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FINAL REPORT

Comparison of the IFT of alkali/surfactant and branched alcohol/surfactant for Surfactant Flooding

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Petroleum Engineering

CERTIFICATE OF APPROVAL

Comparison of the IFT of alkali/surfactant and branched alcohol/surfactant for Surfactant Flooding

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(Petroleum Engineering)

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TRONOH, PERAK

MAY 2011

CERTIFICATE 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.

Mohamed Wahyudeen bin Zakaria

ABSTRACT

Surfactant flooding has been applied commercially for many years, especially in the 1970's and 1980's. The principle of lowering the interfacial tension to release residual oil trapped thus giving a higher oil production. The ultimate challenges in using surfactant as the preferable methods in chemical EOR are the effectiveness of the surfactant and the cost of using surfactant. Researchers have shown additives (e.g.; Alkaline and Branched Alcohol) incorporated with surfactant enhanced the effects of surfactant. These additives can also provide solution to the problems in the reservoir like the effective concentrations of surfactant needed, level of tolerance of surfactant in high salinity, high hardness and high temperature reservoirs and preventing the loss into the rock. This project was undertaken to compare the effects of alkali and branched alcohol on surfactant flooding.

Interfacial tension is one of the important criteria in determining the success of EOR. Interfacial tension values of the surfactant with additives were measured using Interfacial Tension Meter (OPMAN IFT 700). Comparisons were done to show which additives (alkalis; sodium carbonate and sodium hydroxide or branched alcohold; 2-methyl-1butanol, 2-methyl-2butanol) were better and at which concentrations (0.1, 0.25, 0.5, 1.0 wt %). At reservoir condition, pressure ranged between 1000-1800psi with the temperature of 40-45 °C was used. Moreover, physical appearance (precipitation) in hard and soft water was also been observed. Results showed that branched alcohol performed well with surfactant in high salinity water with no precipitation effect and had a very low interfacial tension down to 0.5mN/m. However, further branching in alcohol did not show much effect on IFT. Compared to alkali, some precipitation occurred due to reaction of sodium with hydroxide and carbonate ions.

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CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

Study about Chemical Enhanced Oil Recovery was started a long time ago since 1960. And one of the methods proposed at that time was using surfactant EOR. Surfactant EOR has been applied starting in the 1970's and 1980's (Wu, et. al, 2009). Rule of thumb for surfactant EOR was reducing the IFT of the oil and the aqueous phase to allow residual oil to flow into production well. Study about surfactant EOR was done because of the flexibility of the surfactant to optimize the formulation by varying surfactant and co-surfactant (French, 1991).

The additives that can be used have been well researched. The aims here were to compare about the interfacial tension and the recovery effect cause by the addition of additives. Two types of additives used were alkali and branched alcohol because their effectiveness in becoming co-surfactant had been proven in research papers. The interfacial tension was one of the important criteria in determining the successfulness of the EOR. So, the aim here was to develop systems that cost efficient and also very effective in recovering oil.

1.2 PROBLEM STATEMENT

Surfactant in oil and gas industries was widely used as one of the methods for Chemical Enhanced Oil Recovery. Thus, many researchers came out with many outstanding ideas to generate and modify various types of surfactants. The problems were to find surfactant that excellent in recovering oil and also cost effective. Usage of surfactant were strongly advised to be optimized because surfactant price was as high as $1.75/lb quoted by Pride Solvent & Chemical Co. 2010 (Mwangi, 2010). So, additives (alkali and branched alcohol) that can boost the performance of the surfactant were preferable. The reason for these two types of additives in surfactant to be compared was because these additives had shown both good results in usage. In order to know which additives were resulted in higher performance with regard to the High Pressure High Temperature (HPHT) reservoir and also the ability to perform under high salinity brine, IFT experiment was taken place.

1.3 OBJECTIVES

In comparing the effects of alkali and branched alcohols onto surfactant flooding, first thing to do was to fully identify the utmost objectives or criteria for the project to be succeeded. So, the main objectives were:

1. To compare the IFT values of surfactant flooding using Interfacial Tension Meter after the addition of the additives (alkali; sodium carbonate and sodium hydroxide or branched alcohol; 2-methyl-1butanol, 2-methyl-2butanol).
2. To compare the physical appearances of surfactant with the addition of additives (alkali; sodium carbonate and sodium hydroxide or branched alcohol; 2-methyl-1butanol, 2-methyl-2butanol).

1.4 SCOPES OF STUDY

For this project, some scope of study had been identified. They were divided into 2 main groups as they were actually the stages of the research. For the first stages, the concepts of EOR and the surfactant flooding were focused on. Then second division goes with the extensive experimental work that was plan during the planning period to validate the expected result.

Area of Study	Description
Extensive Research	• Research on The effect of Alkali onto Surfactant Flooding • Research on The effect of Branched Alcohol onto Surfactant Flooding.
Experimental Work	• Research on the plan experimental work of IFT using IFT Opman 700 including solution preparation, machine procedure and guidelines, compatibility between chemical and density measurement.

Table 1 Scope of Study

The research was focused on the effect of two types of additives which were alkali (sodium hydroxide, sodium carbonate) and branched alcohol (2-methyl-1butanol, 2-methyl-2butanol). The surfactant used was only anionic surfactant, sodium dodecyl sulfate (SDS). Together with surfactant and additives was light crude oil of Dulang. For the interfacial tension apparatus, Pendant Rise Method was used due to different density of oil and surfactant solution. The IFT 700 brings the opportunity to analyze in high pressure (10000psi) and high temperature (200 °C) condition. However, in this experiment, the pressure used up only to 1000-1800 psi with regards to Dulang Reservoir (Zahidah et. al 2001). The temperature used was 40 °C-45 °C because of the surfactant will be hydrolyzed if the temperature >60 °C (Flaaten, et. al 2008).

1.5 PROJECT RELEVANCY

This project was relevant to current situation of Oil and Gas industries that focused more on the EOR development. As tertiary recovery was more preferable to recover oil from mature oil field, more efficient and cost effective chemical were needed. Having research on different additives effects with surfactant gave more broad choices for sustainable recovery efforts. Successful result of using alkali and branched alcohol in reducing interfacial tension showed a great tendency of having more oil. Thus, gave the industry and EOR development more choices to generate profits as well as more inputs.

1.6 PROJECT FEASIBILITY

Based on the design project, the 10 month period (FYP 1 and FYP 2) on the researching materials were expected to be fully utilized within the scope of study and time frame. First few weeks will be concentrated on the study about the topic and equipment to be used. The sources will be the books, thesis, website, research paper and some journal. The next few weeks were focused on the detail of the design experiment. Samples of another projects were took from the literature review before proceed with the designated experiments in FYP 2. The project can be done as of all the materials and sources were there in UTP like the IFT Opman 700 and Anton Paar DMA. Chemicals availability period also corresponding well with the time frame and space. And also, the timing for each experiment and sample are designed so that it can fulfill the requirement.

CHAPTER 2

THEORY / LITERATURE REVIEW

2.1 CHEMICAL EOR

Chemical Enhanced Oil Recovery is the Tertiary Recovery in the stages of oil field development. Fluid was introduced to reduce viscosity and to improve flow. The fluid could consist of gases that are miscible with oil (typically carbon dioxide), steam, air or oxygen, polymer solutions, gels, surfactant-polymer formulations, alkaline surfactant polymer formulations, or microorganism formulations.

Three chemical flooding processes include polymer flooding, surfactant polymer flooding and alkaline surfactant polymer (ASP) flooding. Generally, these three flooding having the same purposes of enhancing oil production whether by more efficient displacement of moderately viscous oils or reducing oil water interfacial tension to almost zero (ultra low IFT) to displacing trapped residual oil. The processes have considerable potential to recover oil. [8-10]

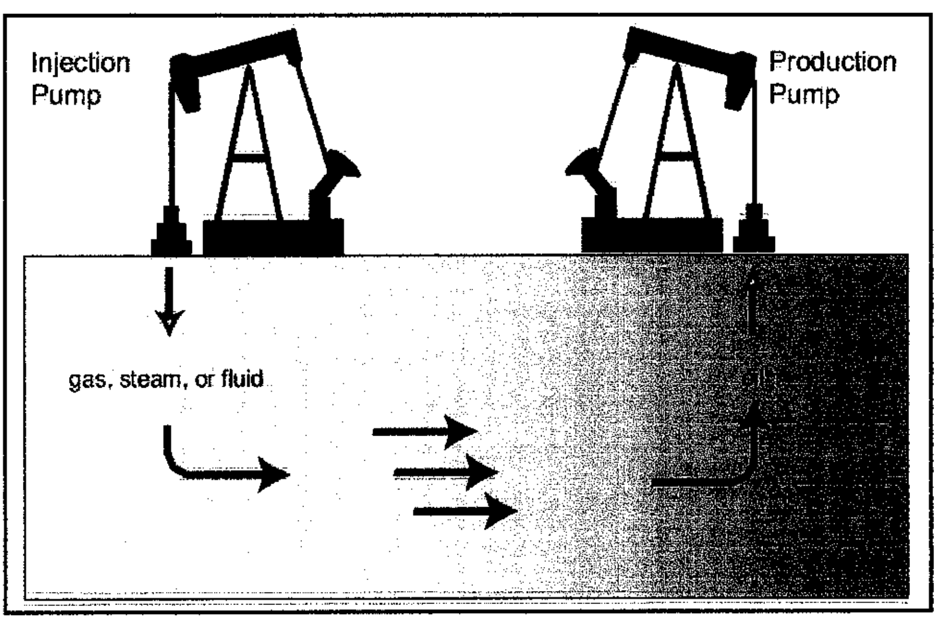


Figure 1 Chemical EOR flooding [7]

2.2 SURFACTANT FLOODING

2.2.1 Surfactant Flooding

Surfactant is abbreviations for surface active agents. Many surfactants will reduce the interfacial tension to low values; for successful surfactant flood is that the interfacial tension between the crude oil and the aqueous phase needs to be reduced to ultra low values, (target 0.0001 mN/m). Besides the requirement to achieve a low in situ IFT, another factor that determines the technical and economical success of surfactant flood is to minimize the injected surfactant (Wu, et al, 2005). Several small commercial projects had been completed and several more are in progress. The problems encountered with some of the old pilots are well understood and had been solved. For example, the new generation of surfactant will tolerate high salinity and high hardness so there is no practical limit for high salinity reservoirs. With regards to the price, current high performance surfactant should cost less than $2 lb of pure surfactant (Pope, 2007).

For surfactant selection criteria, there are some factors that need to be focused on. High solubilization ratio at optimum (ultra low IFT), the surfactant also must be commercially available at low cost, with feasible to tailor to specific crude oil, temperature and salinity, different for highly branched hydrophobe needed for low viscosity micelles and microemulsions. Next, the surfactant most probably have low adsorption/retention on reservoir rock with insensitive to surfactant concentration above CMC and low CMC. However, in this project, the parameter or the selection criteria will be fixed (limited type of crude, fixed temperature and pressure) as of the limitation of the equipment and apparatus and also the time constraint.

2.2.2 Type of Surfactants

Generally, surfactant is usually organic compounds that amphiphilic, meaning it contains both hydrophobic groups (their *tails*) and hydrophilic groups (their *heads*). Therefore, a surfactant molecule contains either a water insoluble (or oil soluble component) and a water soluble component. Surfactant molecule will migrate to the water surface, where the insoluble hydrophobic group may extend out of the bulk water phase, either into the air or, if water is mixed with oil, into the oil phase, while the water soluble head group remains in the water phase. This alignment and aggregation of surfactant molecule at the surface acts to alter the surface properties of water at the water/air or water/oil interface.

Surfactant reduces the surface tension of water by adsorbing at the liquid-gas interface. It also reduces the interfacial tension between oil and water by adsorbing at the liquid-liquid interface. Many surfactants can also assemble in the bulk solution into aggregates. Examples of such aggregates are vesicles and micelles. The concentration at which surfactants begin to form micelle is known as the critical micelle concentration (CMC). When micelles form in water, their tails form a core that can encapsulate an oil droplet, and their (ionic/polar) heads form an outer shell that maintains favorable contact with water. When surfactant assembles in oil, the aggregate is referred to as a reverse micelle. In a reverse micelle, the heads are in the core and the tails maintain favorable contact with oil. Surfactant is also often classified into four primary groups; anionic, cationic, non-ionic, and zwitterionic (Ash, et al, 1993).

2.2.2.1 Anionic surfactant

This is by far the largest surfactant class. Generally it is not compatible with cationic but with some exceptions. Main feature for anionic type of surfactant is that it's generally sensitive to hard water. In other word, the sensitivity decreases in the order of carboxylate > phosphate > sulfate/sulfonate. This type of surfactant can be tailored to a wide range of conditions and widely available at low cost in special cases compared to other classes. Sulfates used in low temperature applications, sulfonates in high temperature applications and cationics can be used as co-surfactants (Pope, 2007).

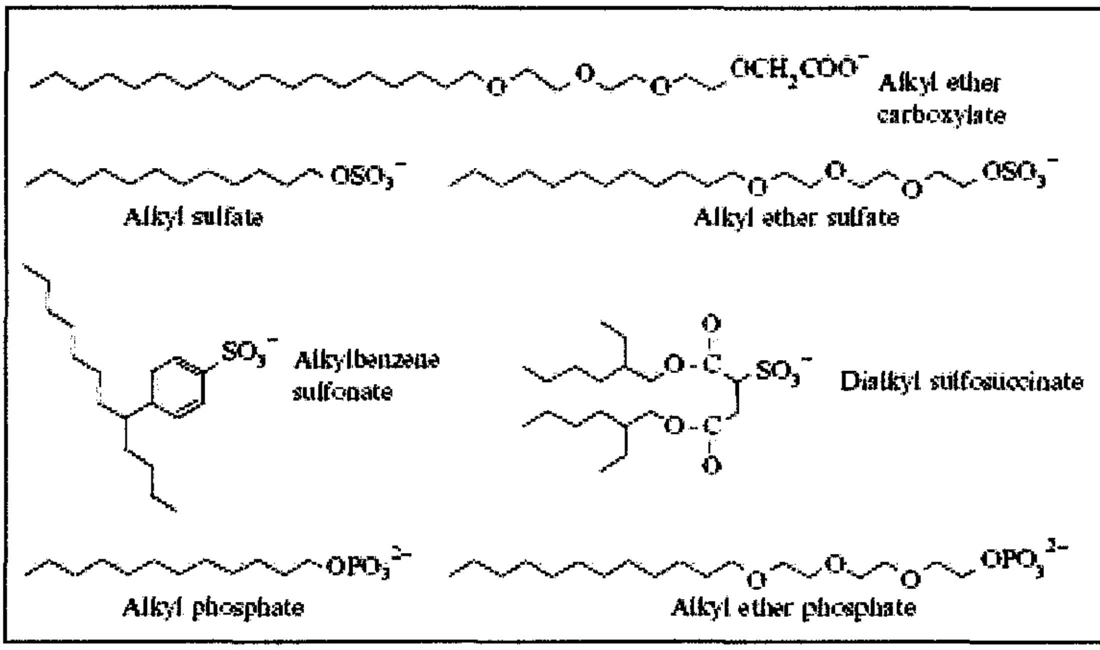


Figure 2 Structures of some representative anionic surfactants (Holmberg, et al. 2002)

2.2.2.2 Cationic Surfactant

Cationic surfactant is the third large surfactant class. As they are generally not compatible with anionic with some exceptions, there are actually hydrolytically stable as it show higher aquatic toxicity than most other classes of surfactant. Adsorb strongly to most surfaces and their main uses are related to in situ surface modification.

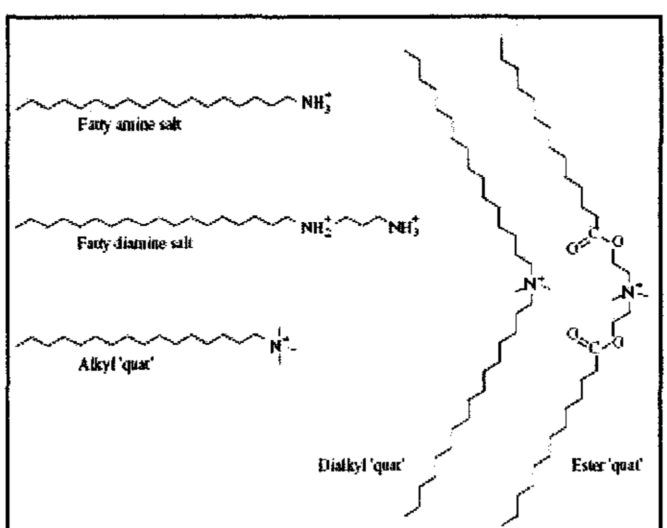


Figure 3 Structures of some representatives of cationic surfactants (Holmberg, et al. 2002).

2.2.2.3 Non-ionic Surfactant

This is the second largest of surfactant class. It is normally compatible with all other types of surfactants. Moreover, it is not sensitive with hard water and in the other hand, contrary to ionic surfactant; their physicochemical properties are not markedly affected by electrolytes.

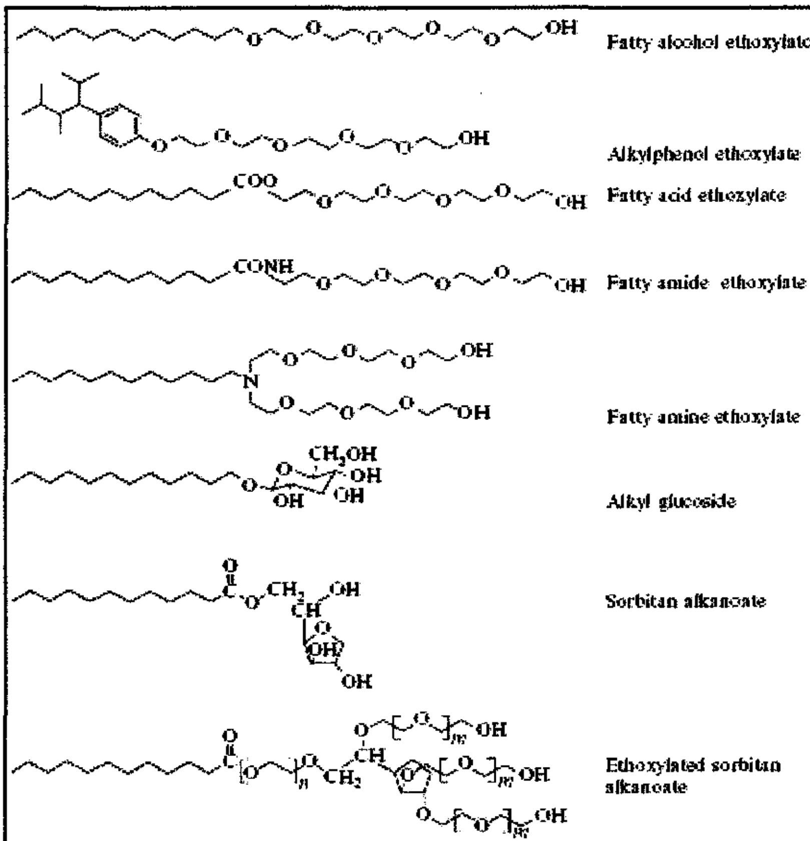


Figure 4 Structures of some representative non-ionic surfactants (Holmberg, et al. 2002)

2.2.2.4 Zwitterionic Surfactant

This is the smallest surfactant class, due to high price of manufacturing it. However, this type of surfactant is compatible with all other classes of surfactant. Not sensitive to hard water and generally stable in acids and bases. Particularly, the betaines retain their surfactant properties in strong alkali. Most types of this surfactant show very low eye and skin irritations, as they are well suited for use in daily care products.

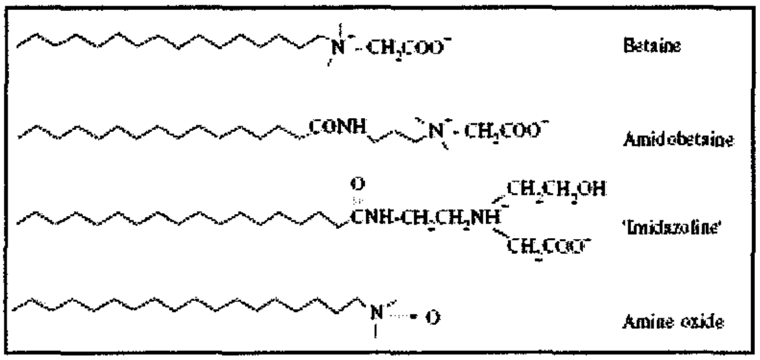


Figure 5 Structures of some representative zwitterionic surfactants (Holmberg, et al. 2002)

2.3 ALKALI IN SURFACTANT

Addition of alkali additives to surfactant formulations has been found to be beneficial by reducing losses of surfactant and polymer, reducing concentrations of divalent cations that cause losses of surfactant by partitioning and precipitation, and by affecting interfacial properties. The effects of alkali/surfactant formulations on heavy, acidic oil have been known for some time. Recent research has shown that weakly alkali additives to surfactant formulations may also be effective for the recovery of light crude oils, and with greatly reduced concentrations of surfactant. Measurements of the dynamic IFT revealed that when the alkali concentration is as high as 0.7–1.0 wt%, the IFT rapidly increases after about 100 minutes (Arihara, et al 1999).

The use of weak alkalis was shown to avoid or reduce some of the adverse reactions that usually occur between reservoir rock and strong alkalis. The lower pH alkalis reacted with acidic components of crude oils to produce surfactants in situ, but the amount of natural surfactants extracted from the crude oil were less than that obtained with stronger alkaline agents (Pope, 2007) meaning that addition of additives is very beneficial. Therefore, the reduction in IFT was also less. Very low concentrations of synthetic surfactants could be added to an alkaline slug and be very effective in oil recovery. It was also observed that alkaline conditions resulted in lower losses of surfactant by precipitation and adsorption. Figure 6 and Figure 7 showing the effect of alkali on oil recovery and interfacial tension. The concentration of alkali also affected the oil recovery and the interfacial tension.

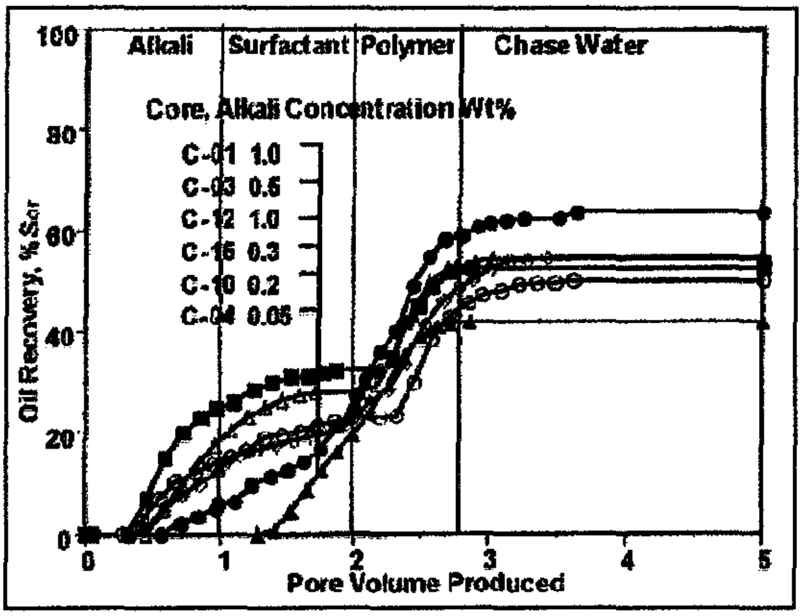


Figure 6 Effects of Alkali Concentration on Oil Recovery (Arihara, et. al. 1999)

Figure 6 showed that the oil recovery increases as the alkali concentration increases until a point that the oil recovery does not affected by the concentration.

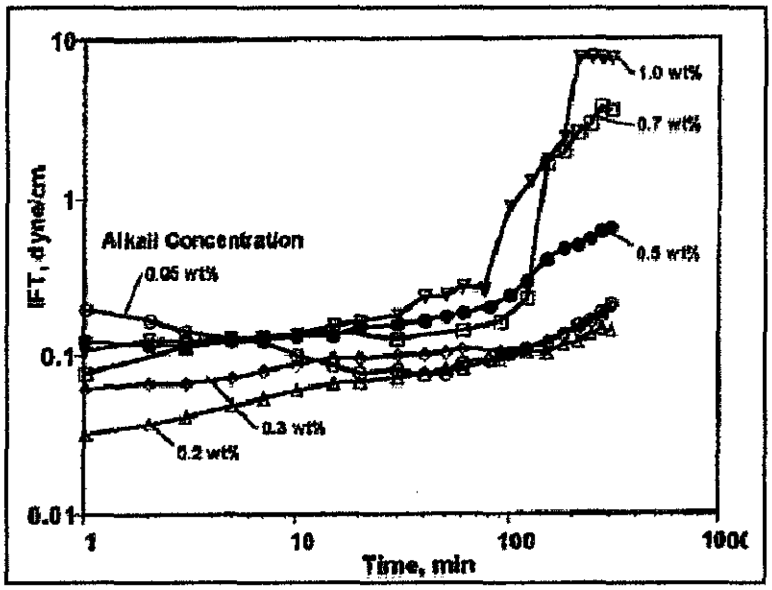


Figure 7 Effect of alkali on IFT (Arihara, et. al. 1999)

Figure 7 showed that the interfacial tensions are affected by the concentration of alkali. IFT increases after the addition of high alkali concentration (0.7-1.0wt%) after about 100minutes. With regard to time, there is a need for polymer added to achieve a better result.

2.4 BRANCHED ALCOHOL IN SURFACTANT

Alcohol surfactant is one class of anionic surfactant types. Experimental results show that a series of branched alcohol as candidates for chemical EOR applications. This experimental result will show that these surfactants may be preferred candidates for EOR as they are effective at creating low interfacial tension (IFT) at dilute concentrations, and without requiring an alkaline agent or co-surfactant. In addition, some of the formulations exhibit a low IFT at several percent Sodium Chloride concentrations, and hence may be suitable for use in more saline reservoirs.

Selected formulation could displace most of the water flood residual oil in place even with a dilute, 0.2 wt% surfactant solutions from Berea sandstone cores [Wu, et. al 2009]. Alcohol is one of the functional group that having –OH. Types of alcohol – based on the degree other C atoms that attached to C atom attached with –OH. There are three main types in alcohol that summarized in the table:

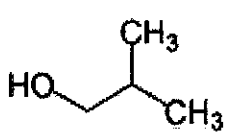
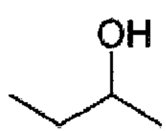
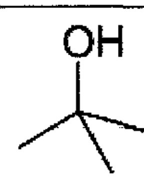
Primary types (straight chain, n-, iso)	Secondary types (sec-, cyclic)	Tertiary types (ter-)
		

Table 2 Types of Alcohol

For straight chain alcohol differs with branched alcohol in terms of the properties. For example, the properties will be differs in polarity and solubility. The branched alcohol is more polar hence it has higher solubility.

2.4.2 Polarity

Polarity is separation of electric charge (+ve / -ve) leading to a molecule or its chemical groups having an electric dipole or multipole moment. The interaction is through the dipole-dipole interaction forces. The molecular polarity is dependent on the difference of electronegativity, between atoms in compounds and compounds in structure. This will affect number of physical properties including surface tension, solubility, melting points and boiling points.

Atom with higher electronegativity attracts electron in higher favor (more attraction forces). Thus, high different of electronegativity exert higher polarity. There are 3 types of molecules that are :

- Non polar – zero different in electronegativity
- Polar – high different in electronegativity
- Polar covalent – middle part (between 0.4 – 1.7 in polarity scale)

Polar molecules tend to dissolve in polar solvent, same goes to non polar molecules that tend to dissolve in non polar molecules. Therefore, high polarity has a high tendency of solubility. For example, sugar (highly polar molecules that have polar groups) able to dissolve easily in water (naturally polar molecules)

Types	Description	Example
AB	Linear molecule	CO
HA_x	Single H molecule	HF
A_xOH	Molecule with an OH at one end	C_2H_5OH (ETANOL)
O_xA_y	Molecule with an O at one end	H_20
N_xA_y	Molecule with an N at one end	NH_3

Table 3 Description of Polar Molecule

The reason of choosing branched alcohol to be added into surfactants is because surfactant itself having hybrid polarity. As the surfactant also having hybrid polarity, the existence of non polar group (hydrophobic) and polar group (hydrophilic) will be enhanced by the addition of the branched alcohol[11-14].

2.5 PENDANT DROP METHOD

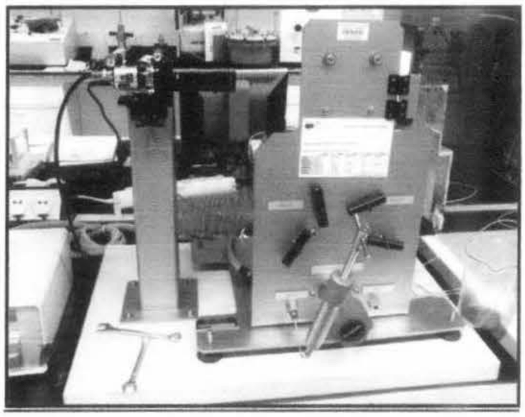


Figure 8 IFT equipment

Pendant Drop method involves the determination of the profile of a drop of one liquid suspended in another liquid at mechanical equilibrium. The profile of a drop of liquid suspended in another is determined by the balance between gravity and surface forces.

$$\gamma = g \, \Delta p \, R_0^2 / \beta$$

$$\beta = 0.12836 - 0.7577S + 1.7713S^2 - 0.5426S^3$$

$$R = \frac{d_e}{2\,(0.9987 + 0.1971\,\beta - 0.0734\,\beta^2 + 0.34708\,\beta^3}$$

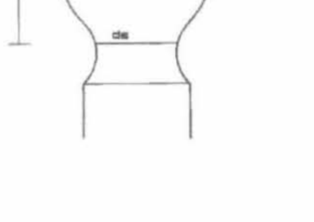
$$S = \frac{d_s}{d_e}$$

γ = interfacial tension

g = gravitational acceleration

Δp = density drop difference

R_0 = radius of curvature of drop apex



S = drop shape factor

R_1 = first radius of curvature

R_2 = second radius of curvature

d_e = maximum drop diameter

d_s = diameter at distance d_e from drop apex

CHAPTER 3

METHODOLOGY

3.1 RESEARCH METHODOLOGY

3.1.1 SAMPLES

- Involving 5 different types of solutions that were
  - Surfactant (SDS – 0.1 wt% and 0.2 wt %)
  - Alkali (Sodium Hydroxide 0.25 wt% and 1 wt %)
  - Alkali (Sodium Carbonate 0.25 wt% and 1 wt %)
  - Branched Alcohol (2-methyl 1-butanol 1.0% and 0.5 wt %)
  - Branched Alcohol (2-methyl 2-butanol 1.0% and 0.5 wt %)
- Involving 2 type of different salinity water
  - Freshwater 500ppm
  - Hard water 35000ppm
- Involving 1 crude sample
  - Dulang Crude
  - Light oil and waxy – pour point (30 ^{o}C)
  - Gravity (API): 37.8

3.1.2 EXPERIMENTAL FLOW

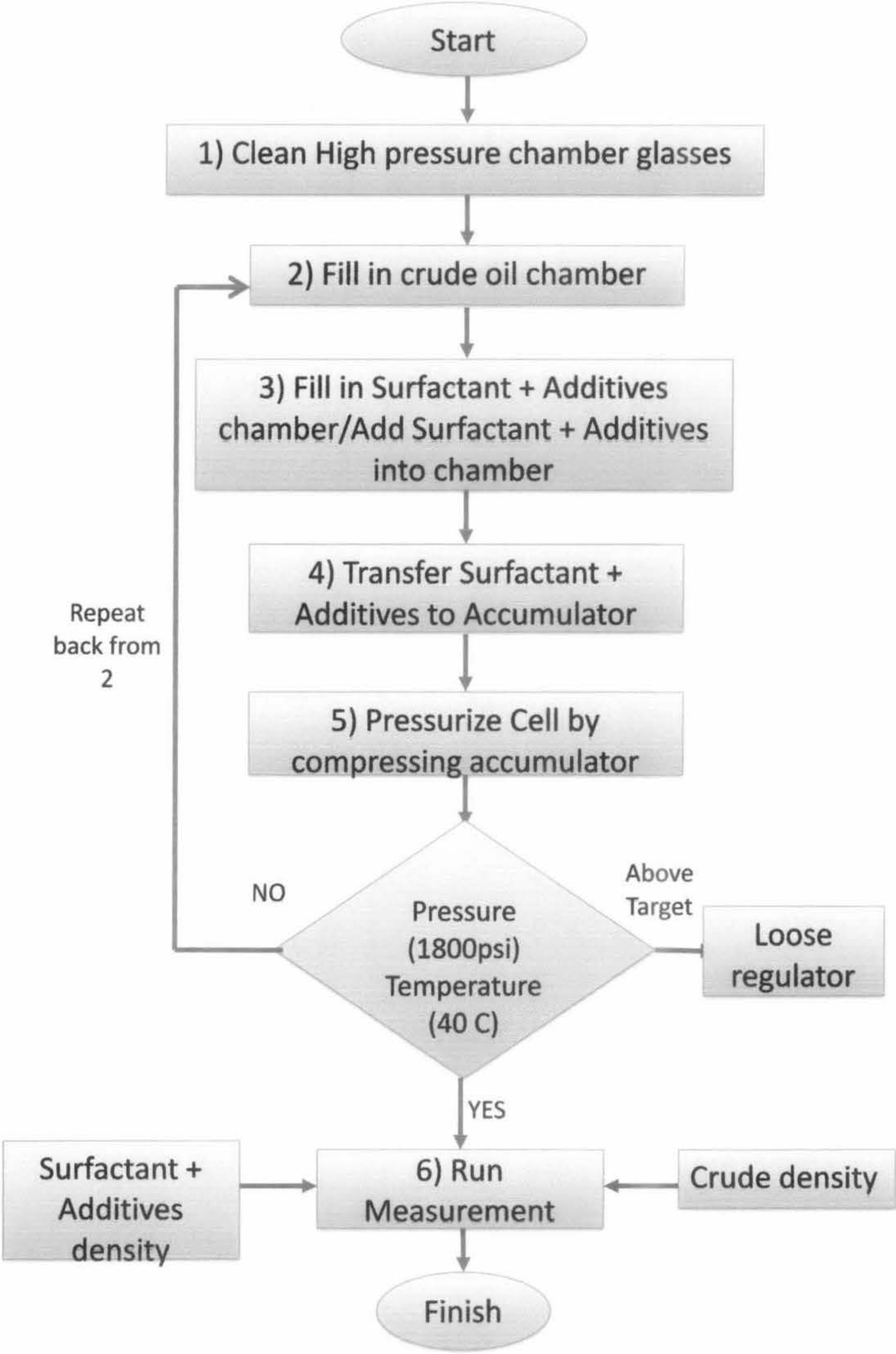


Figure 9 : IFT experiment work flow

3.2 GANTT CHART OF PROJECT MILESTONES

3.2.1 FYP 1

Project Timeline For Semester 1																
NO	**DETAIL/WEEK**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**
1	Project Topic Selection															
2	Preliminary Research Work Literature Review of Effects of Additives onto Surfactant															
3	Submission of preliminary report															
4	**Project Work Continues**															
	a. Literature review on the effects of additives onto surfactant - Alkali - Branched Alcohol															
	b. Project Defence and Progress Evaluation															
	c. Checking on equipment availability - OPMAN IFT 700 - Crude (Dulang) - Surfactant (SDS) - Branched alcohol (2-methyl-1butanol, 2-methyl-2butanol) - Alkali (sodium hydroxide, sodium carbonate)															
	d. Draft of Interim report															
5	Submission of interim report															

Table 4 Gantt Chart for FYP 1

3.2.2 FYP 2

Project Timeline For Semester 2															
DETAIL/WEEK	May		June				July				August				Sept
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Preparing the chemical (Alkali and Branched Alcohol) and checking the machine availability															
Experiment on IFT															
- Experiment of Crude + Surfactant															
- Experiment of Crude + Surfactant + Sodium Hydroxide															
- Experiment of Crude + Surfactant + Sodium Carbonate															
Submission of Progress Report															
- Experiment of Crude + Surfactant + 2-methyl-1butanol															
- Experiment of Crude + Surfactant + 2-methyl-2butanol															
Preparation re-experiment (buffer)															
Analysis and Discussion of the result															
Pre-EDX															
EDX															
Submission of Final Report															

Table 5 Gantt Chart for FYP 2

3.3 KEY MILESTONES

3.3.1 FYP 1

FYP 1 Milestones

No.	Details / Month	Jan	Feb	Mar	Apr	May
1	**Identifying effects of additives onto surfactant flooding (IFT)**					
2	**Identifying equipment to used - OPMAN IFT 700**					
3	**Identifying alkali** (sodium hydroxide, sodium carbonate), **branched alcohols**(2-methyl-1butanol, 2-methyl-2butanol), **surfactant**(SDS) **and Crude** (Dulang)					
4	**Expected Result of IFT**					

Table 6 Key Milestones for FYP 1

3.3.2 FYP 2

FYP 2 Milestones

No.	Details / Month	May	June	July	Aug	Sep
1	**Experiment on the IFT for alkali (sodium hydroxide and sodium carbonate)**					
2	**Experiment on the IFT for branched alcohol (2methyl 1 butanol and 2methyl 2 butanol)**					
3	**Analysis of the result and discussion for IFT**					
4	**Finalizing the result and discussion**					

Table 7 Key Milestones for FYP 2

3.4 TOOLS REQUIRED

Some specific tools were needed for experimenting purpose. The equipments that required were OPMAN IFT 700 and Anton Paar DMA. Procedure and instruction details were discussed with the lab technician from time to time.

EXPERIMENT	DESCRIPTION
DENSITY EXPERIMENT	Equipment used : • Anton Paar DMA Items used : • Distilled water • Toluene • Formulation of SDS, Na_2CO_3, NaOH, dimethyl butanol and dimethl 2butanol
IFT EXPERIMENT	Equipment used : • OPMAN IFT 700 Items used : • Alkali (sodium carbonate, sodium hydroxide) • Branched Alcohol (dimethyl butanol, dimethyl dibutanol) • Aqueous Surfactant (SDS) • HC (Dulang Crude)

Table 8: Experiment Details

- Max Operating Pressure for IFT 700 is 10 000psig
- Max Operating Temperature for IFT 700 is 200 °C
- Range of Temp Measurement for Anton Paar DMA is 0 °C – 40 °C.
- Surfactant Sulfate Hydrolyzed at >60 °C

3.4.1 ANTON PAAR DMA

One of the devices used in this experiment was Anton Paar DMA. This device was used to get the density value of a solution. The accuracy range of using this device was between 0°C – 40 °C. Solution that was prepared beforehand will be heated to >40 °C. Next, the solution will be sucked into the device before the measurement was taken at 40 °C.

3.4.2 IFT 700

The main component of IFT-700 in this experimental set-up was a see-through windowed high-pressure cell. The maximum operating pressure and temperature of this pressure cell were equal to 10,000 psig and 200°C, respectively. Pendant rise was chosen due to lower density value of crude oil compared to bulk volume at the respected condition and also due to the many sample use in this project. The equilibrium pressure inside the pressure cell was measured by using a digital pressure gauge.

A microscope camera was used to capture the digital images of the pendant oil rise inside the pressure cell at different times. The high pressure cell was positioned horizontally between the light source and the microscope camera. The data will be processed by the software of Vinci Technologies (OPMAN IFT 700) to get the data and IFT measurement.

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 RESULTS

4.1.1 Physical Appearances of Solutions combination in Hard Water

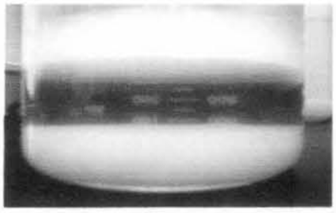
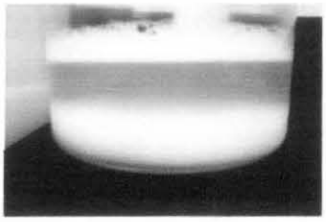
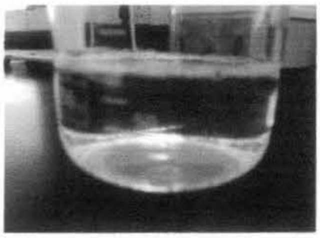
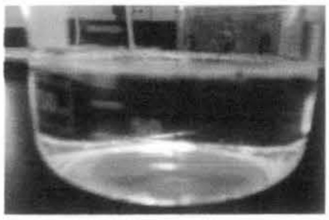
Type of Solution	Physical Appearances	Description
Surfactant (SDS) + Alkali (Sodium Carbonate) in Hard Water (35000 ppm)		- White precipitation occurred at bottom layer of solution
Surfactant (SDS) + Alkali (Sodium Hydroxide) in Hard Water (35000 ppm)		- White precipitation occurred at bottom layer of solution - Hazy upper solution
Surfactant (SDS) + Branched Alcohol (2methyl 1butanol) in Hard Water (35000ppm)		- Crystal clear solution, no precipitation
Surfactant (SDS) + Branched Alcohol (2methyl 2butanol) in Hard Water (35000ppm)		- Crystal clear solution, no precipitation

Table 9 Physical Appearances of Solutions Combination in Hard Water

4.1.2 IFT of Alkali

ALKALI (Fresh Water – 500ppm)						Physical Appearances			
Experiment	IFT at Pressure			DENSITY (40C)					
	1000	1400	1800	Bulk	Drop	1	2	3	4
SDS 0.2wt%	2.4	2.43	1.74	1.005	0.83	1			
SDS 0.2wt% + 1wt% Na_2CO_3	0.66	0.54	0.55	1.0101	0.83	2			
SDS 0.2wt% + 0.25wt% Na_2CO_3	2.28	2.24	2.17	0.9984	0.83	2			
SDS 0.1wt%	2.46	2.45	2.18	1.01	0.83	1			
SDS 0.1wt% + 1wt% Na_2CO_3	0.69	0.7	0.7	1.005	0.83	2			
SDS 0.1wt% + 0.25wt% Na_2CO_3	1.9	1.91	1.88	0.9971	0.83	2			
SDS 0.2 wt%	2.4	2.43	1.74	1.005	0.83	1			
SDS 0.2 wt% + 1wt% NaOH	1.22	1.14	1.06	1.006	0.83	2			
SDS 0.2 wt% + 0.25wt% NaOH	1.95	1.95	1.96	0.998	0.83	2			
SDS 0.1 wt%	2.46	2.45	2.18	1.01	0.83	1			
SDS 0.1 wt% + 1 wt% NaOH	0.63	0.64	0.62	1.0066	0.83	2			
SDS 0.1 wt% + 0.25 wt% NaOH	1.62	1.65	1.59	0.9976	0.83	2			
1- Clear solution	2- Slightly hazy		3- hazy		4- total hazy				

Table 10 IFT result of Alkali

4.1.3 IFT of Branched Alcohol

BRANCHED ALCOHOL (sea water – 35000ppm)						Physical Appearances			
Experiment	IFT at Pressure			DENSITY (40C)					
	1000	1400	1800	Bulk	Drop	1	2	3	4
SDS 0.2wt %	2.4	2.43	1.74	1.005	0.83	1			
SDS 0.2wt % + 1.0% 2methyl 1 butanol	0.78	0.79	0.78	1.0173	0.83	1			
SDS 0.2wt % + 0.5% 2methyl 1 butanol	0.86	0.88	0.9	1.0175	0.83	1			
SDS 0.1wt %	2.46	2.45	2.18	1.01	0.83	1			
SDS 0.1wt % + 1.0% 2methyl 1 butanol	0.62	0.64	0.63	1.0165	0.83	1			
SDS 0.1wt % + 0.5% 2methyl 1 butanol	0.68	0.68	0.67	1.0165	0.83	1			
SDS 0.2wt %	2.4	2.43	1.74	1.005	0.83	1			
SDS 0.2wt % + 1.0% 2methyl 2 butanol	1.12	1.14	1.11	1.0167	0.83	1			
SDS 0.2wt % + 0.5% 2methyl 2 butanol	1.08	1.08	1.08	1.0175	0.83	1			
SDS 0.1wt %	2.46	2.45	2.18	1.01	0.83	1			
SDS 0.1wt % + 1.0% 2methyl 2 butanol	0.87	0.87	0.84	1.0163	0.83	1			
SDS 0.1wt % + 0.5% 2methyl 2 butanol	0.9	0.88	0.91	1.017	0.83	1			

1- clear solution	2- slightly hazy	3- hazy	4- total hazy

Table 11 IFT result of Branched Alcohol

4.2 DISCUSSIONS

4.2.1 Physical Appearances (Precipitation)

For solution of Sodium Hydroxide with Hard water that consists of Calcium Chloride and Magnesium Chloride, layers of white solid occurred at the bottom of the beaker. The reaction that happened between those two chemical had produced a white layer of precipitation. The equation involved was:

calcium chloride + sodium hydroxide → calcium hydroxide + sodium chloride.

$$CaCl_{2(aq)} + 2NaOH_{(aq)} \rightarrow Ca(OH)_{2(s)} + 2NaCl_{(aq)}$$

magnesium chloride + sodium hydroxide → magnesium hydroxide + sodium chloride

$$MgCl_{2(aq)} + 2NaOH_{(aq)} \rightarrow Mg(OH)_{2(s)} + 2NaCl_{(aq)}$$

Figure 10 : Chemical Reaction of Chloride Salt with Sodium Hydroxide

Both of the reactions were producing a white solid or precipitation. They are calcium hydroxide and magnesium hydroxide. Same goes to the solution of Sodium Carbonate with Hard Water that consists of Calcium Chloride and Magnesium Chloride, layers of white solid occurred at the bottom of the beaker. The reactions involved were:

calcium chloride + sodium carbonate → calcium carbonate + sodium chloride.

$$CaCl_{2(aq)} + Na_2CO_{3(aq)} \rightarrow CaCO_{3(s)} + 2NaCl_{(aq)}$$

sodium carbonate + magnesium chloride → sodium chloride + magnesium carbonate

$$Na_2CO_{3(aq)} + MgCl_{2(aq)} \rightarrow 2NaCl_{(aq)} + MgCO_{3(s)}$$

Figure 11 : Chemical Reaction of Chloride Salt with Sodium Carbonate

White precipitation in using sodium carbonate also can be seen as calcium carbonate and magnesium carbonate had the tendency of forming a white precipitation layers.

If the actual surfactant flooding was carried out with these types of alkali, there will be a mass destruction to the reservoir itself. As the white solid precipitation will clog and reduce the permeability of the reservoir. No matter how low the IFT value it was for a reservoir, it will be useless if it cannot flow into the wellbore. For the sake of the experiment, soft water was used in surfactant enhanced with alkali to get the IFT value.

Situations were different with solutions of surfactant of branched alcohols with hard water. Only crystal clear solutions formed instead of white precipitations. These showed that branched alcohol had a tolerance in hard water.

4.2.2 Data Analysis (Alkali)

In this experiment, the objective was to get the IFT value between alkali and branched alcohol with regards to surfactant flooding. The main aim is to show that by using alkali or branched alcohol, it can reduced the IFT of injected oil with surrounding SDS from before the introduction. Two concentration of SDS are used in the experiments that are 0.1wt% and 0.2wt%.

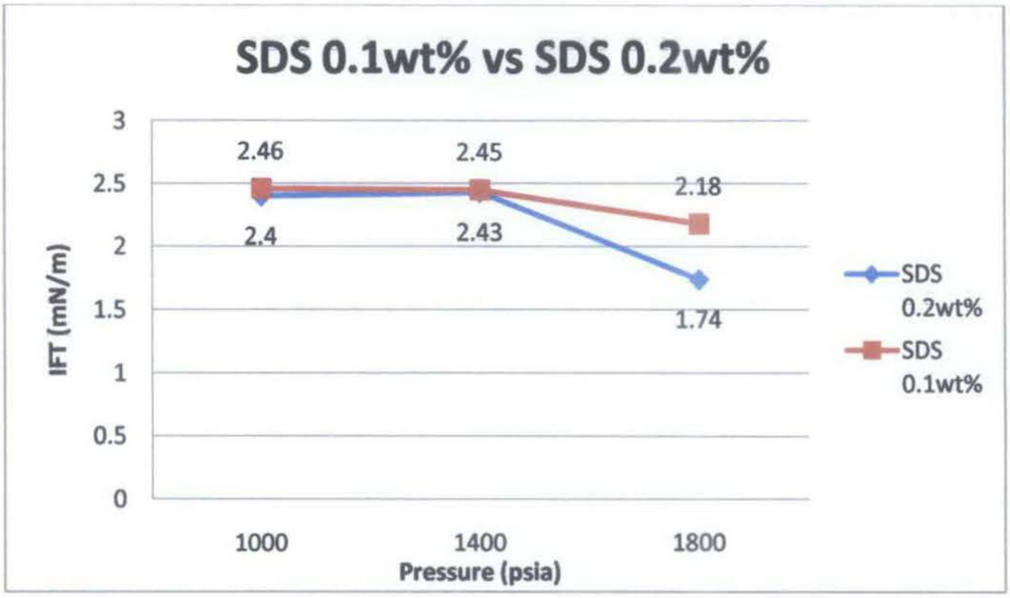


Figure 12 : Graph of SDS concentration

Figure 9 showed a graph of SDS 0.1wt% versus SDS 0.2wt%. From this point, we can see the difference effect in using different concentration of SDS. We can see as the pressure is increased, the IFT number between these two concentrations did not change much. However, at pressure of 1800 psia, the IFT showed a great difference. Here, it's showed that as the concentration of SDS was also influenced the value of IFT. Theoretically, to get lower IFT value for a better sweep of oil in reservoir, more concentration of surfactant needs to be used up to certain point. This may result in a high cost operation for Enhanced Oil Recovery.

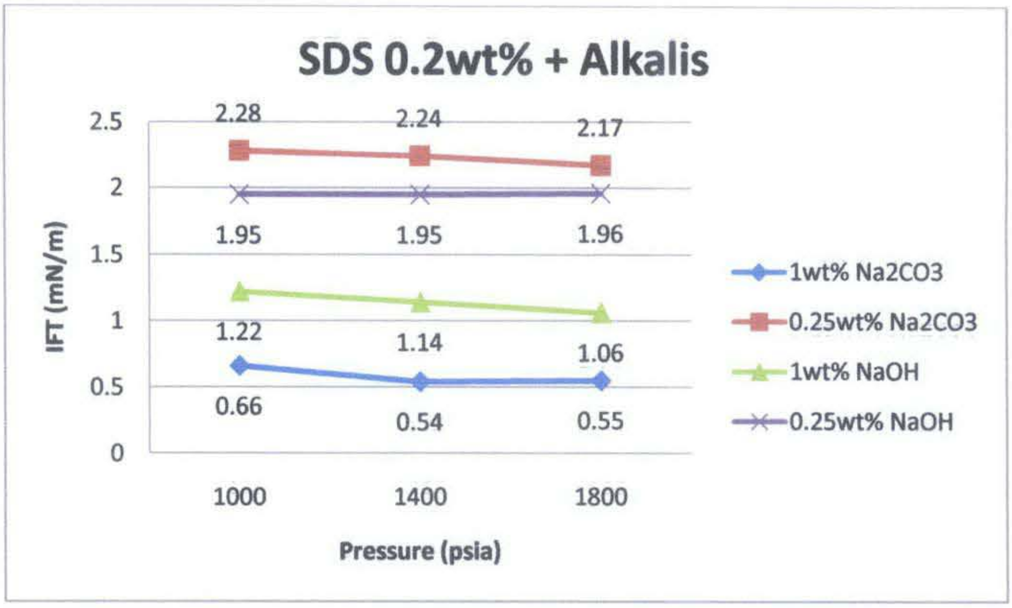


Figure 13 : Graph of 0.2wt% SDS + Alkalis

To avoid of having spending a lot of money on surfactant, a combination of alkali and surfactant are used. Alkali if used in EOR will generates soap in situ by reaction between alkali and naphthenic acids in the crude oil. The soap will further reduce the viscosity or the tension between the oil in the reservoir. Graph in Figure 10 showed the difference of incorporating high concentration of SDS (0.2wt %) with different concentrations of alkalis (0.25wt% and 1.0wt %).

Based on the result, having higher concentration of alkali from 0.25wt% to 1.0wt% were good in terms of having reduced value in IFT. The main point in the result was having alkalis in surfactant were really helpful in reducing the IFT. In fact, the IFT was reduced further from the value of 2.18mN/m to a great extend of 0.55mN/m at 1800 psia. Different alkalis also resulted in different IFT value. This may open opportunity for some different alkali to be applied to different field based on the suitability.

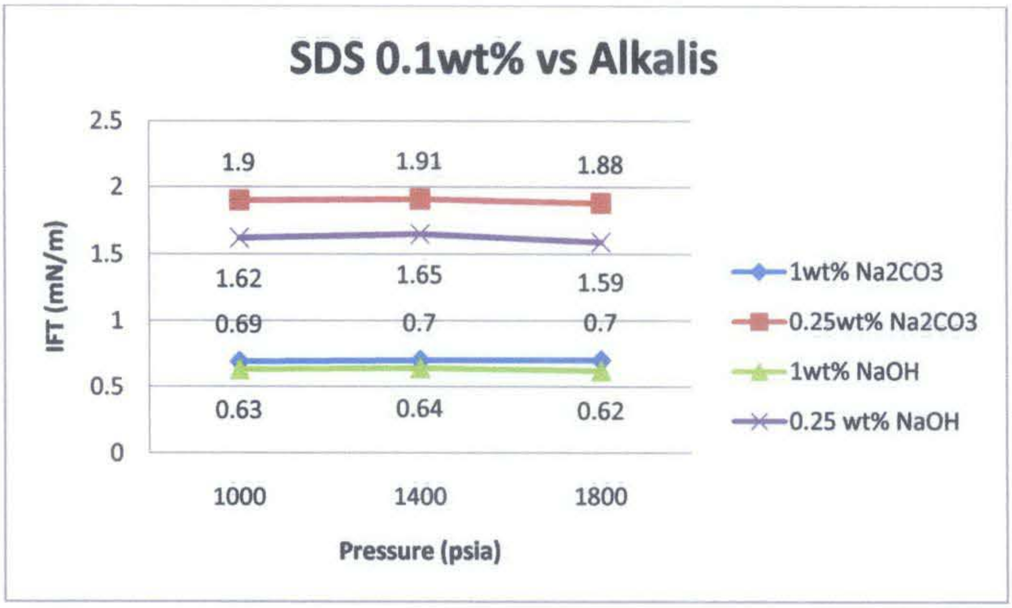


Figure 14 : Graph of 0.1wt% SDS + Alkalis

As concentration of SDS is lowered (0.1wt %) in figure 11, the effect of adding alkali will be further analyzed. By focusing at 1800psi which was the Dulang reservoir pressure, a huge drop in IFT value was studied. Previously, by not incorporating any alkali, the IFT for 0.2wt% of SDS was 2.18mN/m. Then, by having same amount of SDS with a high concentration of alkali (1.0wt %) the value was reduced to a value of 0.55mN/m for sodium carbonate and 1.06mN/m for sodium hydroxide.

Excellent result produced by only incorporation only half amount of SDS (1.0wt %) in the application. Again, higher concentration of alkali definitely resulted a higher reduced in IFT. When using 1.0wt% of sodium carbonate, the IFT is reduced to 0.7mN/m and 1.0wt% of sodium hydroxide resulted in 0.62mN/m of IFT.

The almost same result in IFT dropped can be achieved by using only half of the amount of surfactant. This proved that alkali introduction into surfactant can result a better and can reduce the amount of surfactant used. This can lead to a cost saving operation when running for EOR. Also, based in the result, the concentration amount of surfactant when additives added was not a major factor in reducing IFT. A slight changes was there but was not tremendous. It was only when additives was incorporated in that case.

4.2.3 Data Analysis (Branched Alcohol)

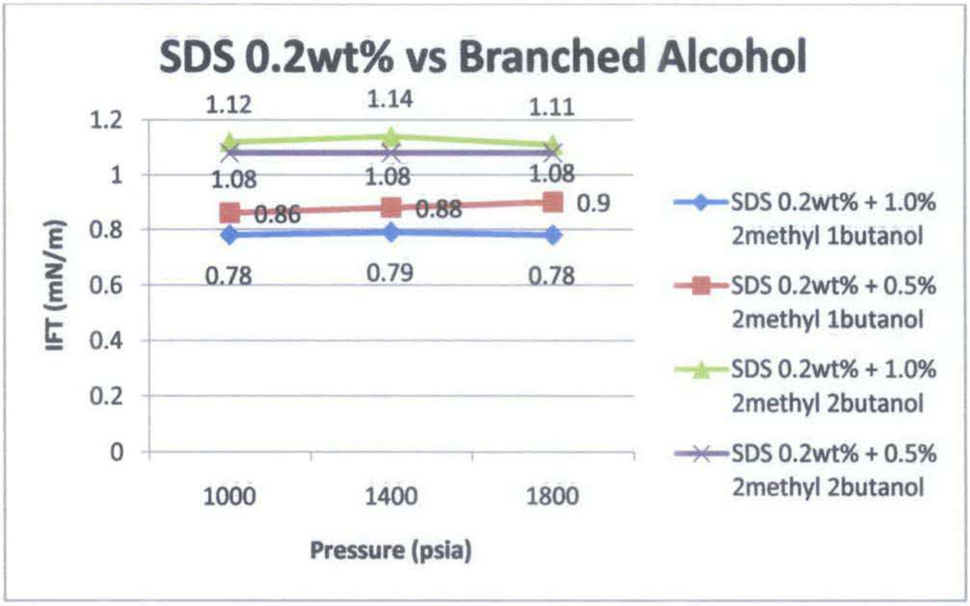


Figure 15 : SDS 0.2 wt% vs Branched Alcohol

As for branched alcohol, previous study showed that alcohol also can help in reducing IFT as alcohol also can behave like surfactant which was to reduce the interfacial tension of oil, thus higher oil recovery. With the combination of surfactant and branched alcohol, a greater and significant doubling reduction of IFT was expected. By focusing in the pressure value of 1800psi, the result showed that by incorporating branched alcohol, the IFT can be reduced down to a range of value 0.78-1.11 mN/m in hard water. However, the polarity in branched alcohol did not make such an impact; because using 2methyl 1butanol (0.5% and 1.0%) can have better result in reducing IFT compared to using 2methyl 2butanol (0.5% and 1.0%).

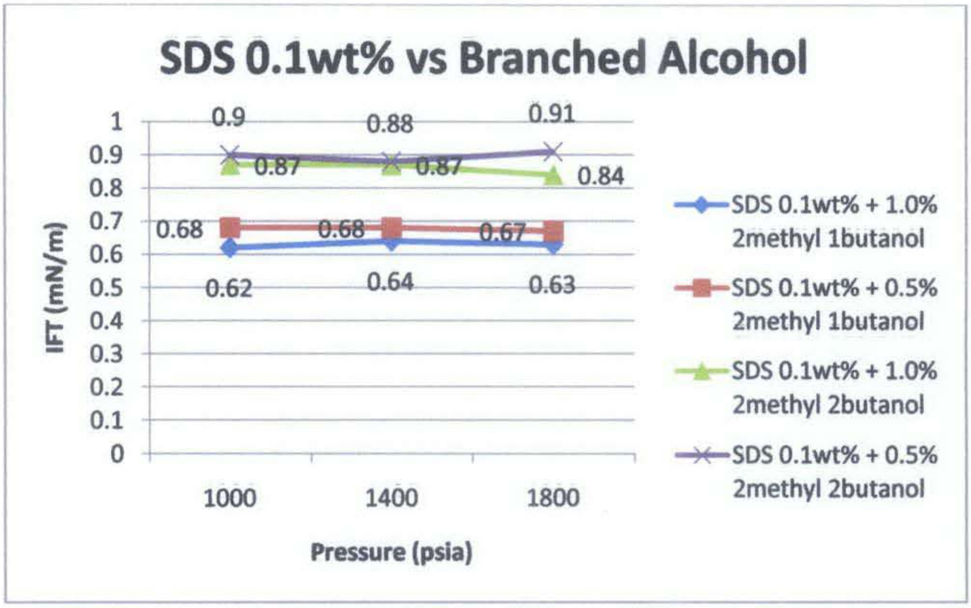


Figure 16 : SDS 0.1 wt% vs Branched Alcohol

By using half concentration of surfactant (0.1wt %), the effect of using branched alcohols were further analyzed. The objective of having better economic prospect can be reflected from the result because the IFT value was reduced further down to a range of 0.91-0.63 mM/m. Again, the result showed that the polarity in branched alcohol did not have a major impact. By using 2methyl 1butanol (0.5% and 1.0%), a desirable reduction was better that having 2methyl 2butanol (0.5% and 1.0%).

4.2.4 Data Analysis (Comparison between Alkali and Branched Alcohol)

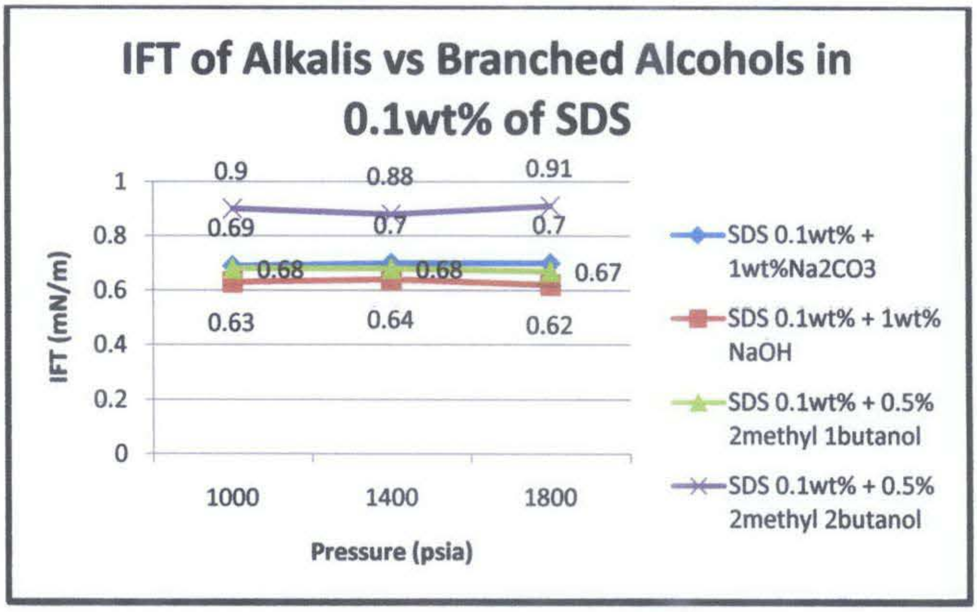


Figure 17 : Comparison of Alkali vs Branched Alcohol in 0.1wt% of SDS

Comparison between the ability of alkali and branched alcohol in this experiment was done. Based on the graph, the best additives that can reduce IFT further down was alkali (0.62mN/m) which was using Sodium Hydroxide. The second best of having reduced in IFT value was 2methyl 1butanol (0.67mN/m). By taking a closer look of both of the additives; a detail contrast had been made.

Reduction of IFT value to 0.62mN/m was done by having 1wt% of Sodium Hydroxide, compared of 2methyl 1butanol, only 0.5% concentration was used to get value of 0.67mN/m. By having less amount branched alcohol used, reduction of IFT can be made possible with alkali with only a little difference. In economic purposes, having half amount of branched alcohol that can give effect almost the same like having one full amount of alkali is much more desirable. It was like using 50% less amount of branched alcohol to get a significant value that only variant in 8% of IFT value.

Furthermore, the application of alkali in surfactant flooding only limited in the situation of having soft brine water (500ppm) to avoid any precipitation. But, branched alcohol can give a better situation where it can be utilized in hard brine water (35000ppm) without any precipitation. In enhanced oil recovery, this is more desirable to avoid any harmful effect to the reservoir.

4.2.5 Economic Viewpoint

Economic was a great indicator to evaluate any project. Categorizing a project whether it was a go or no go, a positive indication means profit must be achieved. In this project, a simple calculation in surfactant's economic shown to further evaluate the results. The SDS's worth was based on the performance earlier in the experiments.

The economic calculation was based on the price of SDS in the market. Cost for 250g of SDS was RM38. Cost of having 0.1wt% of SDS was generally RM3.80.

Vol.	Additives in 0.1wt% SDS	Percentage of IFT reduction (%)	Monetary Saved
1	Sodium Carbonate 1.0 wt%	67.9%	RM 1.22 / RM 3.80
2	Sodium Hydroxide 1.0 wt%	71.6%	RM 1.08 / RM 3.80
3	2methyl 1butanol 0.5%	69.3%	RM 1.17 / RM 3.80
4	2methyl 2butanol 0.5%	58.3%	RM 1.58 / RM 3.80

Table 12 : Economic Viewpoint (Monetary Saved Up)

From the simple calculation in the table, more than 50% can be saved up out of RM3.80 for the usage of SDS. This calculation was based on the price of using 100% SDS with the combination of SDS + additives. Addition of additives showed a very promising future in reducing cost of having only surfactant. IFT value generated was lower and definitely having a lower cost.

However, this was not including cost of additives. The additives cost more than surfactant itself by a factor of 2. Hopefully, in the future to come, additives will cost cheaper.

Vol.	Additives in 0.1wt% SDS	Percentage of IFT reduction (%)	Ability to work in Hard water.
1	Sodium Carbonate 1.0 wt%	67.9%	No
2	Sodium Hydroxide 1.0 wt%	71.6%	No
3	2methyl 1butanol 0.5%	69.3%	Yes
4	2methyl 2butanol 0.5%	58.3%	Yes

Table 13: Percentage of IFT reduction in 0.1wt% of SDS based on different additives

Table 18 summarizes the best option to be considered for surfactant flooding. 2methyl 1 butanol was able to combine with surfactant to reduce the IFT and also able to work in high salinity water.

CHAPTER 5

CONCLUSIONS & RECOMMENDATIONS

5.1 CONCLUSIONS

Enhanced Oil Recovery was booming on its way to achieve a better result in oil production. However, due to high cost of operation, only few can be applied on field. This experiment was meant to prove and compare surfactant application with regards of having different additives that beneficial and also effective in cost. Based on the result and data, the conclusions were:

- By proving that only a 0.1wt% of surfactant used with some alkali or branched alcohol, the result was surpassed the used of higher concentration of surfactant which was 0.2wt% alone.
- The results showed that 1.0wt% of alkali and half of the branched alcohol (0.5%) used were definitely good in reducing IFT to a value that as low as 0.5mN/m with percentage of reduction almost 70%.
- In addition, after introducing additives, the cost of using surfactant was relatively lower up to more than 50%.
- In contrast also, branched alcohol showed a better result in term of the ability to perform in hard and saline brine water.

Expansions in EOR industry were hoped to give a better scenario to deal with high increasing demand of oil with only limited resources yet to be drilled or to be stimulated. Branched alcohol can become an alternative as a co-surfactant for EOR.

5.2 RECOMMENDATIONS

There were several recommendations that can be applied to get a better and more accurate result. They were:

- In the future, this project should be continued by incorporating the polymer in the surfactant flooding. Polymer was important for effective displacement additive. This can result in a better sweep efficiency of oil in reservoir during any enhanced oil recovery technique.
- Furthermore, for the next experiment to come, precipitation effect should be considered. Due to reaction of alkali with calcium and magnesium ion in sea water, precipitation occurred and this was not good for the reservoir itself. Another type of alkali such as sodium metaborate that does not form any precipitation in brine should be used in later experiment.
- All types of surfactants like anionic, cationic, non-ionic and also zwitterionic need to be used for future research; these can make the analysis more accurate and the results are more conclusive.
- Having problem in producing data that can match the real reservoir parameters a close as possible was also crucial. An experimental device that can function in real reservoir pressure and temperature was greatly advised to be used next time to come.
- Next, more branching types in branched alcohol samples need to be incorporated in the study to have a better and conclusive result in the future.
- Last but not least is to incorporate more samples of different concentrations and also different temperature ranges for a higher accuracy result.

APPENDIX

OPMAN IFT 700 Safety Guidelines

Due to the high pressure-temperature levels which can be reached inside the cell:

- Operating staff must not expose themselves directly to the windows. Leakage or blow out can result in ejection of small glass particles and hot pressurized fluids.
- Aggressive organic solvents, e.g. aromatic substances can lead to a leakage in the view cell. In case of doubts, contact the manufacturer. The manufacturer is in no way responsible for leakage through wasted sealing.
- Respect the operating conditions range of the device. Electrical heating is fast and may overshoot the set temperature.
- Never exceed specified maximum operating temperature (180°C).
- Be careful when touching surfaces around the view cell: it might be very hot.
- The equipment must be attended during heating and pressurization operations.
- Working at high pressure requires wearing safety glasses. Especially, if the gas is toxic or flammable, the venting valves and the rupture disk for emergency blow-down (RD) need to be connected to a special venting system

OPMAN IFT 700 Feature

The IFT 700 features basically:

- Two pressure generators (PG1 and PG2) equipped with pressure manometer, each including 4 handles which can be removed for transportation.
- A stainless steel base.
- A viewing chamber (VC) : window diameter 18 mm, electrical heater.
- Temperature is controlled by Pt100, equipped with piezoelectric pressure transducer.
- Capillary injector (inner diameter available from 0.4 to 1.0 mm)
- Two supply tanks for fluids (F1, F2), equipped with Pt100 temperature transducer and electrical heater.
- Rupture disc and support; the (safety) burst pressure is given on the plate attached to the support. Actual burst pressure may vary by ± 5%.

- A back pressure regulator.
- A panel control with two temperature regulator, which enable to set the temperature of the view chamber (VC) and the fluid tanks (F1,F2) ; pressure indicator of the viewing cell.
- Video system: 1 CCD color camera, 1 macro zoom lens , 1 panel light, PCI acquisition board to connect with computer.
- Support for camera with micrometers motion tables (rotation & translation).
- DELL Computer with IFT software installed (1 CD Rom)
- Spare parts, tools

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