Comparison Studies of Surfactant Behavior in Light/Medium Oil

by

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CERTIFICATION OF APPROVAL

Comparison Studies of Surfactant Behavior in Medium/Heavy Oil

by

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A project dissertation submitted to the Petroleum Engineering Programme Universiti Teknologi PETRONAS In partial fulfillment of the requirement for the BACHELOR ENGINEERING (Hons) (PETROLEUM)

Approved by,

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CERTIFICATION OF ORIGINALITY

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

MUHAMMAD SYAFIQ BIN MOKHTAR

ABSTRACT

Depletion and high demand of crude oil had inspired the oil companies to explore other efficient enhanced oil recovery (EOR) methods. This enhancement process is the tertiary recovery method applied even after primary and secondary methods take placed. By conducting this enhancement process, the extraction of oil will increase. However, exploration and further exploitation of residual oil saturation become one of the most challenging activities in the petroleum industry.

Surfactants are well known in the literature which plays the role in improving oil recovery that improve the recovery by reducing the interfacial tension (IFT) between water and oil besides changing the matrix wettability from intermediate or oil wet to water wet and reduce the capillary pressure thus allow the residual oil to flow. However, in term of surfactant itself, there are some factors which have impact on it. Temperature, salinity, concentration of surfactant is a few example of the parameter should be taken into account. However due to time constraint, this study will focus only on salinity and concentration variation on the performance of the new ionic liquid based surfactant. The range of parameters and variables will be based on the laboratory study. The critical micelle concentration (CMC) is known as surfactant concentration in the large amount at which formation of micelle started. Therefore, from the graph of ionic liquid concentration versus interfacial tension, the ability of the new candidate as good surfactant to reduce IFT can be proven as well as the lowest concentration applicable. Additionally, the studies also include the existing anionic surfactant comparison.

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ABBREVIATIONS NOMENCLATURES

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

CHAPTER 1 INTRODUCTION

1.1 BACKGROUND

A large amount of petroleum resources cannot be recovered by conventional methods alone. Even after the primary and secondary recovery production, 60% of the original oil in place (OOIP) still remains in the reservoir [1]. Surfactants flooding is the one of the Enhanced Oil Recovery (EOR) applications in improving oil production by oil companies. Surfactants may be applied in the petroleum recovery and oil processing from the drilling phase, reservoir injection and surface plant processes. There are four categories of surfactant classified as aninonic, cationic, nonionic and zwitterionic. The most common used in industrial applications even in EOR is anionic surfactant. Due to its unique and versatile properties, anionic surfactant has great potential for Enhanced Oil Recovery applications [2].

Many studies and experiments have been conducted to improve the remaining oil production particularly after the reservoir has depleted after primary production. Basically a reservoir has three type of wettability, intermediate wet, water wet (Figure 1) and oil wet (Figure 2). Most of the cases, oil recovery is low due to many reservoirs are mixed wet or oil wet with low permeability. Then, in order to increase the oil recovery surfactants can be used to alter the wettability by reducing the oil-water interfacial tension (IFT) [3]. By reducing the interfacial tension (IFT), the capillary force is strong enough to allow the residual oil flowing in pore spaces.



 Figure 1.1.1: Water-wet phase
 Figure 1.1.2: Oil-wet phase

 Source: Retrieved from http://www.slideshare.net/MTaherHamdani/boundary-tensionand-wettability
 Figure 1.1.2: Oil-wet phase

Many surfactants have been studied in the past experiments. The primary requirement for each surfactant is the ability to mobilize residual oil in reservoir by reducing interfacial tension. In general, there are several factors that can affect the surfactants characteristics in aqueous environment such as temperature, salinity and concentration. However, different crude in the reservoir will need different surfactant to reduce interfacial tension based on different reservoir condition and oil characteristics. One of the reasons anionic surfactants is commonly used in EOR applications is because anionic surfactants has significance high water solubility and capability to low the interfacial tension. However anionic surfactants contained high toxicity level in the surfactants and harmful to aquatic environment and special disposal processes are needed [4]. In this study, an experiment is conducted to identify new candidates of surfactants which can enhance the oil recovery in light/ medium crude oil.

1.2 PROBLEM STATEMENT

Enhanced oil recovery (EOR) is the tertiary recovery method which is applied after primary and secondary recovery stages when there are still oil trapped in the reservoirs. In order to sustain the production of crude oil, efficient enhanced oil recovery methods need to be explored. Chemical flooding can be considered as an efficient EOR method. One of which is surfactant flooding. Surfactant is used in order to reduce the interfacial tension between water and oil. The purpose of this project is to study and propose two new candidates of surfactants which could be effective and economical which are made from ionic liquids. This study will also focus on critical micelle concentration (CMC) to be much lesser or economical than CMC of the existing surfactants in term of amount of surfactants concentration. In order to come out with the best ionic liquid as surfactant, experiment will be run and analysis of data will be conducted. The behavior of the two candidates of surfactants with salinity variation also will be investigated as well the comparison with the anionic surfactant.

1.3 OBJECTIVES

Chemical flooding can be one of the efficient enhanced oil recovery methods. Since the surfactant flooding is one of the chemical flooding methods proposed to be efficient in enhancing oil recovery, it will be studied further in this project.

The objectives of the study are:

- 1) To study the behavior of anionic surfactants in reducing IFT of heavy crude oil.
- 2) To determine the critical micelle concentration (CMC) point of anionic surfactant
- To compare the performance of two new surfactants to existing anionic surfactants.

1.4 SCOPE OF PROJECT

The scopes of study of the project are:

- 1. Study the two new surfactants and one existing surfactant
- 2. Setting up laboratory experiment to determine IFT of the surfactants
- 3. Determine the effects of concentration and salinity for three of the surfactants

1.5 RELEVANCY OF PROJECT

This project is a relevant project because it may give a new idea regarding the suitable candidate of surfactant to be used in EOR process. The surfactant should be able to increase the efficiency of oil recovery. Instead of using conventional surfactant, ionic liquid based surfactant with various parameters will be investigated. Based on the relationship between salinity and concentration with interfacial tension, these variables can be plotted to determine the optimum and economic formulation for each surfactant.

1.6 FEASILIBILITY OF PROJECT

The interfacial tension experiment is a laboratory scale project since the equipment, tools and chemicals can be set up. In this project, only two parameters will be focused on which are salinity and surfactant concentration parameters so the time frame given to run the equipment is also sufficient. It is possible to finish both study and experiment within the time frame if only two parameters are taking into account in this project.

CHAPTER 2 LITERATURE REVIEW

Basically oil recovery has three stages: primary, secondary and tertiary oil recovery. When a reservoir is driven by natural reservoir pressure, its known as primary recovery. While, the secondary recovery usually water is injected into the reservoir to increase the reservoir pressure. For most of the cases, 65% of the original in place (OIIP) still remains in the reservoir even after the secondary oil recovery [1]. The residual oil trapped in the reservoir because of the capillary and viscous force. Tertiary recovery can be applied by modifying capillary number and adding the surfactants to the waterflood [5]. Many researchers had mentioned that surfactant flooding is one of the most chemical EOR processes used. This is because chemicals are less expensive compared to other techniques and many studies and experiment have been conducted in the laboratory and field [6]. The main application of surfactants is recovering the residual oil that still remains in the reservoir after the secondary recovery [2]. The injected surfactant into reservoir will alter the wettability by reducing the interfacial tension (IFT) for increasing oil recovery [3, 7, 8].

Surfactants has 4 classes: anionic, cationic, nonionic and zwitterionic. Among 4 types of surfactants, anionic surfactants is commonly used in EOR processes. This is because anionic surfactants has low cost, wide range of properties and the availability of raw materials in market in large quantities [2]. Many researchers also had mentioned that anionic surfactants can be used in both sandstone and carbonate formations. Surfactants can be effective oil recovery agents by reducing interfacial tension and increasing capillary number, N_C thus the mobility ratio can be increased and aiding the residual oil to flow [7, 9]. Two important concepts that involved in oil recovery are mobility ratio (M) and capillary number (N_C). The mobility ratio is usually defined as the ratio of

injectent divided by that of fluid it is displacing. While the capillary number, N_C is defined as viscosity multiply by darcy velocity divided by interfacial tension (IFT) [6, 8]. There are many surfactants introduced in Enhanced Oil Recovery (EOR) processes but the best surfactants determined based on the crude oil properties, reservoir conditions and also several other requirements. In order to achieve optimum oil recovery by good surfactants, the surfactants agent must has minimum requirement and properties. There are four requirements need to be considered when selecting surfactant: (1) lowering oil-water interfacial tension (IFT), (2) low adsorption, (3) compatibility with reservoir fluids (4) Stability at reservoirs environment (5) low cost [1, 2, 7, 10].

There are some variables that varies the properties and behavior of surfactants in reservoir condition. Factors that affecting surfactant behavior such as pH values, temperature, surfactants concentration, salinity, and reservoirs condition and oil composition [1, 7]. However, in this study it will only focus on salinity and surfactant concentration as the parameters in the experiment. As we know the produced water from a reservoir generally consist of salinity which is Sodium Chloride (NaCl). The salinity of brine at fixed concentration of surfactant relatively reduces IFT values compare with IFT value of surfactant solution in pure water. Basically, the increasing existence of salt in the brine will decrease the solubility of surfactants in the brine. Consequently the surfactants performance is better [2].

Surfactant concentration will also affect the surfactant behavior. When the concentration of surfactants increased, the interfacial tension is decreased till reach the critical micelle concentration (CMC) point. Critical micelle concentration (CMC) is the lowest level and beyond which increasing the concentration of surfactants does not reduce the interfacial tension (IFT) values [1, 2, 11]. Hence, the capillary number is increased due to interfacial tension reduction so more oil can be produced.

Based on the past studies and experiments, the behavior of anionic surfactant also have been affected by salinity and surfactant concentration. Interfacial tension decreases sharply as the surfactant concentration is increased. In anionic surfactant the same trend is observed. IFT decreases with increasing surfactant concentration until the CMC is reached [10, 12, 13]. Furthermore, the water-flooding salinity also affect the anionic behavior. The interfacial tension (IFT) will decrease as the salinity increased [10]. However till the salinity reached a point (optimum salinity), the salinity no longer decrease the IFT values [12, 13].

For this project, ionic liquid is proposed as potential use for IFT reduction in Enhanced Oil Recovery (EOR) processes. Ionic liquid (ILs), organic salts that are composed of organic cations with organic or inorganic anions, which are liquids within room temperature, have received considerable attention recently as potential "green" alternate to anionic surfactants [4, 14]. In term of concentration parameter, recent studies have been conducted using low concentration of surfactant to improve oil recovery. It was found that interfacial tension (IFT) values decreased as IL concentration. However, the effect of temperature on the IFT depended on the type of ILs [4, 15]. Furthermore, the presence of salts also decreased the IFT. As the salinity increased, the interfacial tension (IFT) also will decrease [15]. However different type of ILs will give different behavior and different properties. Therefore, formulation of appropriate chemicals is also needed in order to generate solution with great performance but on low cost. Further laboratory works is needed and extended in modeling and correlating experimental data on ionic liquid properties.

CHAPTER 3 METHODOLOGY

3.1 PROJECT ACTIVITIES



Figure 3.1.1: Flow process of project methodology

Figure 3 shows the flow diagram of project methodology. There are 3 main processes involved in this project. At the beginning of the project, the new surfactants solutions need to be prepared. Then several IFT lab experiments will be running to test the surfactants solution. After that, the data will be collected and analyzed. As this project is quite similar to research and development (R&D) field therefore the results obtained from this research can be compared with the existing one under similar scope of study.

Based on the interfacial tension experiment, measurement of interfacial tension can be made where 3 type of surfactants are used. By having surfactant concentrations and salinity variation on IFT and the optimum salinity and critical point for three surfactants can be determined.

3.1.1 Sample Preparation

Before starting the preparation, bulk solution for brine and surfactants are prepared. The bulk solution for surfactants is 5wt% and for brine bulk solution is 10wt%.

Concentration samples:

Concentration samples for IL-10, CL-10 and sulfonates were prepared and are mixed at 3wt% of salinity and room temperature (23°C). The concentration parameter ranges from 0.01wt% to 0.5wt%.

Salinity samples:

Salinity samples for IL-10, CL-10 and sulfonates were prepared and are mixed at 0.1wt% of concentration and room temperature (23°C). The parameter ranges from 2.3wt% to 3.5wt%.

3.1.2 IFT Measurement

Interfacial tension (IFT) is a measurement of the excess energy present at an interface arising from the imbalance of forces between molecules at an interface. Chemical screening by IFT test is to determine the best surfactant to be used and the optimum surfactant concentration (wt%), and salinity (wt%). For the surfactant concentration, if the concentration is increases, IFT decreases rapidly. This process continues until the point of CMC is reached. After the CMC little change is observed in the IFT. In addition, as the salinity increase, the IFT decreases at some points. By using pendent drop method, interfacial tension between oil and solution in contact with the oil can be determined. The shape of the liquid drop can be seen in the computer with the help of connected camera to the computer in order to derive the interfacial tension and contact of angle properties while keeping rotation as the constant parameter for all measurement.

The methodology of Pendant drop is explained in the procedure below:

1. The crude oil sample is filled in 1 mL syringe.

2. The 5 mL surfactants sample are placed in the container

3. Activated camera icon in the monitor to switch to live video mode.

4. The needle of the syringe is adjusted until a good image is obtained.

5. The stage of is raised up until the syringe is immersed into ionic liquid/container.

6. Make sure the type is Pendant drop.

7. A drop is dispensed in the container and the image of the droplet is captured through the PC camera's window.

8. After that, pressed the "computation" icon and the surface tension reading is measured.

9. The result will be stored in the Result Collection Window

10. The apparatus is cleaned up at the end of measurement.

11. Repeat step 2-10 by using different surfactant sample.

3.2 CHEMICALS AND APPARATUS NEEDED

In the experiments that have been conducted, several chemicals, materials and apparatus are used. List of the chemical and apparatus used in the research study is given below:

Tapis Crude Oil:

Tapis fields are located in Malay Basin, offshore Peninsular Malaysia. These fields contain approximately 1 billion barrels original oil in place (OOIP) [16]. Tapis field has more than 100 wells with recovery factor of 40 to 50% of OOIP. Tapis fields contain saturated, light crude oil. The table below shows the list of reservoir and fluid properties of the Tapis field:

Reservoir & Fluid Properties	Value
Average permeability	50 – 300 mD
Reservoir temperature	200 - 250 °F
Reservoir pressure	1500 – 2500 psia
API	45 °API
Oil viscosity	0.6 cp

Table 3.2.1: Tapis Field Reservoir & Fluid Properties (Selamat et al., 2011)

 Table 3.2.2: List of chemicals and materials

Chemicals/Materials	Amount (g)	Purpose
**CL-10	1.2	Surfactant solution
**IL-10	1.2	Surfactant solution
Sulfonate	1.2	Surfactant solution
Distilled water & Sodium	450	Brine solution
chloride		

**Remarks: CL-10 and IL-10 represent two proposed ionic liquids

Table 3.2.3: List of Apparatus

Apparatus	Quantity
Plastic bottles	10
Beaker	3
Measuring cylinder	3

The model of OCA 15 dataphysics pendant drop equipment is used in this project. Below are the technical specification of OCA 15 equipment:

- Resolution: 0.01 to 2000mN/m
- Temperature: Ambient to 450°C
- Pressure: Ambient pressure
- Power supply: 100 240V AC; 50-60Hz

3.3 KEY MILESTONES

PROBLEM STATEMENT:

Identify the objectives of the project

LITERATURE REVIEW:

Gathering data and information from previous experiments and literature about the project background.

EXPERIMENT DESIGN:

Identify the parameters of interest in the project, experiment procedure, chemical and apparatus needed to conduct the experiment.

DATA ANALYSIS AND INTERPRETATION:

The obtained results were tabulated and compared with existing.

DOCUMENTATION AND PRINTING:

All findings and results were reported in details. Recommendations were proposed for further works or studies.

Figure 3.3.1: Key Milestones

3.4 GANTT CHART

	FYP I										FYP II																	
Detail/Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Identify the objectives of the project																												
Study experimental methodology																												
Running the IFT experiment at different concentration and salinity																												
Analyze the results and make comparison																												
Documentation																												

Figure 3.4.1: Gantt chart

CHAPTER 4 RESULTS AND DISCUSSION

4.1 DATA GATHERING AND ANALYSIS

In this project, CL-10 and IL-10 are the proposed surfactant and sulfonates used as existing surfactant. The selected were varied in parts per million based on weight of chemicals used. Bulk solution need to be prepared based on the calculation. The procedure to prepare the bulk solution and sample was divided into several basic steps as below:

Step 1: Firstly, the amount of each chemical has been used such as CL-10, IL-10, sulfonates, sodium chloride powder and distilled water need to be calculated in unit gram and measured by using weighting equipment as per Attachment 1

Step 2: The chemicals were mixed with distilled water based on required amount by using heater and magnetic stirrer.

Step 3: Then, the surfactants were prepared based on the required surfactants concentrations and salinity parameters.



Figure 4.1.1: Solution samples with various concentrations



Figure 4.1.2: Solution samples with different salinity

Figure 4.1.1 and figure 4.1.2 show a few samples that have been prepared in the laboratory which are sulfonates, CL-10 and IL-10 with various concentration and salinity. The selected surfactant concentrations were varied in parts per million based on weight of chemicals been used.

Interfacial tension measurement:

In this experiment, IFT were measured by using OCA 15 pendant drop equipment through measurement of contact angle of oil droplets in the surfactant solution. The equipment test configuration is bottom up measurement. Before running the Pendant drop equipment, the densities of each solution samples need to be measured by using densitometer.



Figure 4.1.3: Measurement of IFT between crude oil and surfactants solution

4.2 RESULTS AND DISCUSSION

In using pendant drop equipment, solubility of surfactant solution samples must be clear and transparent to enable the camera to capture the crude oil droplets. So, the solubility of solution samples must be considered carefully in screening of IFT measurement. Besides that, the color of solution samples must be contrast with the oil droplets to allow the Pendant drop equipment processes the captured image. After that, the Pendant drop equipment calculated the IFT values accurately based on the size of droplets. Precipitation also will affect the accuracy of the Pendant drop measurement when the boundary line cannot be created according to size of droplets. The accuracy of Pendant drop equipment enhanced by applying these procedures and the experiment can be achieved successfully.

Effects of surfactants concentration on IFT reduction:

The salinity and temperature are constant variables which are 30,000 ppm of salinity and temperature at 23°C. Three types of surfactants solution at different concentration were prepared and measured their IFT values by using Pendant drop equipment.



Figure 4.2.1: Effects of surfactant concentration on IFT for different surfactants at 23°C

Figure 4.2.1 illustrates the effect of surfactant concentration on IFT for three different surfactants. The figure shows clearly that surfactant ability to reduce IFT is different. The IFT values decrease exponentially for both surfactant. After a certain surfactant concentration, the IFT values drop very slight with the increase of surfactant concentration. This point is called as critical micelle concentration (CMC). CMC point is the economical point for surfactant flooding. After reaching the CMC point, the surfactant concentration no longer affects the IFT values as the concentration continually increased. The results from the experiment also found out and investigated by previous researchers [4, 10, 12, 13, 15]. By comparing three of surfactants, it looks like the IL-10 and CL-10 follow the trend of existing surfactant which is sulfonates. This indicates that the IL-10 and CL-10 are the good surfactant behavior in reducing IFT values. Based on the figure, it shows that the CMC point for the sulfonate is 3.07 mN/m at 0.2 wt% of concentration. The IL-10 CMC point is 4.63 mN/m at 0.04 wt% of concentration which is much lower concentration as compared to sulfonates (1:5 ratio). The CL-10 CMC point is 11.59 mN/m at 0.2 wt% which is same as sulfonates CMC point. However, the effectiveness of this concentration has yet to be studied at reservoir conditions

Effects of salinity on IFT reduction:

The surfactant concentration and temperature are constant which are 1000 ppm of surfactant concentration and temperature at 23°C. Three types of surfactants solution at different salinity were prepared and measured their IFT values by using Pendant drop equipment.



Figure 4.2.2: Effects of salinity on IFT for different surfactant at 1000 ppm of concentration

The 10 wt% bulk solutions of brine were prepared and diluting with the surfactant solutions and distilled water. Figure 4.2.2 illustrates the effect of salinity on IFT for three surfactants. The figure shows that IFT decline exponentially as the salinity increased for three surfactants. After a certain salinity, the IFT values drop very slight with the increase of salinity. This point is called as optimum salinity. Optimum salinity point is the economical point for surfactant flooding. By comparing three of surfactants, the IL-10 and CL-10 follow the trend of existing surfactant which is sulfonates. This indicates that the IL-10 and CL-10 are good surfactant. Based on the figure, it shows that the optimum salinity for the sulfonate is 3.51 mN/m at 2.7 wt% of salinity. The IL-10 optimum salinity is 5.45 mN/m at 2.7 wt% of salinity which is same as sulfonates but the value of IFT is higher than sulfonates. The CL-10 optimum salinity is 5.07 mN/m at 2.7 wt% of salinity which is same as sulfonates but the value of IFT is higher than sulfonates. The figure indicates that after the optimum salinity, the IFT no longer affects by the salinity as the salinity continually increased. The results from the experiment also have been seen and investigated by previous researchers [10, 12, 13, 15].

CHAPTER 5 CONCLUSION AND RECOMMENDATION

5.1 CONCLUSION

The recent studies showed capability of ionic liquid based surfactants in reducing IFT. By reducing the IFT value, the capillary number, N_C will be increased thus the mobility ratio can be increased and aiding the residual oil to flow. Concentration and salinity are the parameters that can affect the IFT measurement. Based on the experiment conducted, the IFT tends to decrease with the increasing of surfactant concentration and salinity. The critical micelle concentration (CMC) point for IL-10 is at 400ppm of concentration at 23°C of temperature. While the CMC point for sulfonates is at 2000ppm of concentration also at 23°C. The result shows that the CMC point of IL-10 is lower than sulfonates (1:5 ratio). The capability of sulfonates in reducing the IFT values lower than IL-10. Basically, the trend line and characteristics of ionic liquids are most likely the same as the existing anionic surfactants which is sulfonates in reducing IFT measurement. Further study need to be measured by using selected range to test other parameters. Hopefully the IFT result in this experiment can be used for further adsorption test in coreflooding experiment to investigate the behavior and capability of the new surfactants in recovery oil at reservoir conditions.

5.2 RECOMMENDATION

It is recommended that the lab facilities must be equipped with the high resolution in IFT measurement to obtain accurate data. Besides, the equipment in the lab should be in proper condition so that the students can use the equipment according to scheduled time to prevent any delays and problems to run the experiment. Also sufficient time frame must be scheduled to complete the experiment successfully. Continuation of the study on coreflooding experiment needs to be run to get more data for modeling and correlating the new candidate of surfactants as good surfactants in recovery oil. However, there are some parameters that should be considered such as surfactant behavior by temperature, pressure and any other related parameters.

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APPENDICES



Attachment 1: Weighting equipment



Attachment 2: Heater