.709	1.161	1.753
14	1.797	0.718	1.143	1.761
15	1.747	0.705	1.129	1.755
16	1.74	0.735	1.127	1.714
17	1.762	0.721	1.168	1.746
18	1.798	0.72	1.163	1.719
19	1.792	0.68	1.127	1.749
20	1.749	0.76	1.129	1.75
21	1.759	0.709	1.145	1.719
22	1.747	0.734	1.161	1.72
23	1.75	0.705	1.13	1.749
24	1.763	0.779	1.136	1.714
25	1.761	0.742	1.137	1.721
26	1.787	0.748	1.159	1.721
27	1.796	0.72	1.157	1.774
28	1.751	0.752	1.128	1.715
29	1.798	0.763	1.134	1.708
30	1.787	0.774	1.126	1.748
31	1.793	0.709	1.143	1.75
32	1.748	0.719	1.143	1.707
33	1.762	0.7	1.138	1.711

34	1.749	0.734	1.134	1.756
35	1.745	0.744	1.161	1.771
36	1.797	0.719	1.141	1.77
37	1.839	0.767	1.139	1.776
38	1.84	0.684	1.135	1.764
39	1.845	0.736	1.135	1.773
40	1.854	0.764	1.144	1.758
41	1.743	0.728	1.164	1.758
42	1.834	0.758	1.146	1.763
43	1.863	0.733	1.145	1.768
44	1.807	0.767	1.128	1.788
45	1.748	0.749	1.143	1.709
46	1.795	0.707	1.103	1.762
47	1.796	0.75	1.157	1.755
48	1.832	0.685	1.143	1.719
49	1.776	0.749	1.132	1.718
50	1.843	0.692	1.144	1.722
51	1.846	0.753	1.175	1.739
52	1.808	0.678	1.143	1.808
53	1.844	0.726	1.133	1.772
54	1.866	0.752	1.162	1.76
55	1.877	0.691	1.135	1.774
56	1.799	0.736	1.163	1.76
57	1.811	0.692	1.135	1.783
58	1.802	0.719	1.133	1.769
59	1.812	0.691	1.143	1.762
60	1.868	0.71	1.128	1.772
61	1.812	0.687	1.162	1.767
62	1.801	0.734	1.165	1.764
63	1.87	0.737	1.161	1.748
64	1.819	0.734	1.134	1.758
65	1.846	0.722	1.136	1.756
66	1.858	0.735	1.135	1.75
67	1.846	0.729	1.164	1.756
68	1.876	0.752	1.134	1.757
69	1.865	0.752	1.134	1.784
70	1.855	0.705	1.157	1.767
71	1.807	0.719	1.147	1.773
72	1.808	0.781	1.161	1.761
73	1.861	0.707	1.141	1.752
74	1.863	0.781	1.165	1.765

75	1.864	0.765	1.139	1.761
76	1.87	0.729	1.168	1.772
77	1.869	0.744	1.157	1.773
78	1.856	0.692	1.158	1.757
79	1.861	0.748	1.16	1.783
80	1.862	0.773	1.183	1.756
81	1.818	0.765	1.133	1.766
82	1.801	0.734	1.131	1.756
83	1.867	0.704	1.136	1.752
84	1.868	0.677	1.157	1.756
85	1.806	0.743	1.159	1.763
86	1.864	0.75	1.165	1.763
87	1.863	0.731	1.136	1.749
88	1.801	0.767	1.159	1.766
89	1.805	0.765	1.159	1.718
90	1.845	0.726	1.138	1.725
91	1.815	0.735	1.16	1.713
92	1.815	0.705	1.158	1.748
93	1.867	0.72	1.159	1.752
94	1.845	0.693	1.159	1.76
95	1.842	0.782	1.159	1.772
96	1.872	0.732	1.159	1.76
97	1.816	0.722	1.131	1.753
98	1.863	0.747	1.163	1.759
99	1.862	0.766	1.176	1.716
100	1.857	0.749	1.136	1.753
Average	**1.815**	**0.741**	**1.146**	**1.752**

Table 16 Spinning Drop result for 16400ppm and 21400ppm

Run	16400ppm				21400ppm			
	3a (0.4% NaB(OH)$_4$ + 0.4% SDS)	3b (0.4% NaB(OH)$_4$ + 0.8% SDS)	3c (0.8% NaB(OH)$_4$ + 0.4% SDS)	3d (0.8% NaB(OH)$_4$ + 0.8% SDS)	4a (0.4% NaB(OH)$_4$ + 0.4% SDS)	4b (0.4% NaB(OH)$_4$ + 0.8% SDS)	4c (0.8% NaB(OH)$_4$ + 0.4% SDS)	4d (0.8% NaB(OH)$_4$ + 0.8% SDS)
1	1.158	1.52	0.782	0.678	2.183	0.447	1.402	0.466
2	1.12	1.519	0.828	0.68	2.131	0.495	1.406	0.476
3	1.161	1.507	0.758	0.679	2.223	0.462	1.436	0.47
4	1.154	1.503	0.828	0.692	2.387	0.5	1.429	0.481
5	1.158	1.511	0.73	0.694	2.332	0.456	1.437	0.481
6	1.211	1.517	0.803	0.7	2.291	0.442	1.462	0.469
7	1.156	1.518	0.828	0.71	2.287	0.472	1.49	0.493
8	1.194	1.556	0.781	0.712	2.119	0.472	1.429	0.477
9	1.235	1.505	0.717	0.69	2.281	0.516	1.416	0.482
10	1.183	1.506	0.805	0.716	2.326	0.519	1.404	0.481
11	1.192	1.516	0.784	0.69	2.18	0.471	1.433	0.49
12	1.156	1.557	0.803	0.649	2.392	0.489	1.434	0.49
13	1.158	1.505	0.783	0.692	2.208	0.5	1.464	0.495
14	1.199	1.529	0.802	0.715	2.339	0.445	1.453	0.499
15	1.151	1.504	0.718	0.738	2.237	0.459	1.486	0.479
16	1.195	1.515	0.725	0.676	2.129	0.489	1.43	0.469
17	1.15	1.517	0.759	0.688	2.13	0.503	1.479	0.468
18	1.158	1.509	0.738	0.697	2.102	0.477	1.484	0.467
19	1.143	1.513	0.717	0.7	2.261	0.474	1.402	0.483
20	1.148	1.513	0.757	0.71	2.373	0.465	1.426	0.475
21	1.229	1.537	0.729	0.694	2.169	0.495	1.434	0.498
22	1.201	1.509	0.792	0.709	2.335	0.464	1.458	0.489
23	1.249	1.513	0.759	0.714	2.166	0.458	1.428	0.474
24	1.188	1.503	0.757	0.691	2.169	0.474	1.423	0.52
25	1.191	1.504	0.698	0.694	2.17	0.52	1.48	0.471
26	1.173	1.513	0.737	0.716	2.291	0.471	1.495	0.485
27	1.15	1.518	0.781	0.715	2.166	0.485	1.483	0.505
28	1.167	1.506	0.732	0.695	2.465	0.505	1.382	0.501
29	1.152	1.504	0.718	0.694	2.29	0.501	1.478	0.467
30	1.166	1.513	0.737	0.692	2.275	0.458	1.488	0.5
31	1.226	1.505	0.76	0.698	2.206	0.471	1.461	0.499
32	1.12	1.507	0.781	0.709	2.131	0.464	1.45	0.484
33	1.189	1.516	0.722	0.712	2.113	0.475	1.456	0.484
34	1.192	1.516	0.716	0.709	2.159	0.52	1.459	0.496

35	1.22	1.512	0.737	0.721	2.324	0.467	1.462	0.476
36	1.157	1.504	0.701	0.746	2.434	0.477	1.488	0.47
37	1.221	1.517	0.758	0.695	2.232	0.464	1.464	0.501
38	1.206	1.515	0.739	0.727	2.231	0.501	1.449	0.488
39	1.154	1.513	0.758	0.717	2.115	0.5	1.478	0.477
40	1.151	1.516	0.716	0.745	2.083	0.501	1.434	0.469
41	1.162	1.51	0.759	0.739	2.175	0.471	1.479	0.477
42	1.148	1.504	0.739	0.715	2.171	0.518	1.394	0.482
43	1.151	1.512	0.736	0.69	2.279	0.485	1.483	0.481
44	1.216	1.504	0.74	0.706	2.28	0.502	1.47	0.515
45	1.185	1.518	0.739	0.711	2.122	0.479	1.487	0.515
46	1.187	1.517	0.724	0.693	2.183	0.518	1.406	0.504
47	1.171	1.516	0.804	0.71	2.273	0.435	1.407	0.467
48	1.199	1.516	0.725	0.7	2.171	0.485	1.427	0.483
49	1.185	1.511	0.804	0.693	2.346	0.5	1.431	0.475
50	1.159	1.513	0.803	0.694	2.281	0.476	1.455	0.498
51	1.152	1.504	0.804	0.714	2.206	0.472	1.453	0.462
52	1.158	1.504	0.722	0.719	2.181	0.443	1.428	0.49
53	1.153	1.508	0.739	0.756	2.338	0.502	1.423	0.495
54	1.16	1.515	0.759	0.744	2.263	0.503	1.409	0.499
55	1.168	1.512	0.801	0.727	2.399	0.471	1.494	0.479
56	1.155	1.514	0.781	0.716	2.318	0.501	1.486	0.487
57	1.122	1.516	0.759	0.694	2.213	0.5	1.461	0.478
58	1.235	1.514	0.716	0.712	2.164	0.501	1.424	0.491
59	1.148	1.513	0.758	0.71	2.229	0.479	1.484	0.466
60	1.152	1.504	0.76	0.724	2.13	0.489	1.423	0.476
61	1.189	1.504	0.72	0.71	2.265	0.472	1.467	0.47
62	1.18	1.503	0.718	0.724	2.371	0.464	1.459	0.501
63	1.19	1.519	0.763	0.682	2.3	0.488	1.405	0.5
64	1.156	1.511	0.803	0.713	2.292	0.471	1.456	0.501
65	1.156	1.503	0.727	0.761	2.267	0.471	1.457	0.471
66	1.185	1.516	0.804	0.741	2.107	0.499	1.404	0.518
67	1.204	1.504	0.782	0.748	2.175	0.501	1.479	0.485
68	1.195	1.505	0.727	0.714	2.317	0.472	1.435	0.502
69	1.182	1.517	0.727	0.696	2.179	0.471	1.464	0.479
70	1.183	1.51	0.758	0.694	2.34	0.505	1.445	0.518
71	1.195	1.513	0.758	0.712	2.221	0.512	1.409	0.489
72	1.192	1.516	0.716	0.714	2.263	0.457	1.484	0.503
73	1.177	1.513	0.72	0.752	2.057	0.442	1.455	0.477
74	1.202	1.473	0.757	0.709	2.091	0.502	1.453	0.474
75	1.19	1.539	0.802	0.728	2.208	0.463	1.458	0.465

76	1.134	1.502	0.717	0.696	2.23	0.461	1.52	0.495
77	1.142	1.514	0.804	0.726	2.253	0.444	1.46	0.464
78	1.15	1.506	0.719	0.716	2.335	0.442	1.488	0.51
79	1.088	1.51	0.757	0.761	2.336	0.495	1.457	0.474
80	1.16	1.502	0.802	0.755	2.281	0.473	1.456	0.473
81	1.228	1.531	0.718	0.759	2.234	0.456	1.524	0.483
82	1.23	1.504	0.803	0.695	2.176	0.427	1.505	0.483
83	1.223	1.517	0.803	0.697	2.253	0.448	1.422	0.483
84	1.198	1.504	0.72	0.713	2.179	0.43	1.404	0.52
85	1.182	1.503	0.716	0.757	2.103	0.458	1.459	0.471
86	1.166	1.513	0.761	0.741	2.185	0.495	1.464	0.485
87	1.153	1.502	0.763	0.711	2.089	0.473	1.48	0.505
88	1.177	1.513	0.758	0.713	2.065	0.489	1.446	0.499
89	1.149	1.518	0.718	0.702	2.268	0.427	1.445	0.485
90	1.137	1.555	0.76	0.729	2.155	0.472	1.474	0.467
91	1.205	1.511	0.716	0.761	2.232	0.458	1.423	0.483
92	1.19	1.515	0.76	0.754	2.215	0.495	1.447	0.475
93	1.226	1.511	0.715	0.713	2.082	0.458	1.455	0.474
94	1.189	1.476	0.759	0.738	2.091	0.479	1.483	0.473
95	1.205	1.502	0.716	0.718	2.18	0.455	1.471	0.472
96	1.21	1.506	0.76	0.725	2.196	0.456	1.453	0.471
97	1.158	1.509	0.714	0.724	2.271	0.515	1.485	0.501
98	1.183	1.554	0.738	0.765	2.217	0.515	1.485	0.471
99	1.155	1.518	0.803	0.755	2.174	0.504	1.424	0.495
100	1.15	1.515	0.763	0.712	2.065	0.465	1.417	0.469
Average	**1.176**	**1.513**	**0.755**	**0.714**	**2.225**	**0.478**	**1.452**	**0.485**

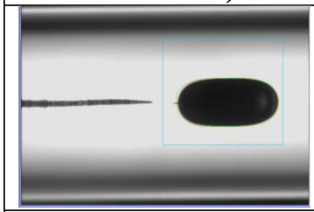
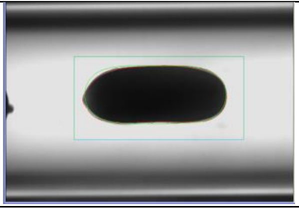
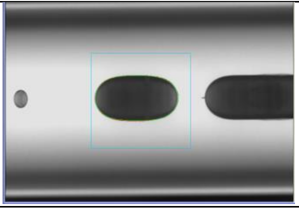
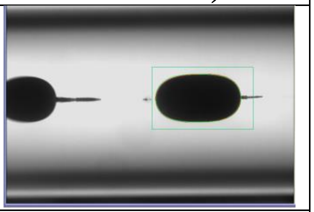
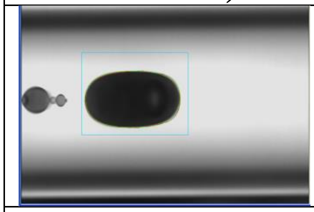
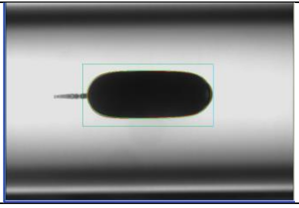
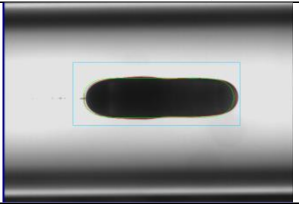
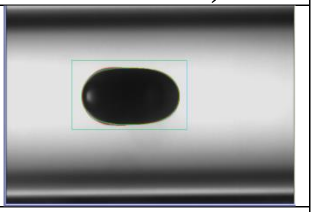
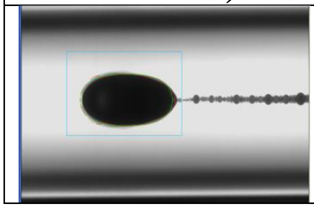
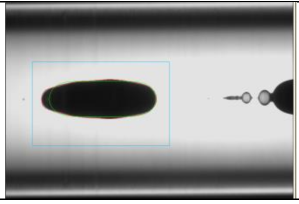
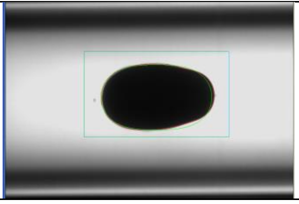
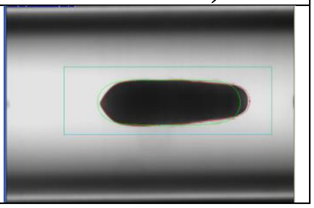
11400ppm			
2a (0.4% $NaB(OH)_4$ + 0.4% SDS)	2b (0.4% $NaB(OH)_4$ + 0.8% SDS)	2c (0.8% $NaB(OH)_4$ + 0.4% SDS)	2d (0.8% $NaB(OH)_4$ + 0.8% SDS)
			
16400ppm			
3a (0.4% $NaB(OH)_4$ + 0.4% SDS)	3b (0.4% $NaB(OH)_4$ + 0.8% SDS)	3c (0.8% $NaB(OH)_4$ + 0.4% SDS)	3d (0.8% $NaB(OH)_4$ + 0.8% SDS)
			
21400ppm			
4a (0.4% $NaB(OH)_4$ + 0.4% SDS)	4b (0.4% $NaB(OH)_4$ + 0.8% SDS)	4c (0.8% $NaB(OH)_4$ + 0.4% SDS)	4d (0.8% $NaB(OH)_4$ + 0.8% SDS)
			

Figure 20 Oil drop for IFT measurement using spinning drop method

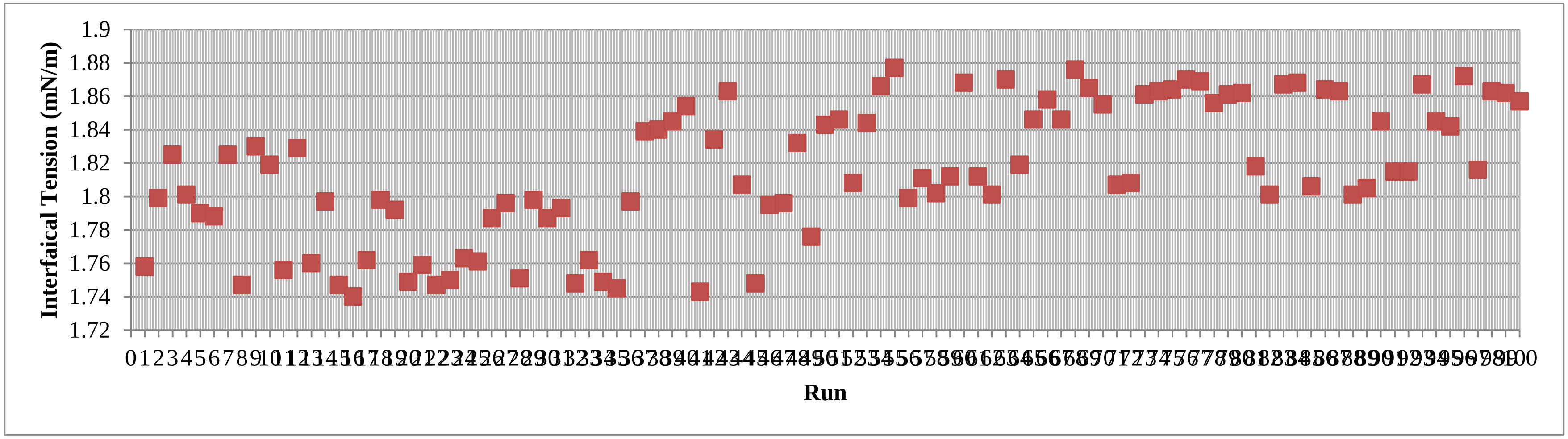


Figure 21 IFT measurement using spinning drop method at salinity of 11400ppm (0.4% $NaB(OH)_4$, 0.4% SDS)

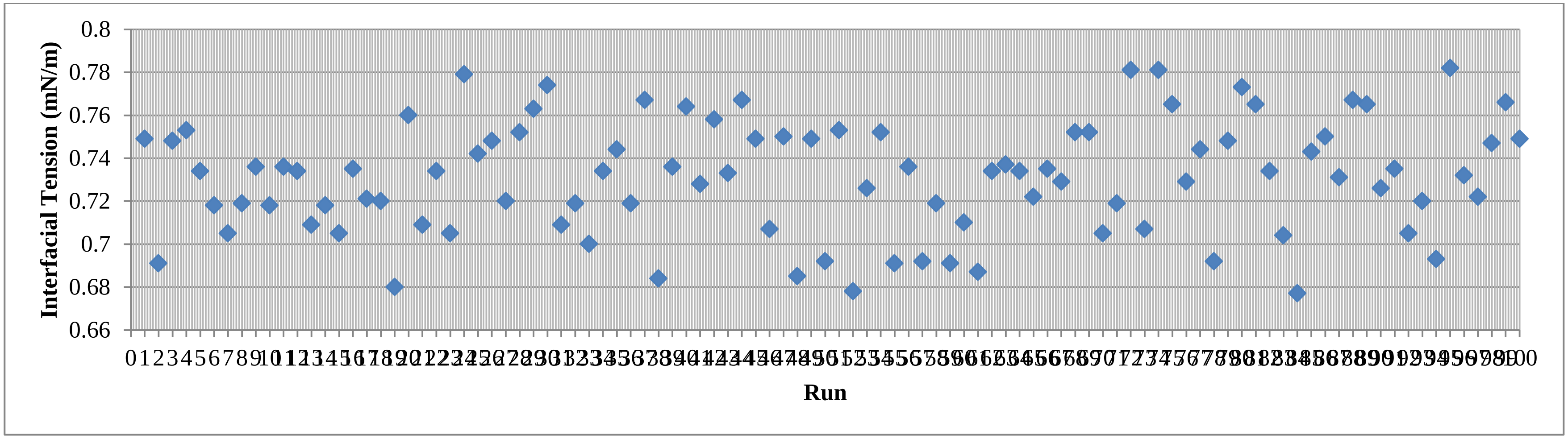


Figure 22 IFT measurement using spinning drop method at salinity of 11400ppm (0.4% $NaB(OH)_4$, 0.8% SDS)

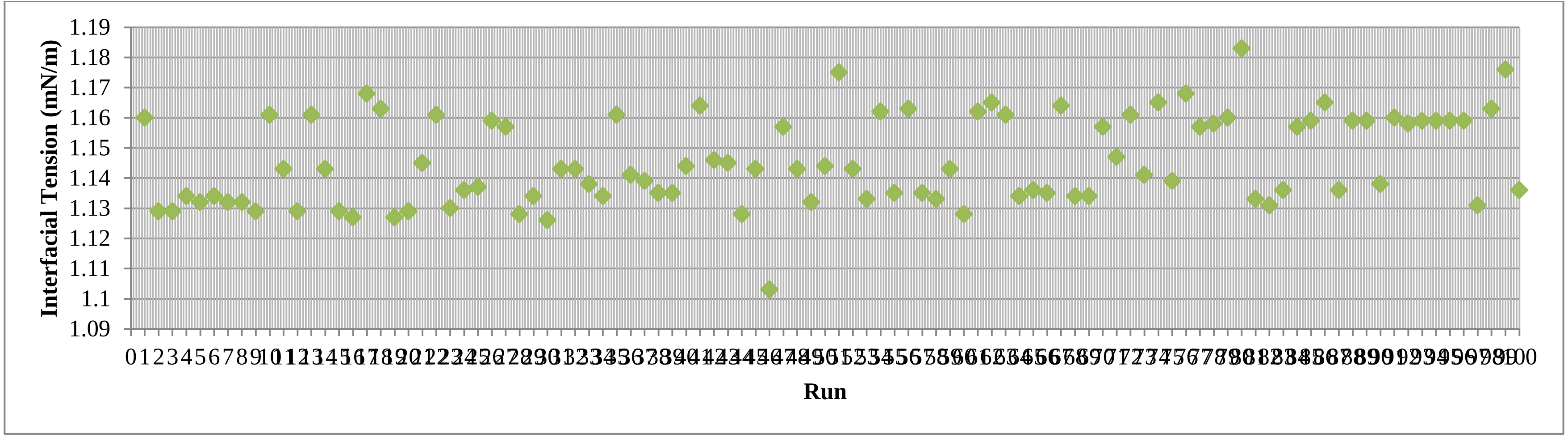


Figure 23 IFT measurement using spinning drop method at salinity of 11400ppm (0.8% $NaB(OH)_4$, 0.4% SDS)

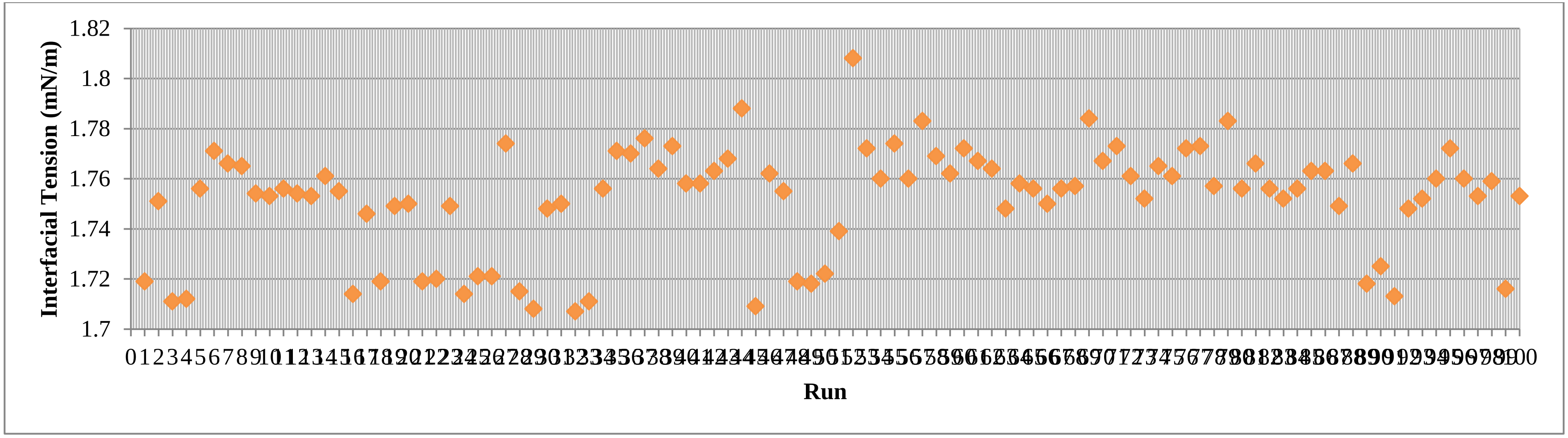


Figure 24 IFT measurement using spinning drop method at salinity of 11400ppm (0.8% $NaB(OH)_4$, 0.8% SDS)

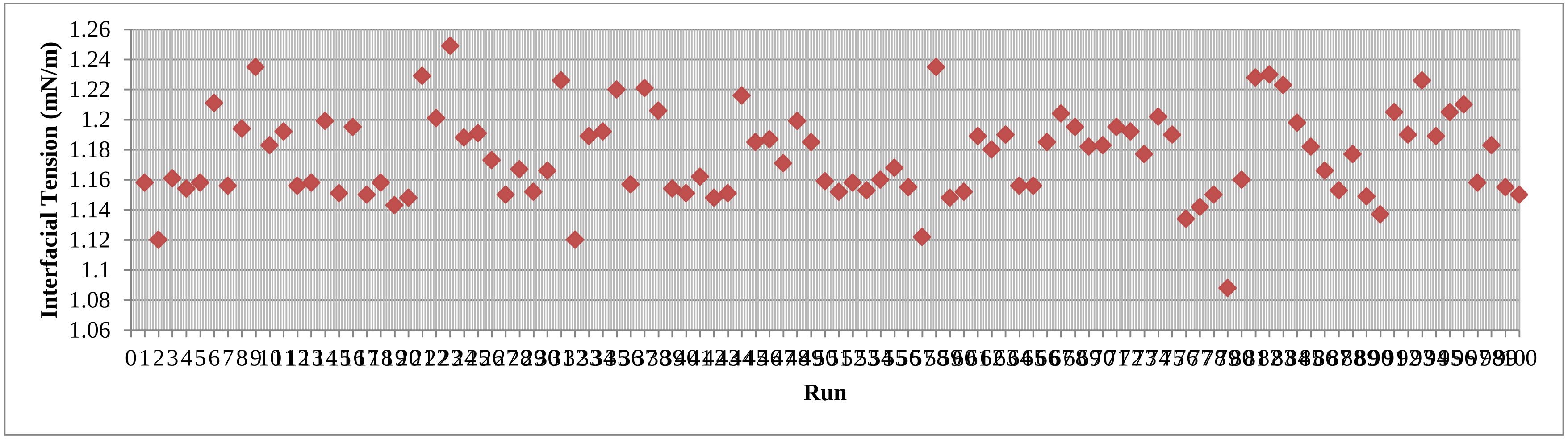


Figure 25 IFT measurement using spinning drop method at salinity of 16400ppm (0.4% $NaB(OH)_4$, 0.4% SDS)

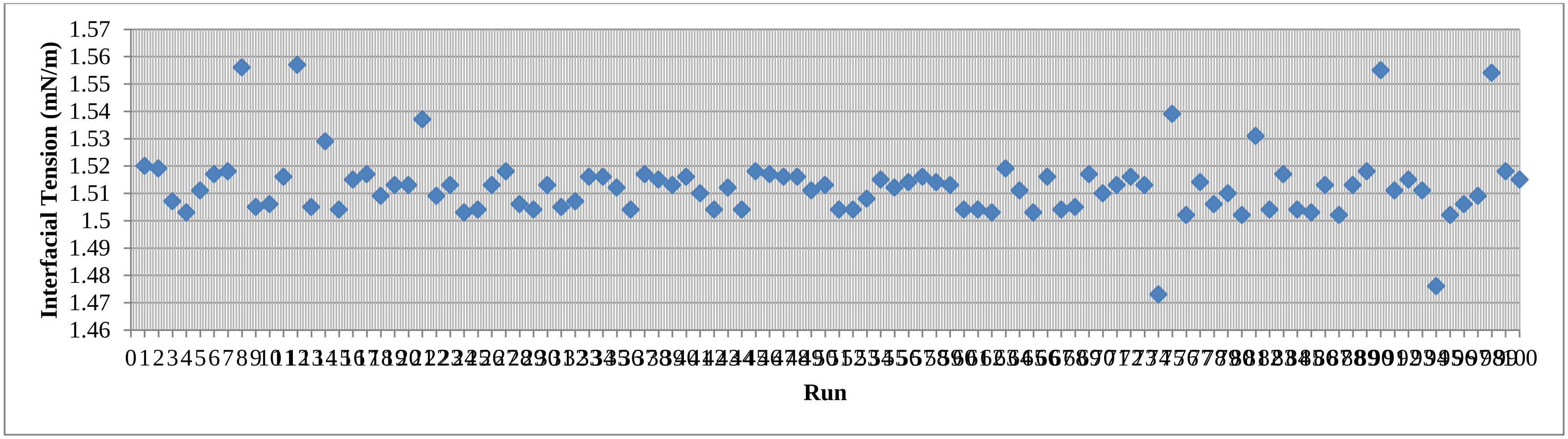


Figure 26 IFT measurement using spinning drop method at salinity of 16400ppm (0.4% $NaB(OH)_4$, 0.8% SDS)

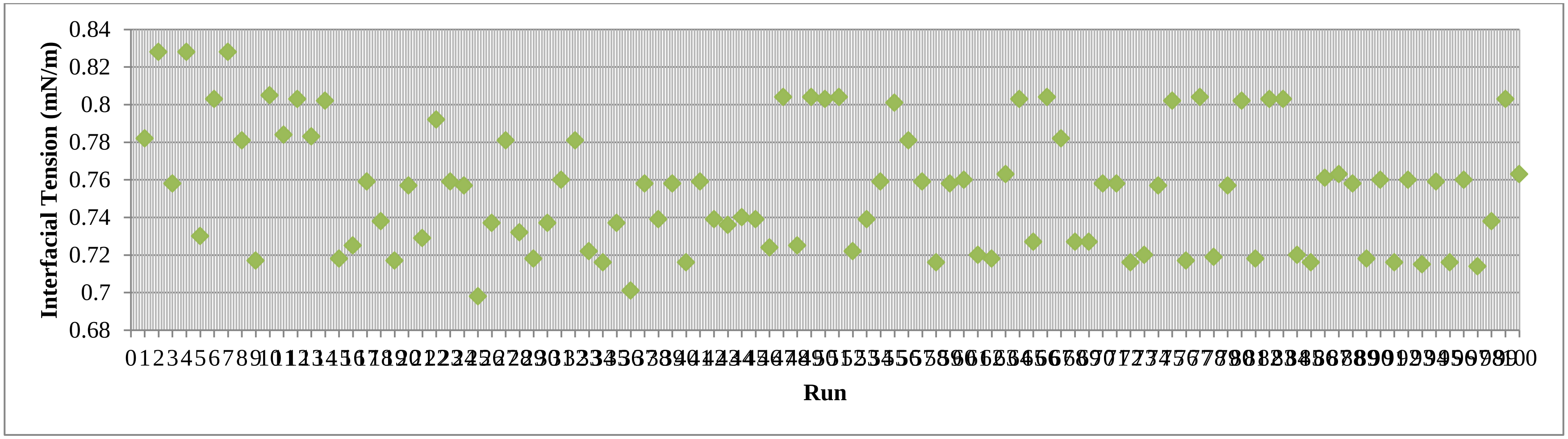


Figure 27 IFT measurement using spinning drop method at salinity of 16400ppm (0.8% $NaB(OH)_4$, 0.4% SDS)

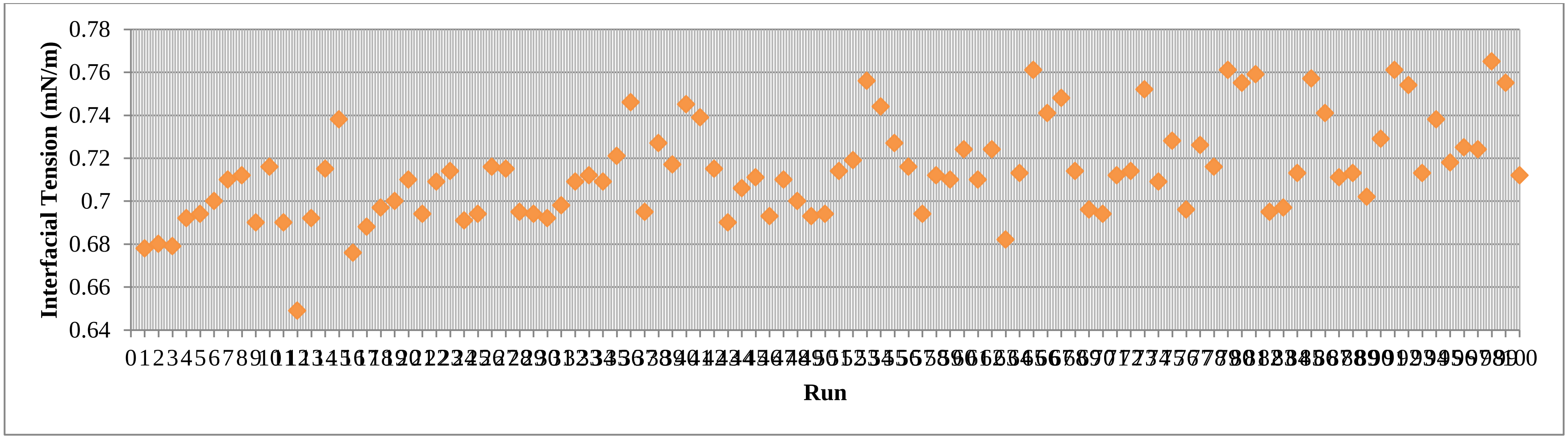


Figure 28 IFT measurement using spinning drop method at salinity of 16400ppm (0.8% $NaB(OH)_4$, 0.8% SDS)

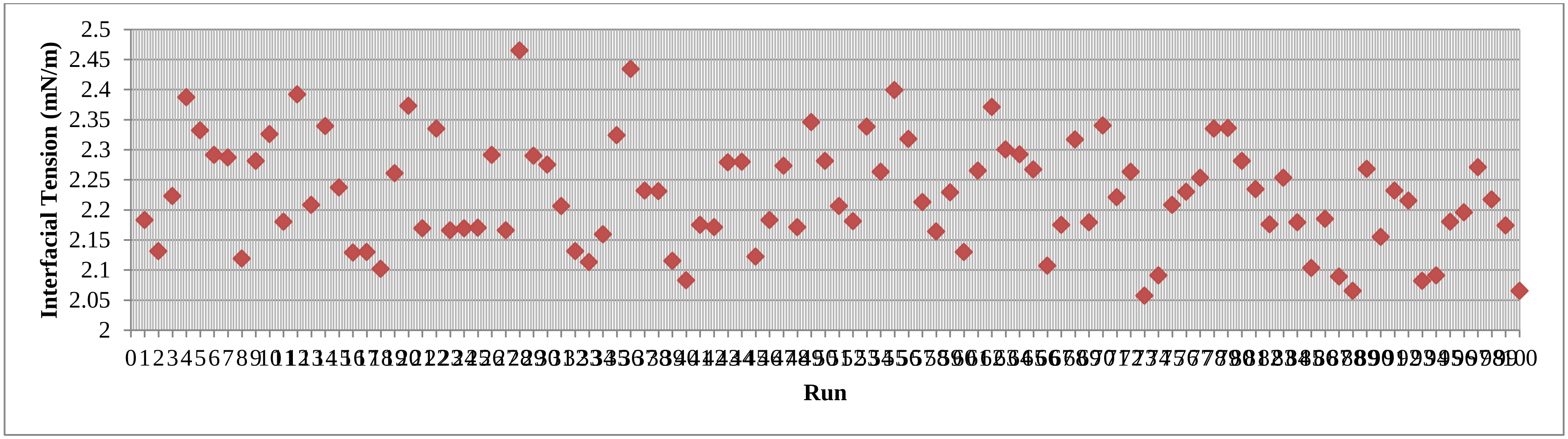


Figure 29 IFT measurement using spinning drop method at salinity of 21400ppm (0.4% $NaB(OH)_4$, 0.4% SDS)

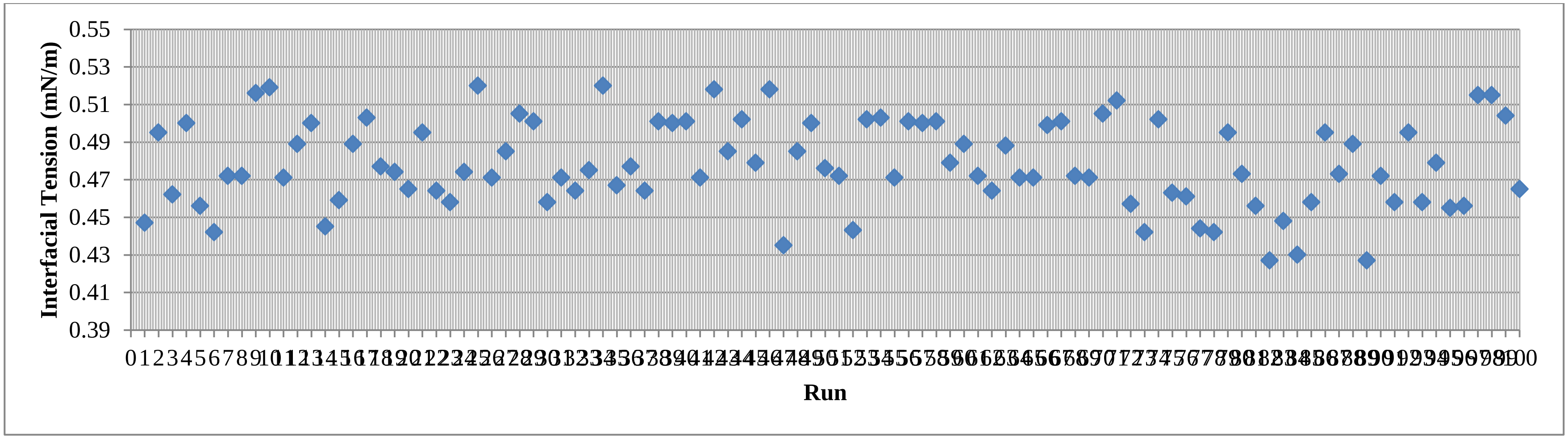


Figure 30 IFT measurement using spinning drop method at salinity of 21400ppm (0.4% $NaB(OH)_4$, 0.8% SDS)

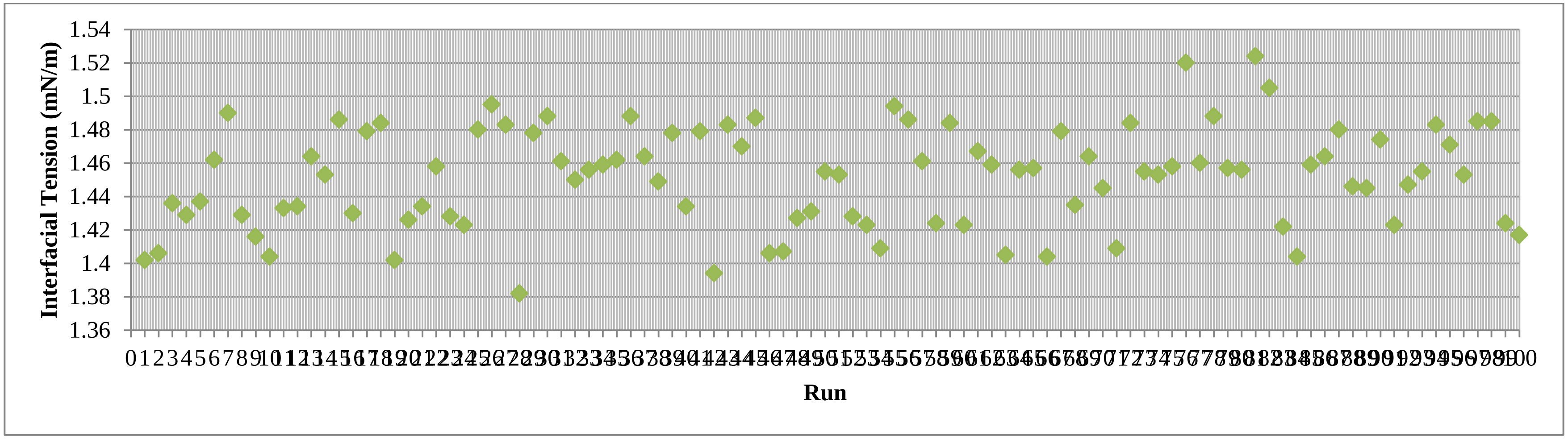


Figure 31 **IFT measurement using spinning drop method at salinity of 21400ppm (0.8% NaB(OH)$_4$, 0.4% SDS)**

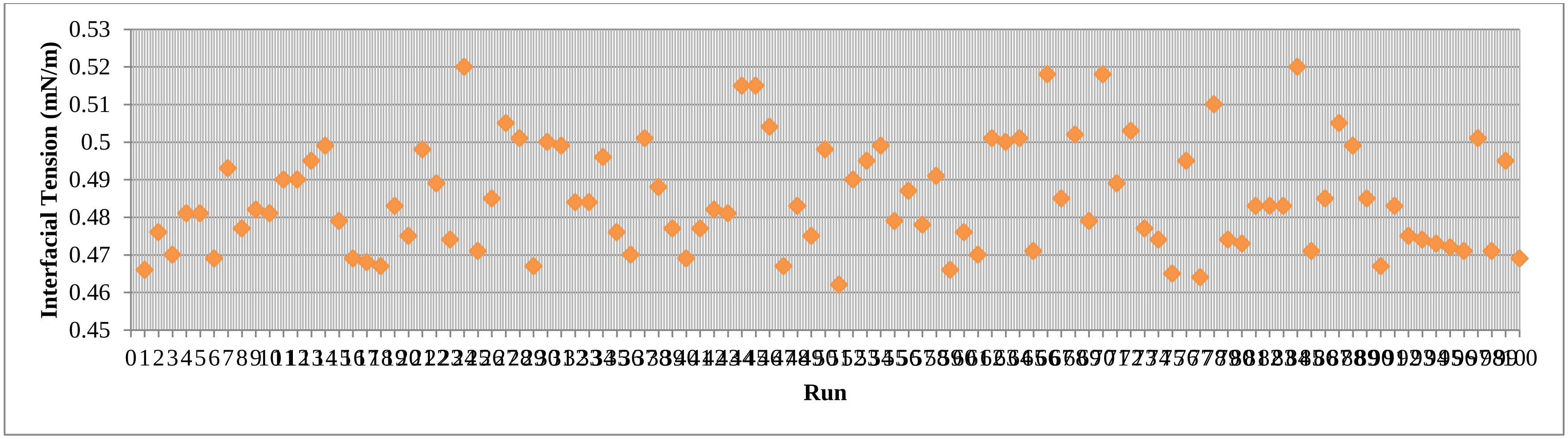


Figure 32 **IFT measurement using spinning drop method at salinity of 21400ppm (0.8% NaB(OH)$_4$, 0.8% SDS)**

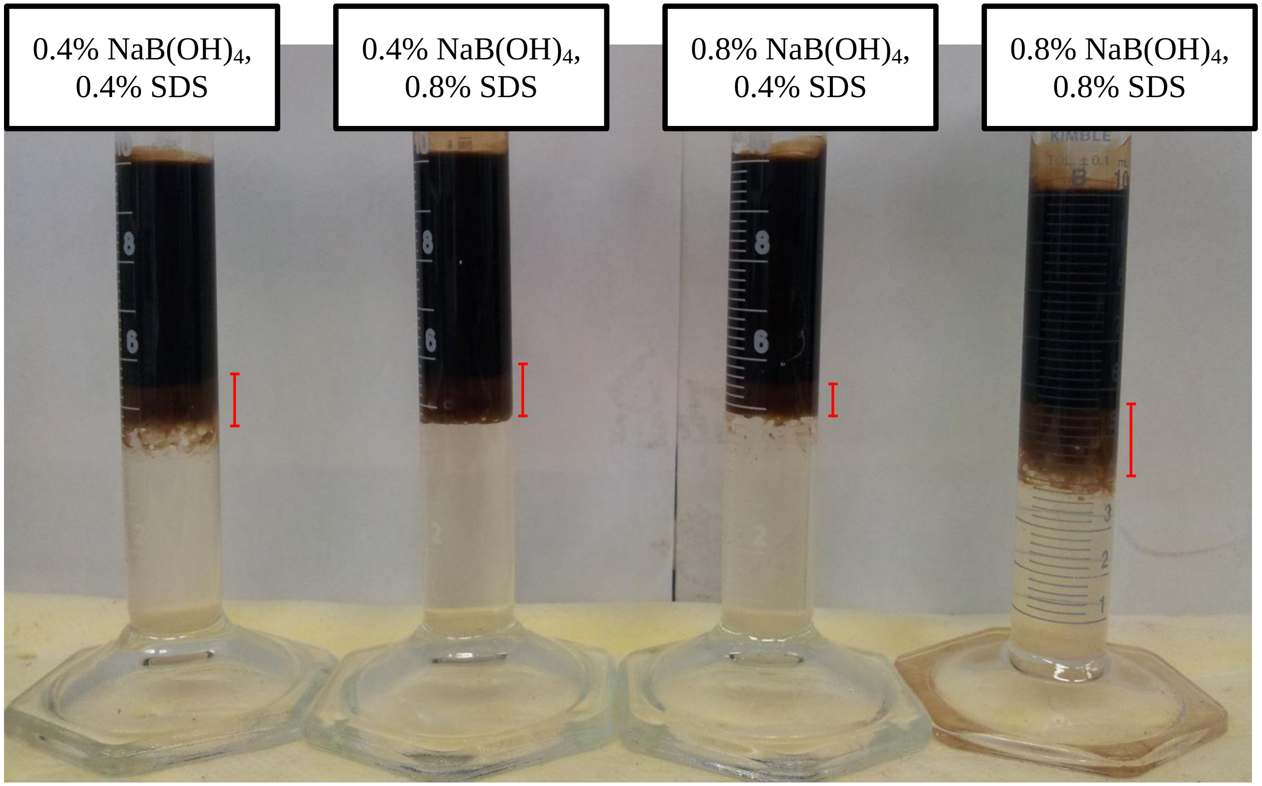


Figure 33 Microemulsion phase behavior test for salinity 11400ppm (1.0 wt% NaCl) after 120 hours

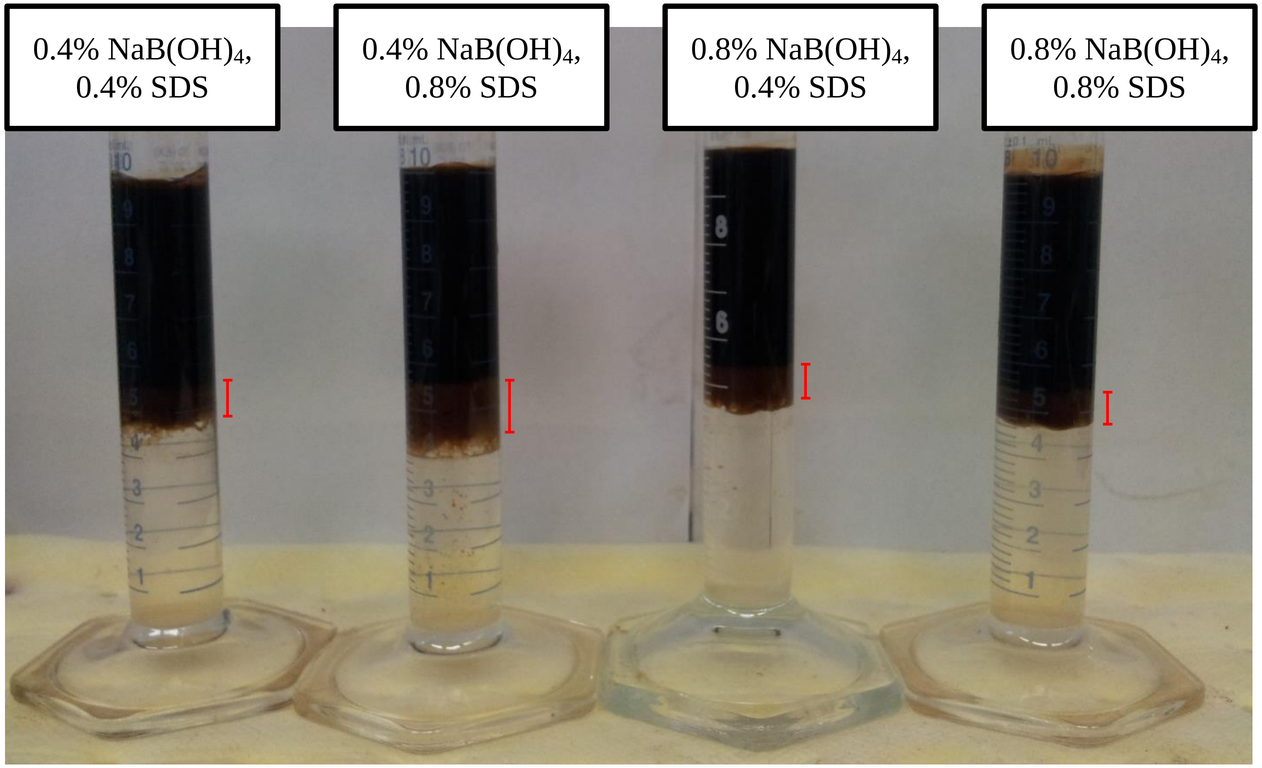


Figure 34 Microemulsion phase behavior test for salinity 16400ppm (1.5 wt% NaCl) after 120 hours

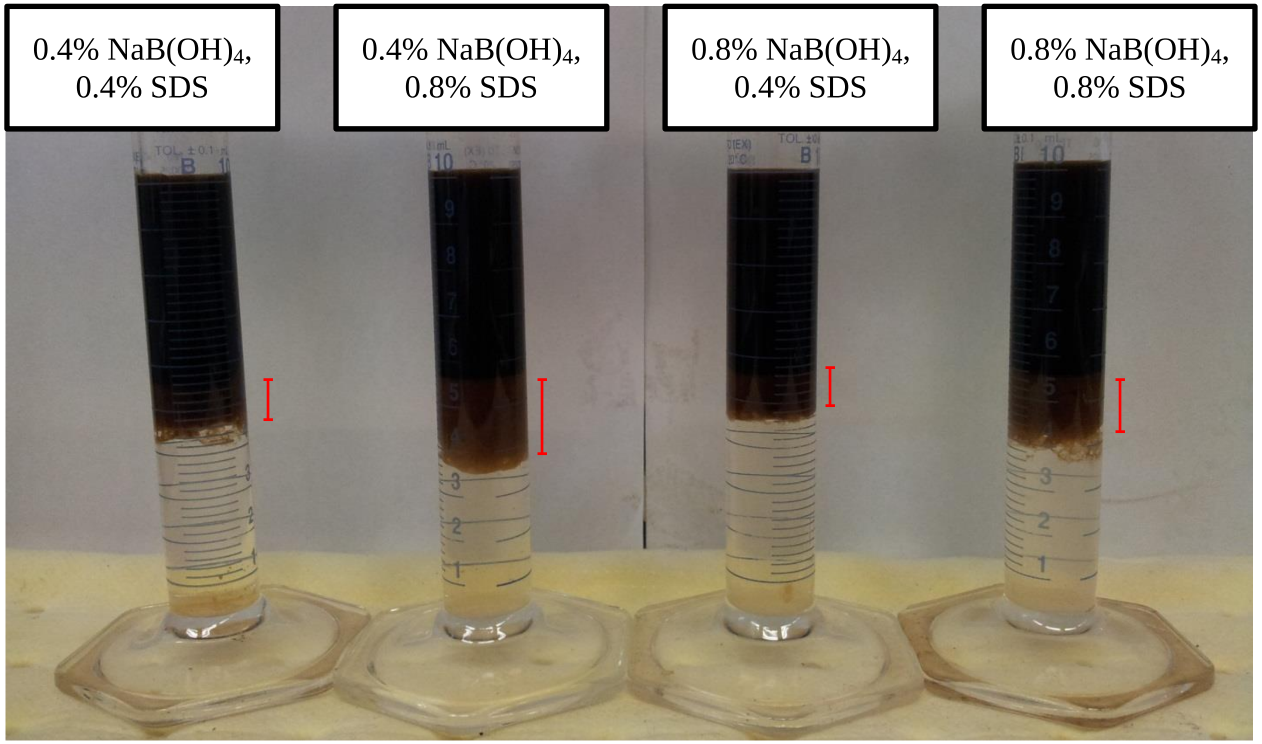


Figure 35 Microemulsion phase behavior test for salinity 21400ppm (2.0 wt% NaCl) after 120 hours

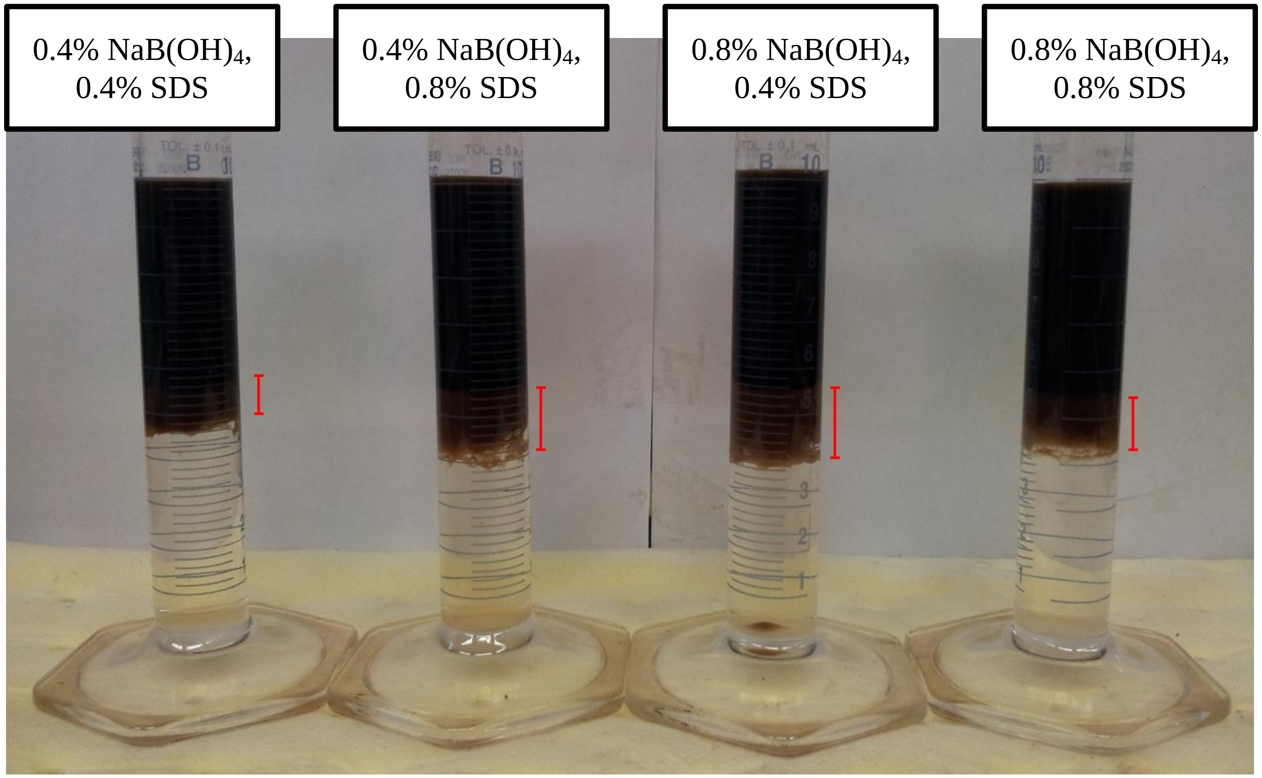


Figure 36 Microemulsion phase behavior test for salinity 26400ppm (2.5 wt% NaCl) after 120 hours

\