PHASE BEHAVIOUR STUDIES IN ENHANCED OIL RECOVERY (EOR) IN DETERMINATION OF PHASE TYPES USING SURFACTANTS

NURUL IZZA BINTI ABDUL RASHID

CHEMICAL ENGINEERING
UNIVERSITI TEKNOLOGI PETRONAS
JUNE 2004

1) secondary recovery of oil
2) CHE -- Thesis

CERTIFICATION OF APPROVAL

Phase Behaviour studies in Enhanced oil Recovery in determination of phase types using surfactants.

By

Nurul Izza Bt Abdul Rashid

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

Approved by,

(Bawadi bin Abdullah)

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
JUN 2004

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.

NURUL IZZA BINTI ABDUL RASHID

ACKNOWLEDGEMENTS

This research is completed in less than six months prior to productive contributions and guidance of individuals and experts. I would like to take this opportunity to express my appreciation to those who had assisted me in making my Final Year Project Thesis a success First of all, I would like to thank my supervisor, Mr. Bawadi Abdullah for giving me the opportunity to do this project and gave a lot of guidance in this research My appreciation also goes to A. P. Dr. Syed Sahkawat Syah that has contributed me a lot of information regarding this research and encouragement on optimizing this research. Special thanks to the Petronas Research and Scientific Services Sdn. Bhd (PRSS) staff, ultimately to Pn. Fauziyah, EOR Senior Chemist and Ms. Hon Vai Yee, Petroleum Engineer who gave me an opportunity to conduct the experimental works at PRSS, Bangi for their guidance, concern and opportunity provided to me. I would like to extend my appreciation to the rest of the lecturers for their co-operation and willingness to share knowledge and experience with me. Finally, I would like to thank others who had also helped me directly and indirectly throughout this course completion My credit also goes to all lab technicians and my friends, who also has given a great deal of contribution and moral support in terms of references and useful data.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

CHAPTER 1

INTRODUCTION

1.1 Background of Study

For decades the international oil industry sought to extract a higher proportion of the available crude oil in a reservoir. It is still a matter of considerable concern, and some embarrassment, to oilmen that they have to leave behind about two thirds of oil in place (OIP). A further improvement in recovery efficiency can be obtained by the application of more expensive and technically more complex production methods enhanced recovery. These methods are often termed tertiary recovery because of their application after the primary and secondary recovery (water or gas injection) phases.

Enhanced Oil Recovery (EOR) has become an important tool in this effort for greater production efficiency. Oil companies are now being encouraged by all sorts of institutions to implement enhanced recovery techniques on a much broader scale. And the industry's own attitude to enhanced recovery has changed considerably from a few years ago.

An improvement in the recovery factor, say 10% worldwide, would provide additional oil existing discoveries of over 250 billion barrels. Only one percentage increase in the average recovery from the world 's currently known oil fields would be equivalent to adding a year's production to the ultimate recovery likely to be obtained from them, this equivalent perhaps to all the oil that could be recovered with great effort and expense from a new ,but as yet undiscovered petroleum province[1].

At the present time the question on EOR methods is "when" and "what type" and not "whether". Based on Malaysian Oil Company's research, the present Malaysian oil reservoirs could be depleted in about 18- 20 years. In order to extend the oil production life, EOR processes should be implemented even in early stage of oil field. Taking into account the Malaysian oil field characteristics, the most appropriate EOR methods seem to be the miscible and chemical flooding particularly surfactant. For this reason, as a future research program, the chemical flooding methods can be looked upon in some details in context of Malaysian oil field characteristic. [1] The major challenge ahead for us is to further increase the recovery rate of oil in production domestically to achieve the optimum value creation from fields in production and to satisfy all demand

In the Exploration and Production (**E&P**) Business, several methods are identified in order to recover the oil from the reservoir and its recovery rate would be the focused essentially from time to time. Reservoir recovery mechanisms are divided into three types namely Natural Drives, Engineering Drives and EOR. All these recovery mechanisms are simplified into three diagrams, Figure1.01, Figure 1.02 and Figure 1.03

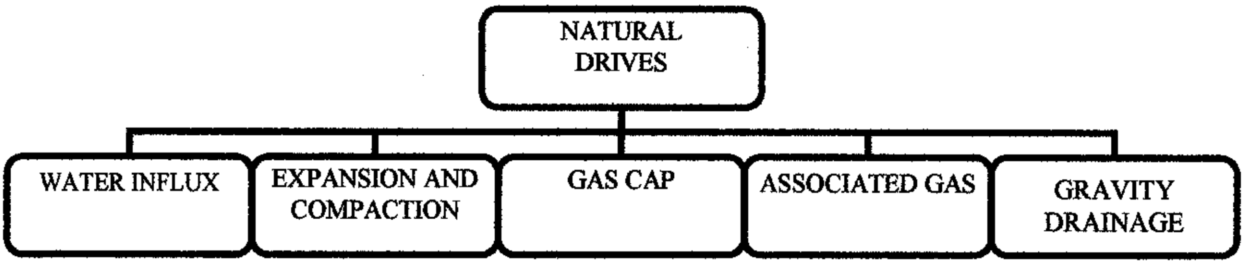


Figure 1.01 Natural Drive Mechanisms

Many oil reservoirs will produce oil, through wells due to natural forces driving oil into those producing wells and up to the surface production facilities. This is referred to as primary recovery or natural drives. The types of natural drives are reflected by Figure 1.01. Typically these forces cannot sustain oil recovery for many years and need to be supplemented by operator imposing extra force, by mean the secondary recovery of water injection or gas injection. The choice of gas or water, or perhaps both, is also dependent on the factors such as geometry and permeability.

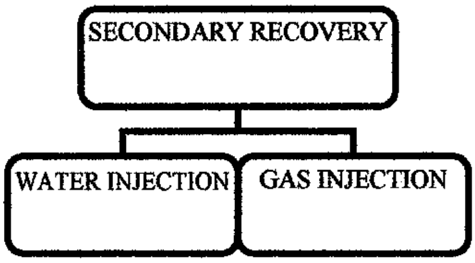


Figure 1.02 Secondary Recovery Methods

The key objective of secondary recovery is to increase the efficiency of oil recovery from and oil reservoir. It may not necessarily increase the amount of original oil in place (OOIP) in the reservoir but should increase the rate of recovery such that most of the recoverable oil can be produce within a useful timescale for example within the life of an offshore platform. In most oil reservoirs, more oil left in the reservoir at the end of the field life than is ever recovered, depending on numerous factors specific to each project, especially the reservoir geometry, litho logy, permeability, fluid saturations and fluid properties.

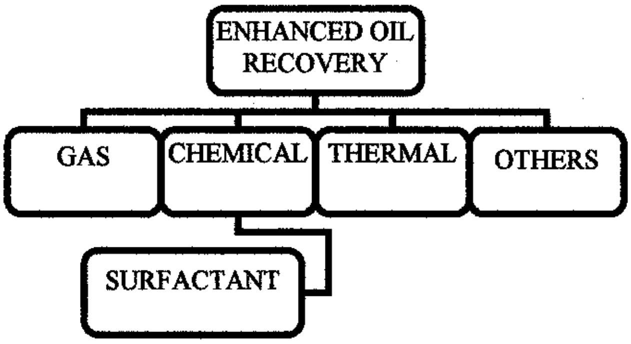


Figure 1.03 Enhanced Oil Recovery Methods

Most Chemical Enhanced Oil Recovery (CEOR) technologies are considered as tertiary application in order to extend the life of a producing field. In most places, the investment has already been made for wells, injection and production facilities and presumably the field has operated economically as a water flood. The operator wishes to recover some of the residual oil left behind by water flooding. Provided that technologies can be applied to add reserves competitively with other investments, CEOR technologies can extend field lie. However the later in the life of a project, the greater the delay in response, which effect the present value and smaller the peak oil cut even though the actual increment production may be little changed, just requiring more time. **[2]**

1.2 Problem Statement

1.2.1 Problem Identification

Initially, the study is aimed to understand the phase behavior of oil and water at the presence of surfactants. To increase the recovery rates, a method used is the injection of surfactants to reduce interfacial tension between the oil and rocks, thus allowing the recovery of oil trapped in smaller pores. The suitability of the surfactant in various conditions such as temperature and pressure however have to be determine as oil are trapped in various size of pores and various type of rocks. The concern of this project is to conduct experimental work and analysis of the selected surfactant used in EOR

1.2.2 Significance of the Project

By identifying and interpreting the effects of surfactant, for example stimulating or fracturing fluids to enhanced oil recovery allow better understanding of the surfactant's nature. Optimization methods would be formulated so that the surfactant is able to be used at its fullest potential leading to better EOR methods

1.3 Objective and Scope of Study

The objectives of this study are:

1.3.1 To understand about EOR and surfactants and its applications

1.3.2 To determine wettability changes at different concentration of surfactant.

1.3.3 To determine the suitable range of surfactant concentration in EOR application

1.3.4 To determine the effect of salinity in EOR

1.3.5 To determine the most desired phase types for EOR

1.3.6 To interpret the physical and chemical property extracted from the surfactant.

The parameters that will be monitor and interpret are the Interfacial tension (IFT) and Phase behavior. Since the facilities for IFT experiment in Petronas Research and Scientific Services Sdn. Bhd. (PRSS) has been shifted back to US, the previous IFT experiment will be verified back to see whether the result is significant to the latest literature review. Further discussion will be done base on the experimental results.

The scope of this study is to produce a detail study discussing the major issues in EOR Surfactants. In depth review of books, and journals would be condone to extract and obtain as much information as possible that are focused on the physico-chemical properties. As the study of EOR Surfactants is very wide, a specific area of research is to be formulated and selected in adherence with the project requirements. The experiment done is listed below;

1.3.7 Phase Behaviour experiment

To study on the fundamentals of surfactants for EOR and basic information on chemical flooding techniques, specifically on the surfactant physico-chemical properties.

1.3.6 Viscosity Test

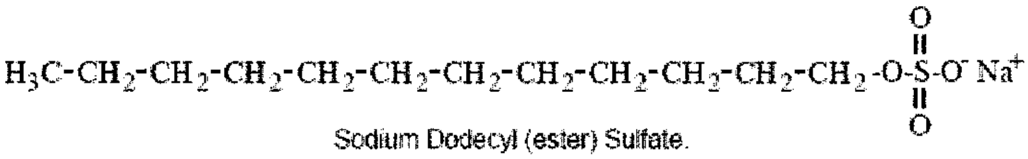
To study whether the viscosity of the phase that will form has a suitable viscosity that can affect mobility of the chemical flooding structure.However, the experiment cannot be done due to time constraint.

The polar portion exhibits a strong affinity for polar solvents, particularly water and it's often called hydrophilic part or hydrophile. The apolar part is called hyrdophobe or lipophile. The following formula shows an amphiphilic molecule which is commonly use in shampoos and this research particularly.

2.2 Tension Lowering Agent versus Surfactant

Because of its dual affinity, an amphiphilic molecule does not feel 'at ease' in any solvent, is it polar or nonpolar, since there is always one of the groups which does not like the solvent environment. This is why amphiphilic molecules exhibit a very strong tendency to migrate to interfaces or surface and to orientate so that the polar group lies in water and the apolar group is placed out of it eventually in oil.

In the following word surface will be used to designate the limit between a condensed phase and gas phase, whereas the term interface will be used or the boundary between two condensed phases. This distribution is handy through not necessary, and the two words are often used indifferently particularly in American terminology.



$$H_3C\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}O\text{-}\overset{\overset{O}{\parallel}}{\underset{\underset{O}{\parallel}}{S}}\text{-}O^{-}\,Na^{+}$$

Sodium Dodecyl (ester) Sulfate.

Figure 2.01: Example of Surfactant

In English the term surfactant (short for surface active agent) designates a substance which exhibits some superfacial or interfacial activity. It is worth remarking that all amphiphiles do not display such activity, in effect, only the amphiphiles with more or less equilibrated hydrophilic and lipophlic tendencies are likely to migrate to the surface or interface. It does not happen if the amphiphilic molecule is too hydrophilic or too hydrophobic, in which case it stays in one of the phases

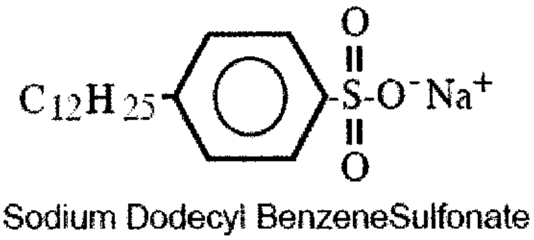


Figure 2.02: Sodium Dodecyl Benzene Sulfonate

2.3 Classification of Surfactants

From the commercial point of view surfactants are often classified according to their use. However, this is not very useful because many surfactants have several uses, and confusions may arise from that. The most accepted and scientifically sound classification of surfactants is based on their dissociation in water. **Anionic Surfactants** are dissociated in water in an amphiphilic anion, and a cation, which is in general an alcaline metal (Na+, K+) or a quaternary ammonium. They are the most commonly used surfactants. Anionic surfactants account for about 50 % of the world production.

Nonionic Surfactants come as a close second with about 45% of the overall industrial production. They do not ionize in aqueous solution, hard water tolerant because their hydrophilic group is of a nondissociable type, such as alcohol, phenol, ether, ester, or amide. A large proportion of these nonionic surfactants are made hydrophilic by the presence of a polyethylene glycol chain, obtained by the polycondensation of ethylene oxide. They are called polyethoxylated nonionics. As far as the lipophilic group is concerned, it is often of the alkyl or alkylbenzene type, the former coming from fatty acids of natural origin. The disadvantages of non ionics are that they are liquids or pastes, more expensive than anionics and less soluble at higher temperatures. This type of surfactant is not practical for CEOR since reservoir temperature is high.

Cationic Surfactants are dissociated in water into an amphiphilic cation and an anion, most often of the halogen type. This surfactant is not suitable for CEOR because of their high adsorption property. It is able to adsorb on negatively charged substrates to produce antistatic and hydrophobant effect, often of great commercial importance such as in corrosion inhibition. A very large proportion of this class corresponds to nitrogen compounds such as fatty amine salts and quaternary ammoniums, with one or several long chain of the alkyl type, often coming from natural fatty acids. These surfactants are in general more expensive than anionic, because of a high pressure hydrogenation reaction to be carried out during their synthesis.

Table 2.01: Surfactant categories

Type	Charge	Product type
Nonionic	None	Ethoxylates, Alkoxylates, Glucosides
Anionic	-	Sulfates, Sulfonates, Disulfonates, Phosphate Esters, Sulfosuccinates
Cationic	+	Quaternary ammonium salts
Amphoteric	-/+	Betaine

When a single surfactant molecule exhibit both anionic and cationic dissociations it is called **amphoteric** or **zwitterionic.** This is the case of synthetic products like betaines or sulfobetaines and natural substances such as amino acids and phospholipids.

Surfactant has the ability to reduce the surface tension of water to a low value is a fundamental characteristic that results in highly efficient and effective performance in a wide range of applications. By changing the surface tension of a solution, the surfactant makes the solution wet better. [4]

2.4 Critical micelle concentration (CMC)

Micelle formation is an aggregated unit composed of a number of molecules of a surface active material as shown in the drawing below. Micelles solubilize oils by lifting these oils of the surface and dispersing them into solution. Micelle formation enables emulsification, solubilization, and dispersion of otherwise non-compatible materials. Critical micelle concentration (CMC) is the surfactant concentration at which an appreciable number of micelles are formed and thus remove oils

Critical micelle concentration (CMC) is a measure of surfactant efficiency. Cmc is defined as the concentration of maximum solubility of the monomer in that particular solvent. It is for this reason that the cmc value is perhaps the more frequently measured and discussed micellar parameter. Cmc values are very important in virtually all of petroleum industry surfactant application. A lower CMC indicates less surfactant is needed to saturate interfaces and form micelles. In this process, surfactant must usually be present at a concentration higher than the cmc because the greatest effect of the surfactant, whether in Interfacial Tension (IFT) lowering or in promoting foam stability, is achieve when a significant concentration of micelles is present. The determination of cmc at elevated temperature and pressure is experimentally much more difficult than for ambient temperature. Typical CMC values are less than 1% by weight .To obtain optimal performance, concentrations of 1-5% are common. This concentration is higher than that needed to achieve micelle formation; therefore, providing a reservoir of additional surfactant molecules to form micelles. Other formulation components and temperature may affect micelle formation. Development of surfactant technology has made it feasible to be applied in EOR methods. [5]

Cmc determinations increase with increasing temperature because at the same time the surfactant aggregation number decreases and the aggregation distribution increases. Another approach is to use dynamic foam stability measurements. Foaming effectiveness and the ease of foam formation, the latter of which promotes foam stability through surface elasticity and other mechanisms. Accordingly, static or dynamic foam height increases with surfactant concentration and then becomes relatively constant at concentration greater than the cmc.

In EOR, the mechanism of surfactant is initiated by injection with solution containing low concentration of surfactant. Large pore volumes of the solution are injected into the reservoir to reduce interfacial tension between oil and water and thereby, increase of oil recovery. Properties of surfactants in EOR must be analyzed so that useful information can be extracted. This would allow optimization methods so that the usage of the surfactant can be fully exploited .Determination of such parameter is done experimentally, and comprises of several methods available, depending which surfactant would be most suitable.

2.5 The Krafft Point

The solubility of micelle forming surfactant shows a strong increase above a certain temperature, termed the Krafft Point (Tk). This is explained by the fact that the single surfactant molecules have limited solubility whereas the micelles are very soluble. The Krafft point the solubility of the surfactant is too low for micellization so solubility above determines the surfactant monomer concentration. As temperature increases the solubility increases until at Tk the cmc is reached. At this temperature a relatively large amount of surfactant can be dispersed in micelles and solubility increases greatly. Above the Krafft point, maximum reduction and surface of IFT occurs at the cmc because the cmc then determine the surfactant monomer concentration for a number of surfactants.

Cloud point is referred to the point where surfactants may begin to lose their surface active properties. This occurs because above cloud point, a surfactant rich phase of swollen micelles separates, and the transition is usually accompanied by a marked increase in dispersion turbidity.[6]

2.6 IFT Measurement Techniques in Industry

The most common method of measuring surface/interfacial tension involves the use of a torsion balance known as the DuNouy instrument (tensiometer), described in ASTM D971:99a and ASTM D1331. In the test (Figures 3 and 4), the force required to lift a horizontal platinum wire ring away from the oil's surface is measured either directly (surface tension) or at an oil/water interface (interfacial tension). The unit of measure for surface tension is dynes per centimeter (equal to mN/m).

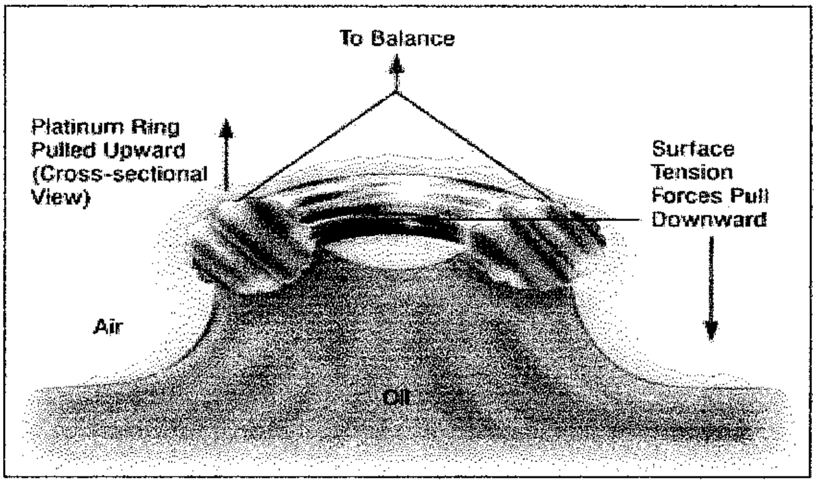


Figure 2.03: The principles of DuNouy Method

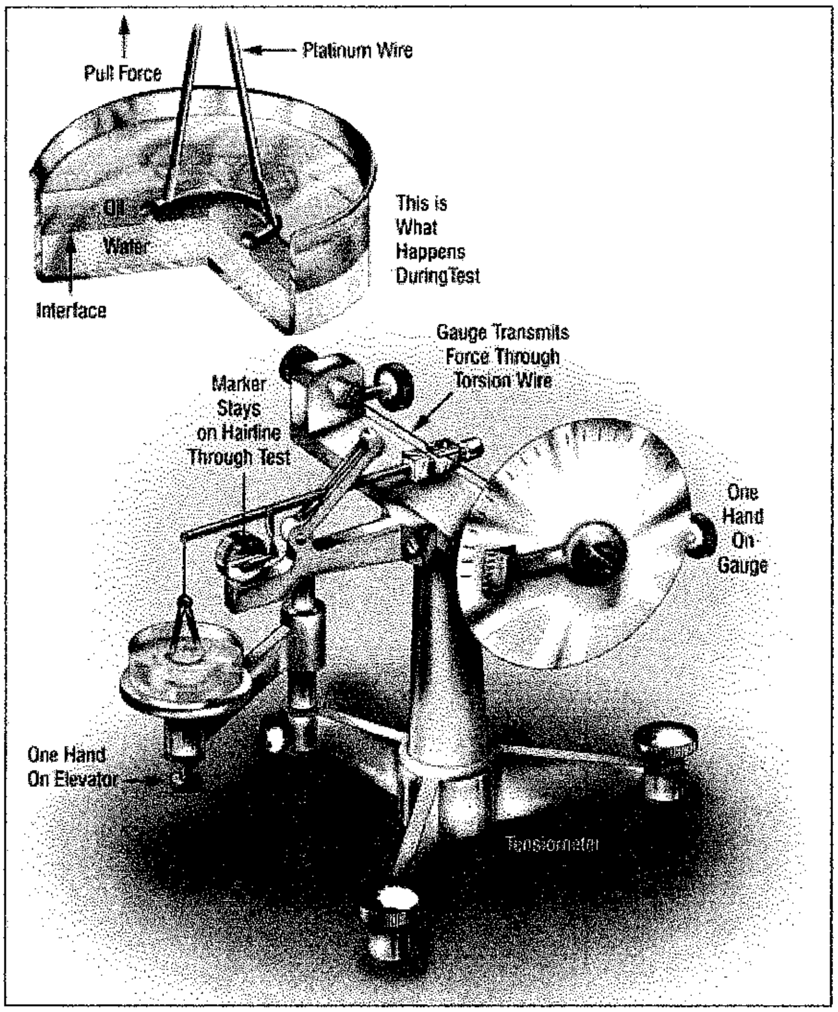


Figure 2.04: The mechanism during the Interfacial Tension Test

Another method to determine interfacial tension is used to characterize the degradation of electrical insulating oils due to oxidation or contamination. It involves the use of a drop-weight procedure and is described in ASTM D2285:99. With any of the prescribed methods, test accuracy is affected by a number of factors including cleanliness of the test apparatus, agitation of the fluid (required to resuspend solids) and the accidental contamination of the fluid by dirty containers and laboratory glassware. In general, good reproducibility of these tests can be difficult to obtain unless care is taken to ensure quality lab test procedures. [7]

2.7 Phase Behavior

The term *phase* defines any homogeneous and physically distinct part of a system which is separated from other parts of the system by definite bounding surfaces.

Phase Behaviour in surfactant property evaluation is represented by phase diagrams. A ternary diagram is used to explain the behaviour of surfactant systems, which associates three different components, which are surfactant, brine and oil.

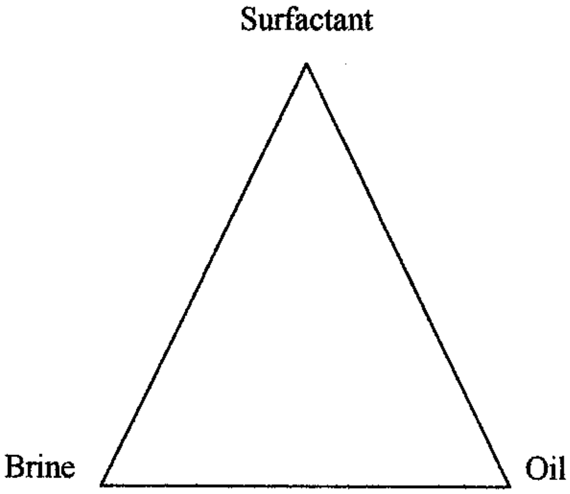


Figure 2.05: Ternary Phase Diagram on Evaluating Phase Behaviour

All reservoirs are heterogeneous varying only in their degree of heterogeneity. This means that the physical properties of rock change with a change in location. One of the very important heterogeneities that need to be considered in reservoir engineering calculation is stratification. Many reservoirs contain layers (strata) of productive rock that can be communicating. These layers can vary considerably in permeability and in thickness. A good description of the layers and their respective properties is critical in planning many EOR operations. A ternary diagram shows the best representation of the phase behaviour and it is reasonably accurate as long as each component has approximately the same composition in each phase. In evaluating phase diagrams, phase behaviour type descriptions are used. Usually, it is classified according too physical observation of the mixture and crude oil. These are the classification of phase types:

Table 2.02: Phase Types Description

Phase Type	Description
II	Two fluid envelopes exist- a bottom aqueous phase and top oil phase. No color is visible in the aqueous phase. The crude oil and aqueous phase volumes are equal to the volumes placed in the tube. Either the alkali has generated no visible surfactant or the surfactant have been driven into the crude oil and no crude oil swelling has taken place
-II	Two liquid envelopes exist a bottom aqueous phase and an oil phase. The bottom aqueous phase is colored indicating the alkali has saponified acids in the crude oil which are now present in the aqueous phase. The crude oil volume can be swollen due to the interaction with the surfactant, but this is not a requirement for this designation
III	Three or more fluid envelopes exist a bottom aqueous phase, one or more middle emulsion phases, and top crude oil phase. The aqueous phase can be colored with saponified acids from the crude oil, however this does not necessarily have to be the case
II+	Two fluid envelopes exist- a bottom aqueous phase and a top crude oil phase. The bottom aqueous phase is clear because the surfactant reside in the crude oil phase. The crude oil phase is swollen due to surfactant carrying water into the crude oil phase

By referring to Table 2.02, type III is the desired phase type to recover additional oil followed by type II-, II and type II+. The relation to ternary phase diagrams explains the equilibrium interaction between of the three major components. Type II- phase behavior refers to the lowest salinity or lowest brine content in the solution. This is because most of the brine water is dissolved in the surfactant, interpreting that the surfactant is water soluble. Should the salinity increases, the surfactant would be more oil soluble, making the phase behaviour to be in the type III region, where the phases are distinguished by the top oil phase, middle emulsion phase, and bottom aqueous phase. Increasing the salinity changes the phase behaviour, and transforming the solution to be in the region of type II+.

Here, it can be concluded that the surfactant is oil soluble, where most oil is dissolved in surfactant and in form of microemulsion followed by brine water. From the phase behaviour explanations, type III verifies as the most desired phase behavior that the evaluations trying to achieve because it shows balanced interaction with the brine and the oil. It is also the target characteristics within the chemical flooding, where the main target is to minimize surfactant losses, and minimize oil solubility to the surfactant so that separation between the oil and the surfactant is easier and economically feasible. **[10]**

2.8 Chemical Flooding

Essentially two different concepts have developed for using surfactants to enhanced oil recovery;

2.8.1 In the first concept, a solution containing a **low concentration** of a surfactant is injected. The surfactant is dissolved in either water or oil and is in equilibrium with aggregates of the surfactant known as micelles. Large pore volumes (about 15 to 60 percent or more) of the solution are injected into the reservoir to reduce interfacial tension between oil and water and thereby increase oil recovery. Oil may be banked with the surfactant with surfactant solution process, but residual oil at a given position in the reservoir will only approach being reduced to zero after passage of large volumes of surfactant solution.

2.8.2 In the second process, a relatively small pore volume (about 3 to 20 percent) of a **higher concentration** surfactant is injected into the reservoir. With the higher surfactant concentration, the micelles become a surfactant stabilized dispersion of either water in hydrocarbon or hydrocarbon in water. The high concentration of surfactant allows the amount of dispersed phase in the microemulsion to be high as compared with the low value in the dispersed phase of the micelles in the low concentration surfactant solutions.

Chemical flooding process is done in the following sequences where Sodium chloride or brine is injected first into the sea water to provide an adequate salinity .After the oil bank is formed, the surfactant solution is injected to lower the IFT of the oil Polymer is later injected to give mobility control to the surfactant and to provides a good displacement of the surfactant solution to prevent any immobilization and trapping that will consequently lead to surfactant losses **[11]**

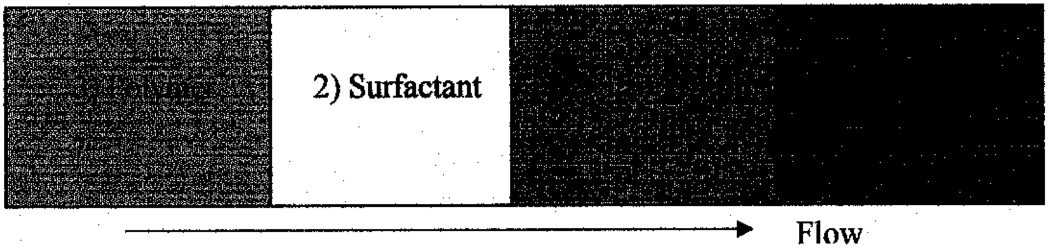


Figure 2.06: Phase Position in chemical flooding

Technical risk was high and traditional chemical flooding methods are subject to several problems, where they are:

- 2.8.3 Difficulty of handling the flow of three liquid phases through an inhomogeneous porous medium
- 2.8.4 Surfactant losses due to reservoir conditions: low porosity, low capillary forces, fingering, and misbehaviour of phase gradient
- 2.8.5 Retention of surfactants, precipitation, and phase trapping

CHAPTER 3

METHODOLOGY

3.1 Research and Literature Review

Detail study has been conducted while several procedures are identified and implement.

3.1.1 Requirement Specification and Preliminary Literature Review

- Specification and requirement for this research are identified.
- All information about mechanism of chemical flooding, surfactant and Enhanced Oil Recovery are gathered by continuous retrieval from the internet and resource centre
- Journals and case studies relevant to this research are also gathered
- All information gathered are rearranged and revised in accordance to the relevance of the research.

3.1.2 Analysis of Experimental Work and Execution

To identify the available experiments that can be conducted for phase behaviour studies. Based on the initial plan, one experiment will be conducted which will takes 2 weeks to finish. All apparatus and chemicals needed are identified and the locations of those are confirmed.

3.1.3 Result gathering and requirement modification

Discussions about the significant of experiment to the research are done after the result of the experiment is obtained. Modification will be done if any minor error detected that may contribute to experimental result. Most of the results gathered are compared relatively to the theory obtained in literature review. Some recommendations are proposed to improve the experimental works and results in the future. Discussions with all lecturers that are relate to this topic are also done to verified some of the founding.

3.1.4 Development and Validation

As results are obtained, conclusion is made after validation is done. Development of discussion part is then started to avoid time constraint in preparation of dissertation.

3.1.5 Preparation of dissertation report

The preparation of report is started earlier since the writing process goes parallel with research and experimental works as there might be some changes required. The report is prepared accordance with the research and course requirements. As addition, the report serves as a future reference of study for further research development.

The simplified diagram for methodology has been constructed as follow

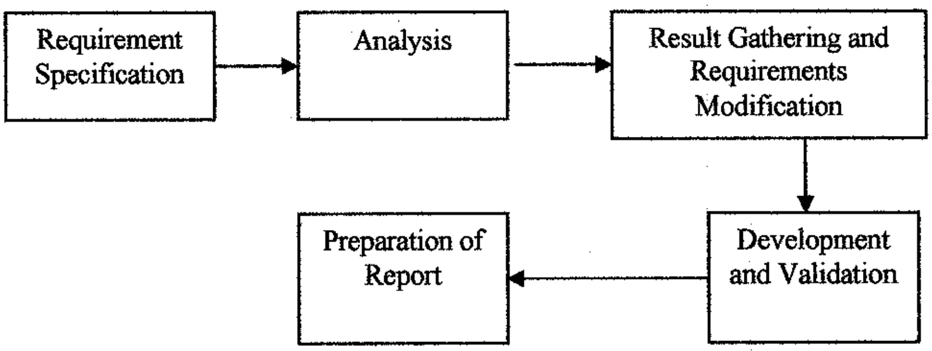


Figure 3.01: The project methodology flow diagram.

3.2 Experimental Equipments and Procedure

Before start the experiment, general safeties in laboratory are reviewed. Form of list of chemicals and equipment are filled to request for apparatus. For the Phase Behaviour experiment, the equipment required is as followed

Table 3.01: Chemical and Equipment for experiment

CHEMICAL	EQUIPMENT /GLASSWARE
SodiumDodecylBenzeneSulphonate Crude oil Seawater Distilled Water	Viscometer Explosion proof Oven 20 Test tubes 3 10 mL graduated cylinder racks Spatula

The experiment procedures for phase behaviour studies are as followed

3.2.1 The surfactant solution in different concentration are prepared of 0.05, 0.1, 0.15 and 0.2 Molar

3.2.2 Prepare a matrix of surfactant to seawater solutions ratio as Table 3.2 below

Table 3.02: Percentage of surfactant to seawater

Percentage of surfactant solution (%)	Percentage of seawater (%)
100	0
75	25
50	50
25	75
0	100

3.2.3 Add crude oil to the surfactant seawater solution into the test tubes to create 10 mL of mixture

3.2.4 Plug top of the test tubes and shake to mix crude oil and surfactant solutions until it becomes homogeneous. The duration of shaking is around 1 minute, depending on the homogeneity of the sample.

3.2.5 Repeat the procedure for the rest of the samples

3.2.6 Place all test in rack and allow the mixture to stabilize.

3.2.7 After stabilize, the characteristic of each phases of the mixture is observed including their colors.

3.2.8 The temperature of Oven is set at 120 deg C and all test tubes are put into the oven and leaved for two weeks.

3.2.9 After two weeks, samples are acquired and each surfactant should give a different reading.

3.2.10 By using a ruler, the amounts of different phase that are settled are measured.

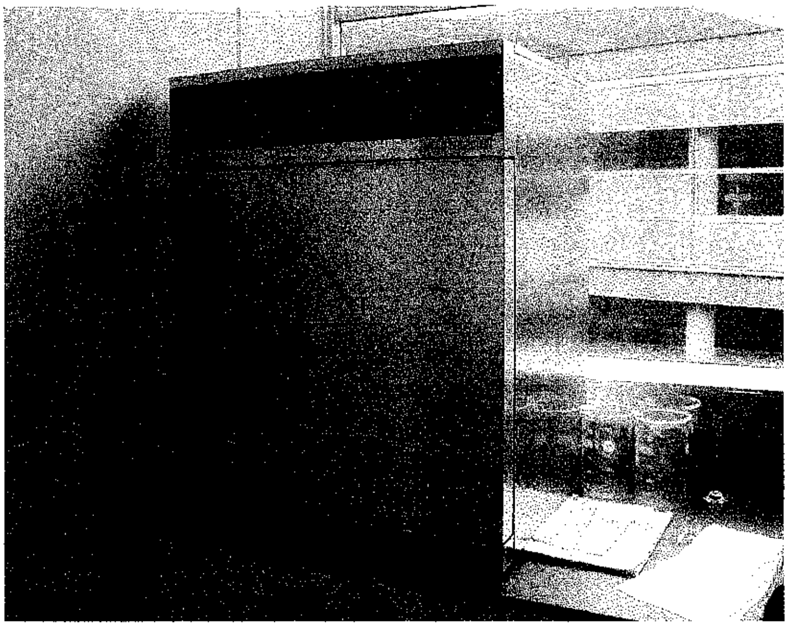


Figure 3.02: Oven

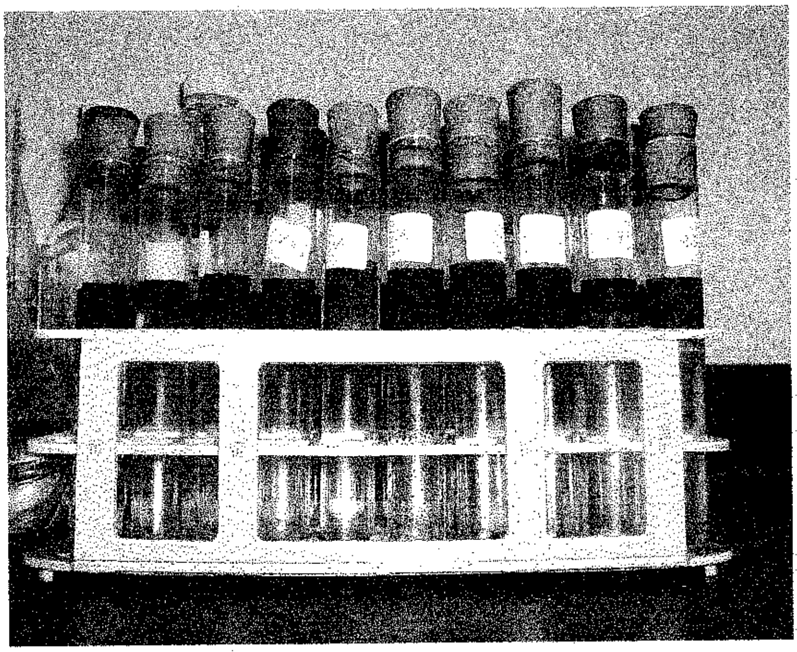


Figure 3.03: Test tubes

CHAPTER 4

RESULT AND DISCUSSION

4.1 Experimental result

By to refer to the experimental procedures conducted, the results are tabulated in Table 4.01 and Table 4.02.

Table 4.01 Experimental Color Observation

Surfactant	**Seawater**	**Color of Phases**							
		Surfactant concentration							
%	**%**	**A=0.05 Molar**		**B=0.10 Molar**		**C=0.15 Molar**		**D=0.20 Molar**	
0	**100**	A1	C,D	B1	C,D	C1	C,D	D1	C,D
25	**75**	A2	C,D	B2	C,D	C2	C,D	D2	C,D
50	**50**	A3	Y,M,D	B3	Y,M,D	C3	Y,M,D	D3	Y,M,D
75	**25**	A4	C,M,D	B4	C,M,D	C4	C,D,M	D4	C,D,M
75	**0**	A5	C,M,	B5	C,M	C5	C,M	D5	C,M

Phase type code follows:

Lower Phase Description Codes as Color - Clarity
Color: B = brown,
C = clear,
G = grey,
M = milky,
W = White,
Y = yellow,
L = light,
D = dark,
Clarity: C = clear,
T = translucent,
O = opaque,
PPT = precipitate

Table 4.02: Experimental Phase observation

Surfactant	**Seawater**	**Type of Phase**							
		Surfactant concentration							
%	**%**	**A=0.05 Molar**		**B=0.10 Molar**		**C=0.15 Molar**		**D=0.20 Molar**	
0	**100**	A1	II	B1	II	C1	II	D1	II
25	**75**	A2	II+	B2	II+	C2	II+	D2	II+
50	**50**	A3	II-	B3	II-	C3	II-	D3	II-
75	**25**	A4	III	B4	III	C4	III	D4	III
75	**0**	A5	II+	B5	II+	C5	II+	D5	II+

Table 4.03 Phase Types Description

Phase Type	**Phase Type Description**
II	Two fluid envelopes exist – a bottom aqueous phase and top oil phase. Color is not visible in the aqueous phase. The crude oil and aqueous phase are equal to the volumes placed in the tube. No crude oil swelling has taken place.
II-	Two fluid envelopes exist, which comprises of bottom aqueous phase and an oil phase. The bottom aqueous phase is colored indicating the alkali has saponified acids in the crude oil which is present in the aqueous phase.
III	Three or more fluid envelopes exist, which comprises of bottom aqueous phase, middle emulsion phases, and top crude oil phase.
II+	Two fluids envelopes exist, where a bottom aqueous phase and a top crude oil phase are present. The bottom aqueous phase is clear because the surfactant reside in the crude oil phase.

Table 4.04 Best and Worst Phase Type Obtained

Type	**Surfactant:** Sodium Dodecyl Benzene Sulphonate
III	A4,B4,C4,D4
II+	A5,B5,C5,D5

4.2 DISCUSSION

4.2.1 Interfacial Tension and Surfactant Concentration

For experiment involving phase behavior, the strategy is to classify the samples in terms of types. As explained in theory, the desired phase behavior of a good surfactant is to have phase type III, where three or more fluid envelopes exist, which comprises of bottom aqueous phase, middle emulsion phases, and top crude oil phase. This can be done through physical observation, and later it is tabulated so that the performance of the samples can be viewed in overall. The fundamental concept of having the phase behavior analysis is to provide the interaction of surfactants with the oil and water so that an effective flooding design can be designated to meet the specific reservoir conditions for CEOR.

From Table 4.04, there are four samples managed from Type III, while there are another four samples managed from Type II-. These samples are considered the ideal samples that satisfy the desired phase type. Unlike type II+, this is the most undesired type of emulsion that needs to be avoided.

The significance of having type III Phase Behavior is to provide clear distinction of all three fluid phases as shown in Figure 4.01

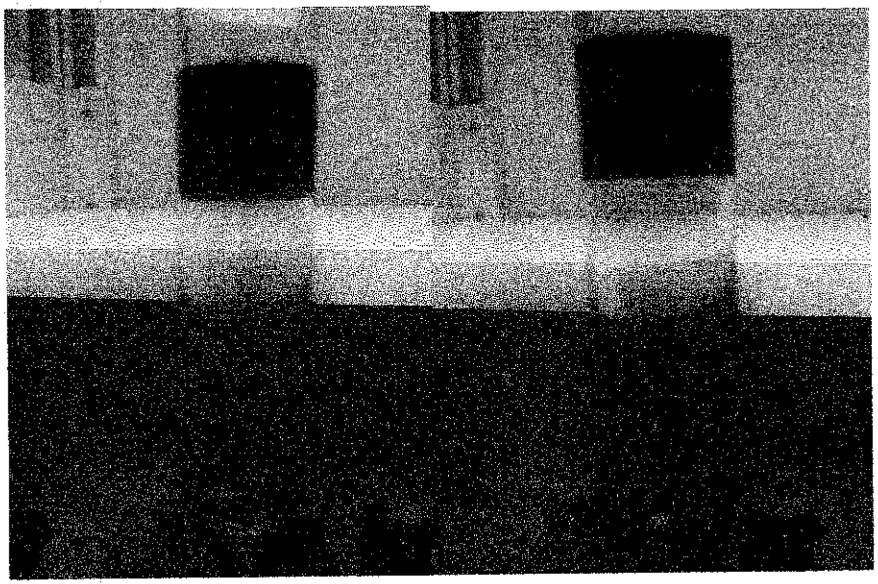


Figure 4.01: Phase Type III and II- the most desired phase in the experiment

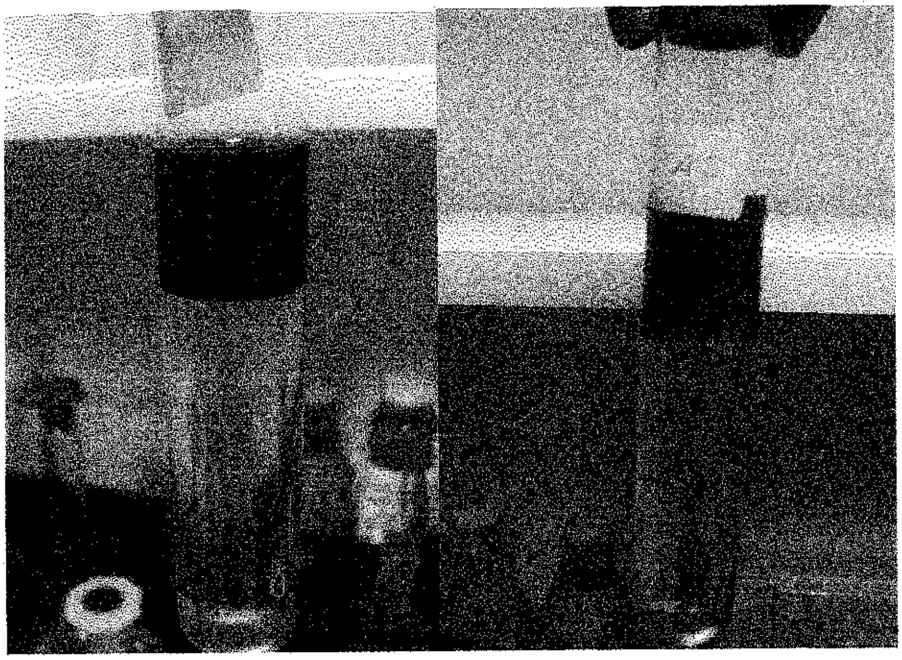


Figure 4.02: Phase II and II + respectively.

In a chemical flooding design, part of the objectives is to minimize the chemical reaction between the oil and the surfactant, while at the same time maintains its recovery performance by lowering the IFT and maximizing mobility control by usage of polymer solution. By having phase type III, less oil is solubilized in a form of emulsion and this is important when the oil is transported to the production well and undergoes the three phase separator, Figure 4.02. From economic point of view, by presence of emulsions, it makes separation of oil, water, and surfactant difficult because the goal is to recover back the surfactant that it can be regenerate again in CEOR. As surfactants are highly expensive chemicals, most flooding designs aim to minimize the surfactant losses; so that the chemical treatment still maintains economic viability of the CEOR. **[7]**

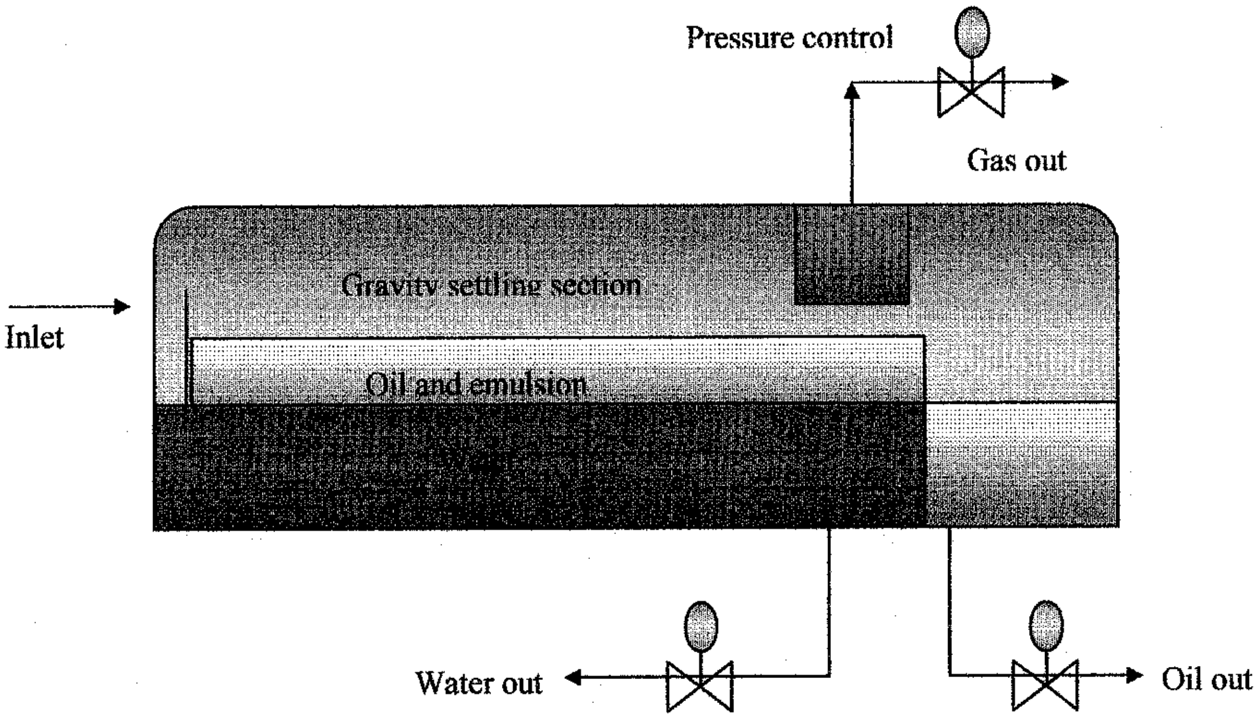


Figure 4.03: Typical Three Phase separator

Phase diagram is one alternative to describe the phase behavior of the oil reservoir, but due to lack of detail in composition, the diagram cannot be plotted. . This is also subject to the true compositions of the reservoir, which is heterogeneous, and the fluids within the reservoir do not behave as absolute true components

One of the options to study the phase behavior is to continuously conducting experiments, particularly at various conditions so that more information regarding the surfactant's nature in phase behavior can be extracted. Experiment using the chromatography can be conducted to know the exact composition of the mixture

The experiment conducted involving phase behavior was done first time in campus, where before this the experiments are done in PRSS for the first time by some students last semester. The previous result has been verified by using other surfactant but basically to monitor the same parameters and concept. Thus, the results gathered during the experiment may deviate from true results, and one of the best options in order to improve the experimental results is to redo the experiments so that the accuracy and the consistency can be achieved. Experiment at various elevated temperatures was also the initial intention at the early stage of the project. As phase behavior classification is done by physical observation, this type of method is subjective, and the classification results may differ due to different kinds of interpretation. The simplest parameters to monitor here is between the solubility in a way of interpreting the IFT measurement with the surfactant concentration.

As from result obtained, those samples shown that as surfactant concentration increases, the solubility increases where they tend to produce more emulsion particularly Phase III and Phase II-

4.2.1 Relationship between wettabillity changes and phase behaviour

The displacement of oil by surfactant is one of the methods used in EOR. The efficiency of oil recovery at low concentration surfactant flooding depends on the partitioning of surfactant molecules in the water or oil phase, which in turn can cause wettability changes. The wettability of a porous medium has a profound effect on flow properties. In order to design a better system of oil recovery for surfactant flooding, it is necessary to clarify mechanism occurring within the pores. The experiment was performed where the desired phase type is either phase III or II- Observation on how different reservoir conditions affect the flow properties of the system was done. The test tube is initially fill with seawater and then flooded with oil to irreducible water saturation. The test tubes were then filled with water flooded to residual oil and finally the surfactant solution was injected. Changes of wettability (from water wet to oil wet) were observed in some regions of the model as the surfactant was flowing through, which was especially noticeable at higher salinities. Wettability changes seem to occur as a result or partitioning of the surfactant into the oil phase and adsorption on to the glass surface. As a consequence, some of the residual oil (non wetting phase) become attracted and attached to the surface. It is observed that wettability changes occurs more readily at high salinities implying that at high salinity the surfactant is more soluble and therefore is more likely to modify the wettability characteristics.

In water wet conditions, a water film exists between the wall of the grain and the oil whereas the oil wet region the oil covers the surface of the grain. Oil water interface is convex in the head meniscus and the contact angle between the non wetting phases and solid is less than 90^0 showing the region is water wet.

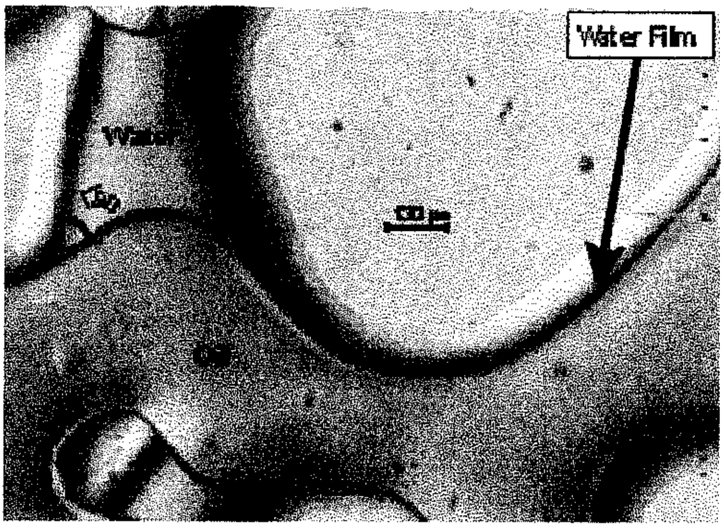


Figure 4.04: Water Wet Region

The oil wet region on the other hand has a contact angle of 180^0 showing of the spread of oil on the surface of the grain. The change in wettability is dependent upon the presence of surfactant molecules and the fluid solid interactions. The change in wettability depends upon the type of adsorption, which in turn depends upon the surfactant molecules and structure of rock surfaces.

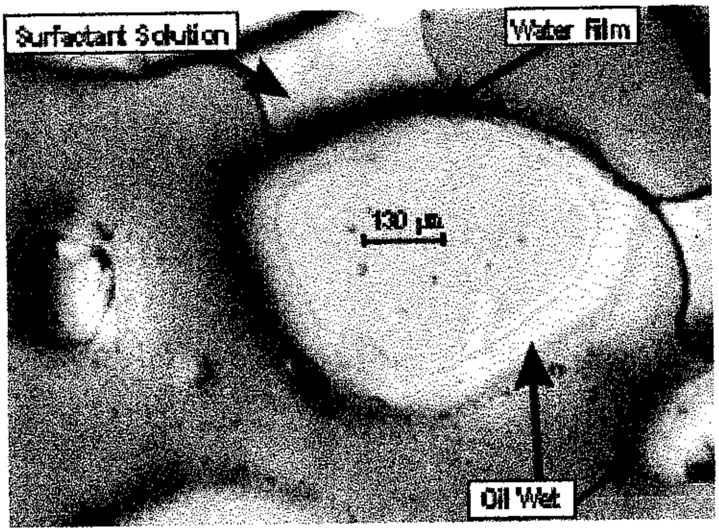


Figure 4.05: Mixed wettability region

In order to achieve a low interracial tension, the surfactant molecule should be able to partition in both the oil and water phases. During the wettability changes two different mechanisms may occur.

- The first mechanism seems to be due to the partitioning of surfactant in the oil phase.
- The second one is due to the presence of surfactant molecules in the aqueous solution.

The effect of wettability changes on the movement of the oil drop during the surfactant flooding is shown in Figure 4.04 a) until Figure 4.04 c). The sequence shown in this figure clearly indicates that the structure of rock is not the same in all parts of the grain. The oil h, with existing surfactant molecules, is moving in the direction of the flow next to the grain g. Since the grain is water wet (hydrophilic), the oil moves through the throat until it reaches a part of glass where the water film can be ruptured. The surfactant in oil phase have already arranged themselves at the interface so that the polar head group sits free at the interface, while the hydrophobic tail is bonded to the hydrocarbon chain (hydrophobic bond) within the oil phase. At this stage, the attraction between the negatively charged head group of the surfactant and the hydrophilic surface results in wettability changes of the grain as shown in Figure 4.04

Figure 4.06a)

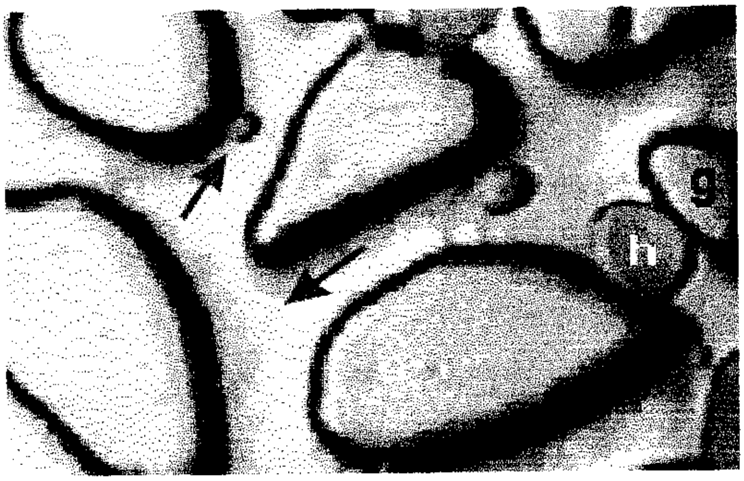


Figure 4.06 b)

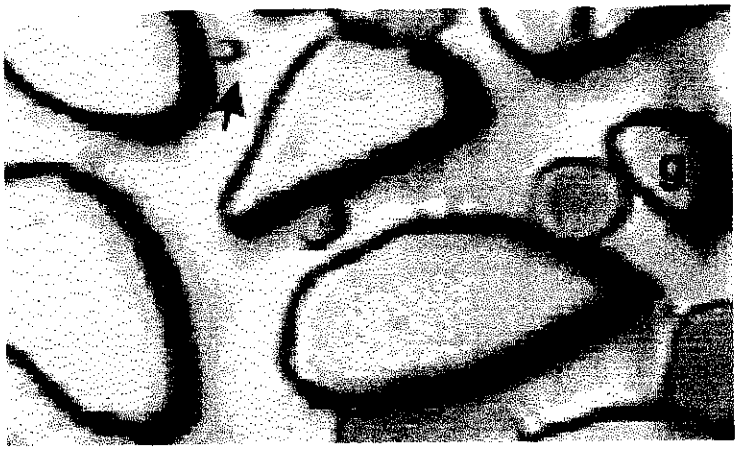


Figure 4.06 c)

Figure 4.04 a-c :Wettability changes due to presence of surfactant molecule at oil water interface

Figure 4.07 :Wettability changes

The attraction forces between the charged head groups of surfactants and solid seem to be quite strong since this occurs within extremely short period of time. However, since the interfacial tension is very low, the oil starts moving in the direction of the flow and at the same time gets pulled back by attractive forces between oil, surfactant and solid as shown in Figure 4.05. The overall results of these forces cause the oil to stretch until there is an instability at the interface of the oil drop causing it to break, leaving a small amount of oil behind (Figure 4.09). This small amount can be removed in the form of emulsion.

Figure 4.08: Forces causes the oil to stretch.

Figure 4.09: Oil drop break

A similar effect is shown in Figure 4.08 a) until Figure 4.08 d). Due to hydrophilic nature of the glass, part of the grain g1 attracts the polar head group of surfactant molecules that present in aqueous phase. As a result, the tail of the surfactant is free at the interface. As the oil filament passes through that region, the attractive forces between the hydrophobic tail of the surfactant and oil chain causes the formation of a " hydrophobic bond" which in turn changes the wettability of the surface (waterwet to oil wet). This process compared to the first one mentioned earlier seems to be slower due to weaker attraction. The uneven wettability changes seem to increase with an increased salt concentration. This is believed to be due to increase in electrolyte concentrations, which in turn decrease the thickness of the ionic atmosphere surrounding the ionic head group. Thus a decrease in electrical repulsion between the charged head group is caused. Resulting in better packing of surfactant molecules at the solid/liquid interface.

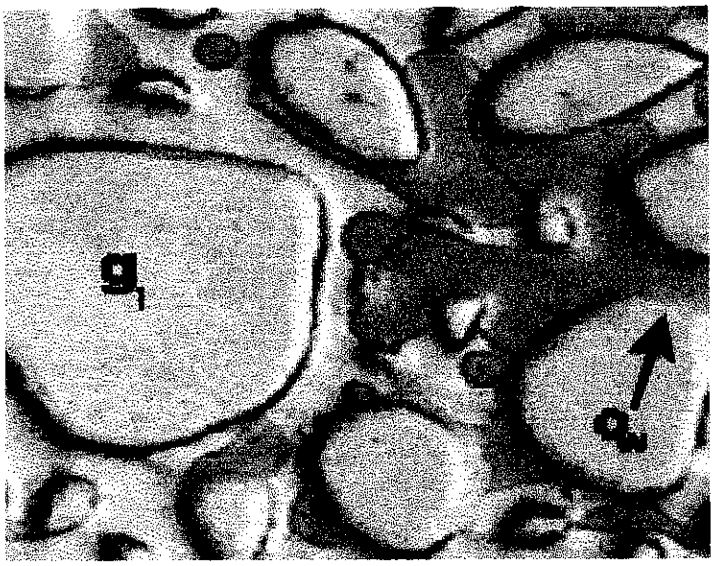


Figure 4.10 a)

Figure 4.10 b)

Figure 4.10c)

Figure 4.10d)

Figure 4.08 a to d: Wettability changes due to absorption of surfactant molecules on solid surface

As the salinity increases the fraction of oil wet region also increases. This is due to an increase of electrostatic repulsion between the ions present in the surfactant solution causing an increase in the amount of surfactant adsorbed on the solid fluid interface. Core flooding experiment (Ashayer- Soltani, 1999) show an increase in the amount of oil produced as the salinity increases from 120 g/l to 140g /l. This is because the interfacial tension between the oil and surfactant solution reaches its minimum at 140 g/l. An increased of salinity from 140 g/l to 160g/l on the other hand causes a deceased in the amount of oil produced due to an increase in the region of oil wet.**[8]**

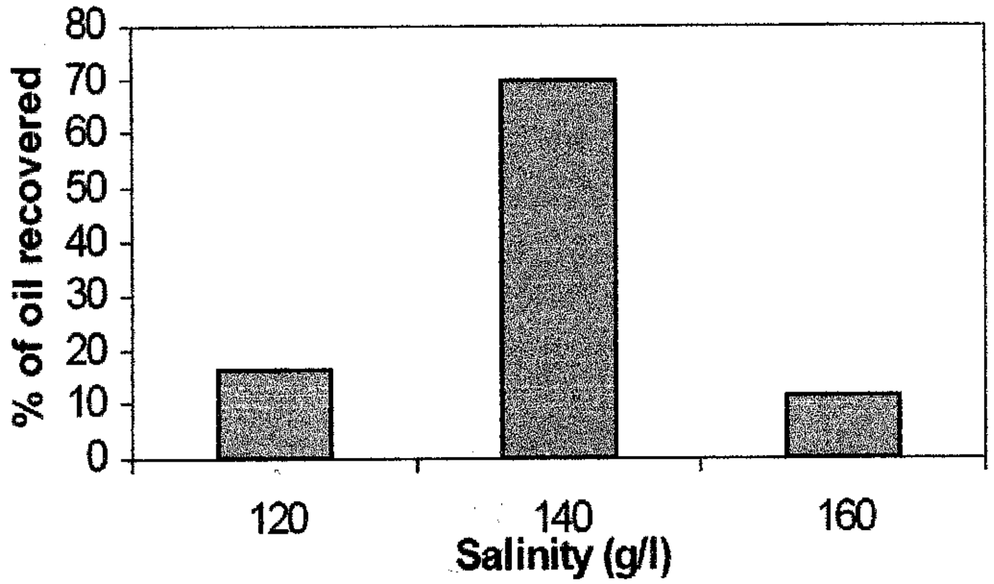


Fig. 5 Percentage of oil recovery after surfactant flooding

Figure 4.11: Percentage of oil recovery after surfactant flooding

4.2.2 Application of Chemical Flooding at Elevated Temperature and Pressure

From the experiment that has been conducted previously, the relationship between the Interfacial Tension (IFT) and temperature and pressure can be made. The initial intention was to varies the temperature in the range of sufficient reservoir condition particularly Malay Basin. The present experiment system was limited to temperature 120 °C and at fixed constant pressure.

A typical plot of dynamic foam height versus solution surfactant concentration is shown in Figure 4.09. Below the cmc there is little or no foam production while beginning at the cmc there occurs a sharp increase in foaming. A tangent is drawn through the approximately linear region of rapid rise, region C. The intersection of the tangent with the horizontal axis is taken as the cmc.

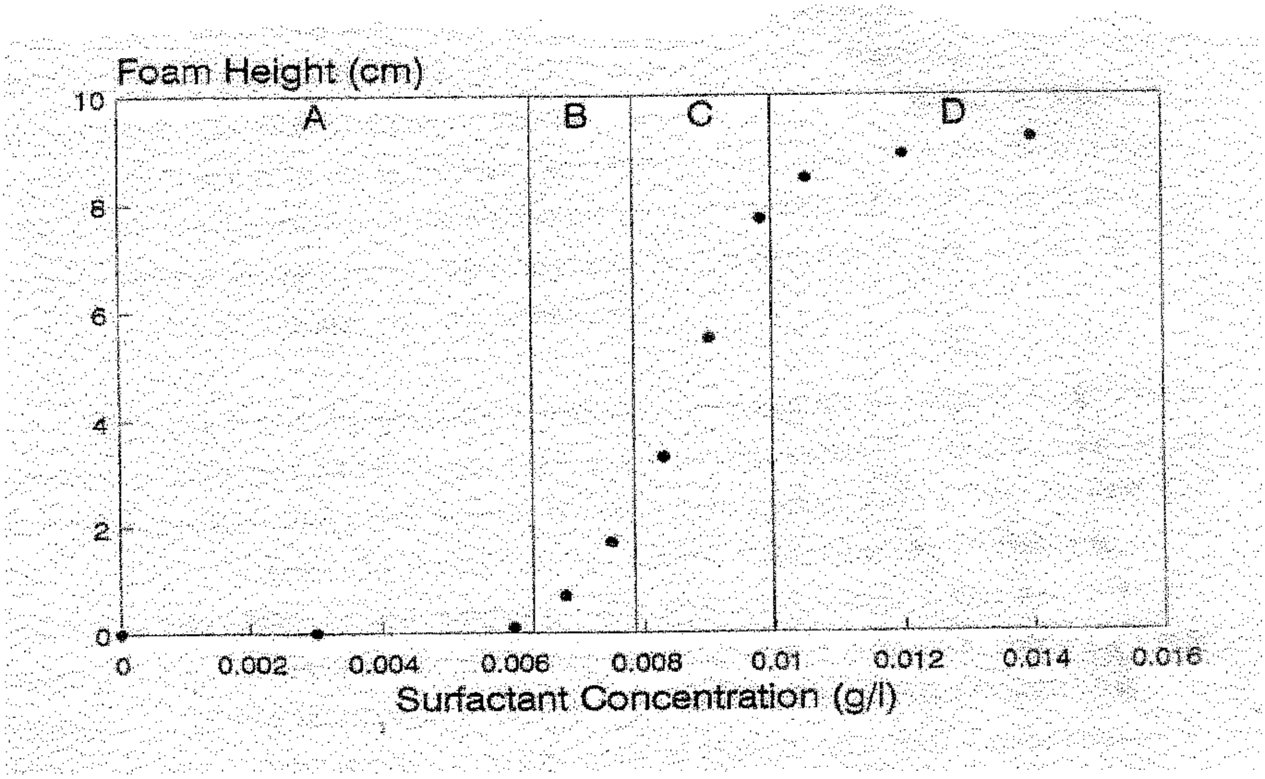


Figure 4.12: Relationship between foam height and surfactant concentration

The new dynamic foam height method, is probably not as accurate as the standard methods for cmc determination at low temperatures and ambient pressure, but is sufficiently accurate for determining reasonably accurate cmc's over a wide range of temperatures and pressures, for determining the minimum cmc as a function of temperature, for identifying the temperature at which the minimum cmc occurs, and for determining how cmc's vary with significant temperature and pressure changes.

The ability of the dynamic foam height technique to determine cmc's at elevated temperature and pressure is illustrated in Figure 4.10 where foam height plots are shown for general surfactant solution at temperature in the range 23 to 180 ° C ,all at constant applied pressure of 1.38 MPa. The occurrence of a cmc minimum between 23 and 75 degrees followed by an increasing cmc with increasing temperature are observed. The exact location of the cmc minimum can be determined by conducting additional cmc titration in appropriate temperature range. When operated at high temperatures and pressures it is extremely difficult to conduct accurate cmc titrations although measurements on individual surfactant solutions quite easy. The difficulty to determine of 15 to 20 individual surface tensions for each temperature and pressure of interest is due to time constraint.

For these letter uses the resent method offers the ability to rapidly determine cmc's without being limited to use for ionic surfactants only. This method has been used to determine the temperature variation of cmc's for a number of commercial foaming surfactants in aqueous solutions, for the deviation of thermodynamic parameters, and to establish useful correlations.[9]

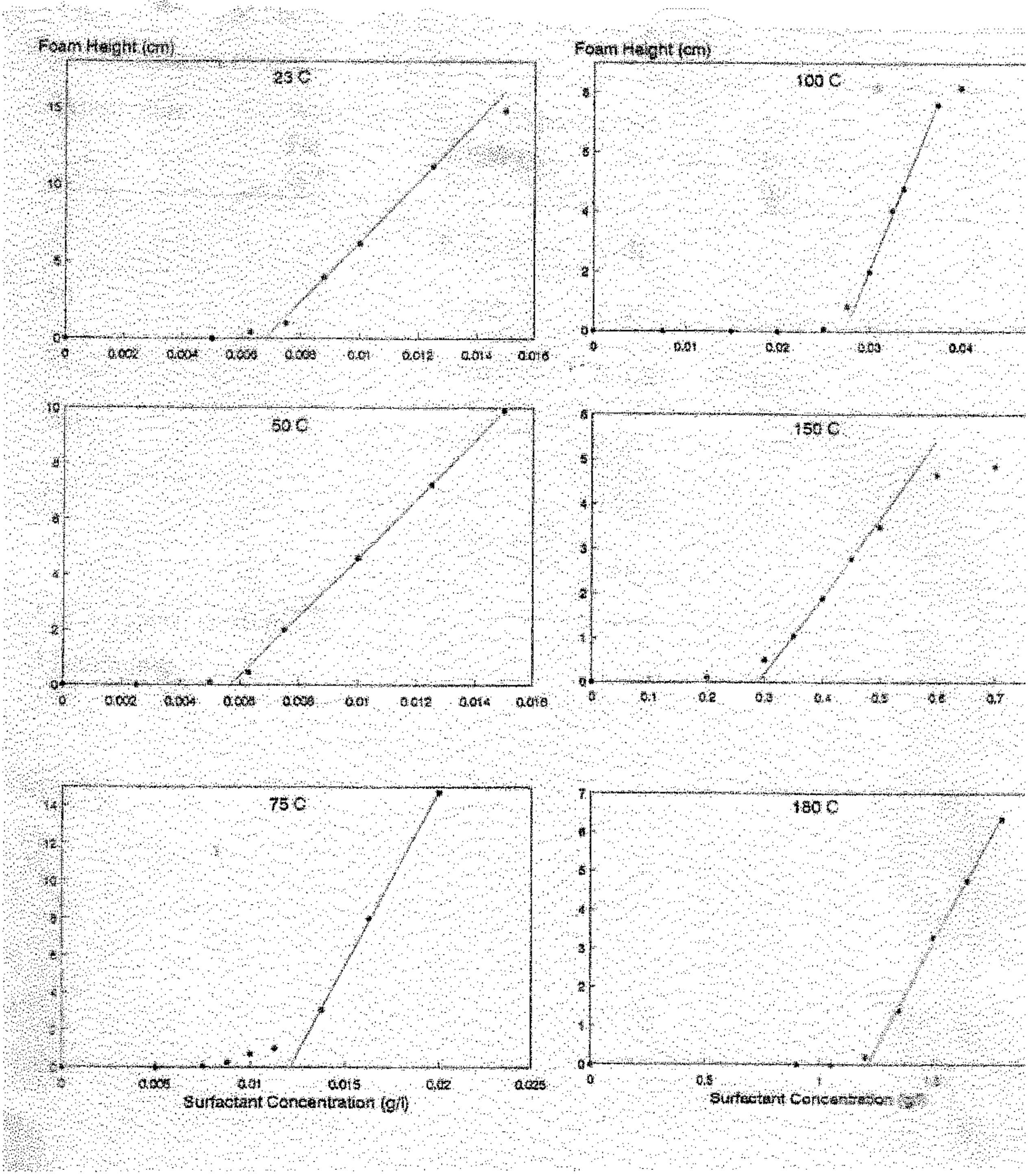


Figure 4.13 Cmc curves of foam height vs concentration at 1.38Mpa and various temperatures.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion and Recommendations

A starting point in considering EOR is to examine primary or secondary recovery from existing fields. Many of these fields were initiated in the 1960's have reached the advanced stages of depletion by primary and secondary production. As it is becoming evident that EOR must be undertaken while the existing wells and surface equipment are still intact and usable. EOR is a valuable area of research because of its potential to further recover more oil. Due to its increasing challenges faced by the petroleum industry, EOR has been the priority and it is up to the engineers to develop and improve recovery techniques in order to design an effective recovery mechanism.

Surfactant floods are generally considered to be suited to the more homogeneous reservoirs. However, the combination of surfactants with polymers in these reservoirs may be attractive and will be the subject of future studies. The chemistry of surfactant behaviour is very complex and oil displacement characteristics are extremely sensitive to the environment conditions of reservoir temperature, salinity of the reservoir brine, the occurrence of divalent ions and the nature of the crude oil.

Surfactant capability to lower the interfacial tension between the crude oil, water and rock due to its hydrocarbon and hydrophilic structure has become the major interest of research and studies about its physical chemistry so that its properties can be very well understood.

Part of the properties that are studied in this research is the IFT and Phase Behavior determination of the selected samples, from the result obtained, conclusions can be made.

5.1.1 As surfactant concentration increases, the IFT will decreases.

5.1.2 As for Phase Behaviour identification, most of the samples yield type II+ and a few of samples managed to obtain type III.

5.1.3 At high concentration of surfactant, the most desired phases are obtained.

5.1.4 The salinity of the reservoir did give some effect in choosing CEOR method.

5.1.5 From observation, as the surfactant concentration increases, foam height will also increases.

CHAPTER 6

REFERENCES

[1] Paul Calin. *Missible and Chemical Enhanced Oil Recovery Methods*, Petroleum Lab Service Department

[2] Ahmad Komarolaili Abu, *Angsi Water Injection System*, Premier Enterprise Corporation (M) SDN BHD.

[3] M. Latil. 1980, *Enhance Oil Recovery*, Institut Francais Du Petrole Publications

[4] Jean Louis SALAGER, *Surfactant, Types and Uses*. Universidad de Los Andes, 2002

[5] Karsa, *Surface Active Behaviour of Performance Surfactant*,New York, Pergoman Press,1995

[6] Bradly, 1987, *Petroleum Engineers Handbook*, Society of Petroleum Engineers

[7] Jim Fitch. *"The Surface Tension Test - Is it Worth Resurrecting?"*, Practicing Oil Analysis Magazine. September 2002

[8] R. Ashayer,C.A Grattoni and P.F.Luckhman, *Wettability Changes During Surfactant Flooding*, Imperial College, 2000

[9] Cassandra Marrison, Baurier L.Schramm, Elaine N. Stanva., *A Review of Methods for Determine of Cmc and a new method for use at elevated Temperature and Pressure*, March 1995

[10] Surtex, *Phase Behaviour Type Descriptions*

[11] W. Barney Gogarty, *Oil Recovery with Surfactants: History and a current Appraisal*, Acedemic Press,Inc,1977

[12] Laurier L. Schramm, 2000, *Surfactants: Fundamental and Applications in the Petroleum Industry*, Cambridge, Cambridge University Press