Experimental Evaluation of SMART Surfactant (UTP-SmartSurf) Derived From Natural Oil for EOR Application

By

Mohammad Hanif Bin Md Rosdi

Dissertation submitted to the Chemical Engineering Programme Universiti Teknologi PETRONAS in partial fulfilment of the requirement for the Bachelor of Engineering (Hons) (Chemical Engineering)

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Certification of Approval

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Approved by,

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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.

MOHAMMAD HANIF BIN MD ROSDI

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I would like to take this opportunity to thank everyone whom had given their support and help throughout the whole period of completing this project.

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ABSTRACT

In this report we will show the progress of the project, understanding and some important ideas that have been developed along the way for the past two months. Surfactants are very important in providing strategies for Chemical Enhanced Oil Recovery (CEOR). The idea behind this project is to modify the surfactant from inedible fatty acid of jatropha oil by epoxidation. Surfactant can reduce the interfacial tension (IFT) of water from 72 mN/m to 0.001 mN/m. To do so, the chemistry of surfactant is analyzed to understand way to modify the surfactant. Initial selection of surfactants is based upon desirable surfactant structure. The characterization of the surfactant will be study in few manners which are IFT that comprised of GC, HPLC, GC-MS and spinning drop method.

This report will show the analysis of microemulsion testing and IFT measurement of Natural Surfactant. The degree of improvement by using Natural Surfactant is compared with few standard bench marks (oil-water IFT value, types of crude oil and commercial surfactants). It is been evaluated quantatively and qualitatively throughout the experiment.

In this paper, IFT of Natural Surfactant is investigated in many ways and methods, and some interesting conclusions are obtained, which will make an important effect on research of SMART Surfactant (Natural Surfactant) theory. Besides, it also includes investigating the reason of ultra-low interfacial tensions and providing suggestions on designing formulations for practical application.

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CHAPTER 1 INTRODUCTION

1.1 Background of study

EOR is enhanced oil recovery to produce incremental oil from a depleted oil well. Oil remains stuck in the rocks due to high interfacial tension IFT between oil and brine. Surfactant will reduce the IFT value so that more oil can be dislodged from the rock. Surfactant is synthesized from natural oil in our laboratory. We report the IFT and microemulsion evaluations of the surfactant and found out that the surfactant performed as well as the commercial surfactants. It is cheaper, environmentally friendly and possesses a high temperature resistance.

World has been concerned of oil depleting and still lack of proven technology for replacing these energy resources since 1960s. One important technology challenge is to increase crude oil production to meet the increasing demand for energy worldwide. Even maintaining current oil production is becoming difficult due to maturity of the well.

In America, out of the total of 649 billion barrels, only 22 billion barrels remain that are recoverable easily by conventional means. On the other hand, new enhanced oil recovery (EOR) methods offer the prospect of recovering as much as 377 billion barrels of oil from already existing properties; this is about twice the amount of cumulative crude oil produced to date [1]. This goes same to any oil and gas plant that important to Malaysia. For an example, as in record from 2005, the Malaysian oil reserves atands at 3.5 billion stock-tank barrels (BSTB) and the cumulative oil production is 4.9 BSTB. These figures translate to an average oil recovery factor of 34%. There is 17.5 BSTB of petroleum resources remaining in the ground. In Malaysia, crude oil reserves have been declining since 1994. Around 66% of the Estimated Ultimate Recovery (EUR) has been produced and now entering maturity stage. Maturity stage normally associated with less production rates, high Gas to Oil Ratio (GOR) and water cut and low reservoir pressure [10]. All of currently available chemical EOR is based on one or more of two principles which are (a) increasing the capillary number means reducing oil-water interfacial tension. Chemical EOR has long been actively involved in many researches around the world.

Chemical EOR methods involve injection of chemicals to the reservoir. These agents modify fluid properties to make them more favorable for oil recovery. The principle chemical EOR methods include injection of polymers, surfactants and alkaline chemicals. Although increasing in some countries, chemical EOR never gained widespread in some countries like USA due to the high cost of chemical agents, and has been declining.

1.2 Problem Statement

Commercial surfactants are expensive and derived from petrochemicals. Because of our dependency on foreign surfactants it does not allow us to tailor make a surfactant that is unique for our oil well. Besides the determination of IFT and phase behavior of the natural surfactants requires and extensive fundamentals study of surfactant and EOR in order to give a better insight and better understanding approach of its physic-chemical properties. In addition, the experimental results of the IFT and behavior of surfactant would give credible information to analyze the ideal specifications and requirements of surfactants for EOR.

1.3 Objective and Scope of Investigation

The objectives of the research are:

- i. To study Interfacial Tension (IFT) and determine the optimum IFT value of SMART Surfactant for Enhanced Oil Recovery (EOR) by using Spinning drop tensionmeter.
- ii. To determine the microemulsion performance and thermal degradation of the SMART Surfactant towards enhanced oil recovery (EOR).

The research will be more specifically by characterizing and investigating natural surfactant from jatropha oil. Further research will be done to investigate the surfactant via detailed characterizations such as IFT.

CHAPTER 2 LITERATURE REVIEW

2.1 THEORY OF EOR

EOR is a technique to increase the production of a crude oil in the oil fields. One way it can be achieved is through Chemical injection or CEOR. There are many surfactants for EOR has largely been studied. It is important to realize that there is no universal surfactant good for every possible application. Different surfactants are needed for different applications, e.g. for wetting and foaming. That is the reason why so many different commercial surfactants are in use. The surfactants studied in this work have different useful properties.

2.1.1 Description of Oil Recovery

The objective of enhanced oil recovery is to economically increase displacement efficiency. The key factor is the mobility ratio - is a function of viscosity and relative permeability, which in turn depends on saturation. The EOR involves mobility control of various kinds that can:

- change oil and water viscosities
- change interfacial tensions
- change oil and water saturations

A. Primary Recovery

Using only the natural energy of reservoirs, typically recover up to 50% of oil originally in place (OOIP), average 19%. The primary production is the oil produced by the original reservoir drive energy. It depends on the type of the reservoir drive, oil viscosity and reservoir permeability but average 30% to 35% of the oil in place and can be as low as 5%. This leave a considerable amount of oil in the reservoir after the pressure has been depeleted, and is classified as improved oil recovery. Ultimate oil recovery is the total production from the well or filed by primary production waterflood and EOR, is justified by economic condition.

B. Secondary Recovery

Involves adding energy to the natural system by injecting water to maintain pressure and displace oil (also known as waterflood). Typical recoveries are 25-45% OIP after primary recovery at average 32%.

C. Tertiary Recovery

Includes all other methods used to increase the amount of oil recovered. Typically recoveries are 5-20% of OIP after the primary and secondary recovery (average 13%). The secondary and tertiary recoveries are together referred to as EOR. Tertiary recovery includes chemical, thermal and miscible gas drive.

There are four principle groups of EOR technologies available:

- CEOR
- Microbial EOR
- Thermal EOR
- Miscible EOR



Figure 1-1: Enhanced oil recovery methods

2.1.2 Chemical Enhanced Oil Recovery

Chemical enhanced oil recovery involves a variety of techniques used to mainly modify the mobility of the aqueous phase during displacement. In the polymer flooding, the objective is to reduce the mobility of the aqueous displacing phase by increasing the viscosity. The overall result is a reduced, and hence more favorable, mobility ratio. Surfactants have a different effect. In surfactant or micellar floods these molecules 'scrub' residual oil from pores by reducing IFT and creating emulsions or dispersions of hydrocarbon in the aqueous phase. The action is to release oil by reducing, initial oil saturation (Soi), and hence increase the moveable oil volume (MOV).

- 1. Polymer Flooding
- 2. Micellar Flooding
 - This method uses the injection of a micellar slug into a reservoir. The slug is a solution usually containing a mixture of a surfactant, co-surfactant, alcohol, brine and oil that acts to release oil from the pores of the reservoir rock [24].
- 3. ASP Flooding
 - ASP flooding is a combination of alkaline, surfactant and polymer which tends to cooperate themselves in its behavior.
- 4. Surfactant Flooding
 - Surfactant flooding is used to reduce the interfacial tension of the oil and rocks in the reservoir. New generation surfactants will tolerate high salinity and high hardness so there is no practical limit for high salinity reservoirs. Sulfonates are stable at high temperatures. Thus, good surfactants are available for both low and high temperature reservoirs.

Favorable Characteristics for Surfactant Flooding

- · High permeability and porosity
- High remaining oil saturation (>25%)

• Light oil less than 50 cp but recent trend is to apply to viscous oils up to 200 cp or even higher viscosity

• Short project life due to favorable combination of small well spacing and/or high injectivity.

- · Good geological continuity
- Good source of high quality water

• Reservoir temperatures less than 300 F for surfactant and less than 220 F if polymer is used for mobility control

- 5. Alkaline Flooding
 - Alkaline flooding or caustic flooding involves injection of NaOH or KOH into reservoir. These chemicals react with organic acids in-situ to produce soap-like surfactants. This process is not well understood in any quantitative way. The technique has yet established itself and only a limited number of field trials have been undertaken with limited success. Because NaOH and KOH are cheap and readily available, caustic flooding is the expensive EOR process. Some recent successes suggest that the method may have considerable potential because of its significant cost advantage. In common with micellar floods, alkaline floods are chased with the polymer pad for mobility control. For this reason only *highly permeable reservoirs* are candidates for the technique.

2.1.3 Technical Challenges in EOR

All Malaysian producing fields are located offshore. Operating EOR in offshore environment is technically challenging. Some of the most common problems associated with offshore operations such as large well spacing and limited space at the platform (surface). So far, only about 9% of world wide EOR application is in offshore environment. Nearly 70% of the 157 existing platforms installed are more than 20 years old. Gas injection pipeline, especially with CO₂ handling capability does not exist. Major infrastructure development is needed, hence major investment is expected for the completion of the project [2] [10].

2.2 THEORY OF SURFACTANT

Surfactants are widely used and of their remarkable ability to influence the properties of surfaces and interfaces. Surfactant may be applies in encountered at all stages in petroleum recovery and processing industries, from oil well drilling, reservoir injection, oil well production and surface plant process to pipeline and seagoing transportation of petroleum emulsion.

2.2.1 What is Surfactant?

Surfactants are wetting agents that lower the surface tension of a liquid, allowing it to be easier to spread and lower the interfacial tension between two liquids [16]. Surfactants work through a process known as "adsorption," which means that they accrete on the surface of a liquid, creating a film which reduces its surface tension [12].

2.2.2 What is Surface Tension?

Surface tension is a tension of a liquid to its surface. Surface tension has the dimension of force per unit length.

2.2.3 What is Interfacial Tension (IFT)?



Figure 1-2: Interfacial Tension

Interfacial tension is almost similar to surface tension. The main forces involved in the interfacial tension are adhesive forces (tension), between the liquid phase and of one phase of one substance. The interaction occurs at the surfaces of the substances involved.

2.2.4 How oil and water make one phase?

Water and oil exist in one phase through emulsion. In the microemulsion, the mixture of oil and water are unstable. It can be stabilize by adding the wetting agent like surfactants. Then a more stabilize one phase (microemulsion) will be formed. These molecules contain a polar group (soluble in water) and an aliphatic tail (soluble in oil). They optimize their interactions and reduce the oil-water interface and the interfacial energy, y [13] [14].

General classification of surfactants

Surfactants are also called active agents. A simple classification of surfactants based on the natural of hydrophilic group is commonly used. Three main classes may be distinguished, namely anionic, cationic and amphteric.

- 1. Anionic surfactants (SDS)
- 2. Non-ionic such as polyoxyethlene alcohol
- 3. cationic surfactants (trimethyllammonium bromide)
- 4. Polymeric surfactants

2.2.5 Emulsification

Microemulsions are macroscopically homogeneous and thermodynamically stable mixtures of a surfactant, oil and water. On a microscopic level, they consist of oil-domains separated from water-domains by a surfactant film (see Figure below).



In general, a surfactant film between oil and water is flexible with regions of both positive (towards oil) and negative (towards water) curvatures [20] [21]. Emulsification thus involves the formation of a liquid-liquid interface.

Microemulsions contain both non-polar and polar domains, allowing many applications. Microemulsions are good solvents of both organic and inorganic compounds, which is a useful property, for example, in catalyzing the hydrolysis of fat compounds. They can be characterized using a range of methods such as rheology or turbidimetry measurements.

Macroemulsions (often called just emulsions), on the other hand, are not thermodynamically stable. Here, surfactants are used to retard the breakdown process. The emulsification properties of a surfactant can be predicted relatively well using the HLB concept. Two surfactants of different HLB values (one low and one high) are often used in emulsification formulations. This gives the best possible performance, since the surfactants can complement each other's properties.

In practical formulations, the emulsion stability and character is also temperature dependent and the character of the oil. Formation of thermodynamically stable microemulsions requires that the surface tension is extremely low (often formed from surfactants having a low CPP-value) or else that emulsions may form instead (see Figure 5). A w/o microemulsion in equilibrium with excess oil is called a Winsor I system, a o/w microemulsion in equilibrium with excess water is called a Winsor III system and a microemulsi on in equilibrium with both excess water and oil is called a Winsor II system [21] [23].

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2.2.6 Critical Micelle Concentration (CMC)

It well known that the physicico-chemical properties of surfactant vary marketable and above a specific surfactant concentration. Below the CMC value, physicico-chemical properties of ionic surfactant like SDS (e.g., conductivity, electromotive force measurement) resemble those of strong electrolyte above cmc values. These properties change dramatically, indicating a highly cooperative association process is taking place.

The CMC values are very important in virtually all the petroleum industry. For instance, a number of improved or enhanced oil recovery processes involve the use of surfactant including micellar, ASP and gas flooding. In these process, surfactant must usually be present at concentration a higher than the CMC because the greatest effect of the surfactant whether in interfacial tension lowering [*fluid displacement studies in uniformly wetted porous media. New york, academic press*] or in promoting foam stability, is achieved a significant concentration of micelles present, the cmc is also of interest because at concentration above the value of adsorption function function of surfactant from which nearly maximum adsorption occurs.

2.2.7 Surfactant Derived from Natural Products (Jatropha)

Why is it important to use naturally occurring starting materials for the syntheses of surfactants? The existing commercial surfactants are mostly based on slowly degradable compounds and in not too few cases they are, or at some point during their degradation become, harmful to the environment or to human beings. The reasons for choosing natural raw materials are several:

1. Renewable starting materials

Natural raw materials are renewable, since they are derived from continuous ecological cycles. They are constantly produced in nature and thus, in principle, available for commercial use with little risk of shortage.

2. Cheap starting materials

Materials produced in nature are sometimes easy to obtain and purify, which results in low prices. Examples are sucrose, lactose, D-fructose, D-glucose, fatty acids and terpenoids.

3. Lower toxicity, less environmental impact

Since nature provides the starting materials, there are microorganisms that are adapted to the degradation of the products. When the surfactants are degraded into their natural, smaller components (i.e. hydrophobic and hydrophilic ones) it is assumed that they are included into the natural ecological cycles, without any significant toxicological impact.

4. Commercially feasible

For the various reasons mentioned (cheapness, non-toxicity etc.) surfactants derived from natural products offer a good substitute for existing surfactant types.

5. Inedible

Jatropha is poisonous and inedible. Thus it has no competition in any food industry.

Fatty Acids	Compositions (Percent)
Oleic Acids	42.4
Linoleic Acids	35.2
Palmatic Acids	14.7
Stearic Acids	6.9

2.2.8 The used of Jatropha oil for chemical EOR surfactant

Table 1: Jatropha Oil Compositions

Advantages:

- It starts producing seeds within 12 months
- Maximum productivity level is 4-5 years
- Plant remains useful for around 35-50 years
- Seeds can produce around 37% oil content
- Kernels can produce up to 60% oil content
- Its seeds yield an annual equivalent of 0.75 to 2 tons of biodiesel per hectare
- It is a "Non-Food Crop"

2.3 THEORY OF CHARACTERIZATION

2.3.1 Interfacial Tension (IFT)

The main characteristic of surfactants is to lower the interfacial tension between an aqueous solution and some other phases. As discussed in 2.3.2, ultra low (0.001 mN/m) IFT can be achieved when middle phase or microemulsion or better known as emulsion is measured between aqueous phase and oil phase. Alkali plays important role and will affect the IFT values during experiment or when oil/ water aged [28].

Degree of trapping is a function of a parameter defined as 'capillary number' as Shown below:

```
N_c = V * \mu / \sigma
```

Where,

V = velocity $\mu =$ viscosity

 σ = interfacial tension.

The higher the Capillary number, the higher will be the oil flow rate and hence oil production. From the equation, IFT is interrelated with Capillary number. Capilary number increases by addition of **Polymers** into the producing well, as polymers increase the viscosity of the displacing fluid – i.e. water. **Heat** reduces viscosity of oil and hence oil flow increases in comparison to water. **Surfactants** added to the water decreases interfacial tension, so the separation between oil and water is faster than without addition of surfactants. Many Secondary recovery processes are variants of water flooding

Injected alkaline is likely to be useless in oil displacement due to alkaline consumption. Generally, alkaline consumption is due to the reactions of alkaline–oil, alkaline–reservoir water, and alkaline–reservoir rock. Alkaline–oil reaction is necessary and useful, because that alkaline reacts with oil to form a low or ultralow IFT favorable for oil displacement.

For IFT measurement, we have used Spinning Drop Tensionmeter. In order to run the experiment accurately, density and Refractive Index of the prepared samples should be determined. Densitymeter of Anton Paar DMA 5000M and Refractometer of ATAGO RX 5000 are used during the experiment was carried out.

2.3.1.1 Overview of Principles of Spinning Drop Tensionmeter

This technique relies on the fact that gravitational acceleration has little effect on the shape of a fluid drop suspended in a liquid, when drop and the liquid are contained in a horizontal tube spun about its longitudinal axis as shown in figure below:



Figure 2-1: Dimension of IFT measurement

At low rotational velocities (o), the fluid drop will take on an ellipsoidal shape, but when o is sufficiently large, it will become cylindrical. Under this latter condition, the radius (r) of the cylindrical drop is determined by the interfacial tension, the density difference (Dr) between the drop and the surrounding fluid, and the rotational velocity of the drop. As the result, the interfacial tension is calculated from the following equation [30].

$$\gamma = \frac{1}{4}r^3\Delta\rho\omega^2$$

Spinning drop method (rotating drop method) is one of the methods that is used to measure interfacial tension. Basically, measurements are carried out in a rotating horizontal tube which contains a dense fluid. One drop of a less dense liquid is placed inside the fluid. Since the rotation of the horizontal tube creates a centrifugal force towards the tube walls, the liquid drop starts to be elongated and this elongation stops

when the interfacial tension and centrifugal forces are balanced. Values obtained at this equilibrium point are used to estimate surface tension of the particular liquid by using appropriate correlations. A device called "spinning drop tensiometer" is generally utilized for this purpose.

The device and software that will be use in the experiment will be SVT-20. Calculation of interfacial tensions from the shape of rotating drops (spinning drops) according to the Young-Laplace equation as well as according to the Vonnegut approximation for sufficiently extended droplets

- a. Laplace Young (Interfacial Tension LY)
- b. Caylas Schechter Wade (Interfacial Tension CSW)

2.3.1.2 Overview of Principles of Densitymeter of Anton Paar DMA 5000M

Almost all laboratory density meters, both the paar range and the instruments derived form them by Japanese company, Kyoto, have a measurement cell comprising a borosilicate glass U tube inside a thermostated jacket. This typically holds about 0.7 ml of sample [29].



Figure 2: Oscillating U-tube density meter DMA5000

The U tube is oscilated at its fundamental frequency, which is a function of the system mass. If we assume that the sample volume trapped between the oscilation nodes is constant, it can be seen that the oscillation frequency is therefore a function of sample density [29].

2.3.1.3 Overview of Principles of Refractometer of ATAGO RX 5000

Refractometry is a technique that measures how light is refracted when it passes through a given substance, in this case, an unknown compound. The amount by which the light is refracted determines the refractive index (RI). Refractive index can be used to identify an unknown liquid compound, or it can be used as a means of measuring the purity of a liquid compound by comparing it to literature values (Chem 211: Refractrometry). The closer the refractive index is to the literature values, the purer the sample. Refractive index is very important since it is related to such fundamental thermodynamic properties as solvent density, phase composition, solute concentration, and interfacial tension. Refractive index is defined as the ratio of the velocity of light in air to the velocity of light in the medium being measured: $\eta D = [V \text{ air}]/(V \text{ liquid})$. The RI of a substance is strongly influenced by temperature and the wavelength of light used to measure it, therefore, care must be taken to control or compensate for temperature differences and wavelength (Answer.com: Refractrometry).

2.3.2 TYPE OF MICROEMULSIONS

2.3.2.1 Winsor Phase Types [22]

The most perfect flooding system in EOR is Winsor type III microemulsion, in which the equilibrium of the middle microemulsion, the low (aqueous) phase and the upper (oil) phase is reached. The microemulsion can solubilize in the oil as well the aqueous, and the IFT will reach an ultra low value between the microemulsion and the aqueous or oil phase under a certain condition, and the surfactant will be concentrated in the middle microemulsion [27].

Type I Type III Type II

Oil
Aqueous Phase
Microemulsion Phase

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Winsor Type I Behavior

- Oil-in water microemulsion
- Surfactant stays in the aqueous phase
- Difficult to achieve ultra-low interfacial tensions

Winsor Type II Behavior

- Water-in-oil microemulsion
- Surfactant lost to the oil and observed as surfactant retention
- Should be avoided in EOR

Winsor Type III Behavior

- Separate Microemulsion phase
- Bicontinuous layers of water, dissolved hydrocarbons
- Ultra-low interfacial tensions (0.001Mn/m)
- Desirable for EOR



2.3.3 IFT & MICROEMULSIONS



Solubilization of oil and water phase with respect to available surfactant forms the basis of the solubilization ratio parameter used for microemulsion characterization. The interfacial tension is estimated using the equation from (1979) as shown above.

The solubilization ratio can be measured while the mixture is in incubated in the oven. By plotting a graph of as in appendix 1 for expected results, IFT can be calculated at optimum solubilization ratio.

The IFT is needed to bring down to ultra low value such as 0.001dynes/cm in order to make the brine and oil miscible.



Figure 2-3: Oil miscible in brine

2.3.4 Screening and Refinement

Phase behavior mixtures had to pass several screening criteria to be further considered for a core flood design. A bi-continuous Type III microemulsion that existed at or near optimum salinity would need to visually appear gel/macroemulsion free, low viscosity, and free-flowing at interfaces. Quantitatively, this microemulsion needs a solubilization ratio equal to or greater than 10 at optimal salinity, and an equilibration/coalescence time of less than 7 days [26]. A high oil and water solubilization ratio at optimal salinity is correlated with an ultra-low interfacial tension, which is the key mechanism driving surfactant-based chemical EOR.

2.3.5 Relation of IFT and Winsor type of Microemulsion

The IFT is related to Winsor type of surfactant described surfactant/oil/water microemulsions as type I (oil in water), type II (water in oil) or type III (bicontinuous oil and water in third phase known as the middle phase microemulsion).

2.3.6 Dispersion

The ability of a surfactant to solubilize ordinarily insoluble particles or aggregates of molecules is called the dispersion ability. Dispersion can be studied by e.g. turbidimetry or rheology measurements [21].

Dispersion is the ability to solubilize ordinarily insoluble particles into a solution by forming micellar structures around those particles. In this thesis, the dispersion properties of a large number of surfactants were studied by solubilizing carbon black into water and then evaluating the turbidity of the solutions.

2.3.7 Detergency and Displacement of Oil

Detergency involves the action of surfactant to alter interfacial properties so as to promote removal of a phase from solid surface. Obviously, wetting agents are used, and usually those that rapidly diffuse and adsorb at appropriate interfaces are more effective. When a drop of oil in water comes into contact with solid surfaces, the oil may form a bead on the surface or it may spread and form a film. A liquid having strong affinity or the solid will seek to maximize its contact (interfacial area) and a form a film. A liquid with much weaker affinity may form into bead; this affinity is termed the wetability. Since there can be a degree of spreading another quantity is needed. The contact angle, in oil-water-solid system is defined as the angle measured through the aqueous phase that is formed at the junction of the three phases. Where, as interfacial tension is defined for the boundary between the two phases, the contact angle is defined for the three phases.

2.3.8 Recent Works

Natural Surfactant synthesized by using Jatropha oil as an ester is first published by UTP [32]. Currently this project is still under ongoing research. The first Surfactant (UTP-SmartSurf) synthesized was evaluated and discussed in this report. Previous experiment also was conducted using different type of Surfactant and was compared with commercial Surfactant (See Appendix 1.A1).

CHAPTER 3

METHODOLOGY

3.1 Synthesis of Unsaturated Fatty acid surfactants

- 1. Jatropha oil will be dried well and then methyl esters and fatty acids will be obtained by transesterification.
- 2. The esters will be analyzed by GC for purity and completion of reaction.
- 3. The esters will be epoxidized by using suitable method like per acid-H₂O₂ treatment.
- 4. Analysis of peroxide will be done by GC.
- 5. The resultant peroxides will be hydrolyzed to hydroxyl groups.
- 6. These hydroxyl groups will be then corrected to esters having long ethyl chains.
- 7. The resultant esters having dry ester chains will be sulfonated by chlorosulfonic acid to synthesize α -sulpho fatty acid methyl esters.
- 8. Resultant surfactants will be characterized for the surface properties like IFT, Surface Tension etc.

3.1.1 Characterization for synthesis

There are several ways to characterize the synthesized surfactant:

3.2.1 Gas Chromatography (GC)

A gas chromatograph is a chemical analysis instrument for separating chemicals in a complex sample. Typical uses of GC include testing the purity of a particular substance, or separating the different components of a mixture (the relative amounts of such components can also be determined). In some situations, GC may help in identifying a compound. In preparative chromatography, GC can be used to prepare pure compounds from a mixture.[17] [18]

3.2.2 High performance liquid chromatography (HPLC)

HPLC is a method to separate, identify, and quantify compounds based on their idiosyncratic polarities and interactions with the column's stationary phase. [15].

3.2.3 Gas chromatography-mass spectrometry (GC-MS)

GC-MS is a method that combines the features of gas-liquid chromatography and mass spectrometry to identify different substances within a test sample [16].

3.2.4 Spinning Drop Method

This method is one of the methods that is used to measure interfacial tension [19]. The spinning drop is used to calculate the elongated oil droplet after it is being centrifuged to a certain revolution and elevated temperature.

3.2 Process Experimental Procedure for Characterization

Evaluation of Natural Surfactant will take place in orderly manner to achieve optimum formation of microemulsion at ultra low interfacial tension value. Variables such as Surfactant, Alkalinity, Salinity and Co-solvents are varied in concentration in order to get the best formulation for microemulsion.

I. Surfactant

Natural Surfactants (Alpha-Sulfonate Methyl Esther) synthesized by Chemical Engineering Department of Universiti Teknologi PETRONAS and Sodium Dodecyl Sulfate (SDS) are used for experimental study.

II. Co-Solvent

The benefits of flushing with cosolvents may result from increase in solubilization within the aqueous phase or through the more efficient process of mobilization. Co-solvent used for this experiment is Iso-Propane-Alcohol (IPA), Butanol and Octanol.

III. Alkali/ Salts

Alkali used in the study is Sodium Carbonate (Na_2CO_3) and is compared with Sodium Hydroxide (NaOH) and Sodium Metaborate. The addition of alkali to surfactant, flooding in the 1980s reduced the amount of surfactant required, reduced the IFT results and increase microemulsion performances [25].

IV. Crude Oil

Crude oils used in the study are from Dulang Oilfield.

Next, steps to achieve for microemulsion variables are shown as below:

- A. Checking the variable of the effect on IFT reduction on alkalinity at 1% Surfactant Concentration, 2% salinity. (with Alkali at 0.2% is used)
- B. Checking the variable of the effect on IFT reduction on types of Co-solvent (2%), 1% Surfactant Concentration, 2% salinity and 0.2% alkalinity (if and only if alkalinity can bring effect on the IFT reduction)
- C. Checking the variable of the effect on surfactant concentration from 0.01% to 1%, 2.0% salinity and 0.2% alkalinity (if and only if alkalinity can bring down the IFT reduction) and Co-solvent (if and only if co-solvent can bring effect on the IFT reduction)
- D. Checking the effect of alkali concentration with optimum surfactant concentration and its effect to IFT from 0% to 1.5%.

*Note that Co-solvent added is at least twice the amount of surfactant concentration.

Summary of details of the whole experimental evaluation can be interpreted as in block diagram below:



Figure 3-1: General evaluation concept for Natural Surfactant for EOR (Green block is where the evaluation is currently concerned)

3.3 Characterization: Evaluation of Natural Surfactant

Surfactants Concentration used are dependable on previous evaluation (0.5%, 1.0%, 1.5% and /or 2.0%). Further evaluation will be done based on different salinities at best formulation for the natural surfactant to form microemulsion at ultra low interfacial tension.

1-1K-NS	1k
1-10K-NS	10k
1-20K-NS	20k
1-30K-NS	30k
1-40K-NS	40k

Table 3-2: Measuring at different salinity and code

```
Notes:
Amount of co-solvent will be double that of surfactant
Key:
CS = With co-solvent
NS = No co-solvent
CS = isopropylalcohol Or iso butanol
pH = 9.5 to 10.0
```

A. Prepare Aqueous EOR solutions and experiment procedure for Microemulsions

- 1. Prepare a solution of brine as shown below*
- * By applying Mass= (M) (V) (MW) \rightarrow E1
- 2. Salt to be use is Sodium Chloride (NaCl).
- 3. Example for solutions preparation is as described below:
 - 1000ppm of salt concentration is equivalent to 1000mg/L. Convert 1000mg/L to molarity (mol/L).
 - Molecular Weight (MW) of NaCl is 58.443 g/mol. Volume of Volumetric flask, 250ml.
 - Thus, $1000 \text{mg/L} \div 58.443 \text{g/mol} = 0.017 \text{M} = 0.017 \text{ mol/L}$.
 - By applying E1, mass of NaCl needed to produce 0.017M of salt concentration is 0.2484g.
 - The solutions are prepared by using the deionizer water

4. However the equal molar volume is produced for the aqueous phase as seen below.

Crude Oil Total Volume = 2ml

Aqueous phase Total Volume = 2ml

Alkəli = 10.09	6 Na2CO3	(5g in 50ml)	UURT = 376
	litition		
1.00%	2.00%		Cor
0.8	1.6		
	de de proven		
2.00%	4.00%		3
Alkat			
0.20%			4
6.4			=

a a casali	
Senter (Senter)	
Û	C
2000	0.04
5000	0.1
8000	0.16
10000	0.2
15000	C.3
20000	0.4
30000	0.6
40000	0.8
50000	1

- $C_1V_1=C_2V_2$ is used to calculate the salinity that should be added at the desired concentration after having the salinity stock ready, say at 10%.
- 5. To evaluate the preparation samples, Brine water, crude oil and surfactant are added in the same volume in each sample to yield 4ml of solution.
- 4 Preliminary observation in order to determine if any gel formation in the samples by shaking them. If the mixture is highly viscous, leave the sample.
- 5 Keep the samples at reservoir condition by setting the temperature in the oven at 50°C.
- 6 For this experiment two ways of measuring the results are by:
 - Quality assessment Observation of the phase types and stability at 50°C
 - Quantity assessment IFT measurement to estimate the desired mixture of microemulsions that produce low interfacial tension value. (See B)
- 7 If possible measure the microemulsion levels using the markings on the pipette or glass tubes. Analyze the volumes (and compare the volumes) and volume fractions with respect to salinity and time.
- 8 Record data.

B. IFT Procedure

- 1. The samples are prepared for IFT testing for at least 10ml aqueous phase separately from crude oil.
- 2. Density meter, Model Anton Paar DMA 5000 is used to determine density of the all aqueous phase and crude oil samples at desired temperature (50°C)
- 3. RI index is measured for all aqueous phase samples at 50°C.
- 4. Spinning drop is used for the IFT measurement.
- 5. IFT between oil top layer and bottom layer will be measured by a spinning drop tension meter
- 6. Place the glass of the mixture in the equipment.
- 7. Set at desired temperature $(50^{\circ}C)$ and rotation speed (17 ms/rev)
- 8. Switch on the equipment and allow the solution to stabilize.
- 9. Spinning continue until observing an equilibrium condition.
- 10. Record data when IFT is measured from spinning drop tension meter.

3.4 Equipments for Experimental Work

No	Parameter	Equipment & Principle	Location
1	Density Temperature range: (20-	Density meter ANTON PAAR DMA5000 The density of a sample is defined as mass divided by volume. It uses	
	90)°C	the principle of oscillating U-tube method. The sample is introduced into a U-shaped borosilicate glass tube that is being excited to vibrate at its characteristic frequency.	Block 4, Level 1 (Ionic Liquid Lab)
2	Refractometer Temperature range: (20- 80)°C	ATAGO RX 5000 - an automatic digital refractometer which can set measurement temperature internally	Block 4, Level 2

		 Has a thermo-module to control temperature, a constant temperature water bath is not necessary. The refractive index at your targeted temperature is speedily displayed. High refractive index ± 0.00004 accuracy can be obtained. 	
3	Interfacial Tension	Interfacial Tension SVT-20 Measurements are carried out in a rotating horizontal tube which contains a dense fluid. One drop of a less dense liquid is placed inside the fluid. The tube creates a centrifugal force towards the tube walls, the liquid drop starts to be elongated and this elongation stops when the interfacial tension and centrifugal forces are balanced.	Block 4, Level 2

Table: 3-2: Equipments' parameters and principles

3.5 Project Flow

Summary for the procedures can be interpreted as shown in diagram below:



Figure 3-2: Summary of steps taken for Characterization experiment for Natural Surfactant for EOR by IFT measurement. (A=Optimum Alkaline, S=Optimum Surfactant, B=Optimum Brine)

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 IFT testing on Surfactant with and without Alkalinity

Density/of (endies of the	0.814 g/ml	
	50 deg Celcius	
Alkalinity	0.20%	Na ₂ CO ₃
Sufferant		
Concentration	1.00%	
Salinty	2.00%	NaCl

Samples en		banely (gm)		
With Alkaline	1-20k-A	0.835	1.33289	0.1583
Without Alkaline	1-20k-WA	0.936	1.33828	0.7804

Table 4-1: Results on IFT testing on Surfactant with and without Alkalinity



Figure 4-1: Effect of combined alkalinity 0.2% with surfactant on IFT

We report our first initial observation and evaluation by comparison of the effect of alkali in surfactant aqueous phase. Sodium carbonate is chosen because of the proven effectiveness in many researches [28]. 0.2% of Sodium Carbonate was injected into the 1% of Surfactant in 10ml aqueous phase solution and another sample was prepared without Sodium carbonate. The result shows a sharp decrease in IFT is recorded between with alkali and without alkali at 0.16 mN/m and 0.78 mN/m respectively. Thus, alkali is useful to bring the IFT to low value with natural surfactant and Dulang crude oil which favorable for oil displacement. Small amount of alkali with surfactant could bring down IFT to a low value. Thus, Surfactant combined alkali is preferable.

4.2 The Effect of Co-Solvents in Natural Surfactant Aqueous Solution

Density of Crude Of	0.814 g/ml	
Temperature	60 deg Celcius	
Alkelinity	0.20%	Na ₂ CO ₃
Stituciant Concentration	1.00%	
Salimity	2.00%	NaCl

Scorpte .	Code - 19 - 1		Rhain San H	
IPA	1-20k-A-IPA	0.99333	1.3388475	0.235 Yellow, Clear Solution
Butanol	1-20k-A-Butanol	0.99728	1.33786	0.258 Yellow, Clear Solution
Octanol	1-20k-A-Octanol	0.9966	1.38342	0.172 Dark Yellow, Slugish Solution

Table 4-2: Results on IFT testing on Surfactant with different co-solvents



Figure 4-2: Effect of different co-solvents on IFT

Three different co-solvents were used to evaluate their effect on surfactant aqueous solutions. All three co-solvents comprises of at least 4 carbon-chains to 10 carbon-chains. Butonol results in the highest IFT (0.258mN/m) followed by IPA and Octanol at 0.235 mN/m and 0.172 mN/m. The data was recorded for 250 runs with 10 seconds interval (Approximately 45 minutes).

Unlike the solubility enhancements caused by partitioning into micelles or microemulsions, solubility enhancements caused by cosolvent addition generally occur because of changes in the bulk properties of the isotropic solution. As with mixed surfactants, advantages are gained by using mixed cosolvents. Short chained linear alcohols are excellent in solubilizing small

chlorohydrocarbons, whereas, larger hydrocarbon cosolvents work best for larger and more hydrophobic contaminants. Addition of short linear alcohols also enhances the solubility of the larger cosolvents. From this graph, emulsion formation was seen fast compared without cosolvent. Thus, the benefits of flushing with co-solvents (Iso-Propane-Alcohol (IPA), Butanol and Octanol) result in increase in solubilization within the aqueous phase or through the more efficient process of mobilization on the reaction with natural surfactant. The IFTs were increasing with time which ensure that the mixture of surfactant solution with cosolvent only increase in tendency of microemulsion formation and not reducing IFT as a whole.

Density of Crude Oil	0.814 g/ml
Temperature	50 deg Celcius
Alkaliziny	0.20% Na ₂ CO ₃
Salinity	2.00% NaCl

		depression (game)	B	EtioNa
0.01	0.01-20k-A	1.002645	1.3389	0.597
0.02	0.02-20k-A	1.002702	1.33522	0.521
0.03	0.03-20k-A	1.002846	1.33522	0.435
0.05	0.05-20k-A	1.00308	1.33526	0.358
0.08	0.08-20k-A	1.00318	1.33542	0.228
0.10	0.10-20k-A	1.00325	1.33531	0.159
0.15	0.15-20k-A	1.003943	1.336695	0.118
0.20	0.20-20k-A	1.003447	1.33601	0.083
0.25	0.25-20k-A	1.003406	1.33567	0.078
0.30	0.30-20k-A	1.003929	1.336785	0.09
0.40	0.40-20k-A	1.003982	1.33581	0.11
0.50	0.50-20k-A	1.00416	1.33573	0.121
0.70	0.70-20k-A	1.004761	1.33592	0.136
1.00	1.00-20k-A	1.005582	1.3361	0.155

Table 4-3: Results on the effect of different concentration of Surfactant toward IFT



Figure 4-3: The effect of Surfactant concentration toward IFT

In this experiment, the main target is to selectively identify the sample which has the lowest IFT values. IFT is decreasing with increasing of surfactant concentration. First IFT is recorded at 0.01% up 1% in order to find optimum concentration that brings the IFT to the lowest. IFT of surfactant 0.01% is the highest and sharply decreased until it reaches 0.25%. At 0.25%, IFT is

recorded the lowest confirmed by extended surfactant concentration up to 1%. IFT can retain optimum at 0.25% and slightly increase after that value. This is because with increasing of surfactant concentration, the surfactant is concentrated to bring the IFT to low value thus taking effect in increasing of IFT. During the reduction of IFT, surfactant in excess of 2% brine been adsorbed into oil and reacted with brine until it reaches equilibrium.

Most of oil reservoirs in Malaysia possess high salinity content compared to other oil reservoirs, and therefore specific CEOR must be design in order to tolerate the salinity content and at the same time maintains recovery efficiency. This explains why various surfactant concentrations are important to be evaluated for fluid-fluid evaluation testing, so that it would comply with the chemical nature f the injection and produced water. This surfactant is optimum at 0.25% which bring to conclusion that this surfactant performed better than any other commercial surfactant that uses crude oil as a synthesize oil that ranging between 1% to 5% to perform at its optimum.

4.4 The Effect of Alkali (Na₂CO₃) Concentration Towards IFT Behavior

Lensity of Crucker Oil	0.814 g/ml	
Temperature	50 deg Celcius	
Surfaciona concentration	0.00%	
Service	2.00%	NaCl
Alkalinity	Na ₂ CO ₃	

Alkan	Gente	Density (d/mil)	RI	
and a matching the first				
0.20	0S-20k-0.2A	1.003161	1.33488	15.173
0.40	0S-20k-0.4A	1.003700	1.33539	13.533
0.60	0S-20k-0.6A	1.005027	1.33561	10.311
0.80	0S-20k-0.8A	1.006397	1.33570	8.197
1.00	0S-20k-1.0A	1.011622	1.33801	7.895
1.20	0S-20k-1.2A	1.013561	1.33834	7.437
1.50	0S-20k-1.5A	1.016417	1.33907	6.911

Table 4-4: Results of the The Effect of Alkali (Na₂CO₃) Concentration Towards IFT Behavior



Figure 4-4: The effect of alkali concentration towards IFT

The effect of alkali is seen through increase in alkali concentration without surfactant. With increase in alkali concentration, further reductions of IFTs are observed up to 1.5% alkali. Alkali

is confirmed to play an effective role in reducing IFT. If surfactants were absorbed at the oil/water interface, the water resistance could be reduced to impulse the residual oil at a proper mobility ratio. Based on this principle, several enhanced oil recovery (EOR) processes, such as the micellar, the alkaline, the polymer and the combination flooding, have been designed for the possible application in tertiary oil recovery, the most simple and low-cost one being the alkaline flooding.

Injected alkaline is likely to be useless in oil displacement due to alkaline consumption. Generally, alkaline consumption is due to the reactions of alkaline-oil, alkaline-reservoir water, and alkaline-reservoir rock. Alkaline-oil reaction is necessary and useful, because that alkaline reacts with oil to form a low or ultralow IFT favorable for oil displacement [31]. The effect of alkaline has brought great attention due to its effect of reducing IFT to 15 mN/m and 7 mN/m with minimum 0.2% and maximum 1.5% respectively (based on determination from end experimental result). Increase in alkali concentration results in lowering IFTs value. At 0.2% alkali is consumed enough into surfactant or aqueous solution and crude oil to naturalize them. Thus results in less IFT value reduction. Increasing alkali concentration results in lowering the IFTs value. However, IFT is slowly reduced from 0.8% to 1.5%. Alkali is almost reaching its equilibrium condition in naturalizing the surfactant aqueous phase and crude oil. Alkali is saturated and cannot function in lowering IFT anymore may result in precipitation. Precipitation should be avoided in reservoir due to high contaminants dissolved solids such as Mg²⁺ and Ca²⁺ that could reacts with alkali to form precipitation. Precipitation may results in damaging the depleted reservoir and blockage the pores of the rock. This result will be discussed further in next experiment on different types of alkali.

4.5 Experimental Comparison Data

- Sample C	Ctate	density /		
Deonized water	0S1-Dw	0.98861	1.3326	46.00
Formation water	FW	1.00334	1.33613	68.75
0 Surfactant with 1% NaOH	0S1-20k-A2	1.01329	1.33872	8.53
Optimum Surfactant w/o Alkali	0.25S1-20k-A1	1.01109	1.33989	0.25

Table 4-5: Experimental Comparisons data

The whole experiment results shown that natural surfactant (UTP-SmartSurf) has high potential to be commercialized in EOR industry by comparing the data obtained with some benchmarks. UTP-SmartSurf has given great impact on lowering IFT to low value by having formation water at IFT of 68.75 mN/m while alkali at 1.5% only able achived IFT at 7 mN/m. On the other hand, 0.25 % surfactant with only 0.2% alkali gives result of the lowest IFT value at 0.078 mN/m. While without alkali at 0.25% gives 0.25 mN/m. This means that the minimum lowering IFT by comparison of surfactant and alkali concentration deviation for desired IFT are:

% Deviation = (Results – Desired Results)/ Desired Results x 100%

Note: 1 Fold = 100% $(7 - 0.001)/0.001 \ge 100\% = \underline{699 \ge 10^3 \text{ or } 699 \text{ folds (minimum deviation for alkali)}}{(0.25 - 0.001)/0.001 \ge 100\% = \underline{24 \ge 10^3 \text{ or } 240 \text{ folds (Deviation for Surfactant without alkali)}}{(0.078 - 0.001)/0.001 \ge 100\% = \underline{7.7 \ge 10^3 \text{ or } 77 \text{ folds (minimum deviation for Surfactant)}}$

Clearly, the deviation values largely deviates from the desired figure based on theory but has also brought down from initial value before formulations. This managed researches from foreseen the effect of chemically synthesized surfactant when combined or reacted in different formulations. Thus, this proven that Surfactant has given great impact in lowering IFT value. This also triggers several possible ideas to enhance the results such as by increasing the alkali and surfactant concentration or trying different types of alkali. Besides, different types of oil also could be tested.

Variables	Na ₂ CO ₃	NaOH	NaBO ₂	NaBO ₂
	1%	1%	1%	2%
	11	13	9	9
	Cloudy, high precipitate	Cloudy. Medium	Clear, No precipitate	Clear, little precipitate
		precipitate		
	10, 10,			
salati kata kata kata				

4.5 Observation of the effect of different alkali in seawater

Figure 4-5: Observation of the effect of different alkali in seawater

Different types of alkali and its concentration were used and varied in the experiment to determine if precipitation occurs. The solutions are mixed with Dulang seawater and kept at 70° C for a week. The results obtained are as shown in the table. pH is important in this case. Higher concentration in alkali might cause precipitation in the reservoir if the alkali selected tends to reacts with seawater having mg²⁺ or Ca²⁺ ion to precipitate. This may cause the pore in the reservoir containing oil to block and might also damage the formation. As a result, no oil could be recover from the well and need to shut down. This experiment shown that Sodium Carbonate reacts with seawater to form higher precipitation as compared from other alkali. Sodium Metaborate shown the most excellent behavior when no precipitation is observed at 1% concentration



4.6 Thermal Gradation Analysis (TGA) of UTP-SmartSurf

Figure 4-6: Thermal Gradation Analysis (TGA) of UTP-SmartSurf

Thermal gradation of surfactant-1 is observed by using TGA. Graph of derivative weight loss in percent with respect to temperature is observed. The surfactant starts to degrade and having a weight loss at 200°C and reaches the highest weight loss at 232°C. At this point some part of of long chain hydracarbon (hydrophobic tails) that used to attract/ dissolves in oil is degrading. More degradation occurs at the point where temperature reaches 388°C. This part, some of hydrophilic is degrading. Long chain hydrocarbon reacts as to attract oil and hydrophilic to attract water. Since some part of long chain hydrocarbon loss at 232°C, the surfactant is assuming to loss some of its effectiveness to able to attract oil. However, this degrading temperature for UTP-SmartSurf has exceeded the actual temperature in Dulang Oilfield. This concludes that, this surfactant is a success for further evaluation in laboratory work or pilot in near future.

4.7 Microemulsion Tests



Figure 4.7: Microemulsion formation (middle phase) between crude oil and aqueous solution

The IFT experiment conducted has results in good behavior of microemulsion generation in tests conducted. The middle phase is very stable after few days and recorded as shown in figure 4.7. The best formulation is selected based on from IFT experiment and compared with microemulsion. The sample is kept at same temperature for few days and shown a good potential result to further investigate on this surfactant. Maximum microemulsion generation showed a good sign of potential maximum oil displacement in reservoir.

CHAPTER 5 CONCLUSIONS

The objectives of the project/ FYP II have been achieved in the given time frame:

- iii. To study the effect of alkali with surfactant
- iv. To study the effect of co-solvents
- v. To find the optimum surfactant concentration
- vi. Extended study of effect of alkali Na₂CO₃
- vii. To study the effect of different types of alkali
- viii. To study Interfacial Tension (IFT) and determine the optimum IFT value of SMARTSurfactant for Enhanced Oil Recovery (EOR) by using Spinning drop tensionmeter.
- ix. To determine the microemulsion performance and thermal degradation of the SMART Surfactant towards enhanced oil recovery (EOR).

Overall results obtained shows that an overall performance of (UTP-SmartSurf) and its effect on alkaline. UTP-SmartSurf performed well by only 2500ppm surfactant needed to bring the IFT to a low value as compared to alkaline performances. Besides that, UTP-SmartSurf has outperformed some commercial surfactant that is more expensive in nature and high dependency on economic fluctuations. This is due to the basic material used to synthesize surfactant as compared to UTP-SmartSurf which is better performance in IFT, cheap and environmental friendly. UTP-Smartsurf has high potential to be further evaluated in detail either in laboratory work or pilot and currently is a success to our own, unique, Dulang Oilfield.

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APPENDICES

Appendix 1

A1: Graph of Interfacial Tension (mN/m) over Surfactant Concentration, %

Resource: Khaled A. Elraies, Isa Bin Mohd Tan, Ismail Saaid (2008), Synthesis and Performance of New Surfactant for Enhanced Oil Recovery, Geoscience & Petroleum and Chemical Engineering Department, Universiti Teknologi Petronas, 2009.



A2: Snapshot of oil droplet in aqueous solution in IFT SVT-20



A3: Structure of Surfactant Type 1, alpha-sulfonated oleic acid methyl ester