INTERFACIAL TENSION BEHAVIOR OF IONIC LIQUID AS SURFACTANT

By

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CERTIFICATION OF APPROVAL

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CERTIFICATION OF ORIGINALITY

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

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SADDAM TAMIMI BIN SHEIKH MOHAMED

ABSTRACT

Fear of depletion of one of the world's most demanding source of energy, crude oil, has made the petroleum industry more concern on sustaining the net volume of production. A crucial phase in petroleum production is applying recovery method to the reservoir as to increase the production of hydrocarbon. A lot of factors influencing the depletion of producing reservoir, primarily because of the declination of reservoir pressure.

There are three steps in the recovery of oil. The process starts from primary oil recovery, followed by secondary oil production and tertiary oil recovery will be the last attempt to take place. Tertiary oil recovery or known as enhanced oil recovery (EOR) will be emphasized by all oil companies as this techniques offer prospects for the producing of 30 to 60 percent of the reservoir's original oil in place. In view of this, surfactant-based chemical systems have been reported by innumerous academic studies and technological operations throughout the years as potential candidates for EOR activities. These chemical compounds are able to reduce interfacial tensions (IFT) as well as to form and stabilize (o/w) or (w/o) emulsions thus allowing the residual oil to flow. However, various parameters such as temperature, salinity and concentration of surfactant should be taken into account as they affect the performance of surfactants.

This experimental study will investigate the influence of surfactant concentration on oil recovery. The IFT between brine and crude oil will be studied with the use of Ionic liquid (IL) based surfactant as a means of lowering the interfacial tension. The pendant drop tensiometer (Vinci, IFT 700) was used to measure the IFT due to its capability to compute ultralow interfacial tensions (ULIFT).

The result will come out with IFT against surfactant concentration graph. As the concentration increases, the IFT will reduce dramatically until it reaches a particular point called critical micelle concentration (CMC) where IFT become less effect on increasing concentration of surfactant. Since the use of surfactants are expensive, determination of this point is vital from the economic perspective.

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ABBREVIATIONS NOMENCLATURES

CMC	Critical Micelle Concentration
EOR	Enhanced Oil Recovery
IFT	Interfacial Tension
IL	Ionic Liquid
Ppm	parts per million

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Chemical flooding is one of the most promising and widely applied EOR. Among the main types of chemical flooding includes alkaline flooding (A), surfactant flooding, polymer flooding (P) and the combination of those either AS flooding or ASP flooding. The development of chemical EOR processes based on operations which involve surfactant is greatly encouraging to enhance oil recovery because it potential to boost recovery rates to as high as 70%.

Surfactants or surface active agents are special classes of chemical compounds that consist of hydrophobic and hydrophilic molecules that tend to form stable configuration at the water and crude oil interface. Generally, they are injected into the injection well as in Figure 1 to reduce the interfacial tension between crude oil and the flooding phase. This procedure result in reducing the capillary forces to improve the microscopic displacement efficiency.

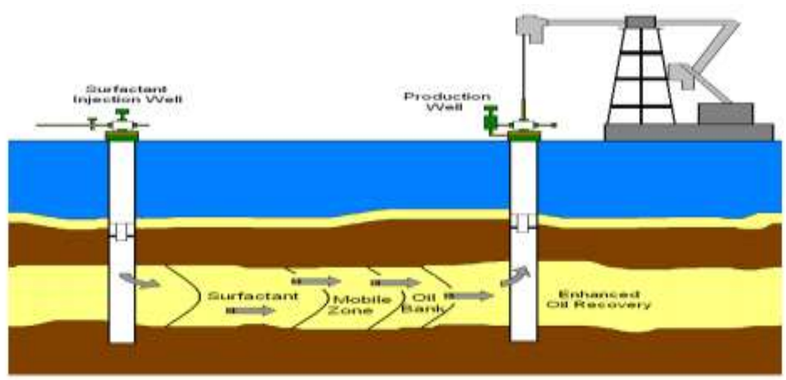

Figure 1: Schematic of a surfactant-based flooding process applied to a petroleum field

However, there are several parameters affecting the performance of surfactant flooding such as surfactant type, surfactant concentration and reservoir condition such as salinity, pressure and pressure. Nevertheless, in this paper, only the effect of surfactant concentration on IFT and determination of its economic concentration will be investigated.

1.2 Problem Statement

The currently used surfactants have many disadvantages or less efficient in reducing IFT need to be replaced with other potential chemical to enable more mobilization of trapped oil in the reservoir. In order to become effective IFT reducing agent, surfactants used in the reservoir must be adaptable with any reservoir conditions such as temperature, salinity, and pressure. Concentration of surfactants also play important role in reducing IFT between water and oil. The use of surfactants in EOR are favorable by oil industry because it's greatly promising. However, due to expensive chemicals this method are considered uneconomic.

In this study, special type of chemicals called Ionic Liquid (IL) which could be more reliable and economical will be investigated. This study will come out with desired CMC value which is expected to be lower than conventional surfactant can give. This value will be retrieved through reaction of crude oil and various concentration of IL surfactant.

1.3 Objective and Scope of Study

The objectives of the project are:

a) Measure the IFT between crude oil and brine without the present of surfactant.
b) Measure the IFT between crude oil and brine with addition of IL surfactant.
c) Determine a critical surfactant concentration (CMC) for very low IFT.

The scopes of study of the project are:

a) Setting of laboratory methodology to determine IFT of surfactants.
b) Study the type of surfactants and use of surfactants in EOR.
c) Study mechanism of surfactant in lowering IFT between two immiscible fluids.
d) Study how surfactant concentration affects the performance of surfactants.

1.5 Relevancy of the Project

This project is relevant and recommended since it may give an improvement to the EOR technique involving surfactant which would lead to increase in oil recovery. This project aims to discover a new surfactant that potentially to give benefit to oil world. Among the features that interest in discovery is capable to reduce interfacial tension between oil-water systems, able to adapting harsh reservoir condition and technically and economically feasible. The performance of the new surfactants will be evaluated from dedicated experiment. At the end of this project, the performance of new surfactants will be compared with the conventional surfactant whether a positive finding can discover or vice versa.

1.6 Feasibility of the Project

The feasibility of this project is in range of intermediate. An experimental based study is estimated to consume a lot of time. Sometime to get a result from an experiment depends on the rate of reaction. The slower the reaction, the more time is consumed. Probability of failure to get chemicals, tools and equipment is also the main concern in this project. Unavailability of this item will cause major catastrophic on the schedule of this project. Consequently, the project cannot be done on time. To prevent this from happening, good time management need to be practiced throughout this project. However, with the time frame given, it is possible to successfully complete the project.

CHAPTER 2
LITERATURE REVIEW AND/OR THEORY

2.1 Enhanced Oil Recovery (EOR)

On average, primary and secondary methods recovered only one third of the total volume of oil in place. Numerous sophisticated methods have been developed to extract the remaining oil. EOR is one of the methods that has been widely used on this day due to its capability to move trapped oil. This method aims to produce the oil that still left behind beyond the secondary recovery method [1]. By applying this method, two third of the total volume of oil in place can be recovered. Thus, production of oil can be increased.

EOR methods are classified into three main categories which is chemical, thermal and miscible gas injection methods. On this day, more advanced method such Microbial Enhanced Oil Recovery (MEOR) has been added under the EOR group [2] [3]. MEOR offer low operating cost compared to the other EOR method [3].

EOR methods work in many mechanisms to move the residual oil trapped in the reservoir either by altering the capillary pressure, interfacial force between oil/water or the wettability of the reservoir rocks [4]. This will lead to displacement efficiency improvement. Surfactant flooding which falls under chemical EOR is an example of EOR method which work on these mechanisms. To displace the trapped oil, surfactant flooding reduce the high interfacial tension between oil and water. Besides, it also can alter the wettability of carbonate rock from strongly oil-wet to water-wet state [5].

2.2 Chemical Enhanced Oil Recovery (CEOR)

Basically CEOR is a method of injecting a particular chemical with the water flood to have a better displacement efficiency. Injected chemicals are designed based on ability to adapt physiochemical properties and specific structural characteristic of a particular reservoir [7].

There are three methods which fall under CEOR family, which is alkaline, polymer and surfactant flooding method [8]. Polymer and alkaline flooding are stated less expensive and simple technique whereas surfactant flooding are stated more complex and more comprehensive which can recover all oil in the region of the reservoir [8]. Surfactant flooding is considered the most efficient among the other method.

Chemical flooding are proven can enhance oil recovery. However, the application is still limited in use due to some reasons. The cost of chemicals is expensive, which would lead to lower rates of return [9]. Besides, most chemicals cannot withstand harsh reservoir condition such as high salinity and high temperature [10]. Other than that, some surfactant suffered adsorption problem when applying to the reservoir that contains clay minerals. Sulfonates type surfactant tends to absorb into clay bodies when being applied [10].

2.3 Surfactant Flooding

Among chemical flooding methods, surfactant flooding is stated the most effective method which can recover a large percentage of remaining oil after applying water flooding which could be as much as 60% [11]. Theoretically, a large percentage of hydrocarbon is still left behind even after applying water flooding. To recover this trapped oil, surfactant solution can be injected into the reservoir to alter the interfacial properties of the oil / water system [12]. This would lead to a strong reduction of interfacial tension force between water and oil, thus the resistance of oil flow is reduced. Proper selection of surfactants is important to achieve a strong reduction of IFT value [13]. The IFT value can lower down to $10^{-3}\,\frac{dynes}{cm} / \frac{mN}{m}$. Approximately 10-20% of the original oil in place can be recovered if IFT value can be reduced down to this value.

2.4 Definitions of Surfactants and its Classification

Surface active agents or shorten as surfactant are wetting agents that reduce the surface tension of a liquid. They also reduce interfacial tension between two liquids. Surfactants are grouped by its tendency to absorb at interfaces and surfaces. Basically, 'interface' represent a border between two immiscible phases, while 'surface' will be used when the present of gas in two phase system. Table 1 further illustrates the different interfaces.

Table 1: Interface Type

Interface	Type
Solid-Vapor	Surface
Solid-Liquid	
Solid-Solid	
Liquid-Vapor	Surface
Liquid-Liquid	

A surfactant molecule is Amphiphilic. Theoretically, the body of this molecule consists of non-polar insoluble hydrocarbon chain (water-hating) and polar water soluble (water-loving) [14] [15]. They tied with each other. This special features enable them to alter the interface properties between organic and aqueous phase. Interference of surfactant between two immiscible liquids will lower down the interfacial tension force and thus make two immiscible fluids become miscible. Figure 2 illustrates a surfactant molecule.

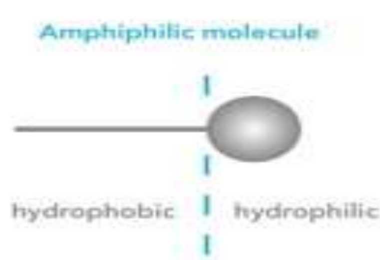

Figure 2[36]: Surfactant molecule

Surfactants can be grouped in different ways commonly by the ionic nature of their head group [14]. Therefore, based on their head nature, surfactants can be divided into four different groups as shown in table 2: (1) Anionic, (2) Cationic, (3) Nonionic and (4) Zwitteronic / Amphoteric.

Categories	Examples	Structures
Anionic	Sodium dodecyl sulfate (SDS)	
Cationic	Cetyltrimethylammonium bromide (CTAB)	
Nonionic	Polyethylene oxides	
Amphoteric	Dodecyl betaine	

Table 2: Categories of Surfactants

2.4.1 Anionic Surfactants

Anionic surfactants contain a negative charge head. This group of surfactants is broadly used in the Chemical EOR process because they are strong against adsorption, inexpensive and stable. When react with clay in sandstone matrix, it tends to repulse each other because both are negative charges. This property makes anionic surfactants highly resistant to adsorption. Meanwhile, Anionics are not suitable to be used in the carbonate rocks environment because positively charged carbonates will attract Anionics, thus contribute to adsorption [16].

2.4.2 Cationic Surfactants

Cationic surfactants contain positive charge head. This group of surfactants is rarely used because they are weak against adsorption. They tend to adsorb to the surface of sandstone rock which are negatively charged. Nevertheless, cationic surfactant can be used with positively charged carbonate rocks to change wettability from oil wet to water wet [16].

2.4.3 Nonionic Surfactants

Nonionic surfactants are usually used as a co - surfactant. Nowadays, it is also used as a primary surfactant. When dissolved in aqueous solutions, nonionic will appear as surfactant properties because of the electronegativity difference between their constituents. Nonionic are much better in adapting high salinity condition compared to anionics. However, in terms of interfacial properties, they are not good as anionic in reducing IFT between oil and water [16].

2.4.4 Amphoteric surfactants

Amphoteric surfactants or zwitteronic surfactants contain both negative and positive charges on their head. They can be nonionic-cationic, nonionic-anionic or anionic-cationic [16].

2.5 Surfactants in Enhanced Oil Recovery

The main intentions of all EOR methods are to increase the volumetric sweep efficiency and to enhance the displacement efficiency [17]. Volumetric sweep efficiency can be increased by reducing the mobility ratio, whereas displacement efficiency can be enhanced by reduction of the amount of oil trapped due to the capillary forces. This goal can be reached by the application of surfactant flooding. Surfactant flooding offers a way to recover a large percent of residual oil by reducing interfacial tension between oil and water. Reducing the IFT would lead to a reduction of the capillary pressure and increase in oil mobility, thus oil can be easily displaced by water drive [18]. Technically, residual oil can be totally displaced if the IFT force can be reduced to zero value. In practice, application of surfactant flooding is impossible to reach this vision. Literatures stated that adding surfactant between two immiscible fluid interfaces such oil and water can reduce its interfacial tension which could lead to increase in mobility ratio between oil and water. In addition, it can also lead to an increment of the capillary number that can assist the residual oil to flow [19] [20].

2.6 Interfacial Tension

Interfacial tension is an attribute of the interface between two immiscible phases. It can be further defined as measurement of the cohesive energy that present at the interface causing from the imbalance of the forces between molecules at the interface. When the phases are both liquids it is termed as interfacial tension, when one of the phases is air it is termed as surface tension. Interfacial tension or surface tension are measured in dynes/cm or mN/m. Interfacial tension is lowered by the surfactant molecule as they spreaded at the interface [21]. There are number of methods to measure interfacial tension as shown in Figure 3. However, among that methods, Pendant drop method will be used in this project.

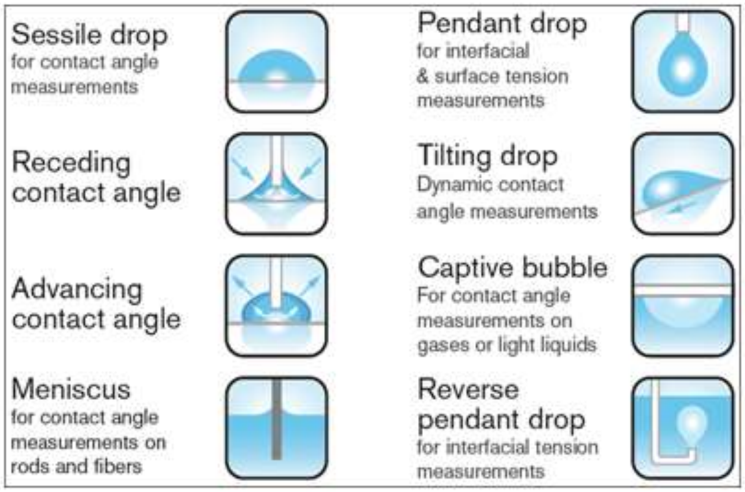

Figure 3[37]: Interfacial Tension measurement method

2.7 Low interfacial tension for oil recovery

Chemical Enhanced Oil Recovery (CEOR) represents the most promising solution that can unblock about 300 billion barrels of oil. To increase the mobility of residual oil, a sufficiently low interfacial tension is essential in order to produce very low capillary forces to allow the oil to flow [22]. Therefore, by injecting various surfactant compounds into the reservoir, interfacial tension can be lowered. Based on fluid flow mechanics theory, the mobility of the residual oil are influenced by two main forces which are viscous and capillary forces. The displacement efficiency depends on the relative influence or the ratio of these two forces. One report suggesting the definition of the capillary number as the ratio of viscous forces to capillary forces [23].

$$\text{Capillary Number } (N_C) = \frac{\upsilon\mu}{\gamma \cos\theta} \qquad (1)$$

Where ν and μ are the velocity and viscosity, respectively, of the displacing phase (brine), γ is the interfacial tension between the displaced and displacing phases and θ is the contact angle. Therefore, by altering the interfacial tension between the water and oil phases, surfactants can cause a significant change in the flow behavior.

2.8 Surfactant and Interfacial Tension

The physics behind the surfactant EOR is that the residual oil is trapped by high capillary forces within the porous media. Residual oil can be pushed to the production well by increasing the fluid flow viscous forces or decreasing the capillary forces that hold the oil. The thumb rule for a successful Surfactant EOR process is to reduce the interfacial tension (IFT) to 10^{-3}mN/m between the oil and the aqueous phases [51]. This is equivalent to increasing the capillary number, N_c to three orders of magnitude. The capillary number is a dimensionless group which reflects the ratio of the viscous to capillary forces. Viscous forces foster the mobilizing oil blobs in the porous media and the interfacial forces trap oil blobs in place.

2.9 Effect of concentration on IFT

Many researchers found that that IFT decreased as concentration increased. One report investigates the behavior of two types of surfactant which are anionic and nonionic. Nonionic Triton X-100, Triton X-400 and Anionic Zonyl FSE were used in the investigation. Then, a plot of IFT variation with concentration was constructed (Figure 3). It was observed that both types of surfactant show similar trends. The plot indicates a sharp exponential IFT decline with the increase of surfactant concentration [28]. Furthermore, previous investigators also reported the same trend was obtained in their experiment [29] [30] [31] [32] [33] [34]. Another project was conducted by using ionic liquid (ILs) as a surfactant. The Ammoeng 102 surfactant (IL) was used and diluted in two concentration of brine at 10% and 20% (w/w) salinity. The oleic phase was medium Saudi crude and the test was conducted at constant pressure and temperature, 2000psi and 60°C respectively. It was observed that IFT measurement for different IL concentrations indicates IFT values exponentially decrease with increasing IL concentration as show in figure 4 [35]. Thus, decreasing trend of IFT value with increasing surfactant concentration was justified and universally acceptable.

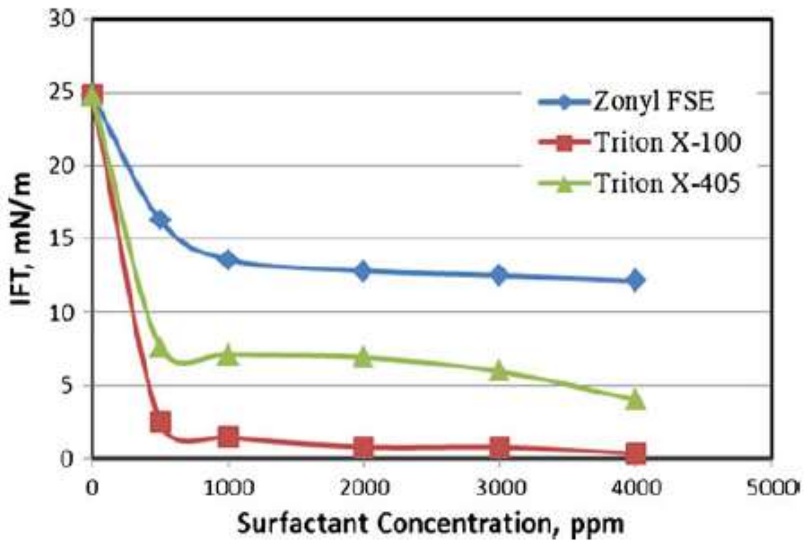

Figure 4[28]: Effect of surfactant concentration on IFT for different Surfactants.

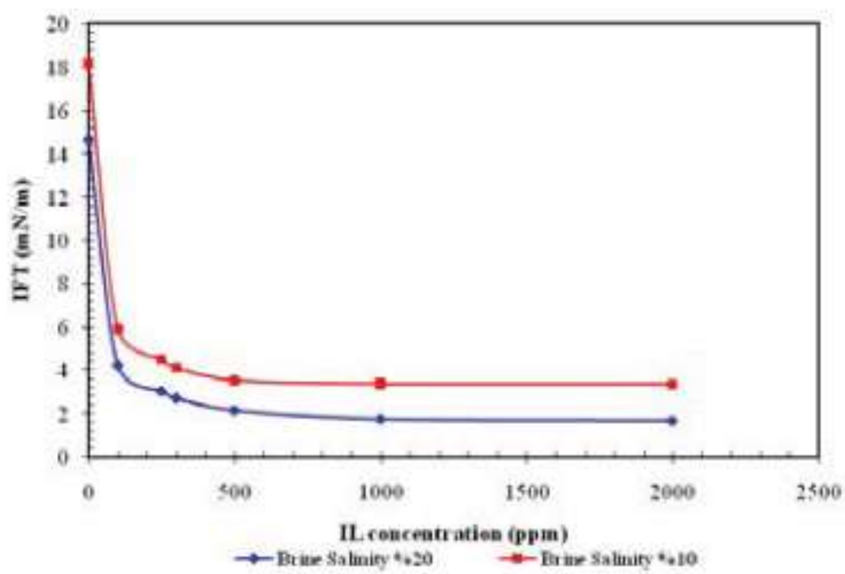

Figure 5 [35]: IFT of Ammoeng 102 Solution-Crude Oil at Different Concentrations and Two Brine Salinities.

2.10 Critical Micelle Concentration

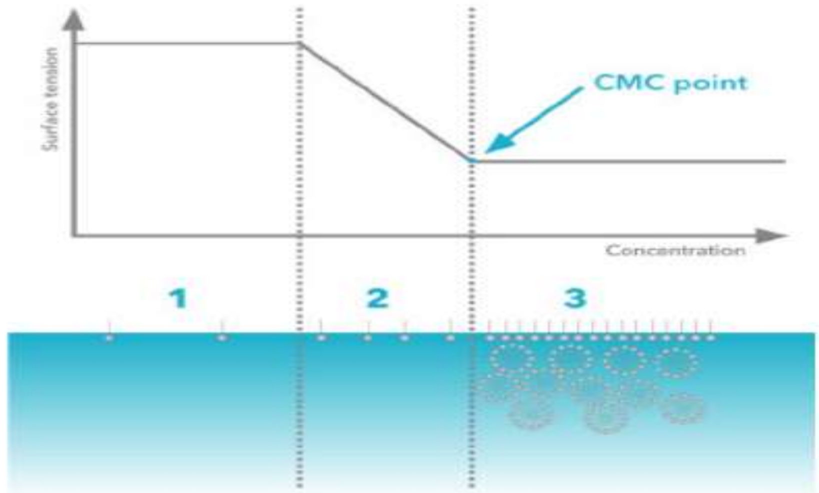

Figure 6[36]: Surface tension against the surfactant concentration

In colloidal and surface chemistry, the concentration above which micelles form is called critical micelle concentration (CMC). Initially, the surfactant molecules will arrange themselves on a fluid surface when a low surfactant concentration is dispersed onto it. The surface tension of the solution starts declining sharply when more surfactant is added. At a point when the surface become saturated, the addition of the surfactant molecules will lead to formation of micelles and the surface tension reduction will become less significant [36].This turning point is referred to critical micelle concentration. Figure 6 illustrates three different phases that show the reaction between surface tension and concentration of surfactant. Each phases are described as below:

1. Very small change of surface tension is observed at low surfactant concentration.
2. Sharp and drastic declining trend of surface tension are observed when concentration of surfactant is increased
3. Insignificant change of surface tension is observed at a point of micelles start to form.

This theory was justified in many experimental studies. Referring to graph plotted in figure 3 and 4, the reporters also state that after a certain concentration, the drop become very slight, and this inflection point is referred to as critical micelle concentration [28][35]. CMC values are significant in all surfactant applications related to the petroleum industry. The surfactants must be present just higher than the CMC, because the greatest effect of the surfactant whether in lowering the interfacial tension or promoting foam stability is achieved when a significant concentration of micelles is present [24]. Nevertheless, CMC can be influenced by pressure and temperature. An experimental study of surfactant has revealed that as the pressure increased, the CMC value will decreased but CMC tend to increase when the temperature was raised [28]. This has been tested on Anionic Zonyl FSE surfactant. However this behavior is not valid for nonionic surfactant CMC because no effect of temperature and pressure has been found on Triton X-405 (nonionic) [28] [29]. Figure below show effect of temperature and pressure on CMC of anionic Zonyl FSE.

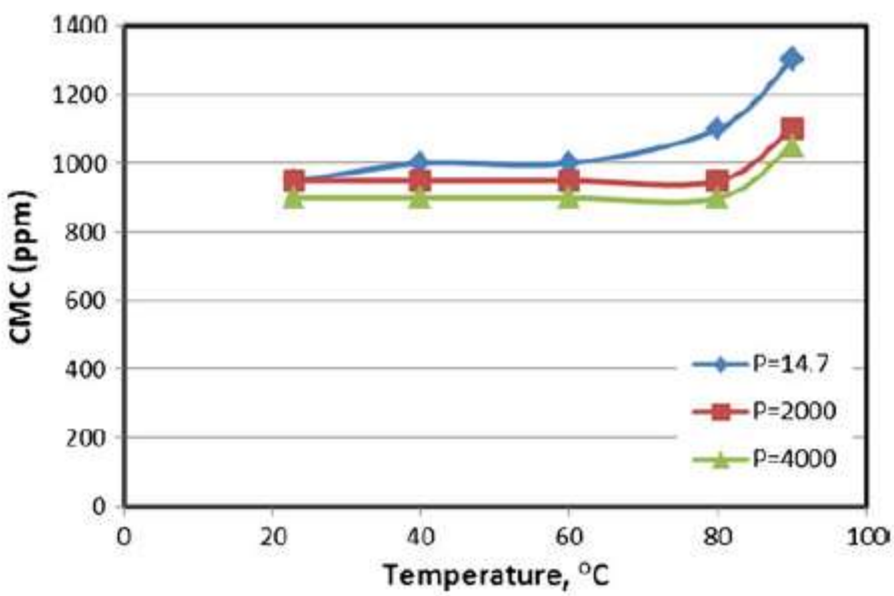

Figure 7 [28]: Effect of pressure temperature on CMC of Zonyl FSE a variable pressure condition

2.11 Economic Feasibility on using Surfactant in EOR

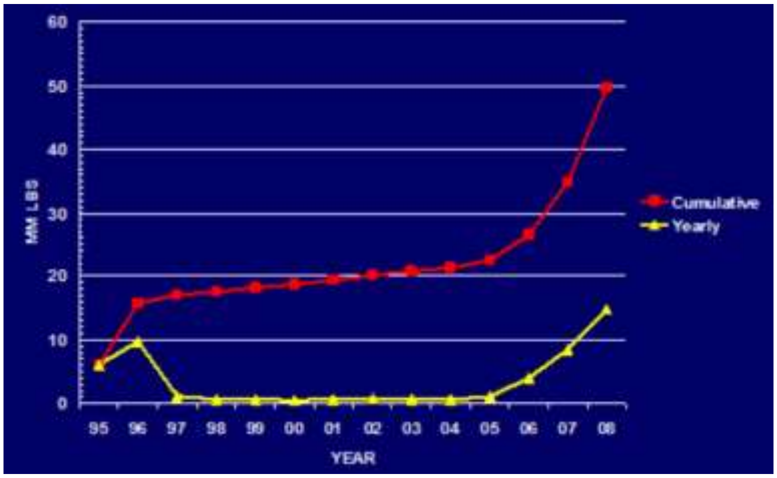

Figure 8 [40]: EOR Surfactants Sale (1995-2008)

As Shown in figure 8, demand for surfactant has increased every year. An assumption can be made that the application of surfactant can give high return to the petroleum operators. Basically, the purpose of using of surfactant is to increase the production of oil by extracting the residual oil. Usually, a chemical project may post a risk to the financial. As the cost of the surfactant is not exceeding the value of remaining oil, the application can be said feasible. For this reason, sensitivity analysis is vital to reach this goal. Thus, optimization of using surfactant is crucial to avoid any undesired result. Concentration of surfactant is the best parameter to be analyzed because it is interconnected with the cost and oil recovery. A simulation study on surfactant concentration has report that a higher concentration gave a worse chemical efficiency ($16.5/bbl) with 35.2% cumulative oil recovery compared to the base case ($14.5/bbl). Conversely, the simulation with lower concentration resulted in an improved efficiency ($13.5/bbl) with 17.55% cumulative oil recovery. These values were calculated using a surfactant price of $2.75 per pound. Thus, regardless of volume of oil recoveries, an optimization of using surfactant is important to ensure profitability [41]. Theoretically, high concentration of surfactant can lower much IFT between oil and water but at certain point of concentration, it not influencing much on IFT reduction (CMC) .Thus it is necessarily to find the very optimum concentration to reduce the operating cost. Thus, investigation of CMC point on IFT versus surfactant concentration is a feasible method to be studied.

2.12 Environmental considerations

Currently surfactant with high demand in the market are made of synthetic mainly petroleum-based. However, these compounds are non-biodegradable and toxic to the environment. They may bio-accumulate and their processes, product and by-products can be environmentally hazardous [42]. As a result, then demand for non-toxic and biodegradable surfactants are increasing due to restrictive laws and environmental issues. Hence, there has been an attempt to use natural surface-active components as surfactants [26]. Ionic liquid surfactants (ILS) have often been labelled ‘green’ due to their negligible vapor pressure. However, their toxicology data are hard to reach until present day. [43]. A number of authors [43-46] already stated this shortage of toxicological data in their report. ILS is not causing air pollution because it does not evaporate. However, it will endanger environment when it dispersed into aquatic systems. ILS can disperse into the aquatic environment by effluents or accidental spills. When the presence of water, most ILS such as [bmim] [PF6] or [bmim] [BF4] tend to decompose. This will lead to the formation of phosphoric and hydrofluoric acids [47]. Therefore, Both ecotoxicity and toxicity information which provides metabolism and degradability of ILs, are vital to label them as green solvents. An ecotoxicological studies can be done by investigating the effects of different ILs on microorganism, cells and enzymatic activities. LC50 (lethal concentration) measured in unit mg/L is used as parameter to determine the level of toxicology of a surfactant. Basically, a decreasing trend of LC50 values indicates higher toxicities according to the toxicity classes of Hodge and Sterner scale (1956) [48]. Surfactants that reads LC50 with a value of 10 or below are that the chemical is tremendously toxic, LC50 value between 10 and 100 shows that chemical is highly toxic, LC50 value between 100 and 1,000 shows that chemical is slightly toxic, and finally LC50 value between 1,000 and 10,000 means that chemical is practically nontoxic. Consideration of the effects of surfactant to the aquatic system is highly important because some ILS very soluble in water. One report investigates two Imidazolium-based ILS with common freshwater crustaceans, Daphnia magna [49]. D. Magna is used because its filter feeders at the base of the aquatic food and their responses to ILS are essential in determining how these new solvents may influence an environmental ecosystem. They found LC50 for Imidazolium-based ILS are toxic to Daphnia as benzene and even far more toxic than acetone. However, its toxicity is much less toxic than chlorine, ammonia, and phenol.

CHAPTER 3

METHODOLOGY/PROJECT WORK

Figure 9: Methodology

In this project, the methodology will be done in two ways, which is experimental and research methodology.

3.1 Experimental Methodology

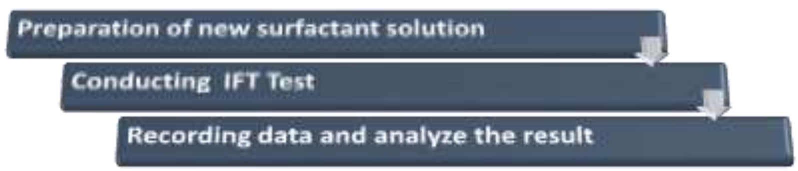

Figure 10: Schematic Diagram of Experimental Methodology

Figure 4 shows the flow diagram of project methodology. There are 3 main processes involved in this project. The sample surfactant solution must be prepared in the early of the experiment in the laboratory. Then, the prepared solutions will be brought up for the IFT test. Several tests will be conducted based on the parameters to be investigated. Later, the data will be collected and further analyzed. The test conducted will measure the interfacial tension between the surfactant and oil. One sample of surfactant will be used in the test and its concentration will act as the parameter. Thus, IFT versus concentration graph can be constructed. As discussed earlier, the aim of this project is to determine the CMC point. This point will be indicated on the constructed graph. This experimental study will be carried out at ambient conditions, hence it do not represent a real reflection of the reservoir conditions. Therefore, this study only reflects IFT measurements in a reservoir at constant temperature and fixed brine salinity for varying concentrations of surfactant.

3.2 Experimental material and apparatus

A number of materials consisting of solids and liquids will be used in this project. Those are surfactant, distilled water, brine and crude oil. Meanwhile, the main equipment to characterize the material attributes are a pendant drop IFT meter and density meter.

3.2.1 Chemicals

(a) Aqueous phase

To form brine, inorganic salt of sodium chloride (NaCl) was used because it is the typical salt found mainly in petroleum reservoirs [26]. The salt will be dissolved in the water using magnetic stirrer. Later, surfactants will be mixed in this solution. As the salinity is constant variable, only one concentration of brine solution will be prepared. The brine solution consisting of 100% NaCl and 3% by weight percent.

(b) Oleic Phase

Crude oil from Dulang Field was used as oleic phase in this project. The Dulang field contains in excess of one billion barrels of oil and a substantial amount of gas, making it one of the largest fields located offshore Peninsular Malaysia. Dulang crude is categorized as saturated, light and waxy with an API of 37. Degrees [25]. The table below illustrates further the reservoir and fluid properties of the Dulang field.

Table 3[25]: Reservoir and Fluid Properties of Dulang Field

Reservoir and Fluid Properties	Value
Pressure	1800 psig
Temperature	96°C
Permeability	200mD
Porosity	30%
Oil Viscosity	0.625 cP
API	37.4°API

(c)Surfactants

As discussed earlier, a type of ionic liquid will be discovered in this project. Among of ionic liquids, IL-10 has been chosen to be investigated. Ionic liquids are believed have a potential to be used for IFT reduction in EOR. Ionic liquids made of organic salts that are consist of organic cations with inorganic or organic anions. Physically, they exist as liquids at room temperature. Recently ILS has received considerable attention as potential "green" alternate to conventional organic surfactants [26][27][35]. Besides, recent studies has discovered ionic liquid effectively can reduce IFT at low concentration [26] [28]. Surface active ionic liquids have the potential to constitute an attractive alternative to the surfactants existing used in EOR processes, with important advantages over the traditional surfactant or polymer flooding methods as below [50]:

- Ionic liquids are exist as liquid form over a wide temperature range and essentially non-volatile.
- Ionic liquid can be optimized by design it for adapting specific reservoir conditions considering different rock properties and fluids.
- Ionic liquids which have high viscosity important to prevent the formation of digitations (phase degradation) resulting from unfavorable mobility rates.
- It is not necessary to use co-surfactant. This is due to strong cohesive forces in ionic liquids. Thus, stable micelles can be formed without the need of additional chemicals.
-

In this project, surfactant solution was prepared at 6 concentration. The unit used for the concentration of the IL or surfactant is ppm, based on weight of materials used. The concentrations ranged from 200 ppm to 5000ppm.

3.2.2 Apparatus/Equipment

(a) Interfacial Tension Meter

Figure 11: IFT Measurement Equipment

Vinci IFT-700 IFT meter (Figure 11) was used to measure the Interfacial tension for this project. This instrument not only can measure IFT but also can measure contact angle and surface tension. This instrument will applied pendant drop method in measuring IFT between liquid-liquid interfaces. For measuring contact angle between liquid and solid interfaces, sessile drop method will be applied. [38]. Pendant drop method is widely used and has been reported excellent in accuracy [39]. The principle approach is to analyze the profile of a drop of one liquid that suspended in another liquid at mechanical equilibrium condition. A liquid drop is created and put in contact with gas or solid in a cell at reservoir conditions. A camera connected to a computer records the shape of the liquid drop to derive the interfacial properties. The profile is determined by the balance between surface force and gravity. Then, The Drop Analysis System software will retrieve IFT value by computing the following equation.

$$\gamma = \frac{\Delta\rho g D^2}{H} \qquad (2)$$

Where $\boldsymbol{\Delta\rho}$, g, D and H are density differences between solution and crude oil, gravitational constant, drop diameter, and a correction factor respectively. A standard pendant drop equipment consist of three parts: a viewing and an illuminating system to visualize the drop, a data acquisition system to interpret the interfacial tension from the pendant drop profile and an experimental cell. Table 4 shows more information about this instrument.

Table 4: Vinci IFT-700 Interfacial Tension Meter Properties

Properties	Description
IFT standard measurement	0.1 to 72 mN/m
Temperature	Ambient to 180°C
Temperature accuracy	0.1°C
Pressure	700 bar (10,000psi)
Wetted parts	Stainless steel
Power supply	220 VAC 50 Hz

(b) Density Meter

Figure 12: Density Meter

MPDS 2000 V3 Anton Paar density meter as shown in figure 12 was used in this project to measure the density of aqueous phase and oleic phase, which are brine and crude oil respectively. The densities of brine and crude oil were measured as a function of temperature. Table 5 be shows further information about this equipment.

Table 5: MPDS 2000 V3 Anton Paar meter properties

Features	Descriptions
Power supply	85 to 260 VAC, 48 to 62 Hz
Power consumption	30 VA
Dimensions (W x H x D)	208 x 160 x 300 mm
Panel cutout	186 x 138 mm
Protection class	Front IP 55
Weight Approx.	5 kg (11 lb)

(d) *Other Apparatus*

A number of basic laboratory apparatus and equipment also has been used in this project. The lists are shows in table below.

Table 6: List of apparatus

Apparatus/ Equipment	Amount
Sample bottle	6
Beaker	3
Measuring Cylinder	3
Magnetic stirrer with heater	1
Micropipette	1
Syringe	3
Needle	3
Weighting Equipment	1

3.3 Experimental procedures

3.3.1 Sample Preparation (bulk phase)

Figure 13: Sample solutions with various concentration

Figure 13 above shows seven samples of IL-10 sample solutions that have been prepared in the laboratory with various concentrations. The selected surfactant concentrations were varied in parts per million based on weight of chemicals used. The concentrations prepared were 0, 200, 400, 1000, 2000, 3000 and 5000ppm. Basically, to come out with these solutions, bulk solution need to be prepared based on the calculation as per attachment in Appendix B. In weight percent, the surfactant solutions were 0.00, 0.02, 0.04, 0.1, 0.2, 0.3 and 0.5wt%. The salinity and temperature is constant parameter which is 3wt% or in parts per million equal to 30 000ppm salinity and 90°C temperature. The procedure to prepare bulk solution and sample was divided into several basic steps as below:

Step 1: Need to know the amount for each chemical used such as IL-10, sodium chloride powder and distilled water in unit gram and measure using weighting equipment as per Attachment 1 and 2 in appendix A.

Step 2: Mix each chemical with distilled water based on required amount using heater and magnetic stirrer in order to form a solution. Refer Figure 14 below and Attachment 3 in appendix A.

Step 3: Then, start preparing the samples with different surfactant concentration according to the mixing volume using equipment as per Attachment 4 in appendix A and Figure 13.

Figure 14: Mixing chemical using heater to form a solution

3.3.2 Density Measurement

Before run the IFT Test, reliable density data for bubble phase and bulk phase at measurement temperature are required as input data in the software in order to calculate the IFT. As discussed earlier, DMA 512P (density meter) from Anton Paar (Mpds 2000 V3), Austria was used to measure the density of Dulang crude and each concentration of surfactant solution. The density of Dulang (light phase) was measured as 0.8115g/cm³ (at 90℃) and that of each surfactant solutions density (heavy phase) was measured at 90℃ and tabulated in table below.

Table 7: Density of Surfactant solutions at 90℃

Surfactant Concentration (ppm)	Density (g/cm³)
0	1.0213
200	1.0215
400	1.0217
1000	1.0214
2000	1.0219
3000	1.0221
5000	1.0223

3.3.3 IFT Measurement

Interfacial tension is an attribute of the interface between two immiscible phases. Chemical screening by IFT test is to find what surfactant and what optimum surfactant concentration to be used to get desired result. Literally, increasing the surfactant concentration can reduce the IFT value. This reducing trend is not continuous, until a point where increasing surfactant concentration does not take action anymore into IFT value. This point is called CMC point. By using pendent drop method, interfacial tension between oil and solution in contact with the oil can be determined. The shape of the liquid drop can be seen in the computer with the help of connected camera to the computer in order to derive the interfacial tension and contact of angle properties while keeping rotation as the constant parameter for all measurement.

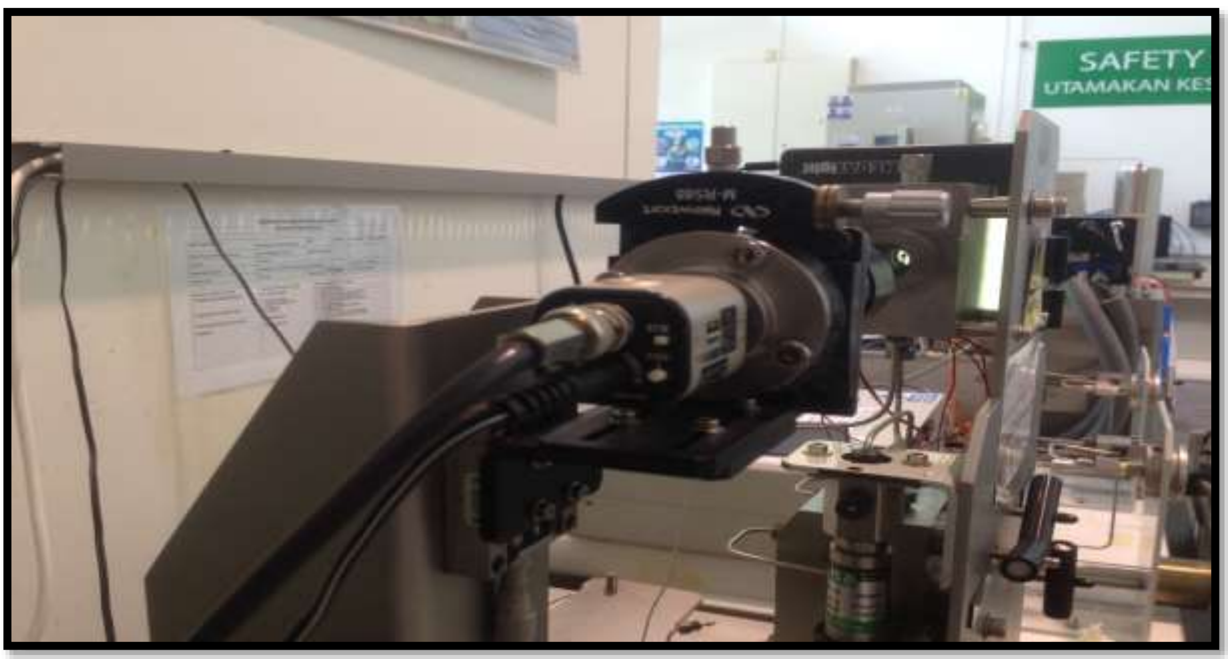

Figure 15: Running the IFT Experiment

There are several steps and precautions that should be taken to measure IFT using Vinci IFT 700 Interfacial Tension Meter. The steps are as below:

1. Crude oil is placed as the rising drop liquid since it has lower density than water while a surfactant solution was placed as bulk liquid
2. The temperature is set to 90°C before generating an oil rising bubble in the cell.
3. The bubble image is captured using a live camera connected to a computer and then analyzed and calculated using Vinci IFT 700 IFT meter Software.
4. For the calculation, densities for both crude oil and surfactant solution are required as input data in software and measured using Density meter.
5. Five measurements of different oil bubbles are recorded and an average IFT are calculated as final results.

The data obtained were tabulated in table shown below. In order to find CMC point, IFT of the IL solutions at different concentration were measured and plotted versus concentration of solution.

Table 8: IFT Measurement Readings

	Surfactant Sample	Surfactant Concentration (wt %)		IFT (Mn/m)			
				R1	R2	R3	Avg
OIL	IL-10	0.00	**3 wt. %**				
		0.02					
		0.04					
		0.1					
		0.2					
		0.3					
		0.5					

3.4 Key Milestone

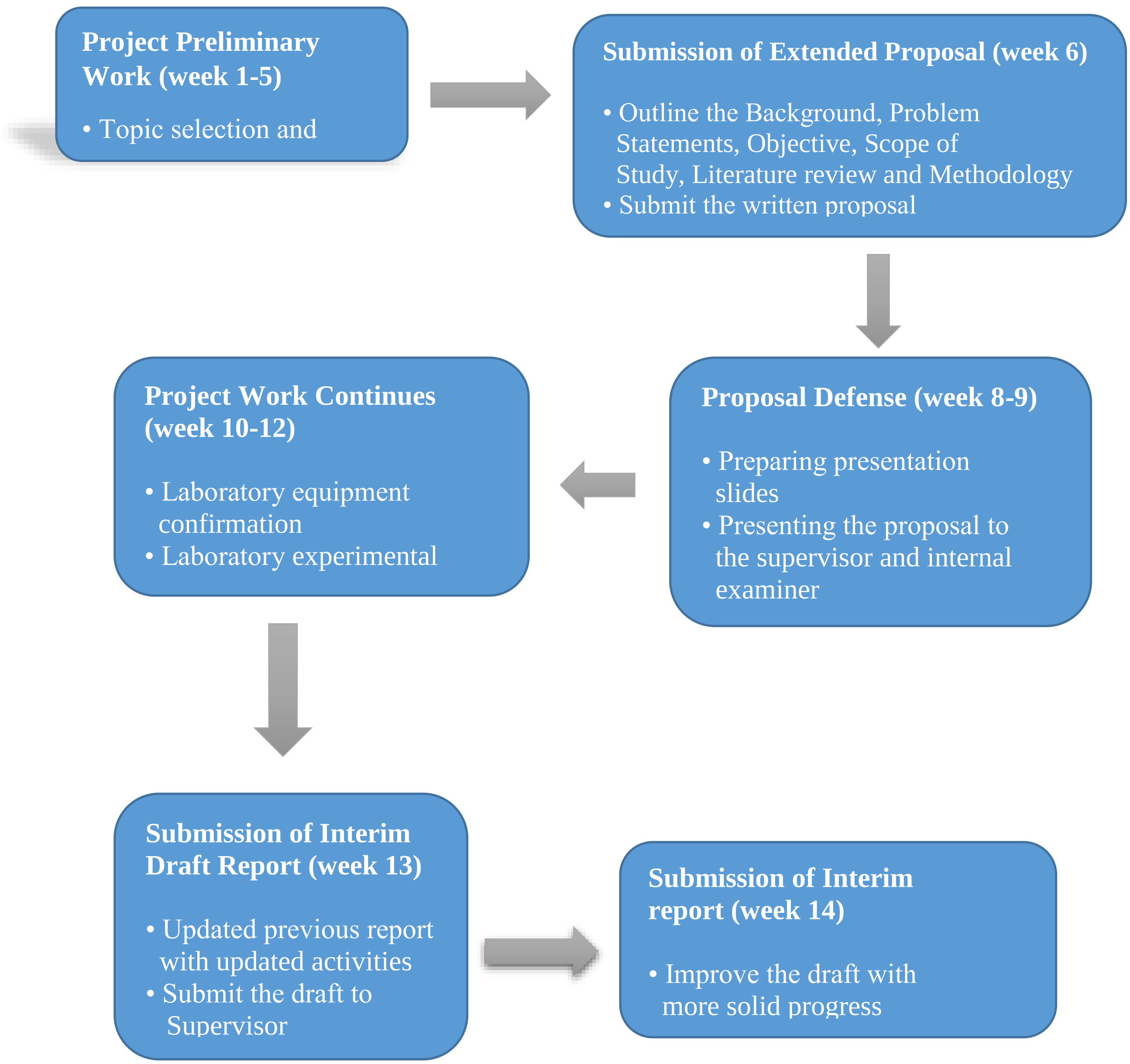

Figure 16: Key Milestone of Project (FYP 1)

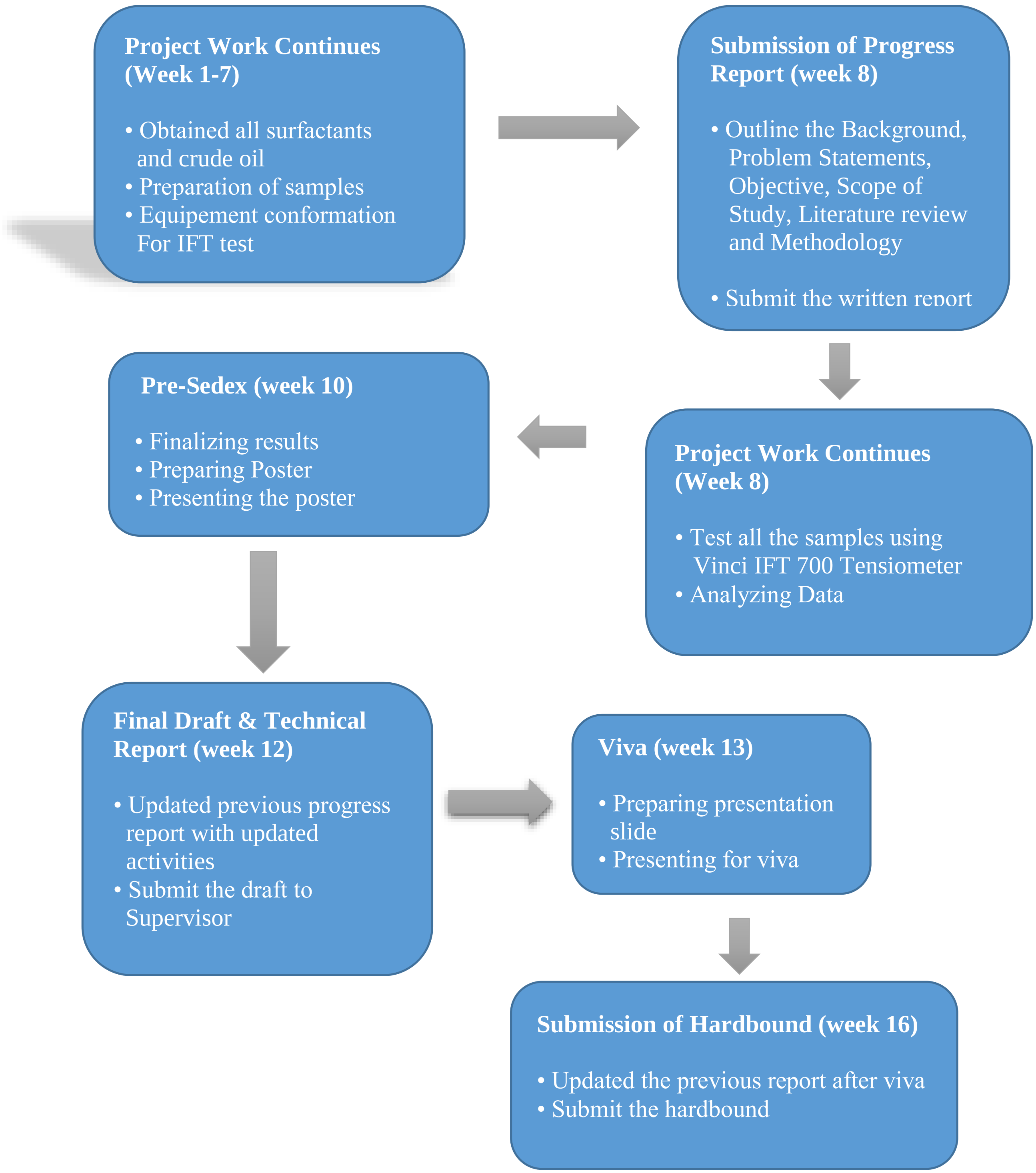

Figure 17: Key Milestone of Project (FYP 2)

3.5 Gantt Chart

	Final Year Project I														Final Year Project II													
Detail/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
Identify the purpose of this project and gather as much information																												
Study the experimental procedure and check the availability of equipment. Prepare the samples that will be used																												
Run the experiment on IFT measurement at different surfactant concentration with several types of surfactant																												
Analyze the result and proceed with determination of CMC point																												
Compile all the documentation including the discussion based on the results obtained in the report																												

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Results

Figure 5.1 shows the IFT results for the Dulang crude oil and surfactant/brine solutions for the first, second and third run.

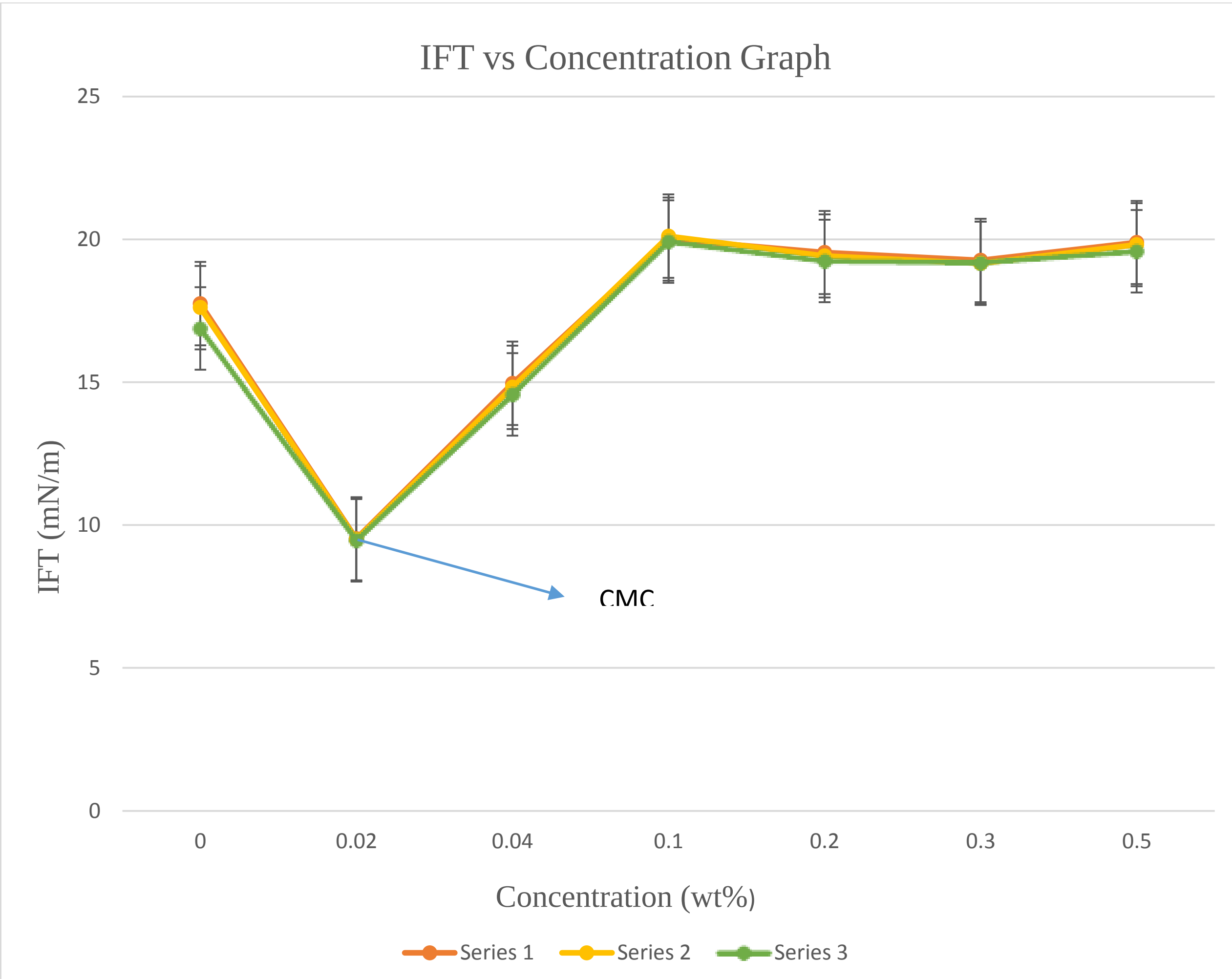

Figure 18: IFT measurements for the crude oil-brine/surfactant system

In the figure 18, the red, yellow and green lines refer to the first, second and third run respectively. Whereas, the graph below represents the average IFT measurements with increasing surfactant concentration in the brine solution.

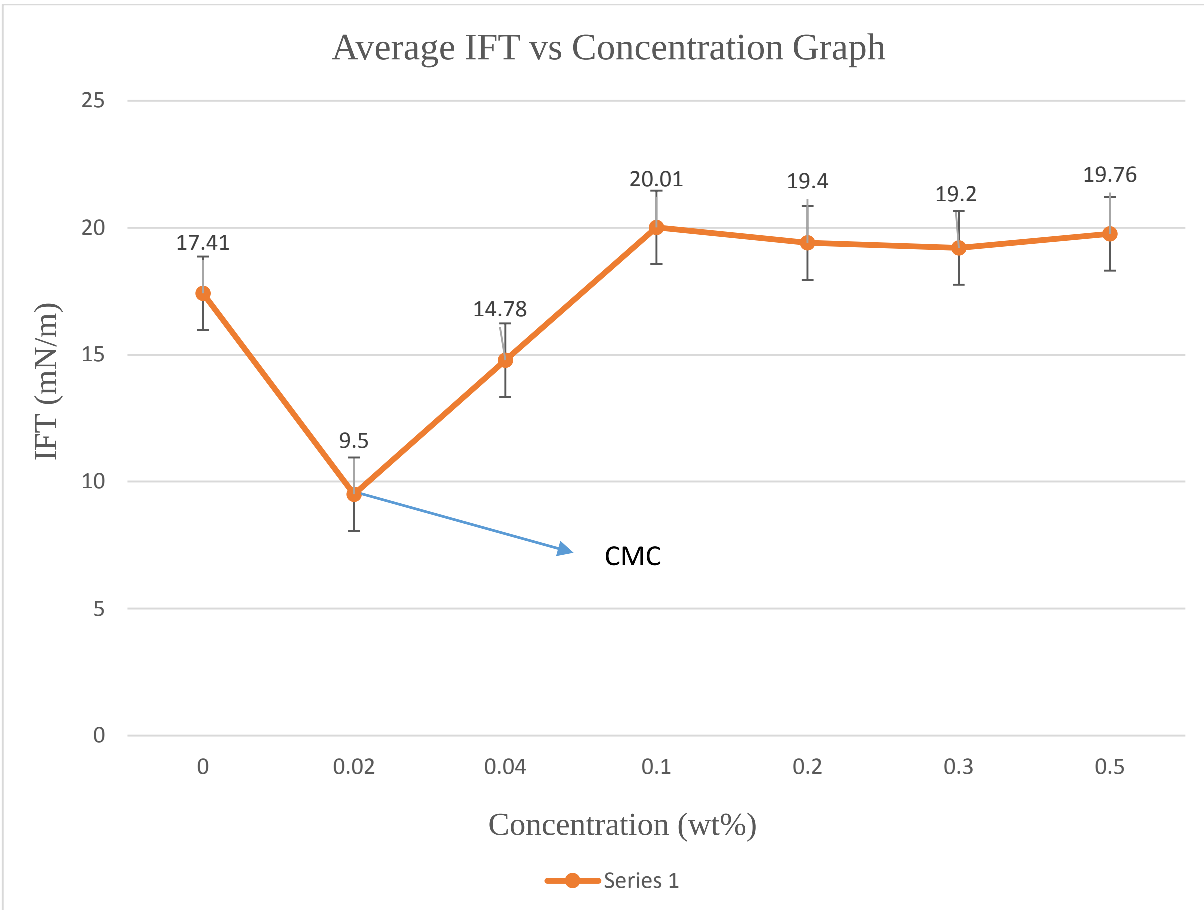

Figure 19: Average IFT measurements for the crude oil-brine/surfactant system

4.2 Discussion

The experiments were carried out to show the effect of varying surfactant concentration on IFT of oil –brine/surfactant system. Initially the experiment was done with no added of surfactant. The temperature was set to 90°C and ambient pressure was used. Three IFT readings were taken for each concentration including 0 wt% for precision. Average reading will be used in this discussion to refer the IFT value. From the next run onwards, IL-10 surfactant was added to the brine solution varying from 0.02 to 0.5 wt%.

Referring to figure 19, without the present of surfactant, IFT was measured to be 17.41 mN/m. This value represents a high IFT and hence a low capillary number. As discussed earlier, water and oil are always in different phases. As oil consists of hydrocarbon molecules which are nonpolar, they do not interact with the polar water molecules. This explains why the high interfacial tension between oil and water.

As the surfactant was added (0.02wt %), the IFT started to drop sharply to the lower value with a magnitude difference of 7.91 mN/m away from the initial run (without surfactant). This observation proves that the addition of surfactant into the oil - water system can reduce its interfacial tension as claimed by previous investigators [22, 24, 26, and 28]. The chemistry behind the reduction of IFT is due to the interaction of surfactant molecules to the oil and brine. When amphiphlic surfactant was dispersed into the interface of oil and water, hydrophilic part will interact with water, whereas hydrophobic part will interact with residual oil. As the consequence a stable microemulsion system was formed between oil and water. This event greatly contributes to a significant reduction of interfacial tension energy. The lower the reduction, the greater the stability of the oil in water emulsion can be formed. In view of this, IL-10 can be considered as an efficient surface active agent.

CMC is another important characteristic that needs to be investigated in this project. As stated in the colloidal chemistry, the lowest reading of IFT may indicate the CMC point. An ideal surfactant concentration for effective implementation of the surfactant EOR process is within range of 0.05 to 0.5 wt% [51]. Referring back figure 19, the lowest IFT was 9.5mN/m measured at 0.02 wt% concentration which is even lower than ideal concentration. This reflection tells that only a small amount of IL-10 is necessary to bring down the IFT value. This can be deduced that IL-10 is effective and economical to be implemented in EOR.

Furthermore, it is clear that an increase in the concentration of surfactant after CMC point had no effect on the IFT reduction as the value continually increased eventually remain less constant. Again from figure 19, when exceeding the CMC point, the IFT reading shows contrast trend where the IFT reading starts to climb up to 14.78 mN/m at 0.04wt% and continue increasing to higher value of 20.01 mN/m at 0.1wt%. Right after that, increasing of surfactant concentration from 0.2 to 0.5wt% seems not give much effect to the IFT reading. This is consistent with the exclamation from previous investigator that stated above the CMC point, the addition of surfactant will just increase the concentration of micelles whilst the IFT reading will stay more or less constant [52].

4.2.1 Experimental Error and Uncertainty

Several factors and errors are taken into account while conducting this project because it may affect the accuracy of the result. To avoid parallax error, the eye are always in the right position while reading are taken. Besides, using appropriate apparatus is important while making any measurement. For example, small volume of solution was measured using micropipette. To ensure the accuracy of the reading such as density and IFT, cleanliness of the equipment is important to be considered. Thus, every equipment was cleaned before use and before proceeding with another sample. For instance, metal syringe that associate with the IFT equipment was used to hold different types of fluid before it was injected into the equipment cell. In this project, oil and surfactant were alternately held by the metal syringe. This will lead to serious dirtiness to the equipment due to waxy oil. When a little mixed, this may alter the properties of the sample surfactant need to be tested due to contamination. As a result, the measurement of the IFT will be not too accurate. Thus, degreaser cleaner was used to clean the metal syringe that is contaminated with waxy oil so that it always clean and clear. Furthermore, while conducting the pendant drop method, the drop image was captured in high definition. This can be done by making sure that the bulk phase is clear and transparent before capturing activity. This will contribute in the precision of calculating the shape or dimension of the drop that to be analysed. A sharp image will give high accuracy of IFT value. Figure 20 shows a typical image of bubble formed by the sample.

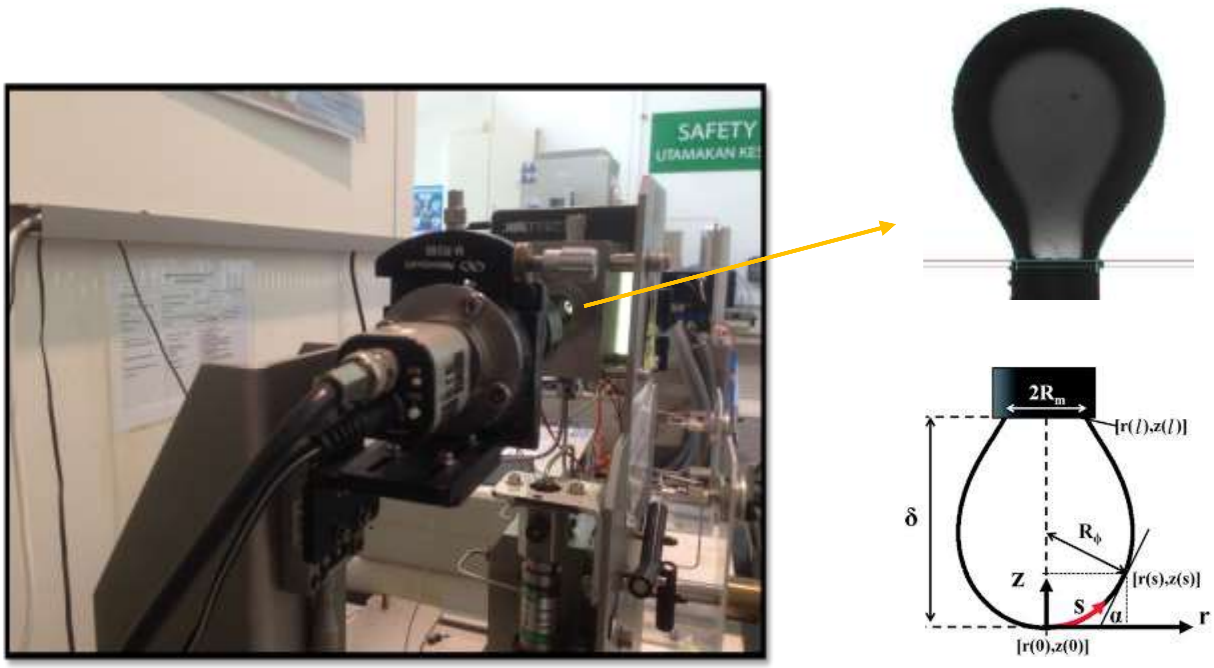

Figure 20: Image of bubble formed

4.2.2 Statistical Analysis

In the graph plotted, statistical analysis to calculate the standard deviation was done. Standard deviations are important because they reflect the measure of fluctuations a set of data will experience. The calculations for the standard deviations are tabulated below in the appendix C. In this study, the following equations were used for statistical analysis:

$$\sum \overline{X} = \frac{(X_1+X_1+X_1)}{3} \tag{3}$$

$$Standard\ Deviation, SD = \sqrt{\frac{\sum(X-\overline{X})^2}{(n-1)}} \tag{4}$$

$$S.D_{spooled} = \frac{\sum((n-1)SDi^2)}{\sum(n-1)} \tag{5}$$

$$Standard\ Error = \frac{S.D}{\sqrt{n}} \tag{6}$$

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

This experiment deals with the variation of interfacial tension with varying surfactant concentration. The experimental data were analyzed to find a critical surfactant concentration. This is very important from the economic point of tertiary recovery (chemical flooding) since the use of surfactants is expensive. The economics of surfactant flooding is a complex function of many elements, such as surface facilities, well operations, reservoir parameters and chemical cost.

Based on the experiment the following conclusions are made:

- There was a decrease in interfacial tension with an addition in IL-10 concentration.
- From the results obtained a critical micelle concentration IL-10 surfactant was obtained at 0.02 wt% of IL-10 which is effective for implementation of the surfactant EOR
- Before the critical micelle concentration (CMC), the present of surfactant reduce the IFT in a brine-oil solution system. Above the CMC, the added surfactant keeps the IFT increasing and eventually remains less constant.

5.2 Recommendations

The following recommendations can be made,

- To best determine the CMC of ILS, the experiments must be carried out using exact formation brine for accurate results.
- To further verify the influence of surfactants on IFT, effects of temperature, pressure and salinity effects must be considered. This report cannot tell the effect of salinity as just one salt concentration was used for the experiment.
- The addition of additives, for example co-polymers and alcohols, along with surfactants should be taken into account

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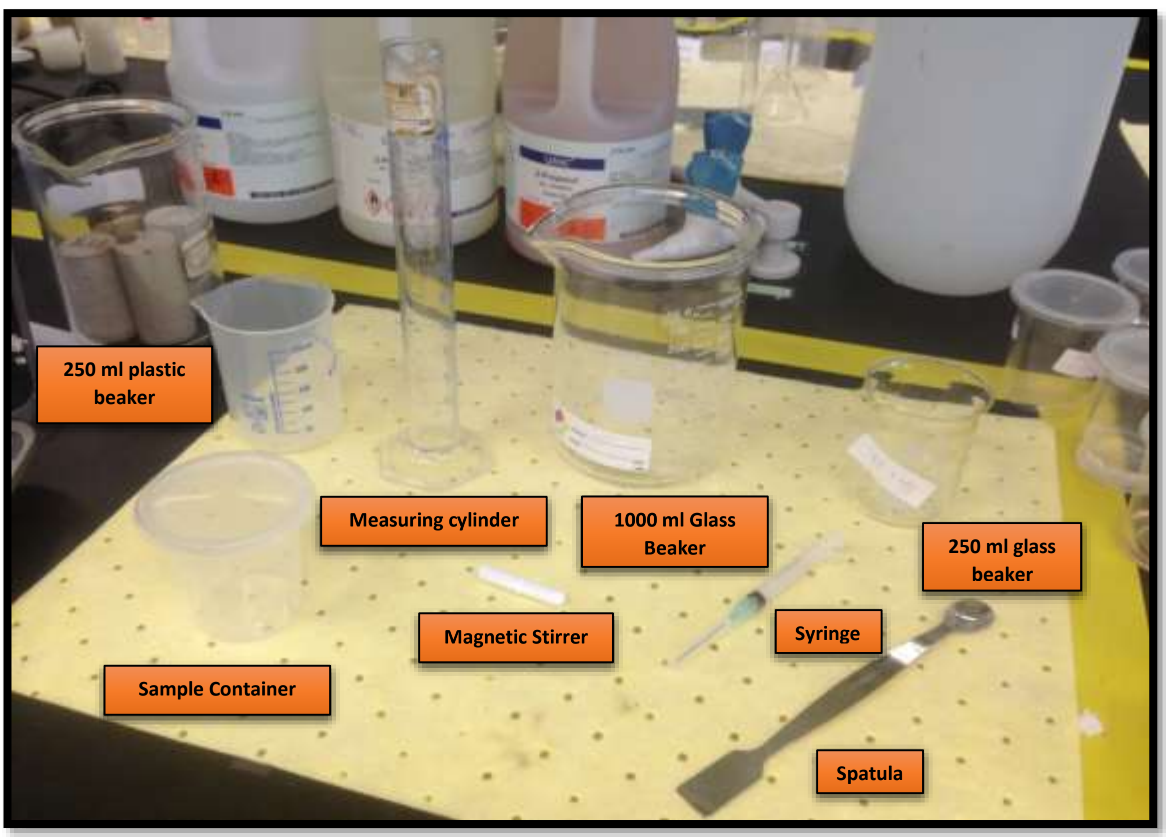
APPENDIX

Appendix A: Apparatus, Material & Method of preparation

Attachment 1: Chemicals - Sodium Chloride [A] & Sample IL-10 [B]

Attachment 2: Weighting Equipment

Attachment 3: Heater



Attachment 4: Equipment used for preparing the samples

Appendix B: Preparation of Solution

1) Brine Solution

$$100\ g\ NaCl + 900g\ Water = \frac{100g\ NaCl}{1000\ ml\ Water} x\ 100 = 10\ wt\%$$

$$\frac{100g}{1000ml} x \frac{1000ml}{1L} x \frac{1000mg}{1g} = 100{,}000\ \frac{mg}{L}$$

$$Stock\ Solution = 100{,}000\ ppm$$

2) Surfactant

$$1g\ (IL - 10) + 19g\ Water = \frac{1g\ IL - 10}{20ml\ Water} x100 = 5wt\%$$

$$Surfactant\ Solution = 50{,}000\ ppm$$

3) Saline Solution

$For\ 3\ wt\%\ of\ salinity$

$$M_1V_1 = M_2V_2 \tag{7}$$

$Volume = 100mL,$

$$V_1 = \frac{M_2V_2}{M_1} = \frac{3.0wt\%\ x\ 100ml}{10wt\%} = 30mL$$

- *Thus, Volume of brine needed in each sample is 30 mL*

(4) Varying Surfactant Concentration

$$M_1V_1 = M_2V_2$$

$$For\ 0.02\ wt\%\ or\ 200ppm$$

$$V_1 = \frac{M_2V_2}{M_1} = \frac{0.02wt\%\ x\ 100ml}{5wt\%} = 0.4ml$$

- *The volume for 400ppm, 1000ppm, 2000ppm, 3000ppm & 5000ppm will be calculated with the same formula. The summary are shown in table below*

Surfactant Concentration (ppm)	***Volume of Surfactant (mL)***	***Volume of Brine (mL)***	***Volume of Distilled Water (mL)***
0	*0.0*	*70.0*	*30.0*
200	*0.4*	*69.6*	*30.0*
400	*0.8*	*69.2*	*30.0*
1000	*2.0*	*68.0*	*30.0*
2000	*4.0*	*66.0*	*30.0*
3000	*6.0*	*64.0*	*30.0*
5000	*10.0*	*60.0*	*30.0*

Appendix C: Standard deviation Calculation

$IL-10$ Concentration (ppm)	$IFT\ (X_1)$	$IFT\ (X_2)$	$IFT\ (X_3)$	$\overline{X} = \frac{(X_1+X_1+X_1)}{3}$	$S.D$	S.E
0	*17.75*	*17.61*	*16.88*	*17.41*	0.4672	0.1045
200	*9.52*	*9.5*	*9.47*	*9.50*	0.0252	0.0056
400	*14.96*	*14.82*	*14.57*	*14.78*	0.1976	0.0442
1000	*20.01*	*20.11*	*19.92*	*20.01*	0.0950	0.0212
2000	*19.54*	*19.42*	*19.24*	*19.40*	0.1510	0.0338
3000	*19.26*	*19.16*	*19.18*	*19.20*	0.0529	0.0118
5000	*19.89*	*19.81*	*19.58*	*19.76*	0.1609	0.0360

$$\sum \overline{X} = \frac{(X_1+X_1+X_1)}{3}$$

$$Standard\ Deviation, SD = \sqrt{\frac{\sum(X-\overline{X})^2}{(n-1)}}\ , where\ n\ is\ the\ data\ points\ at\ each\ IL10\ conc.$$

$The\ spooled\ standard\ deviation\ is:$

$$S.D_{spooled} = \frac{\sum(\ (n-1)SDi^2)}{\sum(n-1)}, where\ SDi^2\ is\ the\ standard\ deviation\ at\ each\ IL10\ conc.$$

$$= \frac{2.68001}{6} = 0.44667$$

$$Standard\ Error = \frac{S.D}{\sqrt{n}} = 0.10447$$