CERTIFICATION OF APPROVAL

Suitability of Surfactants in Enhanced Oil Recovery

by

Azfarizal bin Ahmad Zaki

A project dissertation submitted to the
Chemical Engineering Programme
Universiti Teknologi PETRONAS
in partial fulfilment of the requirement for the
BACHELOR OF ENGINEERING (Hons)
(CHEMICAL ENGINEERING)

Approved by,

(Syed Sakhawat Shah)

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

May 2004

t
TN
23
.A99
2004
1. Petroleum
2. ChE -- thesis

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 acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

AZFARIZAL BIN AHMAD ZAKI

ABSTRACT

As the EOR technology is yet to be introduced in Malaysia, an initial study have to be started to determine its suitability. Thus, chemical EOR or chemical flooding, as a possible candidate of EOR method to be run in Malaysia, has to be studied its compatibility with the Malaysia oil field conditions.

This project intended to study suitability of surfactant with Malaysian crude oil and sea water through analyzing certain parameter in EOR. In this project, the interaction of selected surfactant with water mixture and crude oil from Malaysian oil field is determined through interfacial tension (IFT) analysis. Instead of that, the suitable polymer compatible with the Malaysia reservoir need to be determined to be used along with the selected surfactant.

The analysis began with preparation of water blends and crude oil, before the test on polymer and surfactant is done. The main technique used in this project is the analysis of IFT using spinning drop tensiometer. The final surfactant candidate also undergoes phase behavior test to determine the interaction between surfactant solution with crude oil at different water mixtures and surfactant concentrations.

From the study, the surfactant that has the best performance with Malaysia fluid condition is Sample 6-79 as it shows the lowest range of IFT at all testing condition. Apart from that, the polymer Superfloc BD319 have shown the best results compared to the other polymer tested and have the potential use with the surfactant to be applied in the chemical flooding in Malaysia.

ACKNOWLEDGEMENT

First and foremost, I would like to express my gratitude to Allah SWT for giving me the strength, ability and courage upon completing this Final year research Project course. My deepest gratitude to AP Dr Syed Sakhawat Shah, my personal supervisor for his technical guidance, continuos support, brilliant ideas and suggestion and personal concerns during duration of this final year project.

My appreciation to final Year Research Project Coordinators, Puan Anis Suhaila Shuib and Miss Nor Yuliana Yuhana for taking care of the charity of the Final Year students. An infinite gratitude to PRSS personnel especially Puan Pauziyah abdul Hamid, Miss Hon Vai Yee, Mr Arif Azhan Abdul Manap and Mr Tajuddin Abdullah for guidance, suggestions and helps during my duration there. Gratitude also to Chemical engineering Department, Mr Zaaba, Mr Jamalkhair, Mr Shaharuddin and Mr Jailani for assisting me throughtout my experimental work.

Last but not least, special thanks to both my parents for being there all of the time, continuos aspiration and encouragement for me to proceed with my Final Year Research project.

TABLE OF CONTENTS

CHAPTER 1: INTRODUCTION

1.1 BACKGROUND STUDY 1

1.2 PROBLEM STATEMENT 2

1.3 OBJECTIVES AND SCOPE 2

CHAPTER 2: LITERATURE REVIEW AND THEORY

2.1 DEFINITION OF SURFACTANT 4

2.2 THE HYDROPHOBIC EFECT AND MICELLE FORMATION 6

2.3 MICELLAR-POLYMER FLOODING / CHEMICAL FLOODING 7

2.4 SURFACTANT IN CHEMICAL FLOODING 8

2.5 POLYMER IN CHEMICAL FLOODING 13

CHAPTER 3: PROJECT OVERVIEW/METHODOLOGY/PROJECT WORK

3.1 PROJECT OVERVIEW 14

3.2 METHODOLOGY 14

3.3 TEST PROCEDURES 18

CHAPTER 4: RESULTS AND DISCUSSION

4.1 POLYMER SELECTION/SCREENING FOR EOR 22

4.2 SURFACTANT SELECTION FOR EOR 25

CHAPTER 5: CONCLUSION AND RECOMMENDATION

5.1 CONCLUSION 32

5.2 RECOMMENDATION 32

REFERENCES 33

LIST OF FIGURES

Figure 2.1 Sample of anionic surfactants
Figure 2.2 Example of nonionic surfactant
Figure 2.3 Example of cationic surfactant
Figure 2.4 Example of Zwitteronic surfactants
Figure 2.5 Cross section of a typical micellar-polymer flooding
Figure 2.6 Spinning drop tube filled with the two phases.
Figure 2.7 Micelle formation in Phase Behavior Winsor Type I and Type II
Figure 2.8 Surfactant Micelle structure in respective type of Phase Behavior
Figure 2.9 Respective region for phase behavior type I, II and III
Figure 3.1 Spinning drop interfacial tensiometer Model 500
Figure 3.2 The expanded oil droplet viewed from the microscope (B)
Figure 4.1 IFT of oil - surfactant (Agent 2385-A) solution with various type of polymer
Figure 4.2 IFT reading for different concentration of surfactant Agent 2385-81 A
Figure 4.3 IFT reading for different concentration of surfactant SS-6066
Figure 4.4 IFT reading for different concentration of surfactant Sample 6-79

LIST OF TABLES

Table 2.1 Phase Behavior Type
Table 3.1 Composition of Formation Water in Angsi I-86
Table 3.2 Chemicals mixtures for Formation water/ simulated water prepared
Table 3.3 The list of polymer used for the evaluation
Table 3.4 Matrix table for Phase Behavior Test
Table 4.1 Polymer types and the IFT reading obtain after IFT test
Table 4.2 IFT test results matrix for Agent 2385-81 A
Table 4.3 IFT test results matrix for SS-6066
Table 4.4 IFT test results matrix for Sample 6-79
Table 4.5 Phase Behavior test results for Sample 6-79 with Angsi Crude Oil

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND STUDY

1.1.1 About Enhanced Oil Recovery (EOR)

Because the world oil resources are limited, the exploitation of oil fields to a higher degree is desirable. New methods are required to improve the recovery rates of oil fields and to recover oil found in pores between rock particles. The method to improve the recovery of the oil from the field is classified as the Enhanced Oil Recovery (EOR) methods.

The objective of EOR is to economically increase displacement efficiency. EOR involves mobility control of various kinds that can change oil and water viscosities, change interfacial tensions, and change oil and water saturations. There are four principal groups of EOR technologies available which are thermal EOR, miscible EOR, chemical EOR and microbial EOR.

One of the methods under chemical EOR is the injection of surfactants. This method is use to reduce interfacial tension between the oil and water phases, thus allowing the recovery of oil trapped in smaller pores (surfactant flooding). For a number of reservoirs, chemical EOR methods may be the only viable methods for significantly reducing oil saturation in the field.

1.1.2 Surfactant

Surfactant is the main component in chemical flooding, one of the technique in chemical EOR.A surfactant is a wetting agent that breaks the surface tension between substances. The purpose of the surfactants is to lower interfacial tension and to displace oil that cannot be displaced by water alone.

The other component in chemical flooding is polymer. The purpose of the polymer is to provide mobility control for a more piston-like displacement.

1.2 PROBLEM STATEMENT

Malaysia has the 27th largest Crude Oil Reserves in the world with 3.4 billion barrels, according to Petrochemical & Polymer Industries Division, MIDA, as on January 2003. Like other oil producer country in the world, there is a need to exploits it oil field to higher degree. Thus, the introduction of EOR method in the near future is inevitable.

As the EOR technology is yet to be introduce in Malaysia, an initial study have to be started to determine its suitability. Thus, chemical EOR or chemical flooding, as a possible candidate of EOR method to be run in Malaysia, has to be studied its compatibility with the Malaysia oil field conditions.

1.3 OBJECTIVES AND SCOPE

The objectives of the project is to determine the compatibility of chemical flooding in Malaysia oil field by:

1. Determine the interaction of selected surfactant with water mixture and crude oil from Malaysia oil field through interfacial tension (IFT) analysis.

2. Determine the best polymer to be used along with the surfactant for Chemical EOR in Malaysia oil field.
3. Determine the phase behavior of the selected surfactant suitable for chemical EOR in Malaysia.

1.3.1 The Feasibility of the Project within the Scope and Time Frame

The project is to simulate the actual oil field in Malaysia to the experimental work in lab. Thus, the water sample and crude oil which come from a location of oil reservoir in Malaysia, Angsi I68, is assumed to represent the general condition of the oil field in Malaysia. Instead of that, the study of the chemical EOR aspects only covers the fluid-fluid interaction as stated in the objectives above. This means that the study on interaction of surfactant with solid as the reservoir rock is not covered. To make the project feasible with the time frame and the access to the lab equipment, the project was done at Petronas Research & Scientific Services (PRSS) lab and inline with their study of chemical EOR for PETRONAS.

1.3.2 The Relevancy of The Project

The project is working on the possibility of the introduction of Chemical EOR in Malaysia. As the surfactant analysis in Malaysia is still new, this project could contribute some useful information, which might brought the interest to investors and oil producer to look on the application of chemical EOR and EOR in general in Malaysia.

CHAPTER 2

LITERATURE REVIEW AND THEORY

2.1 DEFINITION OF SURFACTANT

Some compounds, like short-chain fatty acids, are amphiphilic or ampiphatic, i.e., they have one part that has affinity for nonpolar media and one part that has an affinity for polar media. These molecules form oriented monolayers at interfaces and show surface activity (i.e., they lower the surface or interfacial tensions of the medium in which they are dissolved). In some usage surfactant are defined as molecules capable of associating to form micelles. These compounds are termed surfactants, amphiphiles, surface-active agents, tensides, or in the very old literature, paraffin-chain salts.

The unusual properties aqueous surfactant solutions can be ascribed to the presence of a hydrophilic head group and a hydrophobic chain (or tail) in the molecules. The polar or ionic head group usually interacts strongly with an aqueous environment, in which case it is the nature of the polar head group which is used to divide surfactants into different categories.

2.1.1 Type of surfactants

Generally, there are 4 types of surfactants based on its molecules active site:
The types are:

1. Anionic
2. Nonionic
3. Cationic
4. Zwitterionic

2.1.2 Anionic surfactant

In anionic surfactant, the surface-active portion of the molecule bears a negative charge. This includes alkylbenzene sulfonates (detergents), (fatty acid) soaps, lauryl sulfate (foaming agent), di-alkyl sulfosuccinate (wetting agent), lignosulfonates (dispersants) etc.

Anionic surfactants are account for about 50 % of the world surfactant production

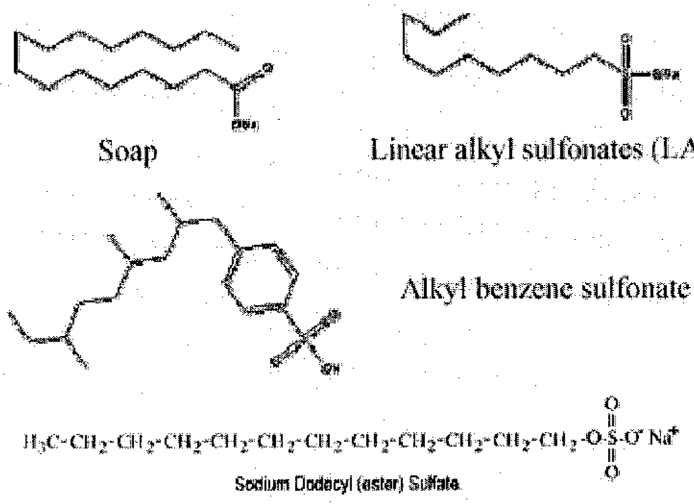


Figure 2.1: Sample of anionic surfactants

2.1.3 Nonionic Surfactants

The characteristic of the nonionic surfactant is the surface-active portion bears no apparent ionic charge. Its hydrophilic group is of a non-dissociable type, such as alcohol, phenol, ether, ester, or amide. This type of surfactant accounted for about 45% of the overall industrial production

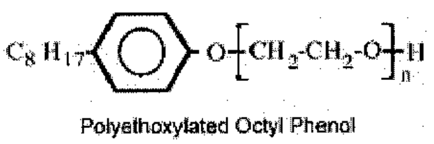


Figure 2.2: Example of nonionic surfactant

2.1.4 Cationic Surfactants

The surface-active portion of cationic surfactant bears a positive charge. This type of surfactant includes long-chain amines and quaternary ammonium salts. Generally, cationic surfactants more expensive than anionicsurfactants.

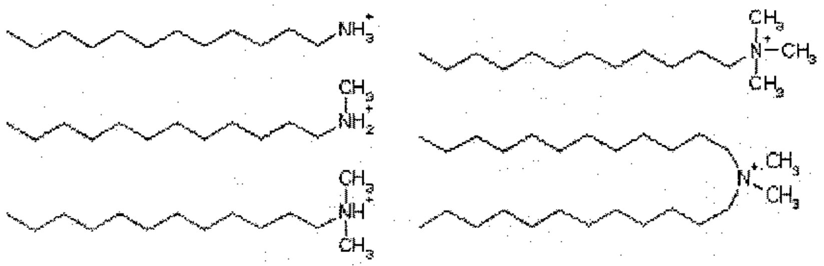


Figure 2.3: Example of cationic surfactant

2.1.5 Zwitterionic Surfactants

For this type of surfactant, both positive and negative charges may be present in the surface-active portion

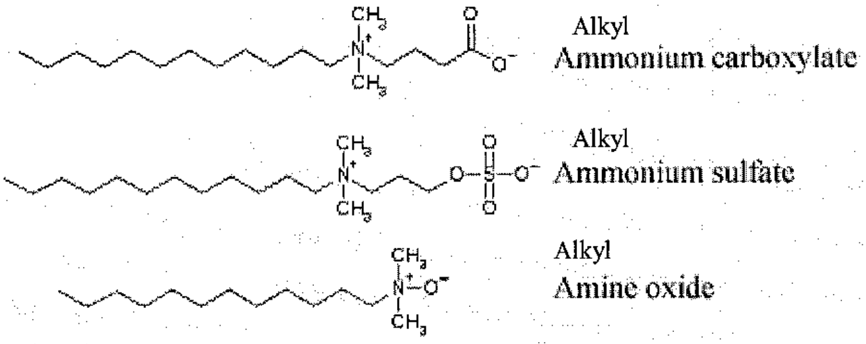


Figure 2.4: Example of Zwitteronic surfactants

2.2 THE HYDROPHOBIC EFECT AND MICELLE FORMATION

In aqueous solution dilute concentrations of surfactant act as much as normal electrolytes, but at higher concentrations very different behavior results. This behavior is explained in terms of the formation of organized aggregates of large numbers of molecules called micelles, in which the lipophilic parts of the surfactant associate in the interior of the aggregate leaving hydrophilic parts to face the aqueous medium. The formation of micelles in aqueous solution is generally viewed as a compromise between the tendency for alkyl chains to avoid energetically unfavourable contacts with water, and the desire for the polar parts to maintain contact with the aqueous environment.

2.3 MICELLAR-POLYMER FLOODING / CHEMICAL FLOODING

In practice surfactant injection alone can not achieve sufficient recovery due to several problems, fingering, adsorption, surfactant-soil interactions, etc. Therefore, a more complex process involving different steps is required to fully realize this technique potential. The process is term micellar-polymer flooding (MP).

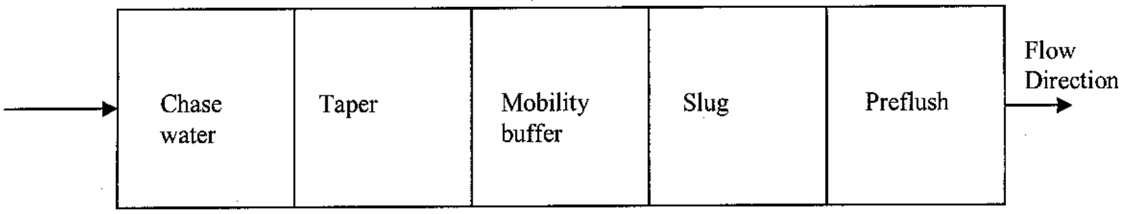


Figure 2.5: Cross section of a typical micellar-polymer flooding

Figure 2.1, shows an idealized version of an MP flooding sequences. The process is applied in the drive mode. The process consist of:

Preflush. A volume of brine to lower the salinity is added first. Preflushes range from 0 to 100% pore volume (PV). Sometimes an agent is added to lessen the surfactant retention.

MP slug. The main surfactant, cosurfactants, and other chemicals are added later. Slug volumes range from 5 to 20% PV.

Mobility buffer. This fluid is a dilute solution of a water-soluble polymer whose purpose is to drive the MP slug and banked-up fluids towards the production wells. The buffer volumes range from 0 to 100% PV.

Mobility buffer taper. This is a volume of brine that contains dilute polymer added to produce a gradual change in polymer concentration from the mobility buffer concentration to zero.

Chase water. This fluid is injected to reduce the cost of continuous injection of polymer.

2.4 SURFACTANT IN CHEMICAL FLOODING

A surfactant is a wetting agent that breaks the surface tension between substances. The purpose of the surfactants is to lower interfacial tension and to displace oil that cannot be displaced by water alone.

2.4.1 Interfacial Tension (IFT)

Capillary forces cause large quantities of oil to be left behind after waterflooding of an oil reservoir. Capillary forces arise from the interfacial tension (IFT) between the oil and water phases that resist externally applied viscous forces and causes the injected water to bypass the resident oil. The predominant mechanism to recover this oil is lowering the IFT through the addition of suitable chemicals (surfactants). Lower interfacial forces recover additional oil by reducing these capillary forces. This trapping of the resident oil can be expressed as a competition between viscous forces, which mobilize the oil, and capillary forces, that trap the oil. According to John Farnell[1] (1987), to get increased oil recovery from lowering the IFT, the IFT needs to be reduced to values in the range of 0.01 to 0.0001 dyne/cm.

2.4.2 Spinning Drop Tensiometer

One of the techniques to determine the IFT of the immiscible fluids interaction is spinning drop. The equipment use is known as spinning drop tensiometer.

The spinning drop measurement principle is based on the fact that the gravitational acceleration has little effect on the shape of a droplet rotating at sufficient speed around its longitudinal axis. The elongation of the droplet due to centrifugal forces is balanced by the interfacial tension between the two phases. A droplet located long the axis of a rotating capillary filled with denser fluid will form a cylindrical shape. With the appropriate drop volume and rotational speed, the drop diameter depends solely on the interfacial tension. The droplet stabilizes in the axis of rotation, while the surrounding fluid is forced toward owing to its higher density.

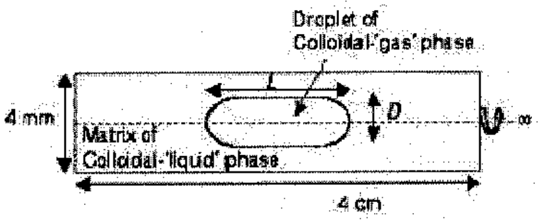


Figure 2.6: Spinning drop tube filled with the two phases. The system is rotating around its axis with a rotational speed w.

Consider a tube filled with the high-density phase and a droplet of the low-density phase. The tube rotates around a horizontal axis at a certain rotational speed w (see figure 2.6). From the measurement of the length L and diameter D of the droplet, the interfacial tension can be calculated using an equation derived by Princen[6] et al.:

$$\gamma = \frac{\omega^2 a^3 \Delta\rho}{2\alpha}$$

Here, a is the curvature of the top of the drop and a is a dimensionless number, both of which are determined by L and D .

2.4.2 Phase Behavior

Phase behavior is one observation that can determine the performance of a surfactant. Observation is done to view the interaction of the surfactant solution with the oil. In general the type of phase behavior was named after the research done by Winsor. Phase behavior related to the hydrophilic and hydrophobic effect of the surfactant with the solution.

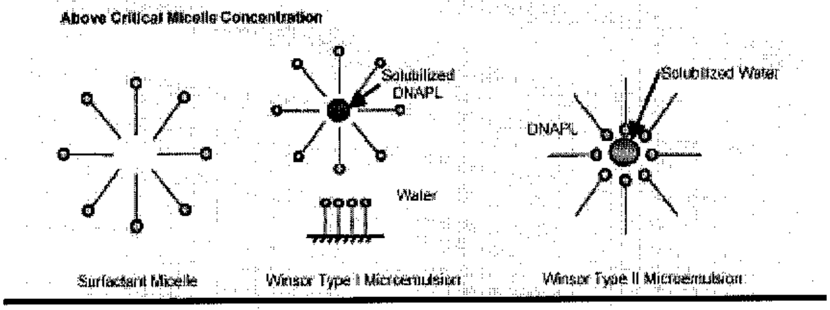
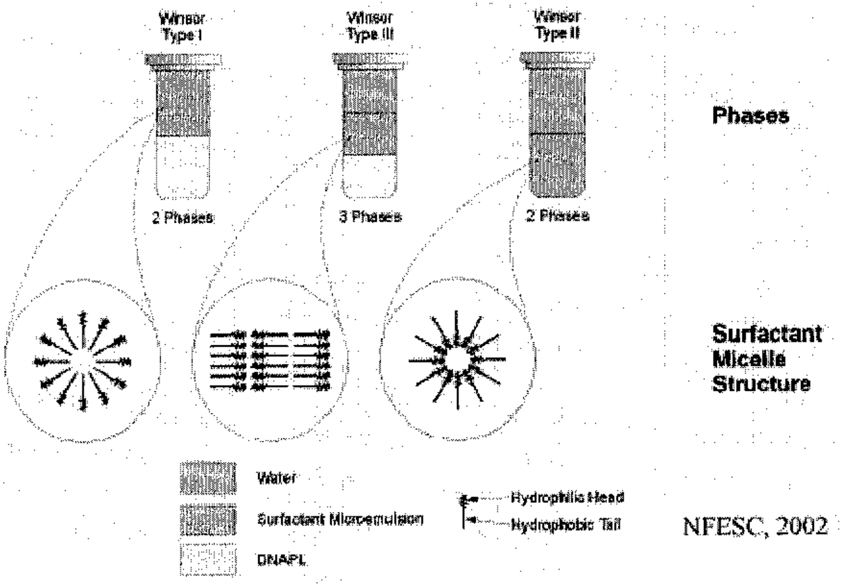


Figure 2.7: *Micelle formation in Phase Behavior Winsor Type I and Type II*

The phase behavior known as Winsor Type I, Type II and Type III are described according the region of where a number of phase exist at certain fraction and the surfactant micelle structure behavior at the respective regions. This micelle behavior is shown as in Figure 2.7 and Figure 2.8.



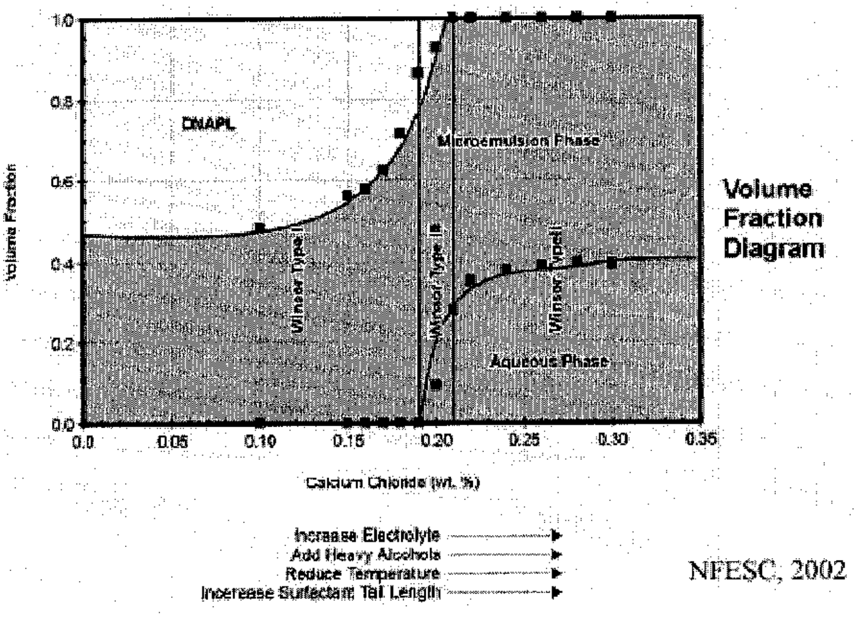
NFESC, 2002

Figure 2.8*: Surfactant Micelle structure in respective type of Phase Behavior*

Winsor Type I micelles have a hydrophilic exterior (the hydrophilic heads are oriented to the exterior of the aggregate) and a hydrophobic interior (the hydrophobic tails are oriented towards the interior of the aggregate). Winsor Type II surfactants are oil soluble (have a low hydrophile-lipophile balance -- (HLB), will partition into the oil phase, and may form reverse micelles). Reverse micelles have hydrophilic interiors and lipophilic exteriors; the resulting phenomenon is analogous to dispersed water drops in the oil phase

Surfactant systems intermediate between micelles Winsor Type I systems and Winsor Type II systems can result in a third phase with properties (e.g., density) between oil and water. This third phase is referred to as a middle phase microemulsion (Winsor Type III system). The middle phase system is known to coincide with ultra-low interfacial tensions; thus, middle phase systems will result in bulk extraction of organics from residual saturation.

The interaction of the hydrophobic and the hydrophilic side of the surfactant with the aqueous solution or oil is different based on the composition. This can be shown in Figure 2.9, which show the phase behavior of water, surfactant and dense non aquoues phase liquid (DNAPL) including oil, and the respective surfactant micelle structure.



NFESC, 2002

***Figure 2.9**: Respective region for phase behavior type I, II and III*

For the project study, as the sample consist of mixture o oil, surfactant and water, the phase which probably will occur are either type III or type II variations. The characteristics for these phases are summarize in Table 2.1.

Type III is considered to have the best probability of recovering additional oil. Type II is considered to have the poorest chance to recover additional oil. Type II- is considered to have the second best chance to recover additional oil because it shows interaction between the aqueous phase and crude oil and saponified acids are observed. Even though Type II+ demonstrates interaction between the crude oil and the aqueous phase, it is considered to have poorer oil recovery potential than Type II-.

***Table 2.1**: Phase Behavior Type*

Phase Type	Phase Type Description
II	Two fluid envelopes exist - a bottom aqueous phase and a top oil phase. No color is visible in the aqueous phase. The crude oil and aqueous phase volumes are equal to the volumes placed in the tube. Either the alkali has generated no visible surfactant or the surfactant have been driven into the crude oil and no crude oil swelling has taken place (Type II+ phase 3behavior).
II-	Two fluid envelopes exist - a bottom aqueous phase and an oil phase. The bottom aqueous phase is colored indicating the alkali has saponified acids in the crude oil which are now present in the aqueous phase. The crude volume can be swollen due to the interaction with the surfactant (added and in-situ), but this is not a requirement for this designation.
III	Three or more fluid envelopes exist - a bottom aqueous phase, one or

	more middle emulsion phases, and a top crude oil phase. The aqueous phase can be colored with saponified acids from the crude oil; however, this does not necessarily have to be the case.
II+	Two fluid envelopes exist - a bottom aqueous phase and a top crude oil phase. The bottom aqueous phase is clear because the surfactant (added and in-situ) reside in the crude oil phase. The crude oil phase is swollen due to surfactant carrying water into the crude oil phase.

2.5 POLYMER IN CHEMICAL FLOODING

The purpose of the polymer is to provide mobility control for a more piston-like displacement. There are two classes of polymers used in oil recovery, which are Polyacrylamides and Polysaccharrides

Polyacrylamides are generally used in concentrations of 50-1000 parts per million. The use of polyacrylamides decreases the mobility of the injected fluid by decreasing the permeability of the reservoir rock. A polysaccharride reduces the mobility of the injected fluid by increasing the viscosity of the fluid with very low levels of permeability reduction occurring in the reservoir rock.

CHAPTER 3

PROJECT OVERVIEW/METHODOLOGY/PROJECT WORK

3.1 PROJECT OVERVIEW

In general, the chemical flooding analysis consists of water analysis, crude oil analysis, and polymer analysis and surfactant analysis. However, crude oil analysis was not done directly during the project and only the relevant data was taken for the other analysis. For water analysis, only water blend preparation was involved directly during the project.

The project started with the water blends preparation. The next stage is the selection of polymer. 14 polyacrylamides polymer types will be tested. The polymer selected is the polymer which produce the best result in the interfacial tension (IFT) test. The selected polymer will be used for further test in selection of surfactant.

Then the next step is the surfactant selection. The first test for selection is using IFT test. IFT test mainly use two main equipment which are spinning drop tensiometer to determine the radius of the oil interact within the surfactant-water solution, and the densiometer, to determine the density of the surfactant solution and crude oil. The surfactant that obtained the best IFT results will proceed for phase behavior test.

3.2 METHODOLOGY

The main method use in the project is determination of interfacial tension (IFT). This method requires the usage of spinning drop tensiometer and densiometer, and applied for polymer analysis and surfactant analysis. However, the methodology for the project started with water blends preparation, then followed by polymer analysis and surfactant evaluation.

3.2.1 Preparation of water blends

To represent the condition of an oil field in Malaysia, the sample need to be taken or produced identical to actual field. For the experiment, the oil field selected is Angsi I-68. This field was selected by PRSS to done their CEOR evaluation, thus the crude oil and water sample from the field are available in the lab.

There are two type of water needed to be prepared. The first type is the injection water. Injection water is the water, which will be injected into the reservoir. For the experiment, the injection water is the seawater taken from the Angsi I-68 area. The second type of water is known as formation water or produced water or simulated water. This water is probably the water composition in the reservoir or the underground water. The water will go out with the oil and interact with the injected water in the reservoir. For the experiment, the formation water needs to be prepared in the lab. The preparation is based on the actual composition of the formation water in the Angsi oil field. The composition of formation / simulated water is shown in Table 3.1 and Table 3.2

***Table 3.1:** Composition of Formation Water in Angsi I-86*

	Ion, mg/L
Calcium	13
Magnesium	2.9
Strontium	1.4
Barium	2.4
Sodium	2360
Potassium	110
Chloride	1080
Sulfate	36
Carbonate	110
Bicarbonate	4070
Total Dissolved Solids	**7780**
pH @ 20 C	8.57

Therefore, it volume is still enough to undergo surfactant testing event after a portion have been used for polymer evaluation.

***Table 3.3:** The list of polymer used for the evaluation*

MANUFACTURER	TYPE	PRODUCT NAME
Ciba	Polyacrylamide	Magnafloc 358 Alcoflood 1285 REL Alcoflood 1275A Alcoflood 1235
SNF Floerger	Polyacrylamide	Flopaam 3330S Flopaam 3430S Flopaam 3530S Flopaam 3630S AN 125
Cytec	Polyacrylamide	Superfloc BD274 Superfloc BD317 Superfloc BD318 Superfloc BD319 Cynatrol 720H

3.2.3 Surfactant Evaluation

After the polymer has been selected, the next test is the surfactant evaluation. There is two part of the surfactant evaluation. The first part is the IFT test and the second part is the phase behavior test.

For the first part, IFT test, three types of surfactant is being tested. The surfactants are the anionic type and named as Agent 2385-A (manufactured by Stepan), SS-6066 and Sample 6-79 (both manufactured by Oil Chem Technologies). There is 5 mixtures of water and the surfactant will be tested at 4 different concentration which are 0.05 wt%, 0.10 wt%, 0.15 wt% and 0.20 wt%. Overall, for a type of surfactant, it should have 20 samples. For each surfactant-water solution, there will be added 500 ppm of polymer chosen from polymer evaluation. The IFT test will be done with Angsi I-68 crude oil. The surfactant that will be chosen is the surfactant, which has the lowest IFT range for all matrices of water ratio and surfactant concentration.

The next part is the phase behavior test. The selected surfactant from IFT test will undergo the test to observe the fluid-fluid interaction with the crude oil.

3.3 TEST PROCEDURES

The test procedures consist of the general procedure for determination of IFT using spinning drop tensiometer and the phase behavior test.

3.3.1 Determination of the Interfacial Tension using Spinning Drop Tensiometer

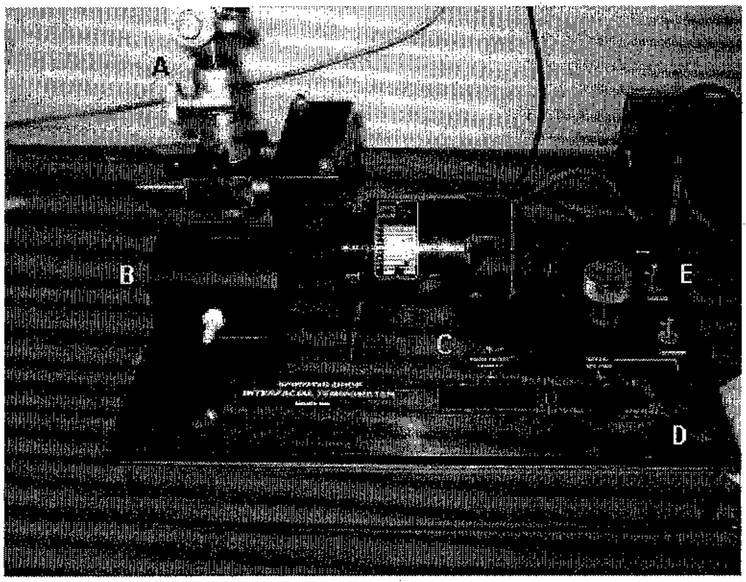


***Figure 3.1**: Spinning drop interfacial tensiometer Model 500*

3.3.1.1 Equipment:

The equipment use is spinning drop tensiometer as shown in figure 3.1

3.3.1.2 Description of the equipment:

Based on Figure 3.1, the main component o the spinning drop tensiometer are:

A: the microscope to determine the final diameter of the oil

B: the inserted slot for capillary tube
C: temperature controller
D: speed-adjusting knob
E: power switch

3.3.1.3 General procedure to use the equipment:

1. The sample solution to be tested (for this experiment, the solution mixed with surfactant) is being put into a capillary glass tube. Fill up glass tubes with surfactant solutions using a pipette.
2. Then a small drop of crude oil is injected into the solution inside the capillary tube. Ensure that there is no trapped air bubble in the oil droplet. The oil drop should be in sphere form, did not disperse, did not stick to the tube wall and can move freely in the
3. The capillary glass tube is inserted into tube slot of the spinning drop equipment (B).
4. The temperature has to be set initially (to avoid overshoot). Then the equipment can be started and adjust to maintain the desired speed and the desired temperature.
5. The movement of the oil drop is observer using the microscope (A), and adjust the microscope location and focus if necessary
6. After the oil size has stabilized i.e. did not expanded anymore; or about five minutes, the diameter of the oil is taken as the figure below.

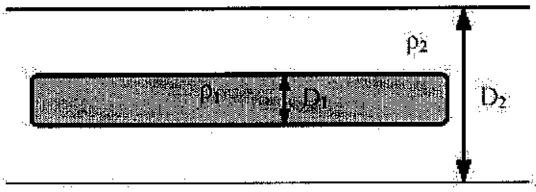


Figure 3.2: *The expanded oil droplet viewed from the microscope (B)*

7. The IFT of the surfactant-solution-oil interaction can be calculated using the general formula

$$\gamma = ((\rho_2 - \rho_1) * \Omega^2 * D_1^3)/32 \qquad \text{Equation (1)}$$

Where:

γ = Interfacial Tension [N/m]

ρ_2 = Density of the Heavier Fluid [kg/m3]

ρ_1 = Density of the Lighter Fluid (fluid of the drop) [kg/m3]

Ω = Angular Velocity [rad/s]

D_1 = Diameter of Drop [m]

However, for the spinning drop tensiometer used, Model 500, the modified equation is :

$$\gamma = 0.520 * (1/R)^2 * D^3 * (\rho_2 - \rho_1) \qquad \text{Equation (2)}$$

where

γ = Interfacial Tension [dyne/cm]

ρ_2 = Density of the Heavier Fluid [g/cm^3]

ρ_1 = Density of the Lighter Fluid (fluid of the drop) [g/cm^3]

R = Speed rotation reading [m.s]

D_1 = Diameter of Drop [cm]

3.3.2 Phase Behavior Test

1. Prepare matrix of surfactant solutions in test tubes by mixing surfactant with synthetic formation water. The surfactant solution in ascending concentration were prepared i.e 0.05%, 0.1%, 0.15% and 0.2%.
2. Prepare a matrix of surfactant to sea water (injection water) solutions ratio of 100% surfactant solutions, 75%-25%, 50%-50%, and 25%-75% and 100% sea water. The matrix table is as per attached below, table 3.4
3. Add crude oil to the surfactant-sea water solutions to create 10 ml of mixture.
4. Plug top of test tubes and shake vigorously to mix crude oil and surfactant solutions.

5. Place all test tubes in rack and allow the mixture to stabilize. The mixtures is left in the oven at temperature of 50 °C for one week.
6. After one week, the mixture should be in two or three phases i.e top oil phase, bottom aqueous phase, and middle emulsion phase (if any). Observe characteristics of each phases and the colour of aqueous phase.
7. The aqueous phase color could be dark brown, yellow, milky or clear.
8. Measure the specific gravity of the surfactant-sea water solutions using densitometer.

***Table 3.4:** Matrix table for Phase Behavior Test*

Injection Water %	Produced Water %	Phase Behavior at surfactant concentration of:			
		0.05%	0.10%	0.15%	0.20%
0	100				
25	75				
50	50				
75	25				
100	0				

CHAPTER 4

RESULTS AND DISCUSSION

4.1 POLYMER SELECTION/SCREENING FOR EOR

The polymer selection for Chemical EOR has to undergo two tests. The first one is to observe the solubility of the polymer in the prepared surfactant-water mixture, and the second test is to determine the IFT reduction by each tested polymer.

4.1.1 Observe on the Clarity of the Solution

Each polymer is mixed with the surfactant and water mixture solution before the IFT test. The clarity of the solution is observed to ensure that the polymer is soluble in the water – surfactant solution. If the polymer is found out insoluble in the mixture, the polymer is considered not suitable for Chemical EOR. However, from the observation, all 14 polymers tested were found out soluble in the water mixtures and thus could be proceed to the next stage, which is the IFT test.

4.1.2 IFT Test For the Polymer

Experiment has been done on the 14 types of polymer (polyacrylamide type) to select the best polymer to be use in further IFT test for surfactant selection. The test on the polymer was done based on the IFT produced from the surfactant solution mixture with the polymer. The best polymer is the polymer that produced the lowest IFT on the oil-surfactant solution. The condition of the test are at 50 ^{o}C at atmospheric pressure, using a same concentration of surfactant (0.10 wt% of Agent 2385-A) in the same ratio of water mixture (50%-50% injection water to formation water), and the concentration of the polymer in the solution is 500 ppm. The crude oil used is Angsi I68 Crude Oil.

The results are shown in Figure 4.1 and table 4.1

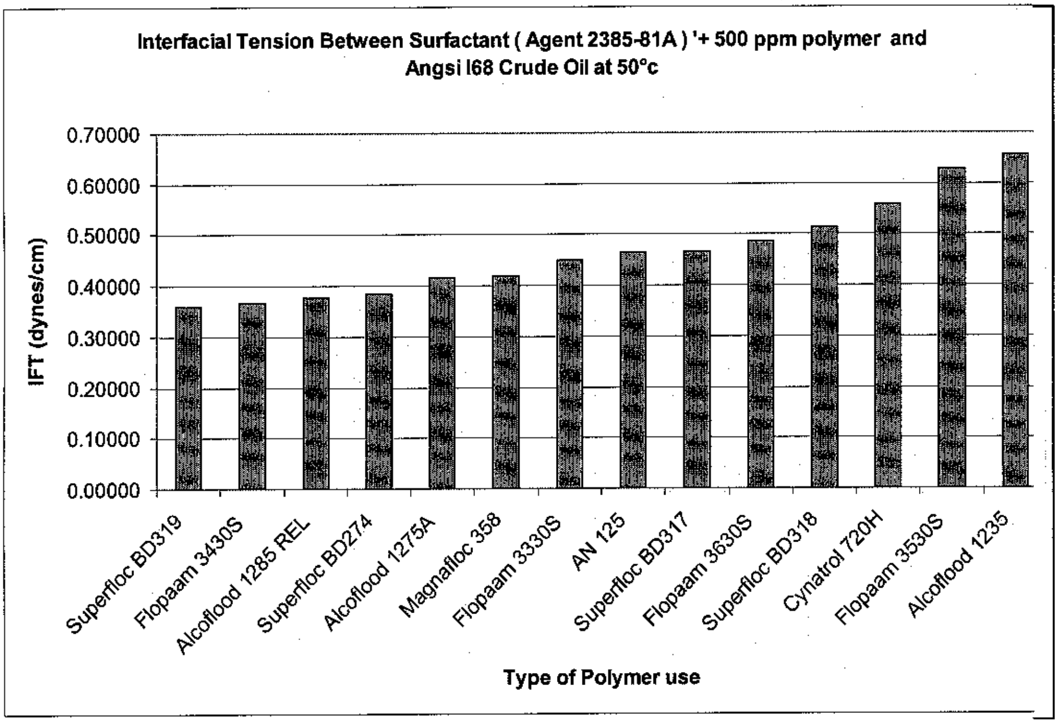


***Figure 4.1**: IFT of oil - surfactant (Agent 2385-A) solution with various type of polymer*

Figure 4.1 shows the result of the polymer screening for use in the Chemical EOR. At the same concentration of surfactant used, water mixtures, and crude oil, different types of polymer (polyacrylamide) have shown a different value on the IFT of the solution surfactant – oil.

As from the analysis, the lowest IFT was achieved using Superfloc BD319, manufactured by Cytec, and followed by Flopaam 3430S, manufactured by SNF Floerger. The range of IFT reading for all polymers is from 0.35914 dynes/cm to 0.65548 dynes/cm.

Table 4.1: *Polymer types and the IFT reading obtain after IFT test in prepared solution (surfactant 0.10 wt % Agent 2385-A, ratio 50% injection water-50% formation water) with Crude Oil Angsi I68.*

Ranking	**Name**	**IFT (dynes/cm)**	***Manufacturer***
1	Superfloc BD319	0.35914	Cytec
2	Flopaam 3430S	0.36608	SNF Floerger
3	Alcoflood 1285 REL	0.37689	Ciba
4	Superfloc BD274	0.38520	Cytec
5	Alcoflood 1275A	0.41552	Ciba
6	Magnafloc 358	0.41753	Ciba
7	Flopaam 3330S	0.45057	SNF Floerger
8	AN 125	0.46531	SNF Floerger
9	Superfloc BD317	0.46554	Cytec
10	Flopaam 3630S	0.48685	SNF Floerger
11	Superfloc BD318	0.51384	Cytec
12	Cynatrol 720H	0.55776	Cytec
13	Flopaam 3530S	0.62657	SNF Floerger
14	Alcoflood 1235	0.65548	Ciba

From the results, it was found out that even the main function of the polymer in the Chemical EOR is as a mobility buffer component, it also can contribute to slight change in IFT between the solution-oil. Thus, the polymer with can produced lower IFT compared to the others polymer is the best possible polymer to be used in the Chemical EOR. Instead help to reduce the interaction force (IFT) between the solution with oil, it will also reduced some cost for the project as the lower surfactant concentration needed to obtained optimum condition for Chemical EOR.

The selected polymer, Superfloc BD319 is then proceed to be the component for the IFT tests for surfactant selection. 500 ppm of Superfloc BD319 will be included in each surfactant solution prepared for the IFT test. This is as per-instruct in the IFT test procedure section.

4.2 SURFACTANT SELECTION FOR EOR

The surfactant selection for Chemical EOR has to undergo two tests. The first one is to determine the best surfactant, which have the lowest IFT range for all the different ratio of water mixtures. Then, the selected surfactant proceeds to the second test, which is the phase behavior test.

4.2.1 Determination of IFT reading for Different Surfactants

Three different surfactants have been tested for the IFT determination test. The surfactants are Agent 2385-81 A manufactured by Stepan, SS 6066 and Sample 6-79, both manufactured by Oil Chem Technologies. All the surfactants used are from anionic type.

4.2.1.1 Agent 2385-81 A

Table 4.2: *IFT test results matrix for Agent 2385-81 A*

Solution	Injection Water (IW)%	Formation Water (FW)%	IFT @ Surfactant Concentration			
			0.05%	0.10%	0.15%	0.20%
A	100	0	2.08	1.48	1.61	1.62
B	75	25	0.44	0.28	0.32	0.37
C	50	50	0.37	0.29	0.36	0.35
D	25	75	0.31	0.29	0.28	0.29
E	0	100	0.34	4.12	0.35	0.30

The table shows the result for the IFT tests for Agent 2385-81 A. Generally, it was found out that the IFT is high when the surfactant solution is made of injection water only. Instead of that one point have been found to be located at extreme position which is the value for IFT at 0.10 % concentration of surfactant in 100% of formation water. The plotting of the IFT value in the graph is shown as in Figure 4.2

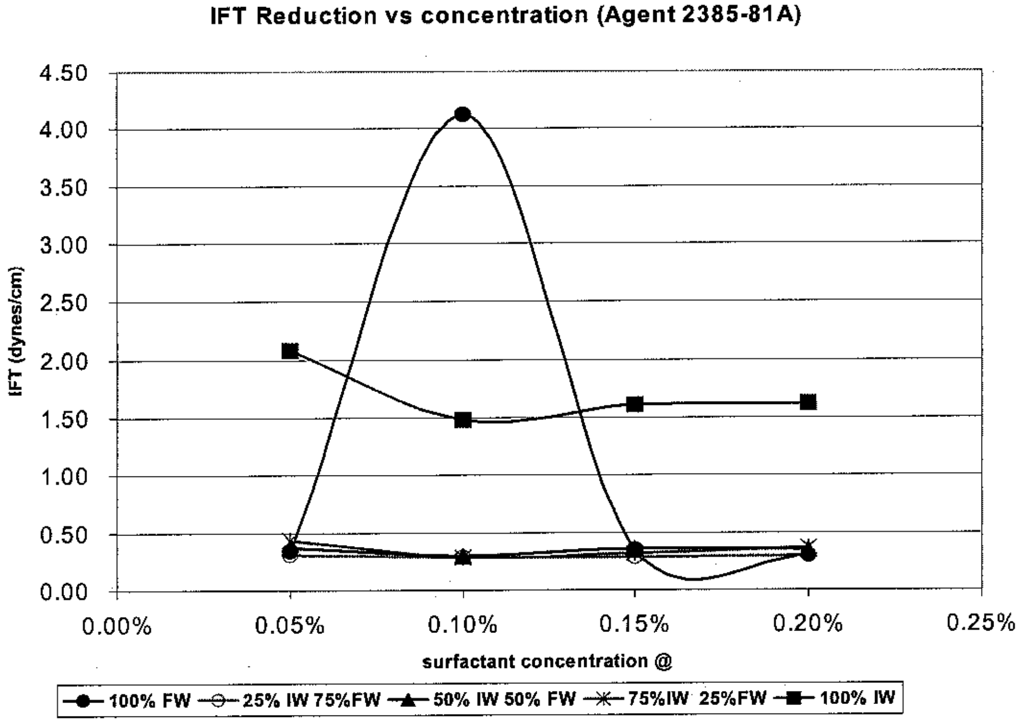


Figure 4.2: *IFT reading for different concentration of surfactant Agent 2385-81 A*

From the graph, it was found out that the IFT range for surfactant Agent 2385-81 A mostly between 0.28 dyne/cm to 0.50 dyne/cm. There is one extreme point that was out from the waiter mixture general trend, which is the IFT value at 0.10 5 of surfactant concentration in 100% formation water. While for water mixture of 100% injection water only, the IFT range from 1.50 dyne/cm to 2.08 dyne/cm, which is quite high and exhibit different behavior than the IFT of the same surfactant at different water composition.

Overall, the behavior shown by the surfactant indicates that the IFT is higher when the water is at 100% injection water only but then reduced when the solution contain the mixture of injection water with formation water. This means that the surfactant solution could not maintain at lower IFT when interact with the crude oil at different water composition.

4.2.1.2 SS-6066

Table 4.3: IFT test result matrix for SS-6066

Solution	Injection Water (IW) %	Formation Water (FW) %	IFT @ Surfactant Concentration			
			0.05%	0.10%	0.15%	0.20%
A	100	0	0.086	0.071	0.072	0.158
B	75	25	0.366	0.277	0.278	0.318
C	50	50	0.209	0.179	0.169	0.190
D	25	75	0.236	0.151	0.134	0.198
E	0	100	0.286	0.223	0.258	0.307

From the table, the lowest IFT value is 0.071 dyne/cm, which is obtained at 0.10 wt % of surfactant in 100% injection water. The is a total of 3 points where the IFT value is below 0.1 dyne/cm and all of them were obtained when the solution is in 100% injection water mixture. The highest IFT value is 0.366 dyne/cm at surfactant concentration of 0.05%, in the solution mixture of 75% injection water and 25 % formation water.

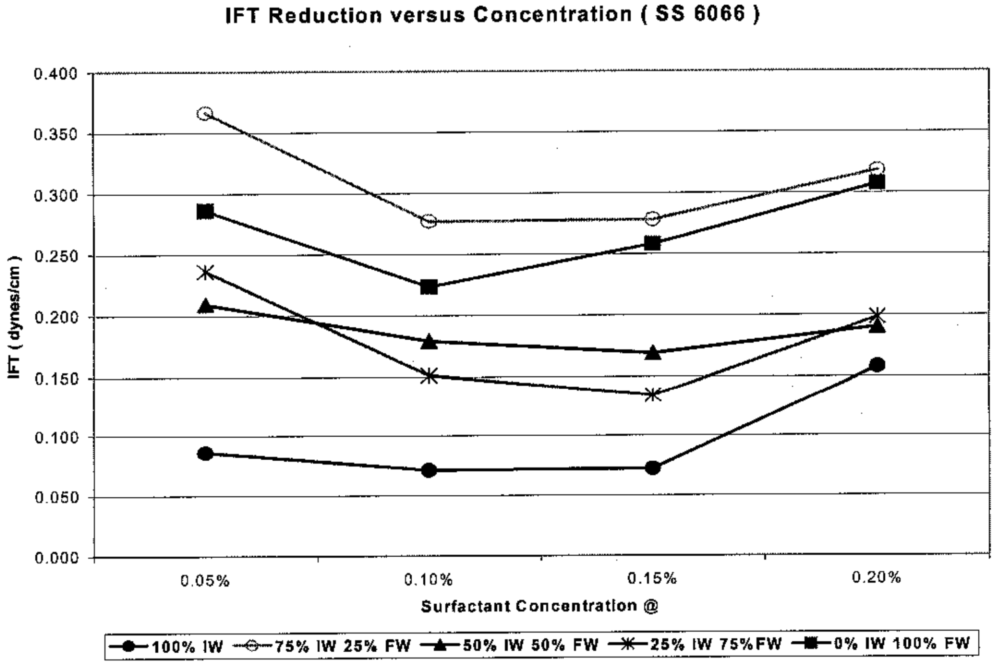


Figure 4.3: IFT reading for different concentration of surfactant SS-6066

In general, the graph shows that the range of the IFT for the surfactant for all condition tested range from 0.071 dyne/cm to 0.3666 dyne/cm. Compared to the performance of surfactant Agent 2385-81 A, surfactant SS-6066 has a lower and narrower range of IFT. The SS-6066 surfactant gives the lower value of IFT at it different concentration when the water solutions consist of 100% of injection water. While this surfactant concentration of 0.10 wt % have the narrow range of IFT at different water composition compared to its other set of surfactant concentration.

4.2.1.3 Sample 6-79

***Table 4.4**: IFT test results matrix for Sample 6-79*

Solution	Injection Water (IW) %	Formation Water (FW) %	IFT @ Surfactant Concentration			
			0.05%	0.10%	0.15%	0.20%
A	100	0	0.033	0.025	0.030	0.046
B	75	25	0.082	0.042	0.060	0.074
C	50	50	0.056	0.026	0.043	0.050
D	25	75	0.058	0.043	0.045	0.076
E	0	100	0.097	0.038	0.076	0.083

From the table 4.4, the lowest IFT value is 0.025 dyne/cm, which is obtained at 0.10 wt % of surfactant in 100% injection water. This is the lowest value obtained from all of the tests including the IFT test done on surfactant Agent 2385-81 A and surfactant SS-6066. All the IFT values achieved using this surfactant (Sample 6-79) are below 0.1 dyne/cm. The highest IFT value is 0.097 dyne/cm at surfactant concentration of 0.05%, in 100% formation water. The graph (Figure 4.4) has shown that, for all water mixtures, the lowest IFT achieved at surfactant concentration of 0.10 wt %. Compared to the other surfactants tested, the surfactant Sample 6-79 have the narrowest range of IFT for all surfactant concentration at different water ratio in the solution.

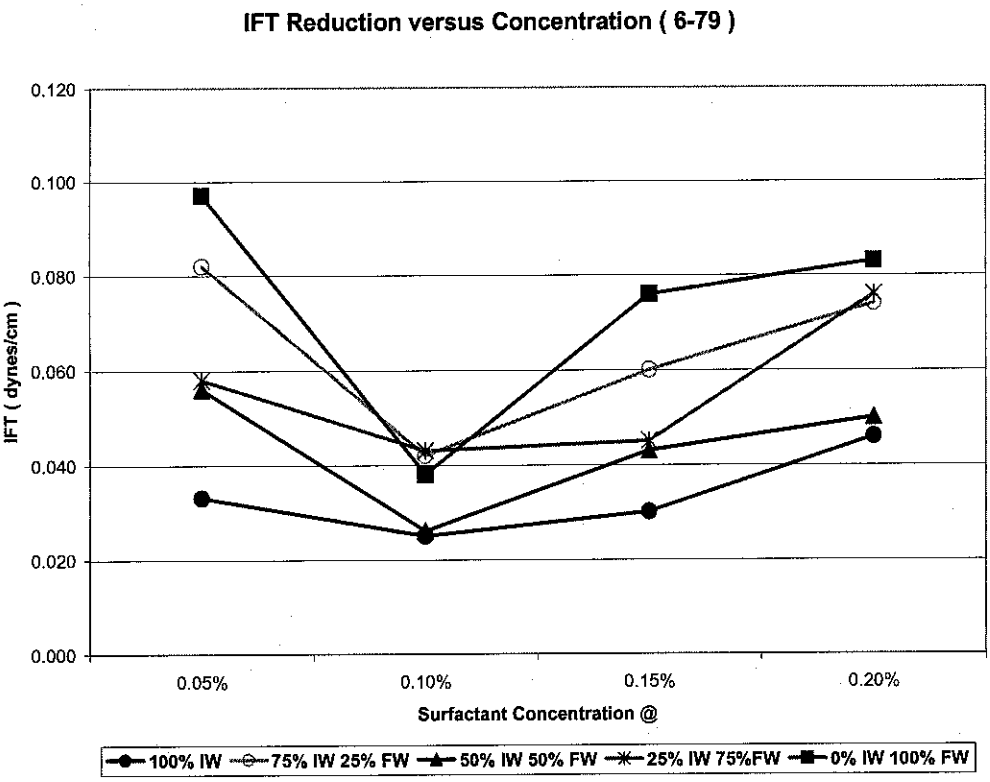


Figure 4.4: *IFT reading for different concentration of surfactant Sample 6-79*

From the IFT test done on the three surfactants, surfactant Sample 6-79 was chosen as the best surfactant. This is because among the surfactants tested, it has the narrowest range of IFT produced for all water condition and surfactant concentration. It overall IFT range is between 0.025 dyne/cm to 0.097 dyne/cm, or in general, below 0.1 dyne/cm, while surfactant SS-6066 exceed 1.0 dyne/cm on most condition and Agent 2385-81 exceed 1.0 dyne/cm when the solution is in 100% of Injection water. Surfactant 6-79 then proceeded for the phase behavior test.

4.2.2 Phase Behavior Test for the Selected Surfactant

From the IFT test, the best surfactant is found out to be the Sample 6-79. Thus, the surfactant was selected to further undergo another test, which is the phase behavior test. The result of the test is as shown in Table 4.5

***Table 4.5**: Phase Behavior test results for Sample 6-79 with Angsi Crude Oil*

Solution	Equilibrated Phase Volumes %			Phase Type	Phase Description Code	IFT (dyne/cm)
	Bottom	Middle	Top			
A1				II -	LY, C	0.033
A2				II -	LY, C	0.025
A3				II -	LY, C	0.030
A4				II -	LY, C	0.046
B1	49.0	1.0	50.0	III	Y, T	0.082
B2				II +	C, T	0.042
B3	48.0	2.0	50.0	III	LY, C	0.060
B4				II -	LY, C	0.074
C1				II +	M	0.056
C2				II +	C	0.026
C3				II +	M	0.043
C4				II +	M	0.050
D1				II -	Y, T	0.058
D2				II -	Y, T	0.043
D3				II -	Y, T	0.045
D4				II -	Y, T	0.076
E1				II -	B, T	0.097
E2				II -	B, T	0.038
E3				II -	B, M	0.076
E4				II -	B, M	0.083

Remarks: B = Brown, C = Clear, G = Grey, M = Milky Y = Yellow, L = Light,
D = Dark, T = Translucent O = Opaque, PPT = Precipitate

Phase behavior tells whether the surfactant have the possibilities to recover the oil by looking at the interaction shown between the surfactant solution and the oil. In type III, there is an existing of a middle emulsion phase between the aqueous solution and the oil, while in type II-, the even the middle emulsion phase did not clearly exist, the colored bottom aqueous phase indicated the present of crude oil.

From the results, it can been seen that the best phase best behavior, which is type III, can be achieved at B1 and B2. B1 is the condition of 0.01 wt % of surfactant in solution of 75 % Injection Water with 25 % Formation mixture. Meanwhile B2 is 0.15wt% of surfactant in the same water ration of 75 % Injection Water with 25 % Formation mixture. Type III indicates the best possibilities of surfactant to recover additional oil. In overall, the surfactant solution have shown the phase behavior mostly at type II- which can be considered the second best condition for recovery of additional oil. However, the solution mixture of 50 % injection water to 50 % formation water have shown type II+ which is poor condition for oil recovery.

In general, surfactant Sample 6-79 has the probability for enhanced oil recovery from its overall performance in IFT test and phase behavior test.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 CONCLUSION

From the study, the surfactant that has the best performance with Malaysia fluid condition is Sample 6-79. Surfactant sample 6-79 has the lowest range of IFT compared to the other surfactant tested. Surfactant sample 6-79 also shows the best result in phase behavior test. For overall, it achieved type II- and III, which indicates the possibility of additional oil recovery.

Apart from that , the polymer Superfloc BD319 have shown the best results compared to the other polymer tested and have the potential use with the surfactant to be applied in the chemical flooding in Malaysia.

5.2 RECOMMENDATION

As the EOR application is yet to be done in Malaysia and there still not much of analysis done on the suitability of chemical EOR with Malaysia oil field condition, there is a need to run further research on this area. This include the analysis on the surfactant interaction at elevated pressure and temperature, modeling of Malaysia chemical EOR in Malaysia reservoir, and interaction of surfactant solution with the reservoir rocks in Malaysia oil reservoir.

REFERENCES

1. Farnell, James. June 1987, *"Foam and Emulsion Effect o Gas Driven Oil Recovery"*, M.Sc Thesis, Stanford University, Stanford California

2. Chapter 15, Enhancing Oil Recovery, *"The Lease Pumper's Handbook"*

3. Schramm, Laurier L., *"Surfactants: Fundamentals and Applications in the Petroleum Industry"*, Cambridge University Press,2000, United kingdom

4. Gerard T. Caneba and Jay Axland, 2002, "Vinyl Acetate-Acrylic Acid Copolymer For Enhanced Oil Recovery", *Journal of Minerals & Materials Characterization & Engineering, Vol. 1*, No.2, pp97-109

5. Dr. Ir. Th. W. de Loos, Applied Thermodynamics and Phase Equilibria: Research, "Enhanced oil recovery" < http://www.dct.tudelft.nl/ttf/enhance.htm>

6. H. M. Princen, I. Y. Z. Zia, S. G. Mason, *J. Colloid Interface Sci.* **23** (1967) 99.

7. de Hoog, Elisabeth H.A., Measurement of the interfacial tension of a phase-separated colloid-polymer suspension", *Interfaces and crystallization in Colloid-Polymer suspensions,* 2001, <www.library.uu.nl/digiarchief/dip/diss/1953133/c2.pdf>

8. Surfactant-Enhanced Aquifer Remediation (SEAR) http://mail.sci.ccny.cuny.edu/~pzhang/EASB5500/SEAR.pdf

9. Norman Alban and Jorge Gabitto, "*Surfactant-Polymer Interaction in Enhanced Oil Recovery*" <http://www.netl.doe.gov/publications/proceedings/ 99/99hbcu/gabitto.pdf>