Adsorption of Anionic Surfactant onto Malaysian Sandstone

by

Mohd Taufik bin Nordin

Dissertation submitted in partial fulfillment of
the requirements for the
Bachelor of Engineering (Honors)
(Chemical Engineering)

MAY 2012

Universiti Teknologi PETRONAS
Bandar Seri Iskandar
31750 Tronoh
Perak Darul Ridzuan.

CERTIFICATION OF APPROVAL

Adsorption of Anionic Surfactant onto Malaysian Sandstone

by

Mohd Taufik bin Nordin

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

Approved by,

(AP DR. ISA BIN MOHD TAN)

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
MAY 2012

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

(MOHD TAUFIK BIN NORDIN)

ABSTRACT

The adsorption of surfactant from aqueous solution study is very significant on chemical enhanced oil recovery (CEOR). One of chemical enhanced oil recovery identified was surfactant flooding. In present, the potential of surfactant flooding in Malaysia is still in development process and needs laboratory data like surfactant adsorption to assist the field data required. Surfactant losses due to the adsorption on the reservoir rocks weaken the efficiency of surfactant to decrease the interfacial tension between oil and water. For final year research project, a study to investigate the adsorption of anionic surfactant onto Malaysian sandstone has been done with assistance from UTP Enhanced Oil Recovery (EOR) Research Centre. The study was started with determination of critical micelle concentration (CMC) of anionic surfactant by conductivity method to get a maximum concentration at which the surfactant is adsorbing onto the sandstone. The main part of the researches was the static adsorption test where the different concentration of anionic surfactant was mixed with Malaysian sandstone in a continuous mixing environment for 24 hours. The unknown surfactant concentration was represented as absorbance detected by UV-Vis spectrophotometer. The amount of surfactant adsorbed was calculated by subtracting the concentration of anionic surfactant after adsorption from the initial concentration. An isotherm relating the adsorption density with final concentration of surfactant has been developed with the isotherm following Somasundran isotherm. The isotherm shows three mechanisms of surfactant adsorption from low to high surfactant concentration. It was concluded that this adsorption study is valid as fundamental and reference to assist the laboratory studies in determining the potential of surfactant flooding in Malaysia.

ACKNOWLEDGEMENTS

Praise to Allah for His guidance and blessings He has given me throughout this Final Year Research Project. It's the strength from Him that is what keeps us going in everything we do in our lives. My greatest appreciation goes to my supervisor, AP Dr. Isa bin Mohd Tan for giving me such tremendous helps, advices, opinions and courage all the way through the completion of this project. I appreciate the time he allocates for me, to sit and discuss the problems I've faced along the way. A million thanks to him for having such confidence in me.

My appreciation also goes to Final Year Project Coordinator, Dr. Norhayati Mellon for her guide to me and all my friends, and also to the efforts she put to ensure the smoothness of this course. Thank you so much.

A token of appreciation also goes to UTP Enhanced Oil Recovery (EOR) Research Centre for their assistance, knowledge, equipments and continuous support especially to Mr. Muhammed Mushtaq and Mr. Muhammad Rizwan Azam.

Special thanks to my parents and all my friends for their continuous support and courage that drives me to keep on going whenever I fall. Last but not least, I also want to thank everybody who have involved directly and indirectly in helping me along this project. Thanks again to all, your kindness and helps will always be remembered.

TABLE OF CONTENTS

List of Tables:

List of Figures:

Abbreviations and Nomenclatures:

EOR – Enhanced Oil Recovery

LABS– Linear alkyl benzene sulfonate

CMC – Critical micelle concentration

UV-Vis– Ultraviolet - Visible

NMR – Nuclear Magnetic Resonance

HPLC – High Performance Liquid Chromatography

CHAPTER 1

INTRODUCTION

1.1 Background of Chemical Enhanced Oil Recovery (CEOR)

In Malaysia, most mature reservoirs are already waterflooded and presently being subjected to secondary and tertiary recovery processes. In Malaysian oil reservoirs, only about 36.8% of original oil in place (OOIP) is produced through the entire life of mature reservoir which has been developed under conventional methods (Hamdan, Darman, Husain, & Ibrahim, 2005). Enhanced Oil Recovery (EOR) is a well known terms in maximizing the oil recovery with the assistance thermal, gas or chemical methods. Chemical Enhanced Oil Recovery (CEOR) was identified as one of the key EOR processes that have a good potential for field implementation to increase recovery in Malaysian oilfields (Othman et al., 2007).

Chemical EOR processes are being considered for large field applications with recent high price of crude oil (Ibrahim et al., 2006). These include surfactant flooding, surfactant-polymer flooding and combination of alkali-surfactant-polymer flooding. Surfactant flooding is used to decrease the interfacial tension between oil and water inside the reservoirs. An ultra low interfacial tension is needed to increase the sweep efficiency of the oil from the reservoir into the production well.

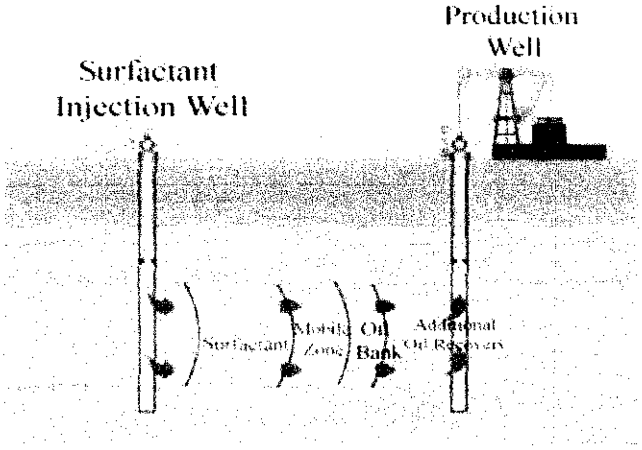


Figure 1: Surfactant flooding

1.2 Background of Surfactant

Surface active agents, usually called as surfactants, have at least one hydrophilic and at least one hydrophobic group in the same molecule. Because of this character that can significantly lower the interfacial tensions and alter wetting properties, surfactants are considered as good enhanced oil recovery agents since 1970s (Healy, Reed, & Stenmark, 1976).

Surfactants are energetically favorable to be located at the interface rather than in the bulk phase (Neogi, 1985). A surfactant molecule has at least one hydrophilic group and at least one hydrophobic group. The surfactant molecule usually is presented by a "tadpole" symbol. While the hydrophilic portion is usually called head, the hydrophobic portion (usually hydrocarbon chain) is named tail. The hydrophilicity of a surfactant is determined by the structure of the head and tail, e.g. the hydrocarbon chain length, the number of branches in chain etc., and the functional groups, e.g. ethoxylated group or propoxylated group etc. Surfactant molecules prefer to aggregate in solutions to form phases such as micellar solutions, microemulsions, and lyotropic liquid crystals (Akstinat, 1981).

According to the charge of the head group, surfactants are categorized into four groups: anionic, cationic, nonionic, and zwitterionic surfactants as Figure 2 shows. Anionic surfactants, which include soap, are negatively charged and the counter ions are usually small cations such as sodium ion, potassium ion, ammonium ion. They are the most used surfactants in the oil recovery process because of their relatively low adsorption in sandstone and clays, stability and relatively cheap price (Akstinat, 1981).

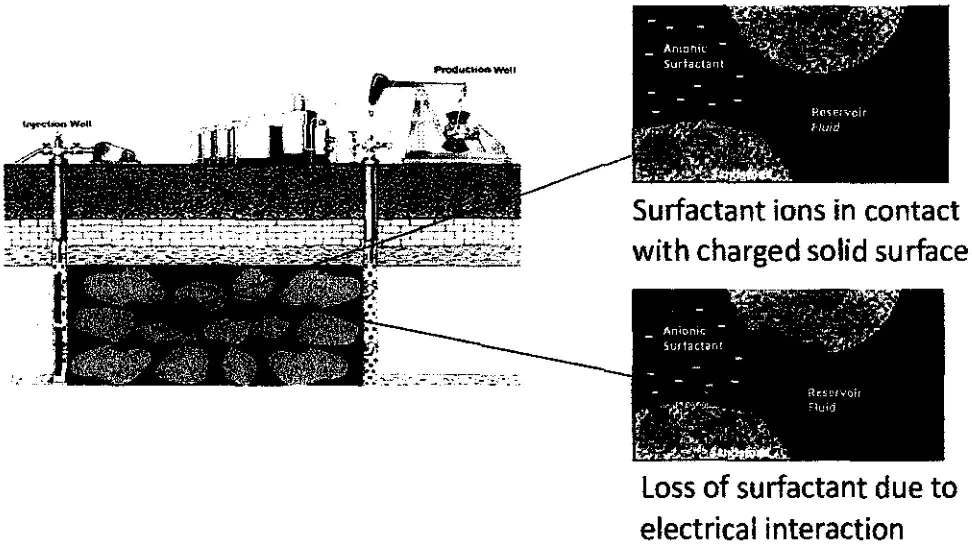
Anionics	Cationics	Nonionics	Amphoterics
Sulfonates Sulfates Carboxylates Phosphates	Quaternary ammonium organics, pyridinum, imidazolinium, piperidinium, and sulfononium compounds	Alkyl-, Alkyl- aryl-, acyl-, acylamindo-, acylaminepolyglycol, and polyol ethers Alkanolamides	Aminocarboxylic acids

Figure 2: Classification of surfactants and examples (Akstinat, 1981).

1.3 Problem Statement

Surfactant loss in a reservoir is caused by several mechanisms such as adsorption of surfactant into the rock, precipitation surfactant in presence of divalent cations, surfactant partitioning into the oil phase and diffusion of surfactant into dead-end pores (Dang, Chen, Nguyen, Bae, & Phung, 2011). The mechanism responsible for surfactant adsorption is mainly the electrostatic attraction between the charged surface of the solid and the charged head group of the surfactant molecule (Somasundaran & Huang, 2000). This is a process of transfer of surfactant molecules from the bulk solution phase to the surface interface. The mechanisms by which surface active molecules

The adsorption of surfactant into the rock may result in the loss of and reduction of their concentration which may render them to be less effective in practical treatment. Besides that, the loss due to the adsorption onto reservoir rock impairs the effectiveness of the chemical solution injected to reduce the interfacial tension and renders the process economically unfeasible (Curbelo et al., 2007). On top of that, the adsorbed surfactant into the rock increases the adsorption of hydrophobic organic compound in the soil-water system, which exacerbate desorption of organic compounds.



Surfactant ions in contact with charged solid surface

Loss of surfactant due to electrical interaction

Figure 3: Adsorption of surfactant onto reservoir rocks in surfactant flooding process

1.4 Objectives

The aim of the project is to study the mechanism of adsorption for anionic surfactant onto Malaysian sandstone. The objectives of the projects are:

1. To develop methods of analysis in characterizing anionic surfactant.
2. To study the mechanism of adsorption for anionic surfactant onto Malaysian sandstone.
3. To provide laboratory data to assist the field data in implementing surfactant flooding in Malaysia.

1.5 Scope of Study

To achieve the objectives mentioned above, the scope of this study was divided into two main parts. The first part focused on the characterization anionic surfactant by critical micelle concentration and absorbance by UV-Vis spectroscopy. The second part concerns the study of mechanism of adsorption possessed by anionic surfactant when it is in contact with Malaysian sandstone. The detailed scope is as follows:

Part I

1. Determination of critical micelle concentration (CMC) of linear alkyl benzene sulfonate (LABS) surfactant by conductivity method
2. Characterization of linear alkyl benzene sulfonate (LABS) surfactant by UV-Vis spectrophotometer.

Part II

1. Examination of adsorption of linear alkyl benzene sulfonate (LABS) surfactant onto Malaysian sandstone by static adsorption test.
2. Determination of adsorption density and amount of surfactant adsorbed.
3. Investigation of adsorption mechanism possessed by LABS surfactant when it is in contact with Malaysian sandstone.

1.6 Relevancy of Project

Determination of critical micelle concentration (CMC) by conductivity method provides the idea of maximum concentration of surfactant where the amount of surfactant adsorbed onto sandstone is constant without going to adsorption test yet. The conductivity method has a simple preparation and equipment setup to determine CMC compared to surface tension and titration method proposed by the past literatures.

There are a number of analysis methods provided to determine the surfactant concentration in any environment for decades. Usage of UV-Vis spectrophotometer to determine the concentration provides an accurate analysis within a short time. The spectrophotometer is available in Universiti Teknologi PETRONAS (UTP) in Block 4, level 2.

Adsorption of surfactant studies have been done for decades for Berea sandstone. Indeed the laboratory data for adsorption on Malaysian sandstone are still needed as PETRONAS attempted to apply chemical enhanced oil recovery covering surfactant flooding, polymer flooding and alkaline flooding in Malaysia. The data obtained from this thesis provides a fundamental basis for further study of adsorption in other parameters.

1.7 Feasibility of Project

This research work has a full support from UTP EOR Research Centre by providing the equipments and materials needed to assist the experimental works. Within eight months, the research work was successfully done with an effective time management and consultation from Dr. Isa bin Mohd Tan and UTP EOR Research Centre members.

CHAPTER 2

LITERATURE REVIEW

This chapter provides a full background about enhanced oil recovery method and reviews the previous work related to adsorption of surfactant. It begins with background information of adsorption and types of porous media and mineral used in adsorption test. The basic structure of surfactant is also described. In addition with that, this section also covers the past literatures done by the researcher in studying the adsorption of surfactant (anionic, cationic, non ionic) at different type of media and parameters. These studies have been used to assist the project in collecting the data needed for static adsorption test.

2.1 Background of Adsorption

Adsorption can be considered as a process of selective partitioning of the adsorbate species to the interface in preference to the bulk and is the result of interactions of such species. Adsorption can be broadly classified into two categories, physical adsorption and chemical adsorption depending on the nature of the forces involved (Adamson, Gast, & NetLibrary, 1967). Physical adsorption is usually weak and reversible and involves energy charges. Van der Waals forces and electrostatic forces are primarily responsible for physical adsorption which is also characterized by a high rate of adsorption and formation of multilayer (Parfit et. al, 1983). On the other hand, chemical adsorption occurs through covalent bonding between the adsorbate and the surface species on the solid. Chemical adsorption normally involves an activation stage and a low rate of adsorption. Such adsorption is usually strong and irreversible and is limited to a monolayer. A distinction between physical and chemical adsorption is identified from temperature dependence where physical adsorption decreases with temperature and chemical adsorption is vice versa.

There are a variety of solids used in surfactant adsorption research. For 'ideal' reservoir materials, the solids are alumina (Al_2O_3 and silica (SiO_2). On the other hand, 'real' materials are represented by kaolinite clays, river alluvium, dolomite, limestone and sandstones (Schramm, 2000). Sandstone is an agglomeration of individual minerals but the primary component is usually quartz. Other minerals comprising sandstone including mica, illite, kaolinite and calcium carbonate. A common type of sandstone used in adsorption research is Berea sandstone.

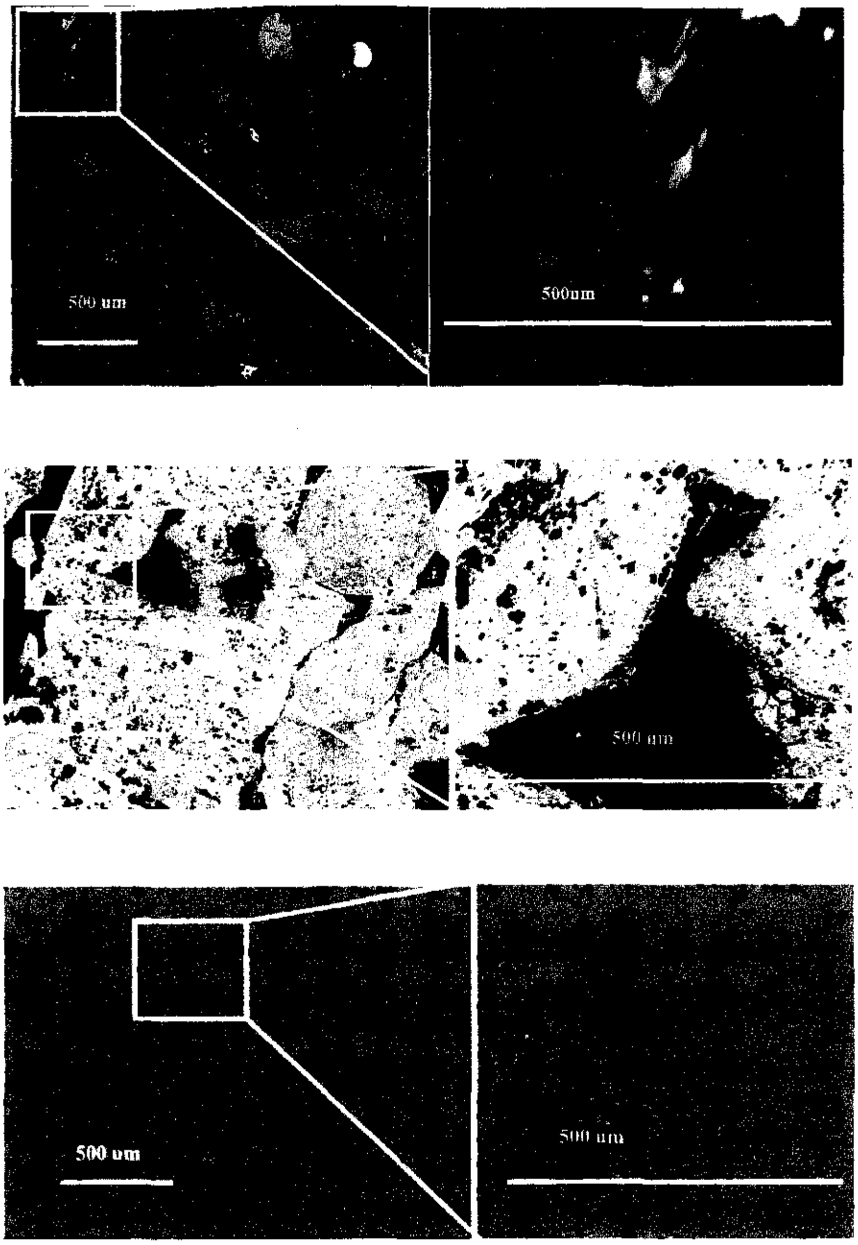


Figure 4: SEM for Berea sandstone (Ou et al.), limestone (*middle*) and dolomite (*bottom*) (Schramm, 2000).

2.2 Past Literatures Relating to Adsorption of Surfactant

According to Zhang (Zhang & Somasundaran, 2006) there are a number of factors which can act as the driving forces for surfactant adsorption on surfactant-solid system. There are including electrostatic interactions($\Delta G^0_{\mathrm{elec}}$), chemical interactions(ΔG^0_{chem}), hydrophobic lateral interactions($\Delta G^0_{\mathrm{c-c}}$), hydrophobic interaction between hydrocarbon chain and hydrophobic sites on solid($\Delta G^0_{\mathrm{c-s}}$) and hydrogen bonding($\Delta G^0_{\mathrm{c-c}}$).

Kwok (Kwok, Nasr-El-Din, & Hayes, 1993) studied the propagation and adsorption of an anionic surfactant in Berea sandstone cores. They reported a dramatic surfactant loss and slower propagation as sodium chloride concentration is increased. Increasing the pH of the surfactant slug from 6 to 12 reduced the surfactant loss by nearly thirty percent at a given sodium chloride and surfactant concentration, surfactant loss decreases as the injection flow rate increases.

Curbelo (Curbelo et al., 2007) investigated the adsorption of two nonionic surfactant (ENP95 and ENP150) with different ethoxylation degree in Acu sandstone. They found that ENP95 with smaller ethoxylation degree adsorbed more into the sandstone compared to ENP159. They reported that less ethoxylation degree surfactant has smaller polar part, hence larger amount of that surfactant required to cover the internal surface of the rock.

Mannhardt (Mannhardt, Novosad, & Jha, 1994) investigated the adsorption of anionic surfactants in Berea sandstone at different conditions of temperature and salinity. They found that the adsorption of the anionic surfactants from low salinity brine is low, but increase substantially at moderate salinities, and observed a trend of increasing adsorption with decreasing surfactant solubility.

Lawson (Lawson, 1978) studied the adsorption of both nonionic and cationic surfactants on sandstones and carbonates. For nonionic surfactants, the adsorption on sandstone was high and is relatively insensitive to solution salinity. Adsorption on carbonates was lower than on sandstone. For anionic surfactants, they found that adsorption isotherms were Langmiurian and multivalent cations were found to increase the adsorption. Salts of large anions and common detergent builders reduce the adsorption of anionic surfactants.

Mazen (Muherei & Junin, 2009) studied the adsorption of anionic, cationic and mixture of them in two local porous media, shale and sandstone. There is no adsorption detected for anionic surfactant on both adsorbents compared to cationic surfactant which adsorbed into both of them. Adsorption of surfactant mixture is lower than cationic surfactant alone particularly on shale. The adsorption fit both of the adsorption isotherms but higher value of R^2 made Freundlich isotherm fit the data compared to Langmuir isotherm.

Trogus (Trogus, Sophany, Schechter, & Wade, 1977) studied the adsorption of anionic and nonionic surfactants on sandstones and found that the adsorption isotherms were Langmuir. The adsorption levels for both anionics and nonionics are of comparable magnitude. Adsorption increases sharply as concentration increases and then levels off at the critical micelle concentration for anionic and nonionic surfactants. The adsorption decreases with the increasing molecular weight for nonionics and the opposite is true for anionics. Negligible adsorption was observed for anionics containing sulfonates with an alkyl chain length of 9 or less.

Kuhlman (Kuhlman, Lau, & Falls, 2000) studied the adsorption and propagation of surfactants in Berea cores and found that surfactant adsorption in sandstones is reduced when the surfactant concentrations are kept below their critical micelle concentration (CMC). They reported that the adsorption can be minimized by reducing the ethoxylate chain length in alcohol ethoxy sulfonates and by blending an ethoxylated with ethoxylated sulfonates.

Table 1: Summary of adsorption of surfactant on specifically mineral sites with the technique used (Zhang & Somasundaran, 2006)

Surfactant	Type	Solid	Technique
Sodium dodecyl sulfate	Anionic	Alumina	Adsorption, electrophoresis
Sodium dodecylbenzene sulfonate	Anionic	Kaolin	Abstraction, deabstraction
Xylensulfonate (meta and para)	Anionic	Alumina, kaolin, anatase	Adsorption, microcalorimetry, electrokinetics, fluorescence
Sodium oleate	Anionic	Calcite	Flotation, SEM, microscope, electrokinetics, turbidity
4-n-Decylbenzenesulfonate (DBS)	Anionic	Kaolin, alumina	NMR, HPLC, adsorption, abstraction
4-n-Octylbenzenesulfonate	Anionic	Kaolin, alumina	NMR, HPLC, adsorption, abstraction
Ethoxylated sulfonate	Anionic	Kaolin, alumina	NMR, HPLC, adsorption, abstraction
Sodium oleate	Anionic	Hematite	Adsorption, calorimetry, abstraction, precipitation
Decylbenzenesulfonate	Anionic	Kaolin, alumina	Adsorption, abstraction
Sodium dodecyl sulfate	Anionic	Alumina	ESR
Sodium dodecyl sulfate	Anionic	Alumina	Raman
Potassium oleate	Anionic	Hemitate	Flotation, surface tension
Na-dodecylbenzenesurfonate	Anionic	Kaolin	Adsorption, abstraction, solubility, precipitation

n-Decylbenzene sulfonate	Anionic	Alumina	Adsorption
n-Decylbenzene sulfonate	Anionic	Kaolin	Adsorption, desorption, HPLC, surface tension
Alkyl pyridinium salts	Anionic	Rutile	Adsorption
Alkyl benzene sulfonate	Anionic	Rutile	Adsorption
Tetradecyltrimethylammonium bromide	Cationic	Alumina	Electronic spin resonance, fluorescence, flotation
Dodecyltrimethylammonium bromide	Cationic	Alumina	Electronic spin resonance, fluorescence, flotation
Alkyltrimethylammonium bromide, C10-C16	Cationic	Silica Sphere	Small angle neutron scattering
Dodecyl amine	Cationic	Hematite	Flotation
Tetradecyltrimethylammonium chloride	Cationic	Alumina	Adsorption, desorption, electrokinetics, fluroescence
Benzyldimethyldodecylammonium ions	Cationic	Silica	Adsorption, calorimetry, electrophoresis

CHAPTER 3

METHODOLOGY

In order to achieve the objectives mentioned in the first chapter, the research methodology was carried out in three main parts. Those three parts consisting of conductivity measurement, ultraviolet-visible range (UV-Vis) absorption method and static adsorption test. The conductivity measurement is related to critical micelle concentration (CMC) of anionic surfactant meanwhile UV absorption method is used to find the unknown concentration of surfactant solution in terms of absorbance. Static adsorption test yield the characteristic of surfactant adsorption to Malaysian sandstone.

3.1 Materials

3.1.1 Anionic Surfactant

In this study, the anionic surfactant used was linear alkyl benzene sulfonate (LABS). LABS are the predominant surfactant used in commercial detergent preparations and often used in specialty cleansers. It was reported to be a mixture of homologues dominated by the docecylbenzene sulfonate although analysis indicated that C11 homologue was the major component.

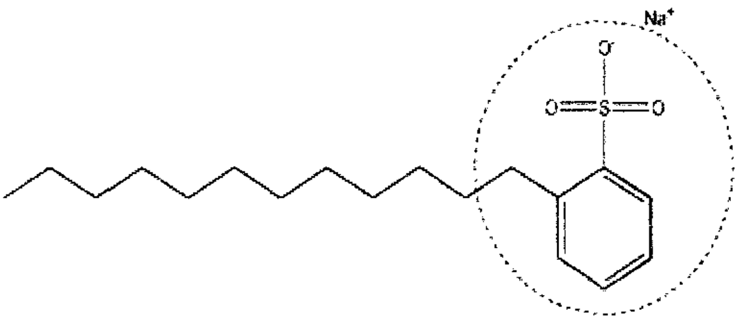


Figure 5: Linear Alkyl Benzene Sulfonate (LABS) surfactant

3.1.2 Malaysian Sandstone

Not much information can be given to describe Malaysian sandstone used in this research project. Malaysian sandstone came in cylindrical core before it was crushed by crusher to become powder. Dr. Isa provided that the specification of Malaysian sandstone used was as same as the sandstone located in Angsi Field, offshore Terengganu.

3.2 Conductivity Measurement

The experiment was done by preparing different concentration of surfactant solution (0 to 750 ppm) from dilution of aqueous stock solution. This experiment took place at Block 15 level 2 and Block 4 level 2 which have the conductivity meter.

Calculation for surfactant dilution is presented as below.

1. 250 mL of 1000 ppm aqueous stock solution LABS surfactant was prepared.

   $$1000\text{ ppm} = 1000\ \frac{\text{mg}}{\text{L}} = \frac{1000\text{ mg}}{1\text{L}} = \frac{250\text{ mg LAS}}{250\text{ mL solution}} = \frac{0.250\text{ g LAS}}{250\text{ mL solution}}$$

2. 14 samples of 20 mL diluted LABS solution were prepared by pipetting different volume of LAS stock solution with water.

3. The volume of LAS stock solution needed for specific diluted concentration in 20 mLwas calculated using the formula below. For example (150 ppm),

   $$C_1V_1 = C_2V_2$$

   $$(1000\text{ ppm})(V_1) = (150\text{ ppm})(20\text{ mL})$$

   $$V_1 = 3\text{ mL}$$

4. The test tubes were placed inside the beaker with water about 1 day for equilibrium and constant temperature.

5. The conductivity was recorded for each samples using conductivity meter.

As precautions, conductivity value of solution is affected by temperature of surrounding. It is recommended to soak all the test tubes into a beaker filled with water for one day to get equilibrium temperature before the conductivity is measured.

Besides that, sometimes the value of conductivity is fluctuating due to the leftover from previous samples. After the previous sample has been removed, it is recommended to wash the sensor carefully with distilled water, wipe the sensor with tissue and inject about 3 to 4 mL of next solution to the sensor with adjustable pipette for more accurate result.

The data is represented as shown in Table 2. From Table 2, graph conductance versus concentration was plotted. The critical micelle concentration (CMC) was determined at the point where two different slopes are intercepting.

Table 2: Data representation for CMC measurement

Volume of LABS added (mL)	Volume of deionized water added (mL)	Concentration of diluted LABS (ppm)	Conductivity (μS/cm)
0	20	0	
3	17	150	
4	16	200	
5	15	250	
6	14	300	
7	13	350	
8	12	400	
9	11	450	
10	10	500	
11	9	550	
12	8	600	
13	7	650	
14	6	700	
15	5	750	

3.3 Characterization of LABS by UV-Vis Spectrophotometer

Characterization of LABS surfactant was started by determining the specific wavelength which gave the accurate absorbance value. The determination of specific wavelength was done by observation on the spectrum obtained from UV-Vis spectrophotometer. At a specific wavelength, a band in the spectrum showed a significant peak corresponding to concentration of surfactant.

After determining the specific wavelength to detect LABS surfactant in UV-Vis spectrophotometer, correlation graph was constructed as reference to determine the unknown concentration of surfactant after static adsorption test. The experiment was done by preparing different concentration of surfactant solution from 0 ppm to 850 ppm. This experiment took place at Block 4 level 2 using UV-Vis spectrophotometer.

In using UV-Vis spectrophotometer, there were a few procedures that have to be followed. First foremost, the calibration of UV-Vis spectrophotometer was performed by clicking *"Connect"*. After calibration of equipment was done, the baseline method was performed in the range of 350 to 90 nm wavelength. The baseline was performed for air, followed by empty cuvettes (both of them) and distilled water (both cuvettes) by clicking *"Baseline"*. Two cuvettes with 1 mm width were used to represent sample and reference. Surfactant solution is consisting of surfactant and water. Therefore, the reference/baseline was taken as distilled water to get the absorbance of surfactant only without mixing with water.

After the baseline method was performed, one of the cuvettes (the right side) was taken out from the equipment and filled with samples. Another cuvette consisting distilled water was left inside the equipment as reference for the sample. The measurement was performed in spectrum method to get more accurate results. The measurement started by clicking *"Measure"*.

The correlation graph was constructed by plotting absorbance versus concentration of surfactant solution. The correlation graph was used to determine the unknown surfactant concentration based on absorbance measured by UV-Vis spectrophotometer.

Table 3: Data representation for correlation graph construction

Volume of LABS added (mL)	Volume of deionized water added (mL)	Concentration of diluted LABS (ppm)	Absorbance at 224 nm
0	15	0	
0.75	14.25	50	
2.25	12.75	150	
3.75	11.25	250	
5.25	9.75	350	
6.75	8.25	450	
8.25	6.75	550	
9.75	5.25	650	
11.25	3.75	750	
12.75	2.25	850	
14.25	0.75	950	

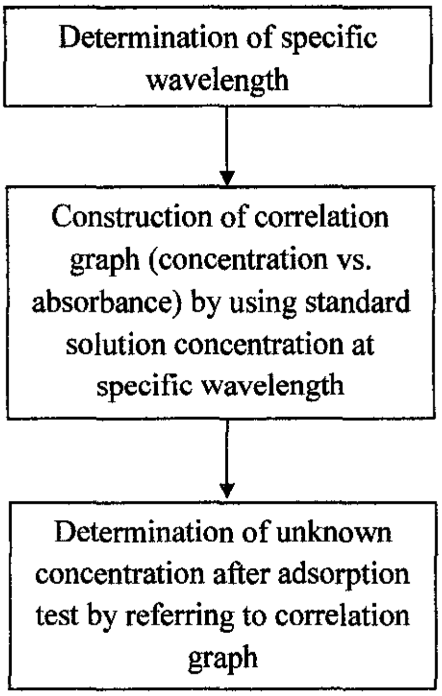


Figure 6: Characterization of LABS surfactant by UV-Vis spectrophotometer

3.4 Static Adsorption Test

There are two types of adsorption test well known in surfactant adsorption study; static and dynamic adsorption test. Simply said, the static adsorption test was carried out with shaking the samples meanwhile the dynamic adsorption test needs more complicated experiment environment such as core flooding test. The core flooding test cannot be done in UTP because core flooding equipment was still in development process. Therefore, static adsorption test was chosen to conduct adsorption study on LABS surfactant.

Malaysian sandstone was received in a cylindrical core. Therefore the sandstone was broken into small pieces before crushed into powder by using crusher in Block 17 level 2. Next, 25 mL test tubes were used to mix 1 gram of sandstone powder with surfactant solution. The mixture was left on the shaker for 24 hours in Block 5 level 1 (microbiological laboratory).

After 24 hours, samples were removed out from 25 mL test tubes to smaller test tubes. These small test tubes were taken to centrifuge equipment to separate solid (sandstone powder) and surfactant solution for 30 minutes at 2500 rpm. The clear surfactant solutions were separated into another test tube before taken to UV-Vis spectrophotometer to observe the absorbance value. The absorbance was observed at 224 nm of wavelength and referred to correlation graph to get the final or equilibrium surfactant concentration. The chronological procedure of adsorption is test is represented in Figure 7.

As precautions, the separation of surfactant solution with solids must be carefully done to get a clear liquid solution. In addition, filter paper was used to remove tiny particles of solids suspended in liquid solution. The existence of these solid particles in liquid solution will result non accurate reading on the absorbance value given by UV-Vis spectrophotometer.

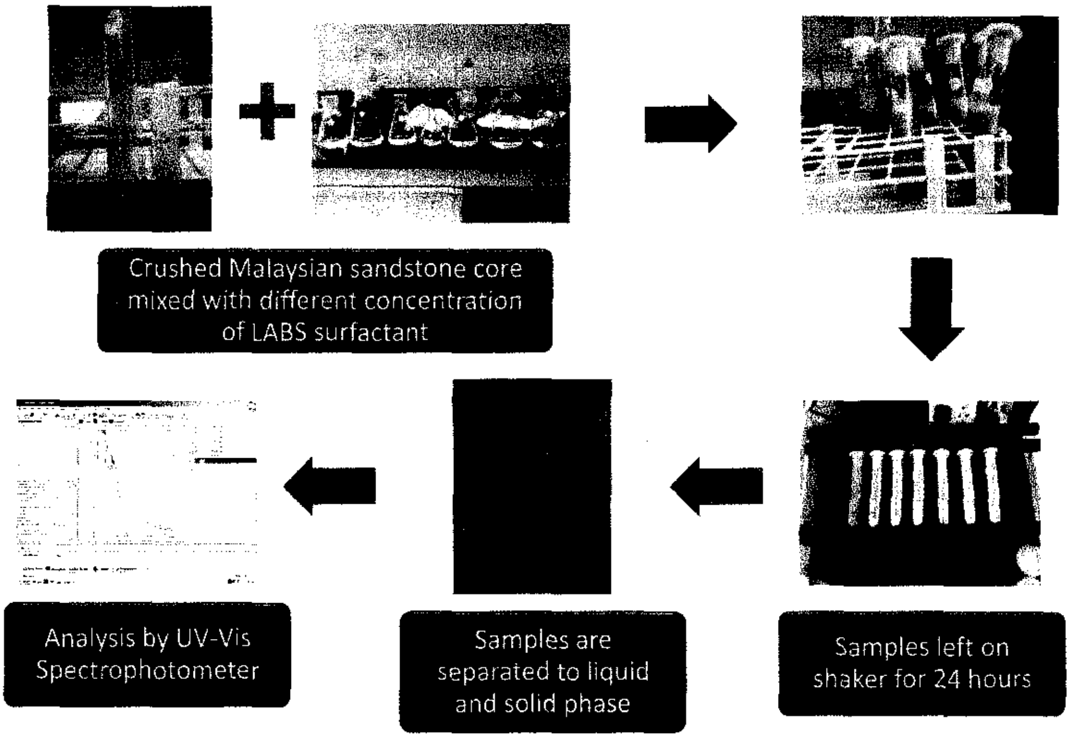


Figure 7: Method on performing static adsorption test

For data analysis, initial and final surfactant concentration, mass of adsorbent (sandstone) and volume of surfactant solutions were recorded to obtain adsorption density as shown in Table 4. In other word, the adsorption density is the amount of surfactant adsorbed per gram of sandstone. The adsorption density was calculated by using formula 1 as below.

$$q_e = (C_i - C_e)\frac{V}{m} \tag{1}$$

Where

q_e = amount of surfactant adsorbed on the adsorbent (mg surfactant/g adsorbent)

C_i = initial concentration of surfactant solution (mg/L)

C_e = equilibrium/final concentration of surfactant solution (mg/L)

V = volume of surfactant solution (L)

m = mass of adsorbent (g)

Table 4: Data representation for static adsorption test

Initial Surfactant Concentration (ppm)	Absorbance	Final Surfactant Concentration (ppm)	Adsorption Density
0			
100			
200			
300			
400			
500			
600			
700			
800			
900			
1000			
1100			
1200			
1300			
1400			
2000			
2500			
3000			
3500			
4000			
4500			
5000			
6000			
7000			
8000			
9000			
10000			
11000			
12000			
13000			
14000			
15000			

3.5 Adsorption Isotherms

Quantitatively, adsorption of a certain compound on a solid surface is described by an adsorption isotherm. It is obtained by plotting the measured amount of the adsorbate on the surface against the equilibrium concentration of adsorbate in solution. Different adsorption models have been developed to describe experimental adsorption data; the most common models used for describing adsorption at the solid-liquid interface are the Langmuir and the Freundlich models (Shaw, 1992).

A basis assumption of Langmuir isotherm is that the adsorption takes place at specific homogeneous sites in the adsorbent. In addition with that, no further adsorption can take at that site when a site is occupied by a solute and the heat of adsorption is independent of surface charge.

$$\frac{1}{q_e} = \left(\frac{1}{C_e}\right)\left(\frac{1}{K_L q_{max}}\right) + \frac{1}{q_{max}} \tag{2}$$

Where

q_e = amount of surfactant adsorbed on the adsorbent (mg surfactant/g adsorbent)

q_{max} = maximum amount of surfactant adsorbed in the sandstone (mg surfactant/g sandstone)

K_L= Langmuir equilibrium constant (L/mg)

C_e = equilibrium/final concentration of surfactant solution (mg/L)

The Freundlich adsorption isotherm can be derived from the Langmuir isotherm by introducing an exponential change to the heat of adsorption with surface coverage. Thus, this model implies adsorption on an energetically heterogeneous surface. The different adsorption sites may be grouped patchwise, with sites having the same heat of adsorption grouped together.

$$lnq_e = lnK_L + \frac{1}{n} lnC_e \qquad (3)$$

Where

q_e = amount of surfactant adsorbed on the adsorbent (mg surfactant/g adsorbent)

q_{max} = maximum amount of surfactant adsorbed in the sandstone (mg surfactant/g sandstone)

K_f = Freundlich equilibrium constant (L/mg)

C_e = equilibrium/final concentration of surfactant solution (mg/L)

n = Freundlich constant

Both Langmuir and Freundlich isotherms are applicable to the adsorption of surfactants on mineral surfaces. However, due to specific properties of surfactant molecules (e.g. their ability to form micelles or adsorbed multi layers) the adsorption of these molecules can be characterized by other types of isotherms. For instance, adsorption of ionic surfactants on oppositely charged surfaces is frequently described by an S-shaped isotherm when plotted using a logarithmic scale and referred to as a Somasundran isotherm (Koopal, Lee, & BÃ¶hmer, 1995) as shown in Figure 8.

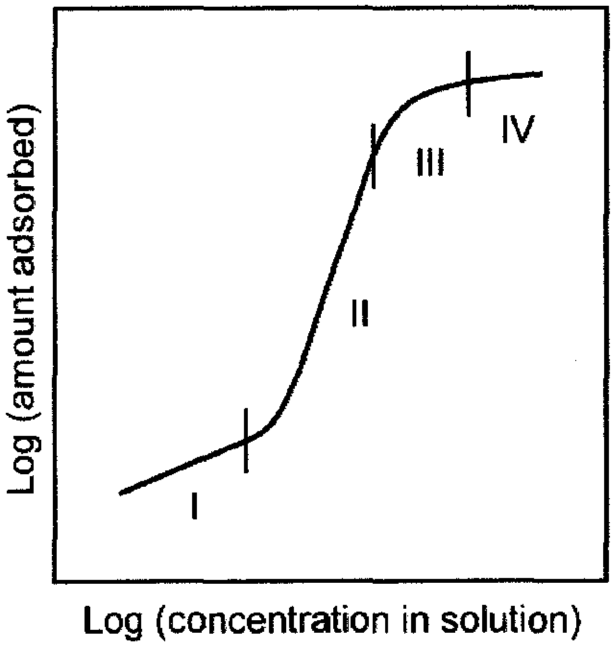


Figure 8: Somasundran isotherm

CHAPTER 4

RESULTS AND DISCUSSIONS

This chapter discusses the result and analysis laboratory data taken to assist the adsorption study of anionic surfactant onto Malaysian sandstone. There are three parts consisting of CMC determination of LABS surfactant, characterization of LABS by UV-Vis spectrophotometer and static adsorption test. In first part, CMC of LABS surfactant was determined to predict the equilibrium concentration which yields constant adsorption density without getting to static adsorption test yet. The second part shows the correct method on using UV-Vis spectrophotometer to represent concentration of surfactant in a function of absorbance. In the last part, an adsorption isotherm was constructed to represent the mechanism of adsorption of LABS to Malaysian sandstone.

4.1 CMC Measurement of LABS Surfactant

The determination of CMC is generally based on the localization of the position of a breaking point in the concentration dependencies of selected physical or chemical properties of surfactant solutions. Because of the surface activity of these substances, measurements of the surface tension of surfactant solutions represent the principal method of CMCs determination (Oremusova et al., 2010).

However, it is rather tedious and time-consuming procedure. In the case of ionic surfactants, the utilization of electrochemical measurements is much more convenient, especially the measurements of the electrical conductivity of their solutions with varying concentration. The conductivity method is based on the finding of a breaking point on the curves, which describe the concentration dependence of conductivity. It is well-known, that the conductivity of any solution is directly proportional to the concentration of its ions. The point, where the micelle formation starts, is indicated on the concentration dependence of specific conductivity (K) as a breaking point. It is easy to find the breaking point, because it marks a significant change of the linear slope of the dependence K =f(c). The requested value of CMC is the intercept of two linear functions with mutually different slopes (Oremusova et al., 2010).

According to Figure 9, CMC for LABS surfactant was found at 480 mg/L. This value was valid according to past literature which reported the CMC value for LABS surfactant by surface tension method to be 433.5 mg/L (Ou et al., 1996). The difference in value may result from temperature inference while doing the experiment and different method used in determining CMC of LABS surfactant.

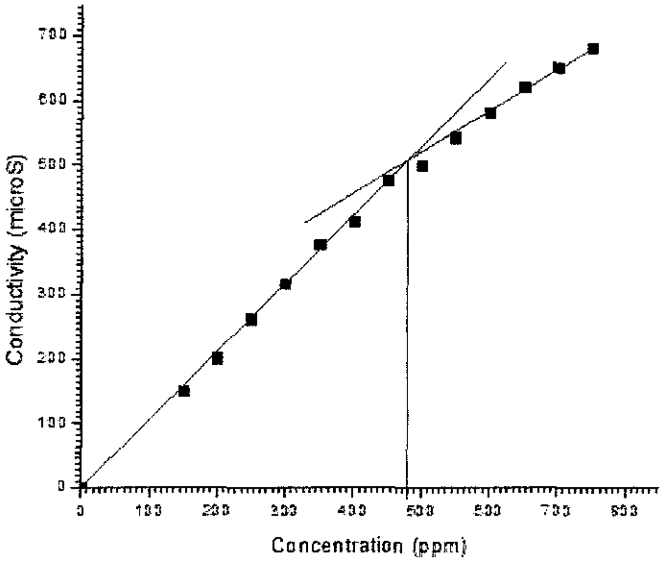


Figure 9: CMC Determination of LABS surfactant

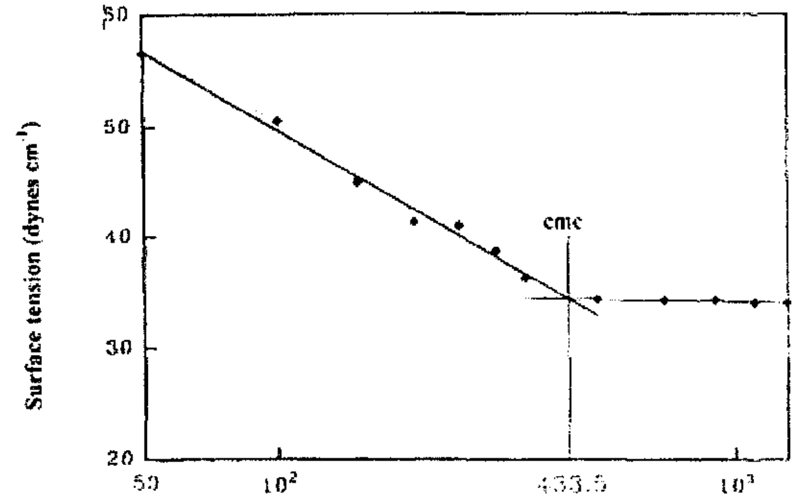


Figure 10: Determination of CMC by surface tension method for LABS surfactant (Ou et al., 1996)

4.2 Characterization of LABS Surfactant by UV-Vis Spectrophotometer

The absorbance value was taken at the highest peak of spectrum which shows a significant value corresponding to the concentration at a specific wavelength shown in Figure 11. Based on Figure 11, LABS surfactant has a significant peak at wavelength of 224 nm. Therefore, the absorbance value for all surfactant solutions was taken at 224 nm. This wavelength is valid based on the literature review done by the past researchers (Schmitt, 2001).

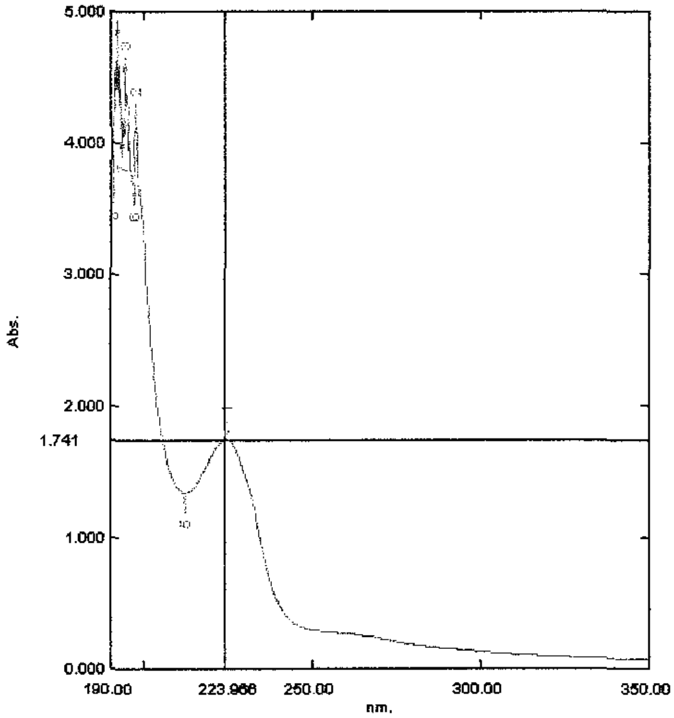


Figure 11: Method of determining absorbance for surfactant solutions

In the initial stage of the experiment, the correlation graph was constructed using 10 mm width of cuvette (path length) for 10 ppm, 20 ppm, 30 ppm, 40 ppm, 50 ppm, 60 ppm, 70 ppm, 80 ppm, 90 ppm and 100 ppm. Based on the spectrum, the absorbance for concentration higher than 100 ppm was not possible because the highest value of absorbance that can be detected by the equipment was five.

Then, the correlation graph is repeated again using 1 mm width of cuvette. By using 1 mm width of cuvette, the absorbance for 10 ppm until 100 ppm concentration of surfactant was lower than using 10 mm width of cuvette.

Determination of absorbance by UV-Vis spectrophotometer follows Beer-Lambert's Law. This law stated that the amount of radiation absorbed or transmitted by a solution or medium is an exponential function of the concentration of the absorbing substance present and of the length of the path of the radiation through the sample (Harris, 2003).

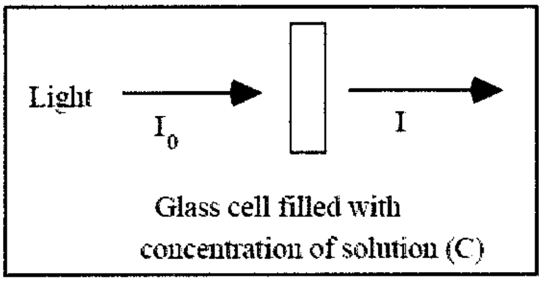


Figure 12: Concept of absorption spectroscopy (Harris, 2003).

Beer showed that, at a given thickness, the absorption coefficient introduced by Lambert's law was directly proportional to the concentration of the absorbing substance in a solution. Combination of these two results gives the relationship of Beer-Lambert's Law (Harris, 2003).

$$A \propto CL$$

$$A = \varepsilon CL$$

Where A = Absorbance

ε = Molar extinction coefficient

C = Concentration of solution

L = Length of the light path through the solution

In Table 5, the absorbance value obtained for different concentration did followed Beer-Lambert's Law by showing increasing absorbance as the concentration of surfactant solution is increased. The absorbance value for 10 ppm until 100 ppm of 10 mm width of cuvette showing increased of 0.366 for 10 ppm meanwhile for 1 mm width of cuvette showing increased of 0.430.

This law also showed that the absorbance of the concentration is dependable on the width of the cuvette. At 50 ppm of surfactant solution, the absorbance value recorded was 1.843 for 10 mm width and 0.212 for 1 mm width of cuvette as shown in Table 12. In Figure 14, the spectrum showed that the absorbance of 950 ppm was still detected in the range of 3.6 for smaller width of cuvette meanwhile the absorbance for 100 ppm was recorded near to 5 (limit) for higher width of cuvette. The results show that the absorbance is proportional to the width of cuvette.

This finding is very important in determining the unknown concentration of surfactant solution after adsorption test. 10 mm width of cuvette gave limit to surfactant concentration until 100 ppm meanwhile 1 mm width gave ease to determine concentration more than 1000 ppm. This finding also is reasonable because the critical micelle concentration (CMC) obtained from conductivity method was higher than 100 ppm and can only be detected by 1 mm width of cuvette.

Table 5: Comparison of absorbance for 10 mm width and 1 mm width of cuvette

Concentration (ppm)	Absorbance	
	10 mm Width	1 mm Width
0	0	0
10	0.366	Not recorded
20	0.745	Not recorded
30	1.111	Not recorded
40	1.477	Not recorded
50	1.843	0.212
60	2.209	Not recorded
70	2.575	Not recorded
80	2.941	Not recorded
90	3.307	Not recorded
100	3.673	Not recorded
150	Cannot be detected	0.576
250	Cannot be detected	1.012
350	Cannot be detected	1.435
450	Cannot be detected	1.753
550	Cannot be detected	2.141
650	Cannot be detected	2.494

750	Cannot be detected	2.976
850	Cannot be detected	3.365
950	Cannot be detected	3.694

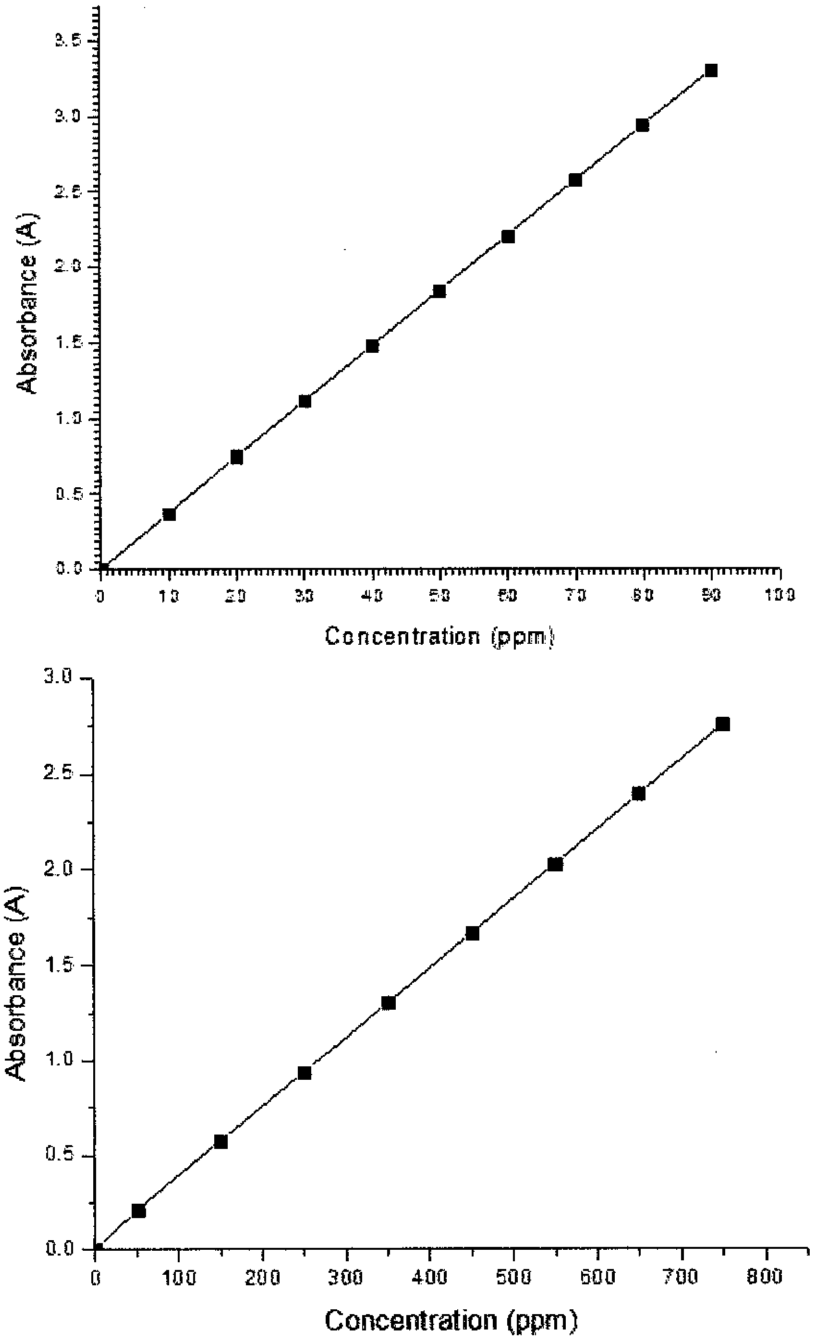


Figure 13: Comparison between correlation graph for 10 mm width (Ou et al.) and 1 mm width (*down*) of cuvette

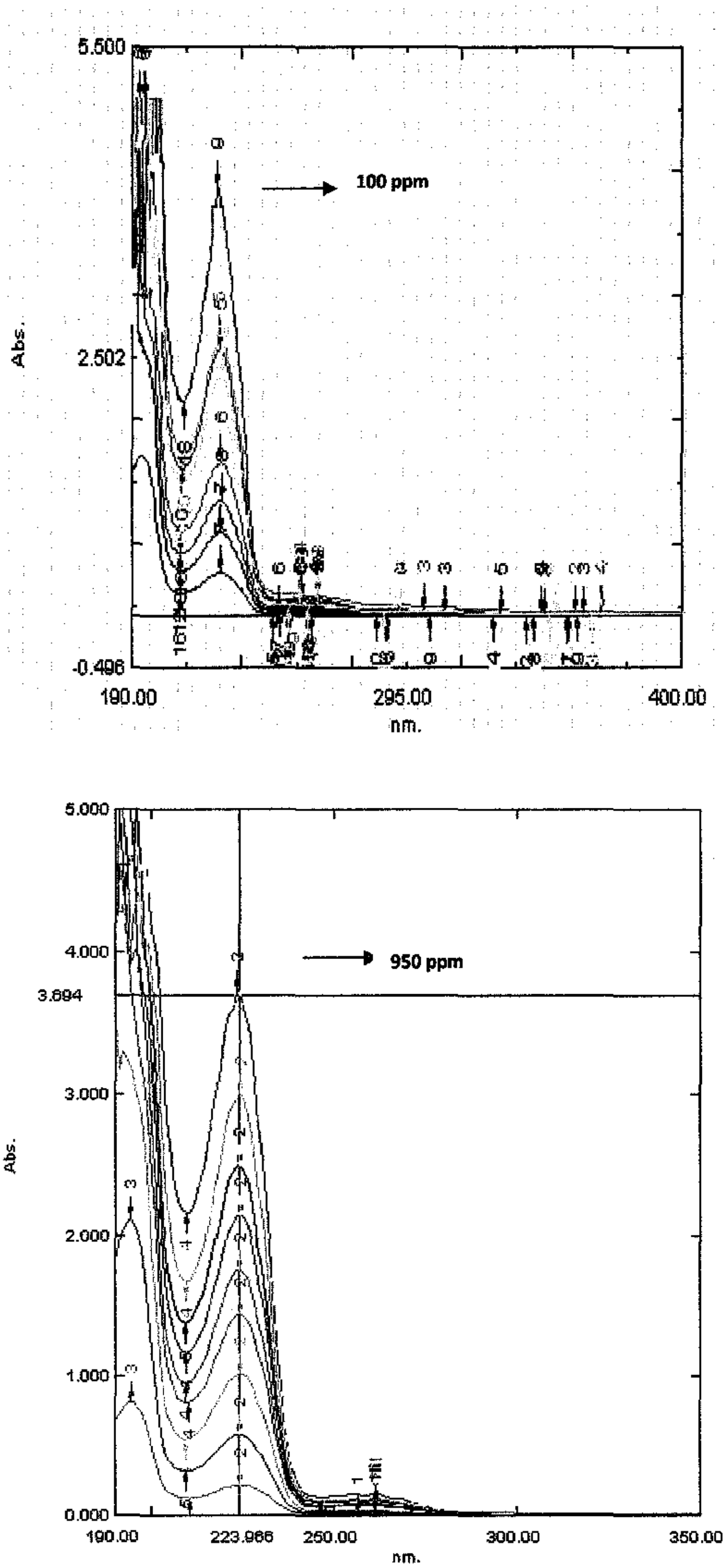


Figure 14: Comparison of absorbance spectrum for 10 mm width (*top*) and 1 mm width (*bottom*) of cuvette

4.3 Static Adsorption Test

Static adsorption tests were done for surfactant solution in range of 100 mg/L to 1900 mg/L concentration. The mass of adsorbent (sandstone powder) used was 1 gram and the volume of each surfactant solution was 15 mL. The findings and result are represented in Table 6.

Table 6: Result of static adsorption test at 25 °C with different initial surfactant concentration

Initial Surfactant Concentration (mg/L)	Absorbance of Final Surfactant	Final Surfactant Concentration (mg/L)	Mass of Sandstone Sample (g)	Adsorption Density (mg/g)
0	0	0	0	0
100	0.376	96	1.0121	0.060
200	0.541	140	1.0056	0.984
300	0.612	158	1.0001	2.220
400	0.659	168	1.0068	3.516
500	0.753	185	1.0257	4.563
600	0.729	192	1.0404	6.027
700	0.859	214	1.0091	7.195
800	0.886	222	1.0156	8.522
900	0.900	225	1.0019	10.091
1000	0.985	244	1.0024	11.253
1100	0.999	247	0.9997	12.724
1200	1.098	272	0.9998	13.848
1300	1.197	278	1.0023	14.936
1400	1.140	294	1.0006	16.670
2000	1.200	295	1.0000	25.455
2500	1.329	318	1.0000	32.445
3000	1.365	334	1.0000	39.810
3500	1.386	335	1.0000	47.235
4000	1.412	345	1.0000	54.630
4500	1.506	372	1.0000	61.770
5000	1.576	395	1.0000	69.000
6000	1.612	406	1.0135	82.748

7000	1.647	417	1.0125	97.511
8000	1.659	421	1.0025	113.401
9000	1.682	428	1.0006	128.518
10000	1.741	426	1.0365	138.307
11000	1.788	459	0.9965	158.731
12000	1.847	474	1.0000	172.950
13000	1.894	488	1.1018	183.500
14000	1.965	506	1.0140	199.704
15000	2.059	529	0.9945	218.326
16000	2.106	542	1.0243	226.457
17000	2.2	567	1.0090	244.386
18000	Cannot be detected	None	0.9976	None
1900	Cannot be detected	None	0.9945	None

According to Table 6, there are a few relationships obtained in terms of initial surfactant concentration, absorbance of final surfactant concentration, final surfactant concentration and adsorption density. Figure 13 shows the relationship between initial and final surfactant concentration. The slope obtained for the first 2000 mg/L is steeper than initial surfactant concentration more than 2000 mg/L. This shows that the adsorption of surfactant onto sandstone is more active at first 2000 mg/L. As reaching to 2100 mg/L and above of that, the adsorption activity is slowing down due to most of the adsorption sites in the sandstone have been filled with the surfactant monomers.

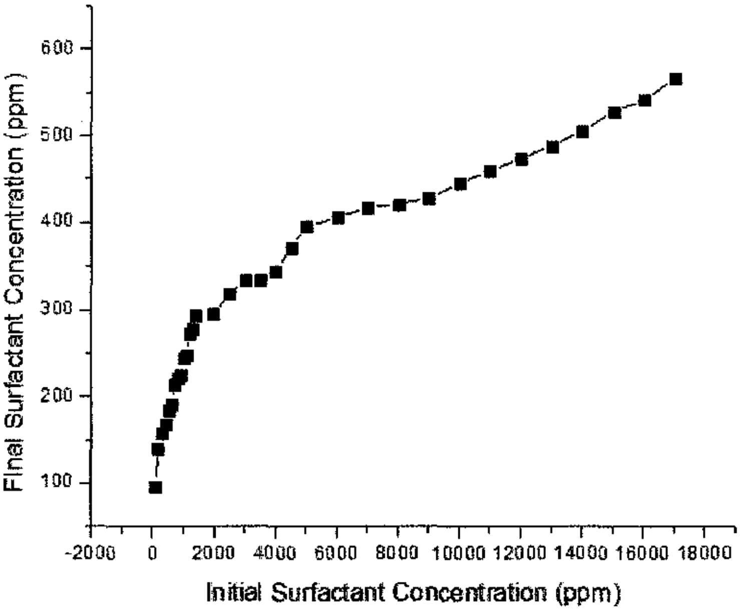


Figure 15: Graph initial surfactant concentration versus final surfactant concentration for static adsorption test

Besides that, a relationship between final concentrations of surfactant with absorbance from UV-Vis spectrophotometer has been observed. According to Figure 15, final concentration of surfactant is proportional to absorbance and provided a perfect linear fit in the graph. These can be explained by Beer-Lambert's Law which stated that the absorbance is proportional to the concentration of solution in a fixed solution molar absorptivity and length of the path (width of cuvette).

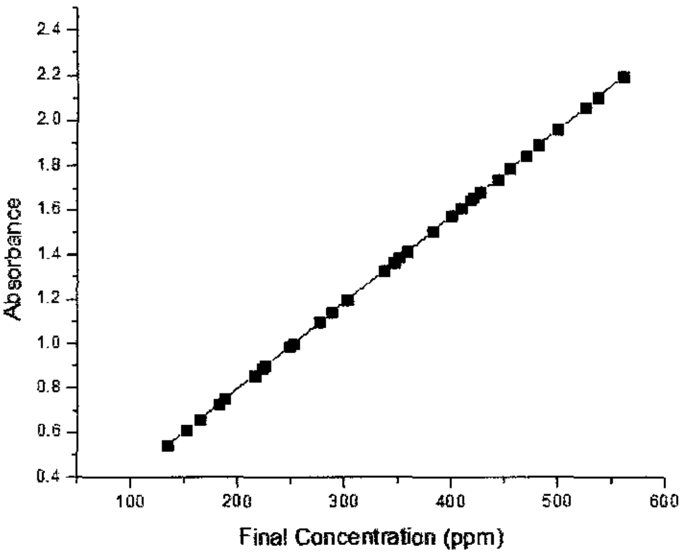


Figure 16: Graph final surfactant concentration versus absorbance from UV-Vis spectrophotometer

After the samples left out on the shaker for 24 hours, the samples were taken to centrifugal equipment to collect a clear surfactant solution only by using centrifugal force to settle down the solids at the bottom. The separation indeed was the most important part in the experiment because UV-Vis spectroscopy is very sensitive and can be only detected a clear liquid solution only. A good spectrum shows a significant absorbance value at 224 nm to represent the surfactant meanwhile the existence of impurities from sandstone in the surfactant solution gave a higher absorbance value as they may also be detected at 224 nm as shown in Figure 16.

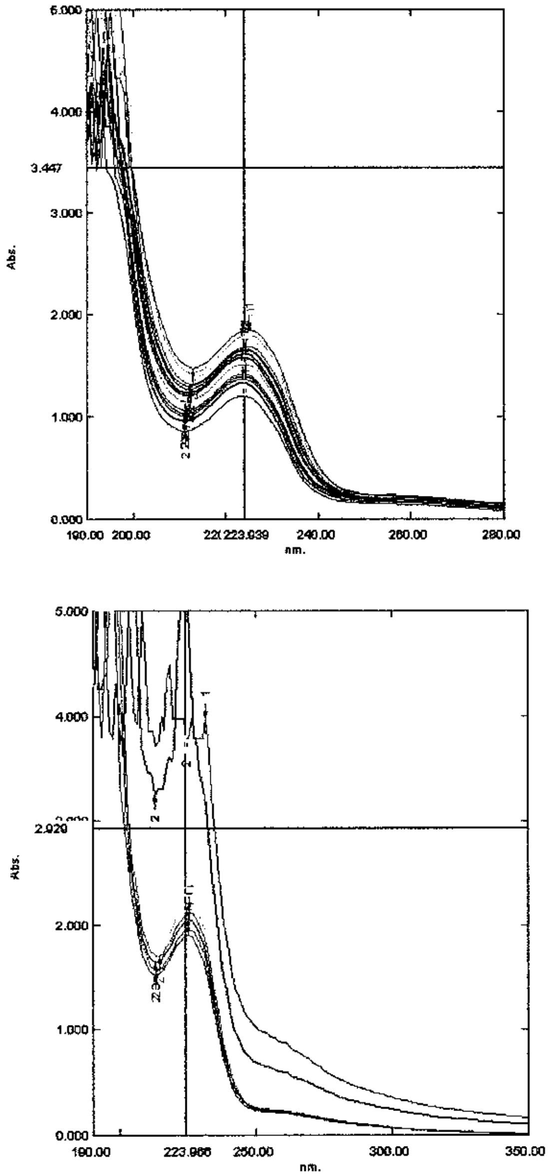


Figure 17: Comparison of spectrum without (Ou et al.) and with (*down*) impurities exist in the final surfactant concentration

The raw data collected from static adsorption test are represented in Figure 17. In order to develop an isotherm, unrefined date were removed without changing the original data collected from the test. Figure 20 shows the adsorption isotherm curve for LABS surfactant after static adsorption test. It is observed that the adsorption isotherms can be divided into three regions (Somasundaran & Hanna, 1979) (Somasundaran & Huang, 2000) (Somasundaran & Krishnakumar, 1997).

According to Somasundran, region 1 is characterized by the existence of electrostatic interactions between LAB surfactant which has negative charge on its head with the oppositely charges in the sandstones. The adsorption in this region can be represented by Gouy-Chapman equation for the diffuse layer by considering an ion exchange process between LABS ions and mineral ions (Zhang & Somasundaran, 2006).

The adsorption of counter ions or potential determining ions of surfactant at relatively low concentration can be represented by electrical double layer concept. According to the electrical double layer concept, an electrical potential exists across an interface when there is an unequal distribution of charges across the surface. This unequal distribution results in each side of the interface acquiring net charges of opposite sign. The idea of the electrical double layer was proposed by Helmholtz in 1879 and modified by Stern in 1924 (Schramm, 2000).

In the Stern modification, the counter ions in the solution which is opposite in charge relative to the surface were divided into two layers as below.

1. A layer of ions adsorbed close to the surface (generally called as the Stern layer)
2. A diffuse layer of counter ions (generally called as the Gouy layer)

As shown in Figure 18, the potential decreases rapidly within the Stern layer (δ) and more gradually within the Gouy layer (d). The net charge in the Stern layer plus the Gouy layer is equal and opposite in sign to the surface charge. For minerals the surface charge is primarily controlled by the pH and the nature of the mineral.

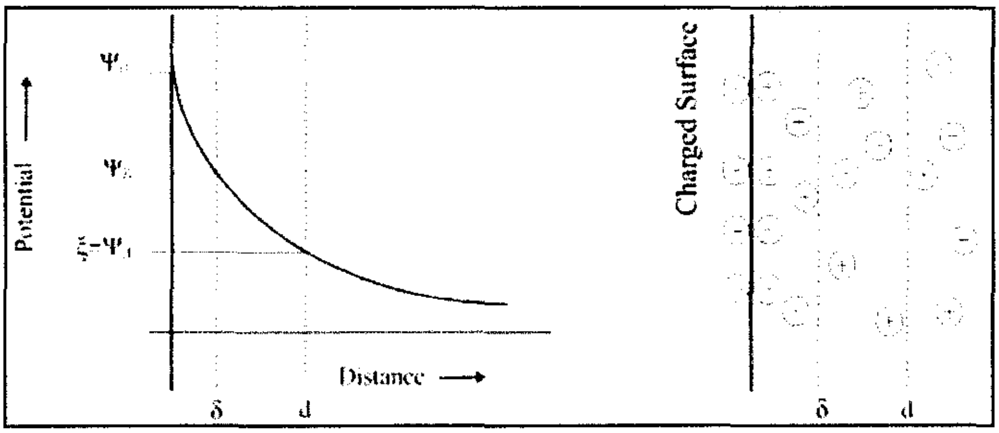


Figure 18: Electrical double layer model (Schramm, 2000)

Region 2 is marked by a sudden increase in adsorption density which is attributed to the onset of surfactant aggregation at the surface through lateral interaction between hydrocarbon chains. The aggregates are generically called as "solloids" or surface colloids and include aggregates such as hemimicelles, admicelles and sef assemblies. In addition with that, it has been concluded that both electrostatic and lateral interaction forces are contributing to the adsorption of LABS surfactant onto the sandstones (Zhang & Somasundaran, 2006).

Region 3 exhibits a marked decrease in the slope of the isotherm as shown in Figure 15. Somasundaran stated that in this region there is an increasing electrostatic hindrance to surfactant adsorption following the interfacial charge reversal caused by adsorption of the charges species in this region and beyond (Zhang & Somasundaran, 2006).

There should be another region exist in the isotherm called as region 4. In region 4, a constant adsorption density will be observed due to maximum surface coverage hence promoting the formation of micelles in the bulk or monolayer coverage, whichever is attained at the lowest surfactant concentration. Increasing surfactant concentration will not alter the adsorption density (Zhang & Somasundaran, 2006).

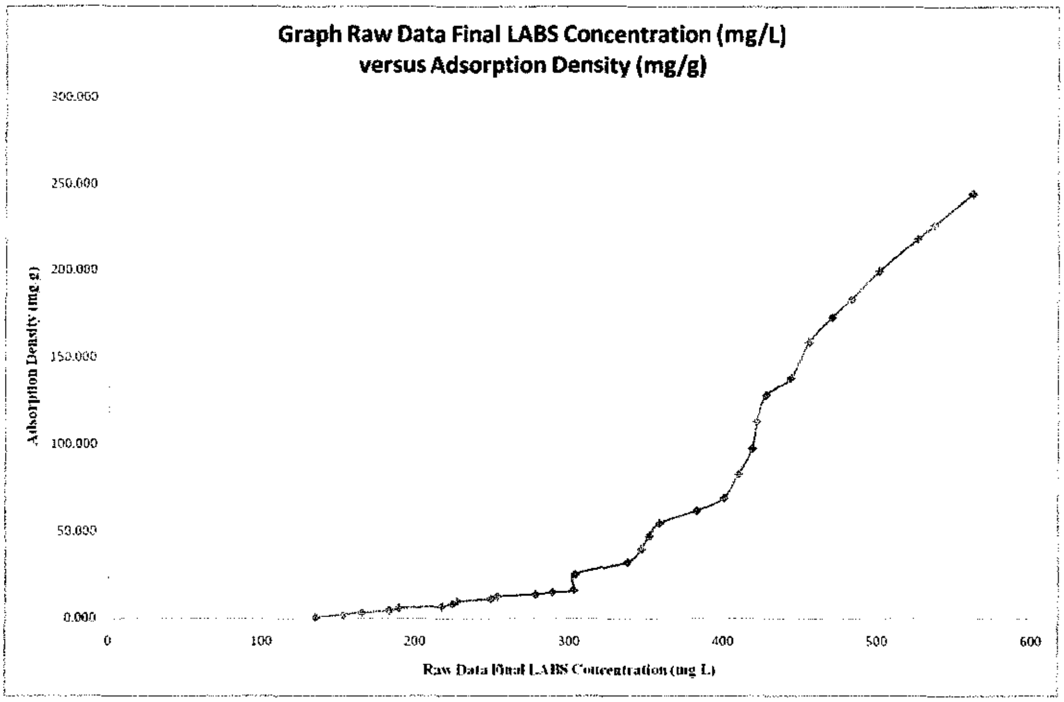


Figure 19: Graph raw data of final LABS concentration (mg/L) versus adsorption density at 25 °C

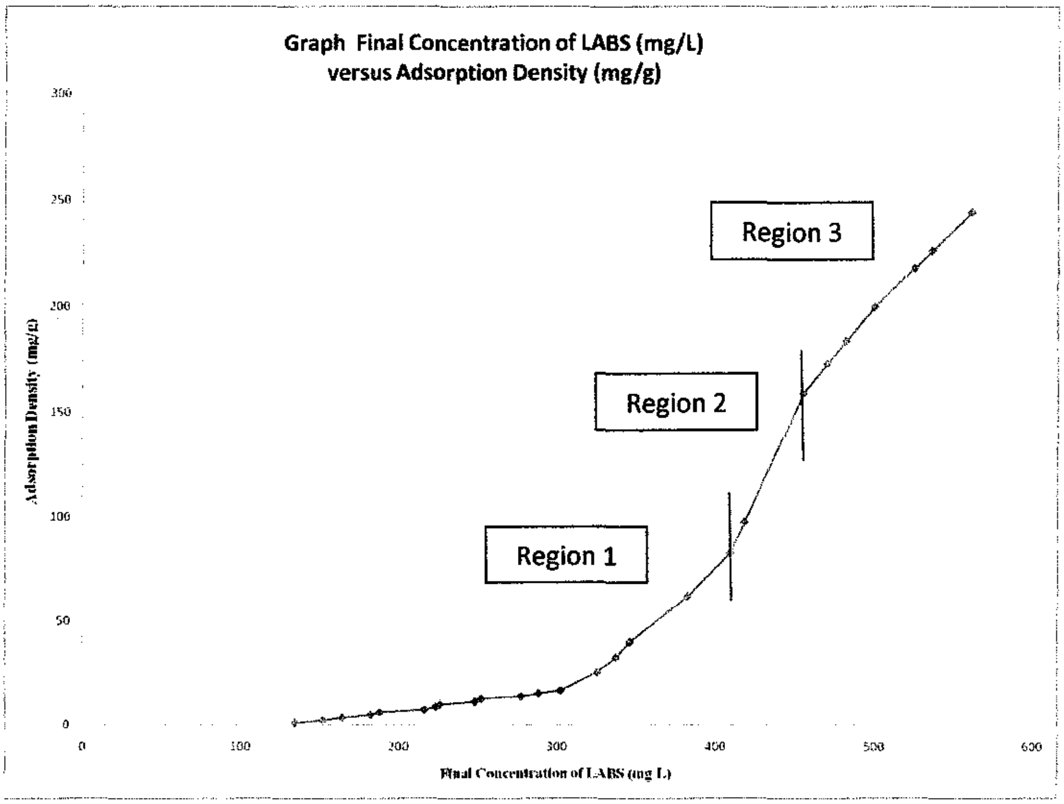


Figure 20: Adsorption isotherm of LABS surfactant onto Malaysian sandstone at 25 °C

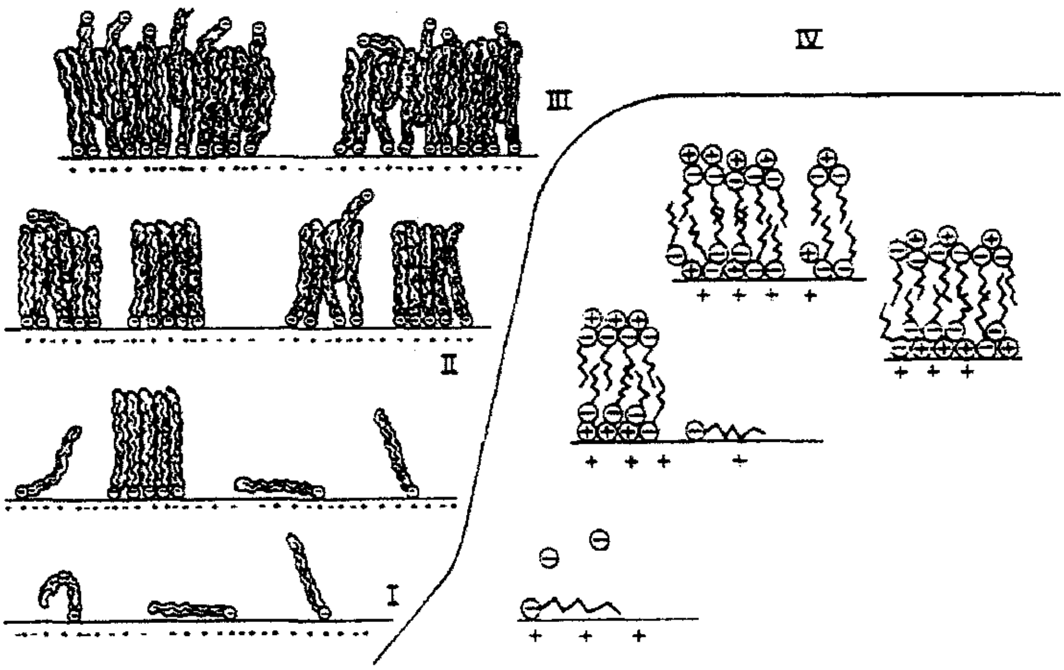


Figure 21: Mechanisms of surfactant adsorption according to Somasundran isotherm (Zhang & Somasundaran, 2006)

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

In this study, the objectives mentioned in the first chapter were accomplished in two main parts. In the first part, the characterizations of LABS surfactant were successfully done by CMC measurement and UV-Vis spectrophotometer. CMC measured for LABS surfactant was 480 mg/L by conductivity method. For characterization of surfactant by UV-Vis spectrophotometer, it can be concluded that the wavelength used to detect the surfactant was 224 nm. Besides, the absorbance can be concluded to be proportional to the path length or width of cuvette. In order to detect a high unknown concentration, smaller width of cuvette should be used for more accurate results. In addition, a detailed method was provided in analysis of anionic surfactant by UV-Vis spectrophotometer.

In second part of this research project, static adsorption tests were successfully done for LABS surfactant with Malaysian sandstone. The samples were left out for one day at room temperature and pressure before taken to UV-Vis spectrophotometer to get the concentration of final concentration before adsorption density was calculated. A plot of final concentration of surfactant with adsorption density provided an isotherm to the adsorption of LABS surfactant on Malaysian sandstone. It was concluded that adsorption of anionic surfactant onto Malaysian sandstone followed Somasundran isotherm which has four regions describing the mechanism of adsorption to sandstone. The first region shows an existence of electrostatic interactions between LAB surfactant which has negative charge on its head with the oppositely charges in the sandstones by following Gouy-Chapman equation. The second region shows adsorption of surfactant is due to the onset of surfactant aggregation at the surface through lateral interaction between hydrocarbon chains. In this region, the formation of aggregation such hemimicelles and admicelles can be found. In the third region adsorption of surfactant is decreasing due to an increasing electrostatic hindrance to surfactant adsorption following the interfacial charge reversal caused by adsorption of the charges species in this region and beyond. In the forth region, the adsorption is not happening and formation of micelles can be obtained. The adsorption density is constant and provides that the there is no more surfactant adsorbed onto sandstone at this high concentration.

5.2 Recommendation and Future Works

Several recommendations are made for future work:

1. To get an accurate result of CMC, it is recommended to use surface tension method which is available in Block 14, level 2. Surface tension measurement has been used widely in adsorption study.

2. The adsorption test can be tested with different parameters such as temperature; salinity of brine, pressure and pH to gives a wide data to support the adsorption study. These parameters have their significant effect on the adsorption of surfactant to sandstone especially pH of surfactant solution.

3. Besides static adsorption test, a kinetic adsorption test should be conducted using core flooding test. The kinetic adsorption test will provide the data on the adsorption from breakthrough time with pore volume of sandstone.

4. A study of comparison between static adsorption test on Malaysian sandstone with static adsorption test on Berea sandstone should be done to compare the efficiency of surfactant flooding in Malaysia.

5. A joint venture should be done between UTM and UTP EOR Research Centre for future research work in providing laboratory data to field application of surfactant flooding because both universities have many publications on EOR research papers.

CHAPTER 6

APPENDICES

6.1 Spectrum of Final LABS Concentration

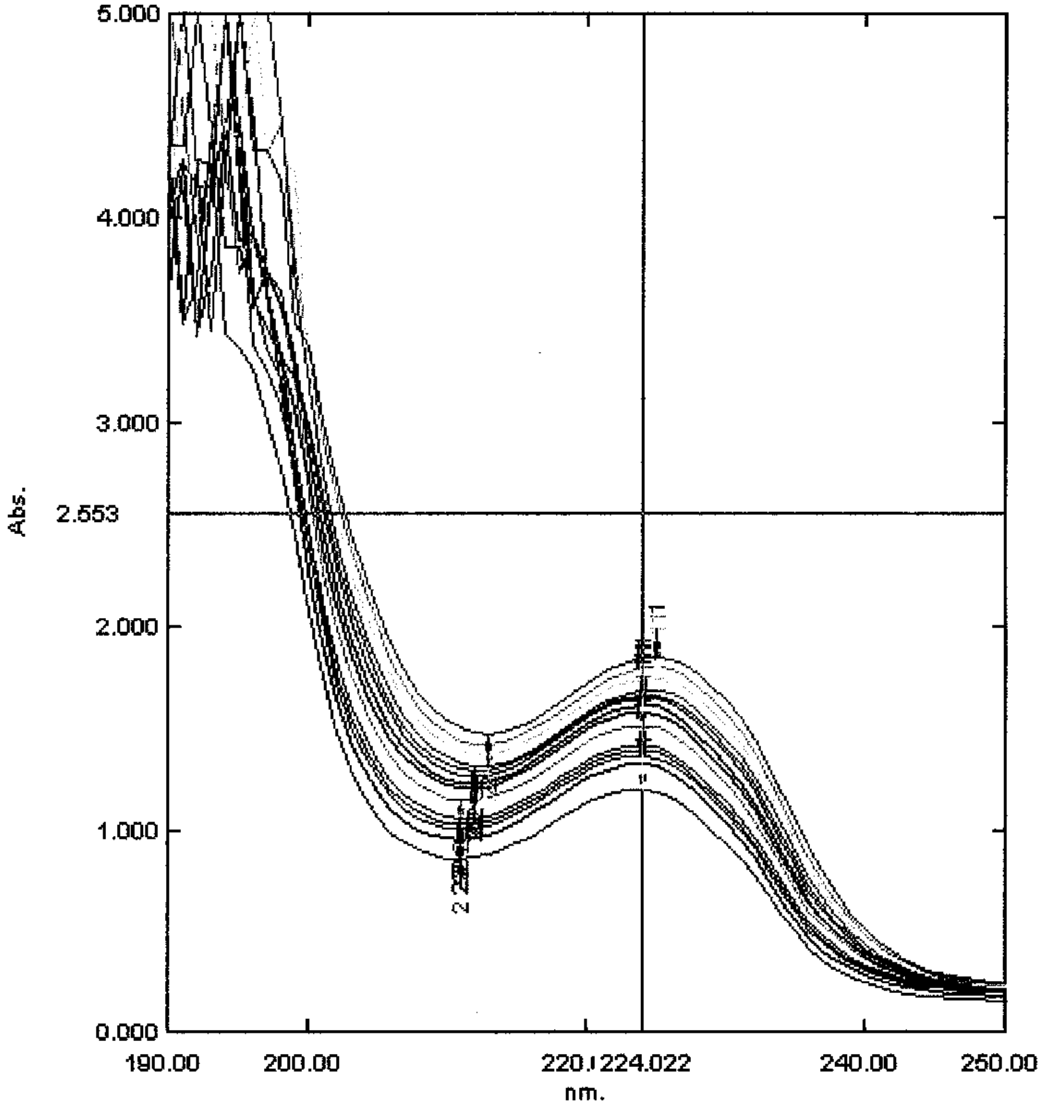


Figure 22: Spectrum from 2000 mg/L to 12000 mg/L

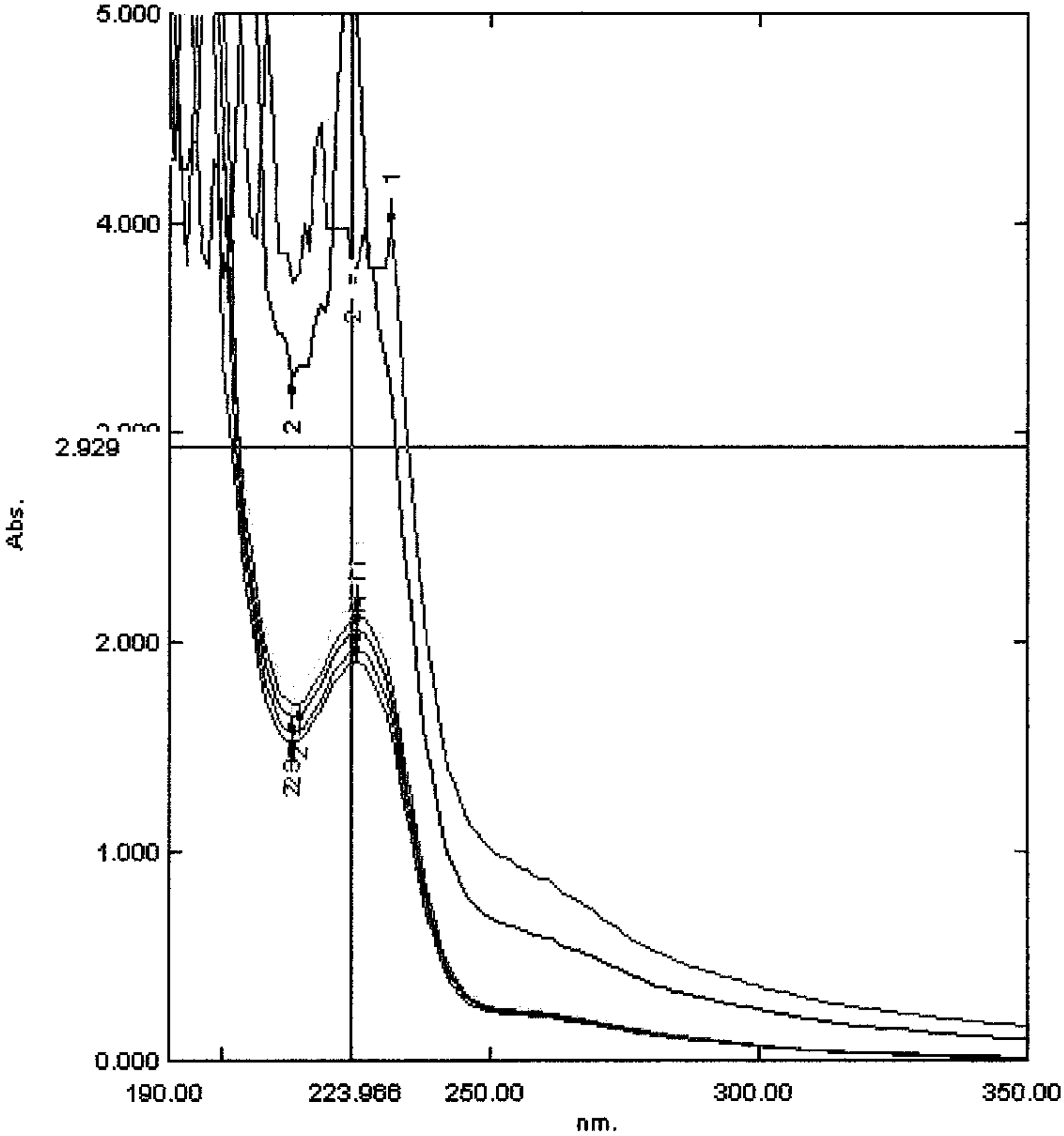


Figure 23: Spectrum from 13000 mg/L to 19000 mg/L

.2 Gantt Chart and Key Milestones

Gantt charts for activities planned along for this final year projects first and second semester are shown in Table 7 and Table 8.

Table 7: Gantt chart for final year project first semester (FYP I)

No	Detail/ Week	1	2	3	4	5	6	7		8	9	10	11	12	13	14
									Mid-Semester Break							
1	Selection of Project Topic															
2	Preliminary Research Work															
3	Submission of Extended Proposal						●									
4	Oral Proposal Defence										●					
5	Project Work Continues															
6	Submission of Interim Draft Report														●	
7	Submission of Finalized Interim Report															●

Table 8: Gantt chart for final year project second semester (FYP II)

No	Detail/ Week	1	2	3	4	5	6	7		8	9	10	11	12	13	14	15
									Mid-Semester Break								
1	Project Work Continues																
2	Submission of Progress Report									●							
3	Project Work Continues																
4	Pre-EDX												●				
5	Submission of Draft Report													●			
6	Submission of Dissertation (soft bound)														●		
7	Submission of Technical Paper														●		
8	Oral Presentation															●	
9	Submission of Project Dissertation (hard bound)																●

CHAPTER 7

REFERENCES

Adamson, A. W., Gast, A. P., & NetLibrary, I. (1967). Physical chemistry of surfaces.

Akstinat, M. H. (1981). Surfactants for enhanced oil recovery processes in high salinity systems-Product selection and evaluation. *Elsevier, New York*, 43-80.

Curbelo, F. D. S., Santanna, V. C., Neto, E. L. B., Dutra, T. V., Dantas, T. N. C., Neto, A. A. D., et al. (2007). Adsorption of nonionic surfactants in sandstones. *Colloids and Surfaces A: Physicochemical and Engineering Aspects, 293*(1-3), 1-4.

Dang, C., Chen, Z. J., Nguyen, N., Bae, W., & Phung, T. H. (2011). *Development of Isotherm Polymer/Surfactant Adsorption Models in Chemical Flooding.*

Hamdan, M. K., Darman, N., Husain, D., & Ibrahim, Z. (2005). *Enhanced Oil Recovery in Malaysia: Making It a Reality.*

Harris, D. C. (2003). *Quantitative chemical analysis*: WH Freeman.

Healy, R. N., Reed, R. L., & Stenmark, D. G. (1976). Multiphase microemulsion systems. *Old SPE Journal, 16*(3), 147-160.

Ibrahim, Z., Abdul Manap, A. A., Abdul Hamid, P., Hon, V. Y., Lim, P. H., & Wyatt, K. (2006). *Laboratory Aspect of Chemical EOR Processes Evaluation for Malaysian Oilfields.*

Koopal, L. K., Lee, E. M., & BÃ¶hmer, M. R. (1995). Adsorption of cationic and anionic surfactants on charged metal oxide surfaces. *Journal of colloid and interface science, 170*(1), 85-97.

Kuhlman, M., Lau, H., & Falls, A. (2000). Surfactant Criteria for Successful Carbon Dioxide Foam in Sandstone Reservoirs. *SPE Reservoir Evaluation & Engineering, 3*(1), 35-41.

Kwok, W., Nasr-El-Din, H., & Hayes, R. (1993). Propagation of an anionic surfactant in radial sandstone cores. *Journal of Canadian Petroleum Technology, 32*(6).

Lawson, J. B. (1978). *The adsorption of non-ionic and anionic surfactants on sandstone and carbonate.*

Mannhardt, K., Novosad, J., & Jha, K. (1994). Adsorption of foam-forming surfactants in Berea sandstone. *Journal of Canadian Petroleum Technology, 33*(2).

Muherei, M. A., & Junin, R. (2009). Equilibrium Adsorption Isotherms of Anionic, Nonionic Surfactants and Their Mixtures to Shale and Sandstone. *Modern Applied Science, 3*(2), P158.

Neogi, P. (1985). Tears-of-wine and related phenomena. *Journal of colloid and interface science, 105*(1), 94-101.

Othman, M., Omar Chong, M., M Sai, R., Zainal, S., Yaacob, A. A., & Zakaria, M. S. (2007). Meeting the Challenges in Alkaline Surfactant Pilot Project Implementation at Angsi Field, Offshore Malaysia. *Offshore Europe.*

Ou, Z., Yediler, A., He, Y., Jia, L., Kettrup, A., & Sun, T. (1996). Adsorption of linear alkylbenzene sulfonate (LAS) on soils. *Chemosphere, 32*(5), 827-839.

Schmitt, T. M. (2001). *Analysis of surfactants* (Vol. 96): CRC.

Schramm, L. L. (2000). *Surfactants: fundamentals and applications in the petroleum industry*: Cambridge Univ Pr.

Somasundaran, P., & Hanna, H. S. (1979). Adsorption of sulfonates on reservoir rocks. *Old SPE Journal, 19*(4), 221-232.

Somasundaran, P., & Huang, L. (2000). Adsorption/aggregation of surfactants and their mixtures at solid-liquid interfaces. *Advances in colloid and interface science, 88*(1-2), 179-208.

Somasundaran, P., & Krishnakumar, S. (1997). Adsorption of surfactants and polymers at the solid-liquid interface. *Colloids and Surfaces A: Physicochemical and Engineering Aspects, 123*, 491-513.

Trogus, F. J., Sophany, T., Schechter, R. S., & Wade, W. H. (1977). Static and dynamic adsorption of anionic and nonionic surfactants. *Old SPE Journal, 17*(5), 337-344.

Zhang, R., & Somasundaran, P. (2006). Advances in adsorption of surfactants and their mixtures at solid/solution interfaces. *Advances in colloid and interface science, 123*, 213-229.