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RHEOLOGICAL PROPERTIES OF SYNTHESIZED SURFACTANTS

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CERTIFICATION OF APPROVAL

RHEOLOGICAL PROPERTIES OF SYNTHESIZED SURFACTANTS

By

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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.

SHAHROL HAIRY BIN SAMSUDIN

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1.0 ABSTRACT

Surfactants are surface-active substances of complex lipids. In nature, surfactants are substances consisting of lipoprotein that is secreted by the alveolar cells of the lung and serves to maintain the stability of pulmonary tissue by reducing the surface tension of fluids that coat the lung [1]. From other point of view, surfactants act as 'soap'. It has the ability to reduce the surface tension of a fluid that is in contact with a solid wall by breaking the strong adhesive forces between the fluid and the wall. A synthesized surfactant can be produced by the reaction of a fatty acid and a base.

Basically, the project is divided into 2 major phases:

1. Synthesizing a surfactant
2. Characterizing the Rheological Properties of The Synthesized Surfactants

For the first phase, fatty acids will be extracted from palm oil and purified. The purification involved 4 steps: bleaching palm oil color, deodorization, hydrolysis, and phase separation. Then, the fatty acids produced from the purification of palm oil process will be reacted with a strong base (potassium hydroxide) in saponification process to form a surfactant. In the second phase, the rheological properties of the synthesized surfactant were evaluated. The study of rheological properties of surfactant will comprised boiling point determination, conductivity of surfactant at different concentrations, and surfactant viscosity over time for various temperature, and phase separation. A critical concentration dependency is demonstrated by the surfactant on the properties investigated.

2.0 TABLE OF CONTENTS

3.0 INTRODUCTION

3.1 BACKGROUND STUDY

Conventional primary and secondary recovery of petroleum operations often leave two-thirds of the oil in the reservoir. In the U.S., enhanced oil recovery methods have the potential to recover much of the remaining oil. However, oil recovery is challenging because the remaining oil is often located in regions of the reservoir that are difficult to access, and the oil is held in the pores by capillary pressure [2]. During primary recovery, the natural pressure of the reservoir drives oil into the well bore, and artificial lift techniques (such as pumps) bring the oil to the surface. Only about 10 percent of a reservoir's original oil is typically produced during primary recovery. Since shortly after World War II, producers employ secondary recovery techniques to extend the productive life of oil fields, often increasing ultimate recovery to more than 20 percent. For the most part, those techniques involve injecting water to displace oil, driving it to the well bore [2]. In some cases, natural gas is re-injected to maintain reservoir pressure, thus driving oil into the well bore (natural gas is often produced simultaneously with the oil from a reservoir).

However, by injecting high pressure into the reservoir will cause instability to the reservoir structure. It may cause the reservoir to collapse. Thus, there is a limit in the pressure that can be used to push the oil to the surface.

3.2 PROBLEM STATEMENT

The Enhanced oil recovery technology by using synthesized surfactants basically deals with the removal of residual non-aqueous-phase liquids (NAPLs) trapped in the pore spaces of the aquifer. The removal of NAPL is frequently inefficient and expensive using conventional technologies such as pump-and-treat, due to the low solubility and rates of dissolution of NAPL **[2]**. The problem is overcome by injecting a surfactant solution while simultaneously extracting water to maintain hydraulic control over the movement of the surfactant solution and the mobilized contaminants. Surfactant flooding is followed by water flooding to remove residual oil and injected chemicals. Conventional wastewater treatment technologies may be used to process the extracted effluent so long as surfactant foaming can be controlled, such as with the addition of an anti-foaming agent. Fluid mechanics and the understanding of the it's phases are essential. The flow properties have become crucial in using surfactant as oil recovery strategy. A study on the rheological behaviors of the synthesized surfactant is performed over wide temperature condition.

3.3 OBJECTIVES AND SCOPE OF WORK

The objectives and purposes of this project are:-

1. To prepare a fatty acid by extraction of palm oil
2. To prepare a surfactant by saponification of a fatty acid by using a strong base
3. To study and define the rheological properties of synthesized surfactants through experiments

4.0 LITERATURE REVIEW

The conventional way of oil recovery process could achieve at most 40%-50% of the total quantity of oil in a certain oil reservoir. Thus, research and development of enhanced oil recovery technology has been extensively carried out to optimize oil recovery. The research and development of enhanced oil recovery could be divided into six areas: chemical methods; gas flooding; microbial processes; thermal processes; novel methods, and computer simulation. For this project, we will focus on the use of a synthesized surfactant.

Chemical Methods

Chemical method focuses mainly on alkaline-surfactant-polymer (ASP) that involves the injection of micellar-polymers into the reservoir. Chemical flooding reduces the interfacial tension between the in-place crude oil and the injected water, allowing the oil to be extracted. Micellar fluids are composed largely of surfactants mixed with water. Goals of polymer floods are to shut off excess water in producing wells, and to improve sweep efficiency to produce more oil. Chemical field trials by industry indicate that surfactants can recover up to an additional 28% of reservoir oil; however the economics have not been favorable when the price of oil is factored against the cost of surfactants and polymers.

Chemical flooding technologies are subdivided into alkaline-surfactant-polymer processes, polymer flooding, profile modification, and water shut off methods. Surfactants are surface-active substances of complex lipids and acting as 'soap'. It has the ability to reduce the surface tension of a fluid that in contact with a solid wall by breaking the strong adhesive force between the fluid and the in contact wall. Surfactants are usually organic compounds that contain both hydrophobic (oleophilic) and hydrophilic groups, and are thus semi-soluble in both organic and aqueous solvents.

Surfactant

A synthesized surfactant could be produced from the reaction of a fatty acid with a base. The fatty acid could be obtained from the extraction of palm oil. There are 2 main steps to produce surfactant; purification process and saponification process. The purification process is done to produce fatty acid for the saponification process. The purification process is divided into 4 steps; Bleaching oil color, deodorization, hydrolysis and distillation of fatty acid from oil contaminant.

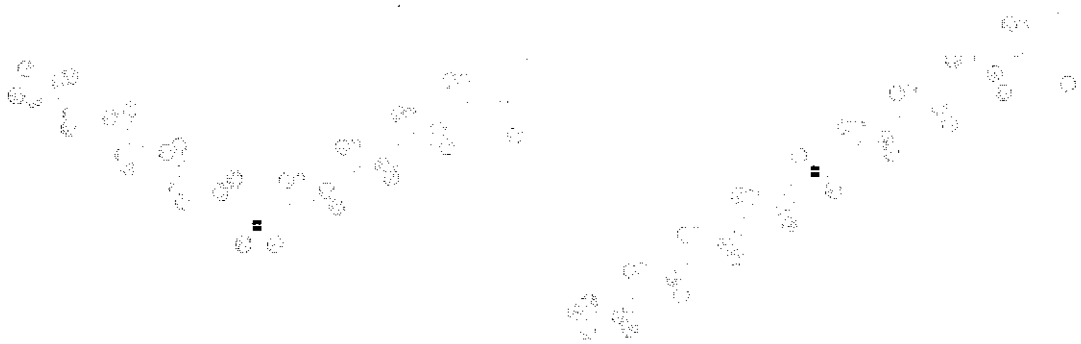
Lipids consist of numerous fatlike chemical compounds that are insoluble in water but soluble in organic solvents. Lipid compounds include monoglycerides, diglycerides, triglycerides, phosphatides, cerebrosides, sterols, terpenes, fatty alcohols, and fatty acids. Dietary fats supply energy, carry fat-soluble vitamins (A, D, E, K), and are a source of antioxidants and bioactive compounds. Fats are also incorporated as structural components of the brain and cell membranes.

Common Fatty Acids

Fatty acids consist of the elements carbon (**C**), hydrogen (**H**) and oxygen (**O**) arranged as a carbon chain skeleton with a carboxyl group (**-COOH**) at one end. **Saturated fatty acids** (SFAs) have all the hydrogen that the carbon atoms can hold, and therefore, have no double bonds between the carbons. **Monounsaturated fatty acids** (MUFAs) have only one double bond. **Polyunsaturated fatty acids** (PUFAs) have more than one double bond. Refer Table 1.0.

Fatty Acid Configurations

Double bonds bind carbon atoms tightly and prevent rotation of the carbon atoms along the bond axis. This gives rise to *configurational isomers* which are arrangements of atoms that can only be changed by breaking the bonds.



Cis-9-octadecenoic acid (Oleic acid)

Trans-9-octadecenoic acid (Elaidic acid)

Figure 1.0: Fatty acids configuration

These three-dimensional molecular projections show the *Cis* and *Trans* configurational isomers of 9-octadecenoic acid with the hydrogen atoms shown in blue. The Latin prefixes *Cis* and *Trans* describe the orientation of the hydrogen atoms with respect to the double bond. *Cis* means "on the same side" and *Trans* means "across" or "on the other side". Naturally occurring fatty acids generally have the *Cis* configuration. The natural form of 9-octadecenoic acid (oleic acid) found in olive oil has a "V" shape due to the *Cis* configuration at position 9. The *Trans* configuration (elaidic acid) looks more like a straight line.

Cis Configuration

Trans Configuration

Figure 2.0: Fatty acid –cis and –trans configuration

Extraction Methods

There are numerous oils and fats obtained from plant and animal sources that are used for hundreds of culinary, pharmaceutical, and cosmetic products. Some of the oils and fats are produced with refining or rendering processes that usually involve heat and some are simply obtained through pressing. Oils that are obtained through cold extraction, such as olive oil, are usually more expensive than highly refined oils and fats obtained through high heat extraction methods.

Cold Extraction Methods	
Cold Pressed	Cold pressing refers to oils obtained through pressing and grinding fruit or seeds with the use of heavy granite millstones or modern stainless steel presses, which are found in large commercial operations. Although pressing and grinding produces heat through friction, the temperature must not rise above 120°F for any oil to be considered cold pressed. The maximum temperature for cold pressed olive oil is somewhat lower. Olive, sesame, peanut, and sunflower are among the oils obtained from cold pressing. (Highly refined versions of these oils are also produced.) Cold pressed oils retain all of their flavor, aroma, and nutritional value.
Vacuum Extraction	Vacuum extraction is another method of cold extraction that produces oils with an expeller process. The process occurs in an atmosphere with no oxygen or light. The temperature during the expeller process may be as low as 70°F.

Heat Extraction Methods	
Expeller Pressed	Expeller pressing is like cold pressing except that extreme pressure is added during the pressing. As much pressure as 15 tons per square inch is used to squeeze the oil from the fruit or seeds. The high pressure also produces high heat (as high as 300ºF) through friction, so the oils produced with the expeller process cannot be considered cold pressed. The oils obtained with this method retain much their flavor, aroma, and nutritional value, but not to the extent of cold pressed oils.
Solvent Extraction	Chemical solvents are used to extract oil, which is then boiled to eliminate most of the solvents. Further refining such as bleaching, deodorizing, and heating to high temperatures cleanses the oil, resulting in a product that has very little of the original flavor, aroma, or nutrients contained in the seeds or fruit before processing. Most of the oils produced with this method have a high smoke point and a long shelf life.

Table 1.0: Palm oil extraction method

Saponification Process

The saponification process can be simply done by titration of a fatty acid with a strong base such as potassium hydroxide or sodium hydroxide. A fatty acid is titrated with a strong base (NaOH or KOH) to form a salt with polar end (hydrophilic) and non-polar end (hydrophobic or oilphilic). Phenolphthalein is used as the indicator.

$$\begin{array}{lllllll} CH_2OOC\text{-}R & & & & CH_2OH & & \\ \vert & & & & \vert & & \\ CHOOC\text{-}R & + & 3\ KOH & \longrightarrow & CHOH & + & 3\ R\text{-}COOK \\ \vert & & & & \vert & & \\ CH_2OOC\text{-}R & & & & CH_2OH & & \end{array}$$

Oleic Acid, R = $CH_3\ (CH_2)_7\ (CH)_2\ (CH2)_7$

Palmitic Acid, R = $CH_3\ (CH_2)_{14}$

Stearic Acid, R = $CH_3\ (CH_2)_{16}$

Figure 3.0: Titration process of fatty acid with potassium hydroxide

Rheological Measurements of Surfactant

Rheological measurements of surfactant involved the studies of the surfactant's flow properties. Rheological measurements and properties of synthesized surfactant consist of the investigation of shearing flow, extensional flow and mixed flow. For the shearing flow, the test will further divide into; flow geometries, transient shear viscosity, steady-state shear viscosity, storage and loss moduli, types of rheological response and defining Deborah Number, Weisseberg Number and Peclet Number. For this project, the rheological test or measurements of surfactant consists of the conductivity of surfactant at different concentration, test of turbidity, and pH test for surfactant at various concentrations.

5.0 METHODOLOGY

5.1 EXPERIMENTAL PROCEDURES

For this final year research project, the methodology of the project has been divided into three major parts which are:

i. Research and Literature Review

Basically, this is the most important step in order to complete the task successfully. The research and literature review process is done by internet surfing, books reference, and journal review. The research is divided into 3 main topics; extraction of fatty acids from palm oil, saponification process of a fatty acids and a strong base, and the rheological test or measurement for surfactant.

ii. Synthesizing a surfactants by extraction of Palm Oil

This process is divided into 2 main phase; extraction of fatty acids from palm oil and saponification process of a fatty acids and a strong base. For the first phase, there are 4 steps involved in order to purify the palm oil and to extract fatty acids from the palm oil. Those steps are:

i. Bleaching palm oil color

Palm oil is filled into a 1000mL beaker and heated up to 70 °C. Hydrogen peroxide (30%) is slowly added into the palm oil and the mixtures are continuously stirred. The mixture is left for 3-4 hours while the mixture is continuously stirred and the temperature is maintained at 70 °C. After 3-4 hours, it is observed that 2 layers occurred. The upper layer is yellowish in color and the lower layer is colorless. The upper layer (yellowish) is the bleached palm oil and the lower layer is the hydrogen peroxide. The mixture is physically separated. The upper layer is prepared for the deodorization process while the lower layer is considered as waste.

ii. Deodorization

A few spatula of activated carbon added into the sample (bleached palm oil). The mixture of bleached palm oil and activated carbon is left for 1 day. Activated carbon is used to deodorize the palm oil. After 1 day, the color of the mixture of bleached palm oil and activated carbon is observed to be darker than before adding the activated carbon. The sample (palm oil and activated) is separated by the aid of TSS apparatus. After the filtration, the color of the palm oil is observed to be clearer. The activated carbon obtained from the filtration process is considered as waste.

iii. Hydrolysis

This step is done using hydrolysis apparatus. A heating mantle is used to heat up the distilled water in the 500mL round bottom flask. Distilled water is heated up to its boiling point (100 °C). The distilled water is observed to start to boil at a temperature of higher than 100 °C (102 °C – 103 °C). This is might be because of the distilled water or the round bottom flask itself containing impurities. A beaker is placed at the outlet of the distillate for the hydrolysis apparatus. The stem produced is supplied into the sample oil (distillate outlet of the apparatus). The task of this process is to initiate the hydrolysis process of stem and the palm oil. After half an hour, the sample is observed to have 2 layers. The upper layer is yellowish in color (fatty acids) and the lower layer is colorless (alcohol). The process is stopped when there is no change in the sample oil anymore.

iv. Phase separation/ Distillation of ester from oil contaminants

The purpose of this process is to separate the fatty acids from the alcohol. The process is done based on the phase separation principle, which the solution with lower boiling point will be evaporated and separated from the solution with higher boiling point. In this case, alcohol has lower boiling point compared to the fatty acids. The boiling point of various alcohols is in the temperature range of 70 °C -80 °C. In this process, the same hydrolysis apparatus is used, but the sample (fatty acids and alcohols) is placed in the 500mL round bottom flask. The sample oil is heated up to 70 °C -80 °C. The temperature is maintained throughout the experiment. The vapor formed (alcohol) is collected at the distillate outlet. The process is stopped until the lower layer of the sample oil (alcohols) is disappeared. At this point, the substance in the round bottom flask is the purified fatty acids and the substance in the beaker is the alcohols. The purified fatty acid is keep for the saponification process and the alcohols gained are considered as a waste.

Saponification of a fatty acid and a strong base

After completing the first phase, the fatty acids gained will be reacted with a strong base (potassium hydroxide) thru saponification process. The purified fatty acids containing phenolphthalein as an indicator will be titrated with potassium hydroxide until the color of the fatty acids turn pink (neutral). The volume of potassium hydroxide used is recorded. The process is repeated at different Molarity of potassium hydroxide. The state of surfactant formed is observed and recorded.

iii. Characterizing the Rheological Properties of The Synthesized Surfactant

For this process, the purposes are to study and characterize the rheological properties of surfactant through several experiments. Those experiments are;

a. Conductivity of surfactant at various concentrations

A few samples of surfactants are prepared at different concentration (10M, 1M, 0.1M, 0.01M, and 0.001M). The conductivity of each sample is determined by using conductivity meter. A graph of conductivity versus surfactant concentration is plotted.

b. Turbidity Test for Surfactant at various concentrations

A sample of surfactant solution is prepared at certain concentration (0.001M). The wave length of the solution is determined. The value of the wavelength is used for the UV absorbance test on different concentration of surfactant. A graph of UV absorbance (%) versus concentration (M) is plotted.

c. PH Test for Surfactant at various concentrations

A few samples of surfactants are prepared at different concentration (10M, 1M, 0.1M, 0.01M, and 0.001M). The pH of each sample is determined by using pH meter. A graph of pH versus surfactant concentration is plotted.

5.2 LIST OF CHEMICALS AND APPARATUS

Purification of Fatty Acids from Palm Oil

No	Process	Apparatus and Chemicals
1	Bleaching Oil Color	Weight balance, beaker, heater, thermometer, stirrer, Hydrogen Peroxides (30%), Palm Oil
2	Deodorization	Beaker, TSS Apparatus with pump, filter paper, activated carbon (charcoal)
3	Hydrolysis Process	Round Bottom Flask, Distillation Set, Thermal Heater (heating mantle), Thermometer, Silicon Tube, Conical Flask, Distilled water
4	Distillation of ester from oil contaminants	Round Bottom Flask, Distillation Set, Thermal Heater (heating mantle), Thermometer, Conical Flask

Saponification of Fatty Acids and Base

No	Process	Apparatus and Chemicals
1	Base Preparation	Weight balance, Volumetric Flask, Potassium Hydroxide (pellets)
2	Titration	Burette, Conical Flask, Volumetric Cylinder, Phenolphthalein (Indicator), Potassium Hydroxides solutions

Characterizing the rheological properties of the Synthesized Surfactant

No	Test	Apparatus and Chemicals
1	Conductivity of surfactant at various concentrations	Conductivity meter, beakers, surfactant at various concentrations (surfactant-solvent volume ratio) such as: 0.001, 0.01, 0.1, 1, 10, and distilled water
2	Turbidity Test for Surfactant at various concentrations	Shimadzu UV spectrophotometer, surfactant at various concentrations (surfactant-solvent volume ratio) such as: 0.001, 0.01, 0.1, 1, 10, and distilled water
3	PH Test for Surfactant at various concentrations	pH meter, beakers, surfactant at various concentrations (surfactant-solvent volume ratio) such as: 0.001, 0.01, 0.1, 1, 10, and distilled water

5.3 EXPECTED RESULTS

Purification of Fatty Acids from Palm Oil

No	Process	Expected Results
1	Bleaching Oil Color	- Reduction in palm oil color - Layers created between oil and hydrogen peroxide - Less palm oil collected during the separation of palm oil and hydrogen peroxides. Some hydrogen peroxides collected in the palm oil during separation process
2	Deodorization	- The oil mixed with activated carbon is black in colour - The mixture still contains hydrogen peroxides in it - The oil colour is slightly clearer than oil after bleaching process
3	Hydrolysis Process	- During hydrolysis process, two layers of oil exist - Upper layer: Yellow colour - Lower layer: Colorless

4	Distillation of ester from oil contaminants	- Bottom layer (alcohol) disappear - The colour of the oil turns pale - Fatty acid is obtained.

Saponification of Fatty Acids and Base

No	Process	Expected Results
1	Base Preparation	- Potassium Hydroxide (pellets) dissolve in the distilled water (solvent)
2	Titration	- Color of fatty acid turned pink after titrated with potassium hydroxide - Two layers exist after sometimes - The physical properties of the surfactant is more soap-like

6.0 RESULTS AND DISCUSSIONS

6.1 EXPERIMENTAL RESULTS

Purification of Fatty Acids from Palm Oil

No	Process	Results
1	**Bleaching Palm Oil Color**	- Reduction in palm oil color - 2 layers created which are upper layer (palm oil) and lower layer (hydrogen peroxide) - The upper layer is yellowish in color and the lower layer is colorless - A little amount of hydrogen peroxide collected during the physical separation of palm oil and hydrogen peroxides. - The lower layer (hydrogen peroxides) is considered as waste - The upper layer (bleached palm oil) collected is prepared for the deodorization process
2	**Deodorization**	- The color of the oil mixed with activated carbon is a bit darker than the bleached palm oil - The mixture still contains hydrogen peroxides in it - Activated carbon collected during the filtration process and considered as waste

		- After the filtration process, the oil color is slightly clearer than oil after bleaching process
3	**Hydrolysis Process**	- Distilled water boiled at temperature higher than 100 °C (102 °C – 103 °C) - The higher boiling point of distilled water might be caused by the presence of impurities in the distilled water or the round bottom flask itself - During hydrolysis process, colorless layer of substance slowly occurred at the bottom of the oil - **Upper layer**: Yellow color (fatty acids) - **Lower layer**: Colorless (alcohols)
4	**Distillation of ester from oil contaminants**	- The lower layer (alcohol) did not boil after heated up to 80°C - The lower layer (alcohol) still not boil after heated up to 95°C - The lower layer (alcohol) starts to boil at temperature of more than 100°C - The temperature is suddenly overshoot to more than 110 °C and drop back to 70 °C - The mixture temperature is out of control and some of the upper layer (fatty acids) pass through the distillate outlet of the apparatus - It's suspected that the lower layer is water instead of alcohol

Saponification of Fatty Acids and Base

No	Process	Results
1	Base Preparation	- Potassium Hydroxide (pellets) dissolved in distilled water (solvent)
2	Titration	- No change in color when phenolphthalein powder is added into the fatty acid - After sometimes, fatty acid's color change to pink in color and the titration is stopped - After a few hour, the pink solution changed into 2 layer solution: - The lower layer is purple in color - The upper layer is yellowish is color - The upper layer showing the physical properties of a soap - The upper layer dissolve in water when the solution is shake

Characterizing the rheological properties of the Synthesized Surfactant

a. Conductivity of surfactant at various concentrations

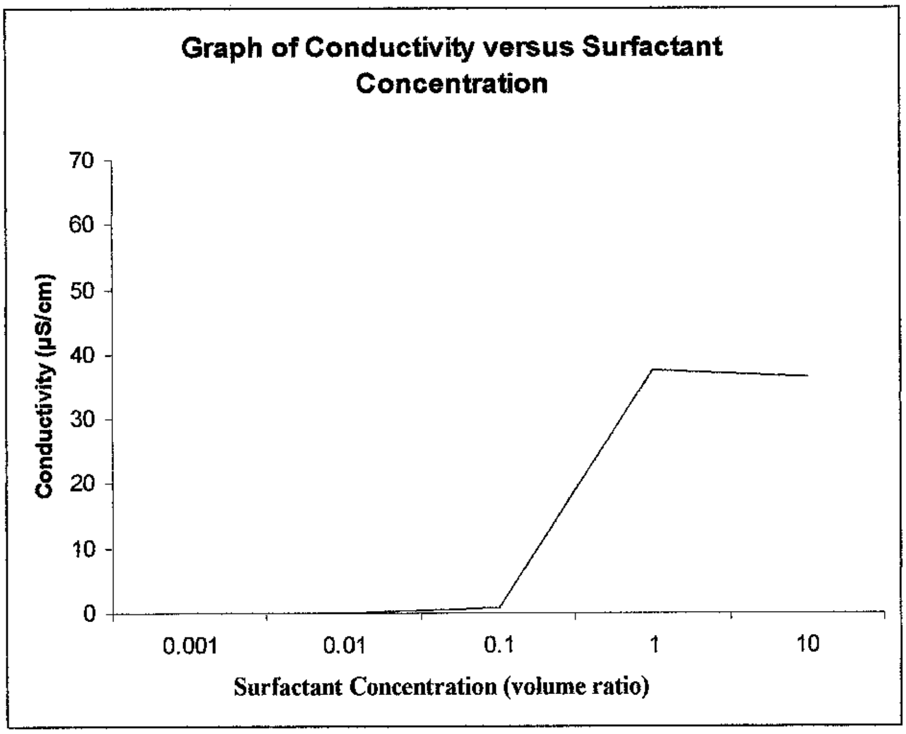


Figure 4.0: Graph of conductivity versus surfactant concentration

Surfactant Concentration (volume ratio)	Conductivity (µS/cm)	Sample's Temperature (°C)
0.001	0.01	26.5
0.01	0.06	26.4
0.1	0.93	26.5
1	37.6	26.5
10	36.4	26.4

Table 2.0: Table of conductivity at various surfactant concentrations

Conductivity (distilled water) = 1.85 µS/cm

b. Turbidity Test for Surfactant at various concentrations

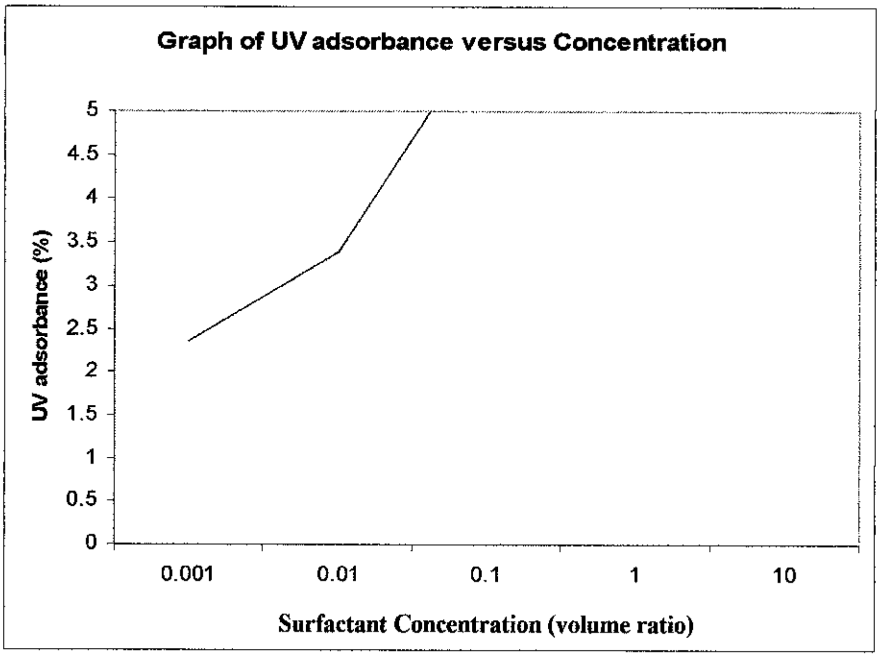


Figure 5.0: Graph of UV absorbance versus surfactant concentration

Surfactant Concentration (volume ratio)	UV absorbance (%)
0.001	2.357
0.01	3.385
0.1	-
1	-
10	-

Table 3.0: Table of UV absorbance at various surfactant concentrations

Surfactant's Wavelength = 210 nm

c. pH Test for Surfactant at various concentrations

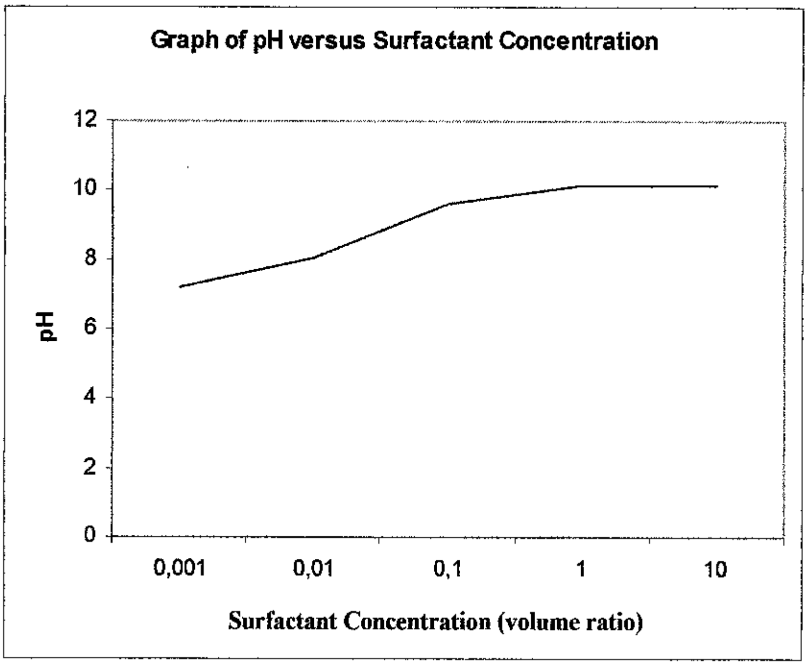


Figure 6.0: Graph of pH versus surfactant concentration

Surfactant Concentration (volume ratio)	pH
0.001	7.19
0.01	8.03
0.1	9.60
1	10.13
10	10.14

Table 4.0: Table of surfactant pH at various concentrations

pH (Distilled Water) = 7.04

6.2 DISCUSSIONS

6.2.1 Extraction of Fatty Acids from Palm Oil

Palm oil consists mainly of glycerides and, like other oils in their crude form, small and variable portions of non-glyceride components are also present. In order to render the oils edible, some of these non-glycerides need to be either removed or reduced to acceptable levels. In term of solubility study – glycerides are of two broad types: oil insoluble and oil soluble. The insoluble impurities consisting of fruit fibers, nut shells and free moisture mainly, are readily removed. The oil soluble non-glycerides which include free fatty acids, phospholipids, trace metals, carotenoids, tocopherols or tocotrienols, oxidation products and sterols are more difficult to remove and thus, the oil needs to undergo various stages of refining. The aim of refining is therefore to convert the crude oil to quality edible oil by removing objectionable impurities to the desired levels in the most efficient manner. This also means that, where possible, losses in the desirable component are kept minimal.

The purpose of the bleaching process is to remove any undesirable impurities (all pigments, trace metals, oxidation products) from Crude Palm Oil and this improves the initial taste, final flavor and oxidative stability of product. In this experiment, hydrogen peroxides are used as the bleaching agent. There is a reduction in the palm oil color after the bleaching process. Two layers of liquid are observed to occur after the bleaching process. Bottom layer is the waste hydrogen peroxides and the upper layer is the bleached palm oil (yellowish). The upper layer is separated from the bottom layer and prepared for the deodorization process. Some of hydrogen peroxides get into the bleached palm oil during the physical separation process. Thus, there are still some impurities in the bleached palm oil. The bleached palm oil is further treated by deodorization process to remove undesired components in the palm oil. During the filtration of palm oil from the activated carbon process, a TSS apparatus is used in order to accelerate the filtration process. The oil is prepared for the hydrolysis process.

Hydrolysis process is a process where palm oil is cleaved to its components by using steam. In this experiment, steam is supplied to palm oil and producing fatty acids and alcohol by using a hydrolysis apparatus. From experiments, distilled water boiled at 100 °C showing that less impurities in the distilled water. The steam is supplied to the palm oil and white bubbles appeared after sometimes. After a few hour of hydrolysis process, there are 2 layers of liquid formed. The upper layer (yellowish) is a fatty acid and the bottom layer (colorless) is an alcohol. During the experiment, some of the steam is condensed in the distillate outlet and formed water droplet which led into the palm oil. Thus, the bottom layer of the palm oil is suspected to consist of alcohol and water. This is proved during the phase separation process, where alcohol did not boil at 70-80 °C, but only boiled at temperature more than 100 °C. This shows that the major component of the bottom layer is water, rather than alcohol. The hydrolysis process was performed over 5-7 hours to make sure the palm oil is fully reacted with the steam. During the hydrolysis, palm oil color is observed to fade. This shows that palm oil is cleaved to fatty acids and alcohol. The 2 layers of liquid did not dissolve into each other.

During the phase separation process, the temperature of the bottom layer of the hydrolysis product is to be maintained at 70-80 °C. This is the boiling point temperature of common alcohols. The bottom layer (alcohols) boiled and vaporized at the temperature (70-80 °C) and the vapor is condensed and collected at the distillate outlet of the apparatus.

This process is temperature sensitive, thus the temperature needs to be closely controlled. During the process of phase separation, the bottom layer (alcohols) did not boil at the temperature of 70-80 °C (boiling point temperature of common alcohols). The temperature is increased to 85 °C as the author suspected some impurities exist in the alcohol, but did not boil after sometimes. The temperature was slowly increase at an interval of 5 °C and held for a moment. The bottom layer (alcohols) started to boil at a temperature more than 100 °C. Water is the main fraction in the bottom layer. At this point, the temperature could not be controlled as it goes up and down dramatically. Some of the upper layer (fatty acids) is pushed to flow into the distillate outlet. Some adjustment is done to the distillation apparatus to improve the results of the distillation process. The distillate outlet end is raised a bit higher so that the steam condensed in the tube will not flow into the distillate outlet but flow back into the round bottom flask. This is done to reduce the amount of water getting into the distillate outlet.

6.2.2 Saponification of Fatty Acids and Base

During this process, fatty acid is titrated with a potassium hydroxide. Phenolphthalein powder is added into fatty acid solution as for the pH indicator. There is no change in color when phenolphthalein powder is added into fatty acid. The fatty acid is slowly titrated by using strong base (potassium hydroxide) until the color of the fatty acid turned pink (showing neutral solution is achieved).

From the experimental results, a pink fatty acid solution was achieved during the titration process but after few hours left, the solution is observed to form 2 layers liquid. The upper layer is clear pink in color and more likely to act like oil and the bottom layer is light-purple in color.

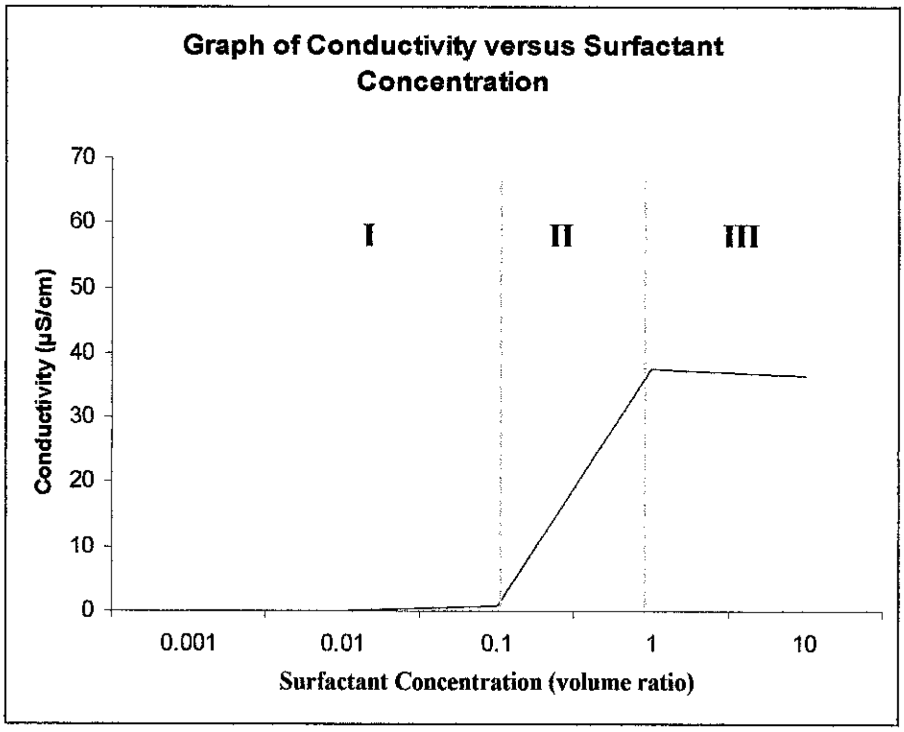
Two layers exist when the solution is left for a few hours. The upper layer and bottom layer of the titration product dissolves in each other when shake.

6.2.3 Characterizing the Rheological Properties of The Synthesized Surfactant

a. Conductivity of surfactant at various concentrations

The conductivity of material is determined by the electronic structure of the atoms. Conductivity of materials can be change by influencing the mobility, μ, of the carriers. The mobility is proportional to the drift velocity, $\bar{\upsilon}$, which is low if the electrons collide with imperfections in the lattice. In the reservoir, oil which is isolated structure of rock is immobilized because drift velocity has collided with imperfection of the rock lattice. Thus, surfactant in oil-surfactant injection is important to act as a material which influences the mobility of oil. The mean free path is the average distance between collisions; a long mean free path permits high mobility and high conductivities. Since surfactant have properties of lowering the interfacial tension, it is predicted to act as one of the best mobility agent for oil conductivity. However, surfactant has properties of micelle concentration, which in certain concentration governs oil in emulsion form.

From the experiment, we can see that surfactant has a low conductivity value at low concentration. As surfactants concentration increased, the value of surfactant conductivity increased. The values of surfactant conductivity slowly increased as the surfactant-distilled water volume ratio increased from 0.001 to 0.1. Surfactant conductivity after this point dramatically increased as the surfactant-distilled water volume ratio increased from 0.1 to 1. The conductivity of surfactant stayed unchanged as the surfactant-distilled water volume ratio increased from 1 up to 10.



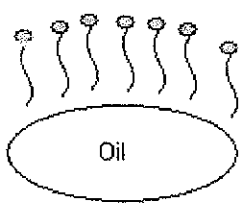
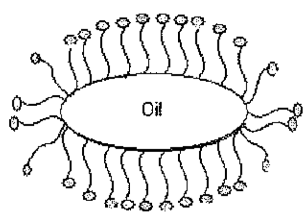
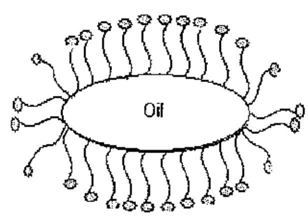
Before CMC (I)	During CMC (II)	After CMC (III)
		
No emulsion between surfactant molecules and oil molecules. Provides low conductivity	Emulsion between oil and surfactant molecules start to occur. Conductivity starts to increase dramatically.	All surfactant molecules capable to emulsify with oil molecules. Provides high conductivity

Figure 7.0: Table of surfactant molecules behaviors before CMC, during CMC and after CMC

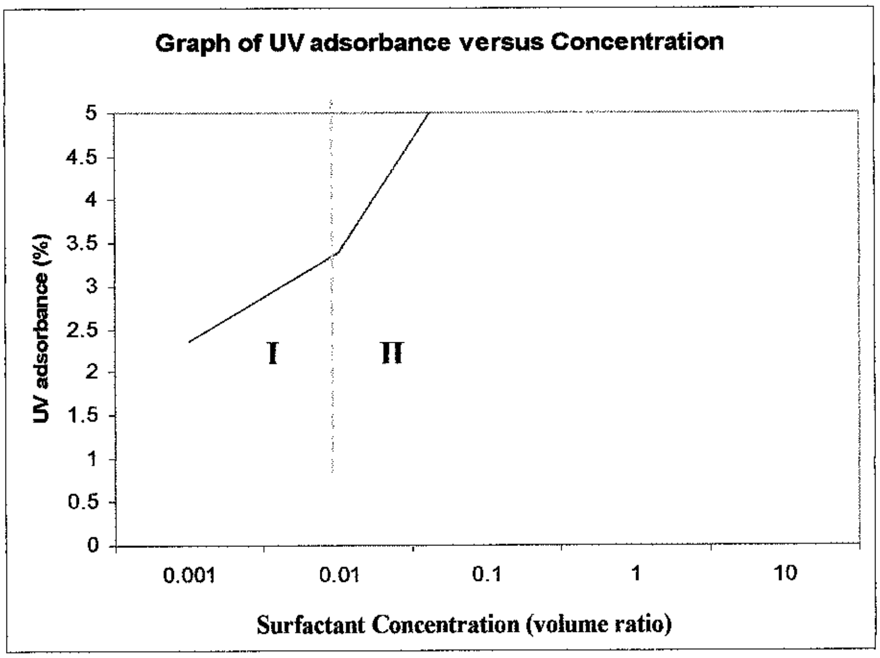
From the result, we can clearly see the 3 phases of surfactant behaviors: before Critical Micelle Concentration (CMC), during CMC and after CMC. At the region I (before CMC) we can see that surfactant conductivity is low. This is because of there is no emulsion between oil and surfactant molecules, thus providing low conductivity.
At the region II (during CMC), the conductivity of surfactant is dramatically increased as the concentration increased. This is because of the emulsion starts to occur between oil and surfactant molecules in this region. This is the region where surfactant molecules start to reduce the interfacial tension of oil.
At region III (after CMC), conductivity of surfactant is high but the value approaching constant as the surfactant concentration increased. During this region, all surfactant molecules emulsify with oil molecules and at the same time resulting on the high conductivity.

b. Turbidity Test for Surfactant at various concentrations

Basically, the Turbidity Test for Surfactant is to observe and measure the degree of turbidity of surfactant at various concentrations. Theoretically, the surfactant's solution becomes turbid as the surfactant concentration increased. This is because of the increasing amount of surfactant particles in the surfactant-distilled water solution as the surfactant concentration increases.

The surfactant observed most intensely at a wavelength of 210 nm as measured by using the Shimadzu UV spectrophotometer. The Shimadzu UV spectrophotometer can measure the UV absorbance of a solution up to 5%. The value of UV absorbance at surfactant concentration of 0.001 is 2.357 % and the value increased as the surfactant concentration increased. At the surfactant's concentration of 0.1, the value of the UV absorbance already exceeded the range of the

UV absorbance value that can be measured by the Shimadzu UV spectrophotometer (0% - 5%). The increasing value of UV absorbance as the surfactant concentration increase showed that the solution become more turbid as the surfactant concentration was increased beyond the concentration of 0.1.

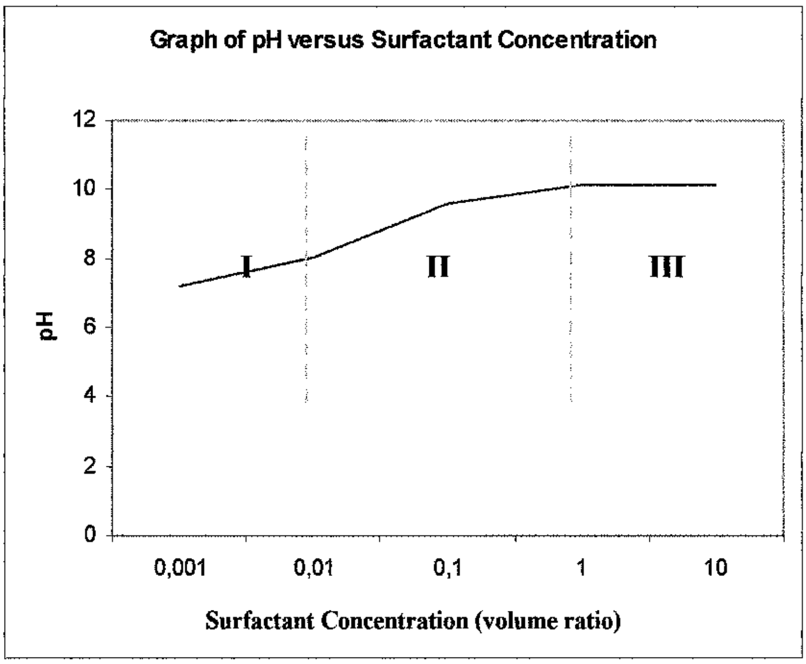


From the result, we can see that 2 phases occurred: region I (before CMC) and region 2 (during CMC). At region I, we can see that the value of UV absorbance increased as the surfactant concentration increased. This is because of the increasing number of surfactant molecules in the solution causing the solution to become turbid. Surfactant molecules still not emulsify with oil molecules causing more UV light can passes through the solution molecules resulting in low UV absorbance value.

At region II, surfactant molecules start to emulsify with oil molecules causing less UV light passes through the solution molecules. This caused high UV absorbance value. The increasing amount of surfactant molecules emulsify with oil molecules caused the solution to become turbid.

c. pH Test for Surfactant at various concentrations

Basically, the pH test for surfactant is to determine the degree of acidity for surfactant-distilled water solution at various concentrations. From the experiment, we can see that the pH value of the surfactant-distilled water solution increase as the surfactant concentration increased. The solution getting more alkali-like as the surfactant concentration increased. The pH value of the solution starts to be constant at the surfactant concentration of 1M.



From the result, we can see 3 different phases: region I (before CMC), region II (during CMC), and region III (after CMC).

At region I (before CMC), there is no emulsion occurred between surfactant and oil molecules causing the solution to have low pH value. This is because of the low concentration of surfactant in the solution, thus less polar end in the solution resulting in low pH value.

At region II (during CMC), surfactant molecules start to emulsify with oil molecules. The pH value dramatically increased as the concentration increased. This is because of the surfactant polar end (hydrophilic) attracted the free hydrogen ion near the molecules. This caused the solution to be more alkali. At region III (after CMC), all surfactant molecules emulsify with oil molecules. All the free ions are attracted near the surfactant polar end caused the solution to have high pH value and the pH value become constant as the concentration increased.

7.0 CONCLUSIONS AND RECOMMENDATIONS

7.1 CONCLUSION

As for the conclusion, a fatty acid can be extracted from palm oil by the hydrolysis process of palm oil with steam. Surfactant can be synthesized by saponification of fatty acid with strong base such as sodium hydroxide or potassium hydroxide.

The conductivity of surfactant-distilled water solution increase as the surfactant concentration increased. The value of conductivity starts to be constant at the surfactant concentration of 1M and larger.

The value of UV absorbance (%) for surfactant-distilled water solution increase as the concentration of surfactant increased.

The pH value of surfactant-distilled water solution increase as the concentration of surfactant increased. The pH value starts to be constant at surfactant concentration of 1M.

7.2 RECOMMENDATIONS

1. To prepare the back up experimental procedures for all the experiments. This is to ensure that the project will not be delayed due to problems occurred such as unavailability of apparatus or chemicals, unexpected results, and malfunctioned machines.
2. It is recommended that Chemical Engineering Department can elongate Final Year Research Project (FYP) course so that this idea can be further attest with the simulation instead of experimental research only.
3. It is recommended that Chemical Engineering Department can provide a device that can measure the viscosity of fluid, such as capillary viscometer.

8.0 REFERRENCES

1. http://education.yahoo.com/reference/dictionary/entry/surfactant
2. http://enviro.nfesc.navy.mil/erb/restoration/technologies/remed/phys_chem/phc-33.asp
3. http://www.clu-in.org/products/aatdf/chap4.htm
4. The Structure and Rheology of Complex Fluids,
   Ronald G. Larson,
   University of Michigan, Ann Arbor,
   New York, Oxford
   Oxford University Press,
   1999
   Chapter 1 and 12
5. Organic Chemistry,
   4th Edition,
   L.G. Wade, Jr
   Prentice Hall International, INC
   1999
   Chapter 25
6. http://www.snowdriftfarm.com/fatproperties2.html
7. www.akzonobel-oleochemicals.com/fatty_acids.htm
8. http://www.scientificpsychic.com/index.html
9. http://www.hormel.com/templates/knowledge/knowledge.asp?catitemid=42&id=568#extraction
10. http://www.thesoapkitchen.co.uk/soap_making.htm
11. http://www.andrew.cmu.edu/user/jitkangl/Palm%20Oil/Refinery%20of%20Palm%20Oil.htm

9.0 APPENDICES

Table 4.0: Chemical Names and Descriptions of some Common Fatty Acids

Common Name	Carbon Atoms	Double Bonds	Scientific Name	Sources
Butyric acid	4	0	butanoic acid	butterfat
Caproic Acid	6	0	hexanoic acid	butterfat
Caprylic Acid	8	0	octanoic acid	coconut oil
Capric Acid	10	0	decanoic acid	coconut oil
Lauric Acid	12	0	dodecanoic acid	coconut oil
Myristic Acid	14	0	tetradecanoic acid	palm kernel oil
Palmitic Acid	16	0	hexadecanoic acid	palm oil
Palmitoleic Acid	16	1	9-hexadecenoic acid	animal fats
Stearic Acid	18	0	octadecanoic acid	animal fats
Oleic Acid	18	1	9-octadecenoic acid	olive oil
Vaccenic Acid	18	1	11-octadecenoic acid	butterfat
Linoleic Acid	18	2	9,12-octadecadienoic acid	safflower oil
Alpha-Linolenic Acid (ALA)	18	3	9,12,15-octadecatrienoic acid	flaxseed (linseed) oil
Gamma-Linolenic Acid (GLA)	18	3	6,9,12-octadecatrienoic acid	borage oil
Arachidic Acid	20	0	eicosanoic acid	peanut oil, fish oil
Gadoleic Acid	20	1	9-eicosenoic acid	fish oil
Arachidonic Acid (AA)	20	4	5,8,11,14-eicosatetraenoic acid	liver fats
EPA	20	5	5,8,11,14,17-eicosapentaenoic acid	fish oil
Behenic acid	22	0	docosanoic acid	rapeseed oil
Erucic acid	22	1	13-docosenoic acid	rapeseed oil
DHA	22	6	4,7,10,13,16,19-docosahexaenoic acid	fish oil
Lignoceric acid	24	0	tetracosanoic acid	small amounts in most fats

$$
\begin{array}{lllll}
CH_2OOC\text{-}R & & & CH_2OH & \\
| & & & | & \\
CHOOC\text{-}R & + \ 3\,KOH & \longrightarrow & CHOH & + \ 3\,R\text{-}COOK \\
| & & & | & \\
CH_2OOC\text{-}R & & & CH_2OH &
\end{array}
$$

Oleic Acid, $R = CH_3\,(CH_2)_7\,(CH)_2\,(CH_2)_7$

Palmitic Acid, $R = CH_3\,(CH_2)_{14}$

Stearic Acid, $R = CH_3\,(CH_2)_{16}$

Figure 8.0: Reaction of fatty acid and strong base

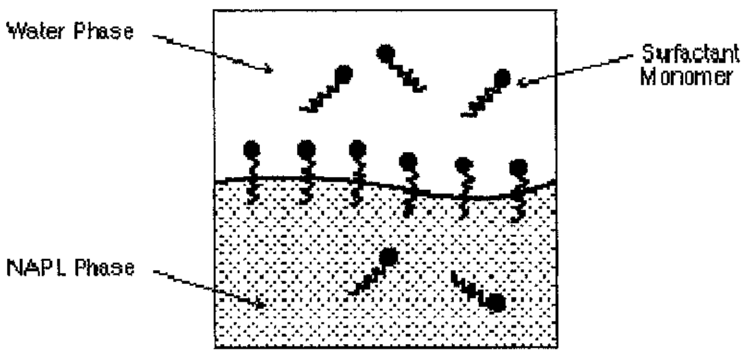


Figure 9.0: Surfactant monomer accumulation at the NAPL-water interface

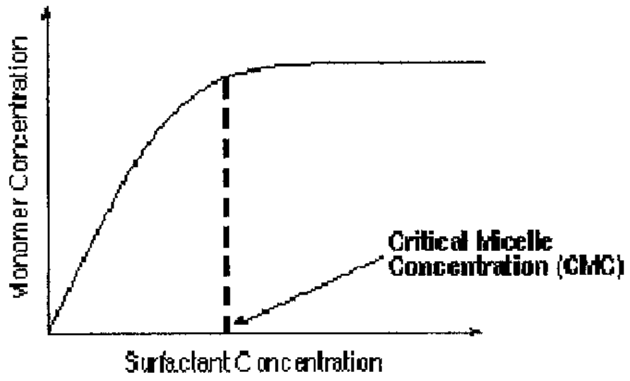


Figure 10.0: Formation of micelles at critical micelle concentration (CMC)

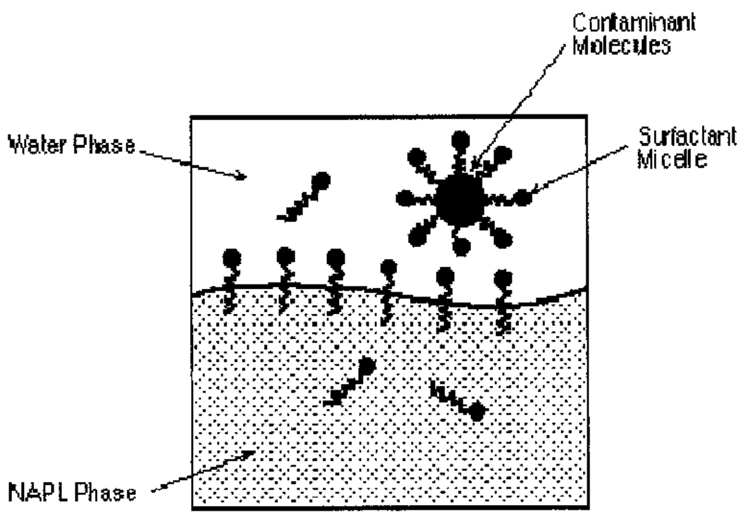


Figure 11.0: Surfactant Monomers and micelles in equilibrium with contaminant molecules and solution interface

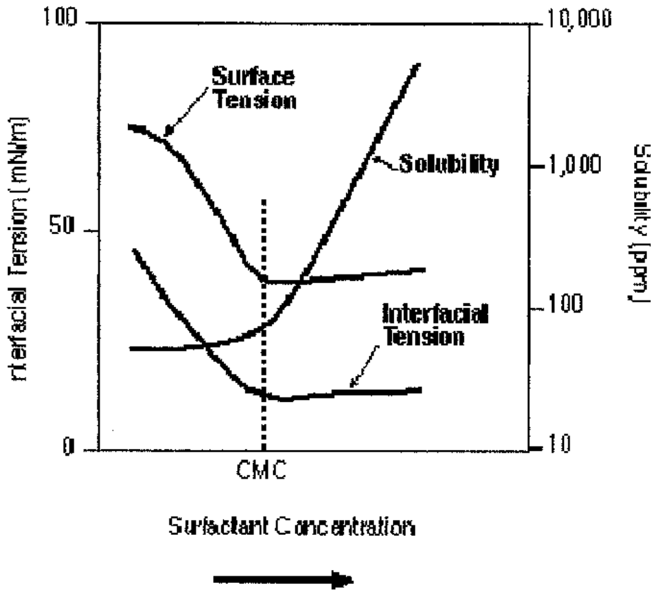


Figure 12.0: Variation of surface tension, interfacial tension, and contaminant solubility with surfactant concentration