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UNIVERSITI TEKNOLOGI PETRONAS

# DESIGN AND APPLICATION OF A NEW ACID-ALKALI- POLYMERIC SURFACTANT FLOODING FORMULATION FOR ENHANCED OIL RECOVERY

by

KHALED ABDALLA ELRAIES

The undersigned certify that they have read, and recommend to the Postgraduate Studies Programme for acceptance this thesis for the fulfilment of the requirements for the degree stated.

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# DESIGN AND APPLICATION OF A NEW ACID-ALKALI- POLYMERIC SURFACTANT FLOODING FORMULATION FOR ENHANCED OIL RECOVERY

by

KHALED ABDALLA ELRAIES

A Thesis
Submitted to the Postgraduate Studies Programme
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BANDAR SERI ISKANDAR,
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# DECLARATION OF THESIS

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hereby declare that the thesis is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at UTP or other institutions.

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# DEDICATION

*In the name of Allah, Most Gracious, Most Merciful*

*All praise and thanks are due to Allah Almighty and peace and*
*blessings be upon His Messenger*

*The results of this effort are truly dedicated to my mother and father whose*
*example as devoted professionals, as well as, parents taught*
*me to be perseverant, responsible and loyal*
*to my belief.*

*To my brother, sisters, and my uncle for all their support, encouragement,*
*sacrifice, and especially for their love.*

*Thank you all and this work is for YOU.*

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Thanks to all of my colleagues and friends with whom I had the opportunity to learn, share and enjoy. It has been a pleasure. Last but not least, special and infinite thanks to the most important people in my life, my parents, for their love, prayers, sacrifice and support.

# ABSTRACT

In this study, new chemical flooding formulations have been developed to overcome the precipitation problems caused by the divalent metal cations prevalent with conventional ASP flooding. The purpose of the new design was to make an economical and effective chemical flooding project using natural sea water. To accomplish this objective, this research work was divided into two parts. In the first part, a series of new polymeric surfactants (PS) were produced by the sulfonation and polymerization of methyl esters derived from non-edible Jatropha oil. The PS was designed to graft the sulfonated group to the polymer backbone as one component system for interfacial tension (IFT) reduction and viscosity control. In the second part, two chemical formulations were developed using the screened PS. The first formula consists of acid-alkali-polymeric surfactant (AAPS) and second formula consists of alkali and polymeric surfactant (APS). The AAPS formula was aimed to overcome the precipitation problems using natural sea water. The second formula was developed to simulate the conventional ASP flooding and also to examine the performance of the polymeric surfactant with alkali using softened water. A comprehensive approach has been taken to study the feasibility of the new formulas with the produced PS. The approach included fluid-fluid interaction tests, interfacial tension measurements, phase behavior tests, and, surfactant adsorption tests, and physical simulation using Berea core samples. The purpose of these tests was to establish the optimum chemicals concentrations for Angsi crude oil and to determine the technical feasibility and the injection strategy of the proposed formulas.

As results of various experiments, the polymeric surfactant showed an excellent performance for IFT reduction and viscosity control with Angsi crude oil. The compatibility tests showed that all alkali employed were not compatible with either sea or softened water. However, the acid effectively prevented calcium and magnesium precipitations and all solutions remained clear in the presence of sea water maintained for 90 days at 90$^{o}$C. A combination of alkali and surfactant was found to significantly reduce the IFT and surfactant adsorption with the use of softened water. The IFT measurements indicated an increase in the IFT as the acid concentrations increased with either surfactant or alkali, despite a slight decrease on the IFT when the three components were combined. It is of note that the viscosity of the AAPS solutions increased in the presence of the alkali and remained constant when the alkali concentration was as high as 0.2-1.2 wt%.

Based on series of core flood tests, the optimum chemicals concentrations were found to be 0.99% acid, 0.6% alkali, 0.6% polymeric surfactant for the usage of sea water and 0.8% alkali, 0.6% polymeric surfactant for the softened water. Injection of 0.5PV of the formulated AAPS slug followed by chase water produced an additional 18.8% OOIP. Meanwhile, 16.3% OOIP was recovered when 0.5PV of the formulated APS slug was injected and followed by extend water flood. The benefit of the new system is the use of sea water rather than softened water while maintaining the desired slug properties. This makes the new AAPS formula an attractive and cost-effective agent for chemical EOR particularly for offshore field application.

# ABSTRACT

Didalam kajian ini, formulasi suntikan bahan kimia telah di kembangkan untuk mengatasi masalah pengendapan yang disebabkan oleh logam kation daripada kaedah suntikan bahan kimia terdahulu (kaedah ASP). Tujuan utama kaedah baru ini dihasilkan adalah untuk menjadikan formulasi suntikan bahan kimia menggunakan air laut semulajadi adalah lebih berkesan dan berpatutan. Untuk mencapai matlamat ini, kajian telah dibahagi menjadi dua bahagian. Pada bahagian pertama, beberapa surfaktan polimer baru (PS) dihasilkan oleh sulfonasi dan polimer metal ester yang dihasilkan daripada benih buah Jatropha. PS direka untuk menjadikan kumpulan polimer tersulfonasi ke tulang belakang sebagai salah satu komponen untuk mengurangkan tegangan permukaan (IFT) dan mengawal kelikatan. Pada bahagian kedua, dua formulasi kimia tersebut dikembangkan dengan menggunakan PS yang telah dipilih. Rumus pertama terdiri daripada asid-alkali surfaktan-polimer (AAPS) dan formula kedua terdiri daripada alkali dan surfaktan polimer (APS). Formula AAPS bertujuan untuk mengatasi masalah pengendapan dengan menggunakan air laut semulajadi. Rumus kedua digunakan untuk mensimulasikan kaedah suntikan bahan kimia yang ASP yang terdahulu dan juga untuk menyemak prestasi surfaktan polimer dengan alkali dengan menggunakan air. Pendekatan yang menyeluruh telah diambil untuk mempelajari kelayakan formula baru dengan PS yang telah dihasilkan.

Pendekatan ini meliputi ujian interaksi fluida-fluida, pengukuran teganganpermukaan, ujian kelakuan fasa (pengemulsian), dan ujian jerapan surfaktan, dan simulasi fizikal dengan menggunakan sampel Berea teras. Tujuan dari ujian ini adalah untuk membina konsentrasi bahan kimia yang optimum untuk minyak mentah Angsi dan untuk menentukan kelayakan teknikal dan strategi injeksi formula yang dicadangkan. Sebagai hasil dari berbagai percubaan, surfaktan polimer menunjukkan prestasi yang sangat baik untuk pengurangan IFT dan kawalan viskositas dengan Angsi minyak mentah. Ujian keserasian menunjukkan bahawa semua alkali yang digunakan tidak serasi dengan air laut mahupun air biasa. Namun, asid secara efektif mencegah pengendapan kalsium dan magnesium dan semua larutan kekal jelas didalam air laut yang dibiarkan selama 90 hari pada suhu 90$^o$C. Kombinasi alkali dan surfaktan didapati dapat mengurangkan IFT dan jerapan surfaktan dengan menggunakan air. Pengukuran IFT menunjukkan IFT dan kadar kepekatan asid meningkat dengan alkali mahupun surfaktan, , walaupun sedikit menurun di IFT ketika tiga komponen tersebut digabungkan. Perlu ambil kira bahawa kelikatan AAPS meningkat dengan kehadiran alkali dan tetap ketika kepekatan alkali adalah setinggi 0,2-1,2%.

Berdasarkan beberapa set ujian terhadap suntikan bahan kimia, kepekatan optimum bahan kimia yang ditemui menjadi asid ialah 0,99%, alkali 0,6%, 0,6% surfaktan polimer untuk kegunaan air laut dan alkali 0,8%, 0,6% surfaktan polimer untuk air. Suntikan 0.5PV dengan daya kuat dari AAPS dirumuskan dan diikuti oleh aliran air menghasilkan 18.8% OOIP tambahan. Sementara itu, 16,3% OOIP dicapai apabila penggunaan suntikan 0.5PV dengan daya yang kuat APS dan diikuti dengan memanjangkan pengaliran air. Manfaat yang di peroleh daripada sistem baru adalah penggunaan air laut berbanding air biasa dalam masa yang sama dapat mengekalkan sifat daya yang di kenakan. Hal ini membuatkan formula AAPS yang baru ini adalah menarik dengan perbelanjaan yang berpatutan untuk CEOR khususnya untuk pelaksanaan di kawasan dalam laut.

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# ABBREVIATIONS AND SYMBOLS

| | |
|---|---|
| EOR | Enhanced Oil Recovery |
| IFT | Interfacial Tension |
| OOIP | Original Oil in Place |
| ROIP | Residual Oil in Place |
| ASP | Alkali-Surfactant-Polymer |
| WAG | Water Alternating Gas |
| PS | Polymeric Surfactant |
| AAPS | Acid-Alkali-Polymeric Surfactant |
| APS | Alkaline-Polymeric Surfactant |
| SMES | Sodium Methyl Ester Sulfonate |
| PMES | Polymeric Methyl Ester Sulfonate |
| KOH | Potassium Hydroxide |
| $Ca^{++}$ | Calcium |
| $Mg^{++}$ | Magnesium |
| Na | Sodium |
| $C_3H_4O_2$ | Acrylic Acid |
| $Na_2CO_3$ | Sodium Carbonate |
| $H_2O$ | Water |
| $C_3H_3NaO_2$ | Sodium acrylate |
| GC-MS | Gas Chromatography-Mass Spectrometry |
| FTIR | Fourier Transform Infra-Red |
| TGA | Thermogravimeter Analyzer |
| ppm | Part Per Million |
| cp | Centipoise |
| $^oC$ | Celsius |

# CHAPTER 1

# INTRODUCTION

## 1.1 Research Background and Motivation

Crude oil makes a major contribution to the world economy today. The provision of heat, light and transport depends on oil and there has not been a single energy source to replace crude oil that is widely integrated [1]. Moreover, the global economy currently depends on the ability to supply the energy sources, and it is indisputable that oil is the main contributor to this demand. Technology has not been able to find an energy source that could compete with oil, making the world, and mainly the high energy consumers to rely on countries with large reserves [2].

During most of the twentieth century, great economies flourished because of the presence of a secure, inexpensive supply of oil. The United States was able to satisfy most of its own demand of energy for most of the century [3]. As the USA domestic oil production peaked during the 1970's, OPEC countries took control over most of the world's supply of crude oil due to their immense reserves and production capabilities [3].

There is a wide range of opinions with respect to the availability of conventional oil, and whether the present energy demand, will cause unstoppable oil production decline. Opposed opinions are characteristic for groups of economists and scientists [4]. Past reservoirs management can not be changed, but the present and future strategies in the production of conventional oil may be critical in recovering more oil that would be otherwise left in the ground using traditional production techniques [4].

Traditionally oil production strategies have followed primary depletion, secondary recovery and tertiary recovery processes. Primary depletion uses the natural reservoir energy to accomplish the displacement of oil from the porous rocks to the producing wells [5]. As a general rule of thumb, it is expected that only one third of the original oil in place (OOIP) can be recovered through primary methods [6]. Secondary recovery methods are processes in which the oil is subjected to immiscible displacement with injected fluids such as water or gas. It is estimated about thirty to fifty percent of OOIP can be produced through the entire life of a mature reservoir that has been developed under primary and secondary recovery methods [7]. The remaining oil is still trapped in the porous media. This is attributed to surface and interfacial forces, viscosity forces and reservoir heterogeneities which results in poor displacement efficiency [7]. Recognition of these facts has led to the development and use of many enhanced oil recovery (EOR) methods. EOR methods hold promise for recovering a significant portion of the remaining oil after conventional methods.

In Malaysia and many other countries, most mature reservoirs were already waterflooded, or are presently subjected to secondary or tertiary recovery methods. A considerable amount of hydrocarbon resource is suspected to remain in the ground even after primary and secondary recoveries. In Malaysian producing fields, only approximately 36.8% of OOIP is produced through the entire life of a mature reservoir that has been developed under conventional methods [8]. It can be clearly seen that 63 percent of the discovered recourses will not be produced with the use of current production strategies, making EOR as attractive techniques for the unrecovered oil.

Various modifications of EOR methods have been developed to recover at least a portion of the remaining oil. Thermal processes are the most common type of EOR, where a hot invading face, such as steam, hot water or a combustible gas, is injected in order to increase the temperature of oil and gas in the reservoir and facilitate their flow to the production wells [7]. Another type of EOR process consists of injecting a miscible phase with the oil and gas into the reservoir in order to eliminate the interfacial tension effects. The miscible phase can be a hydrocarbon $CO_2$ or an inert gas [7]. Another common EOR technique is chemical flooding which includes alkalis, surfactants, and polymers, or combinations thereof. The injected alkali and surfactant agents can lower interfacial tension (IFT) between oil and water, thereby mobilize the immobile oil. Alkali can also reduce surfactant adsorption by increasing the pH of flooding water. Polymers are used to viscosify the aqueous solution and maintain mobility control [7].

Planning for improving or enhancing oil production strategies through EOR methods is one of the most critical challenges facing the industry today. EOR not only will extend the life of this important non-renewable resource, but it will also delay a world production decline and shortage in the energy supply. Realizing the significant potential of EOR, PETRONAS embarked on a massive journey to realize the EOR benefits domestically and overseas.

The earliest feasibility study for EOR in Malaysia was conducted in 1985 with the objective to investigate the technical potential of miscible enriched gas and surfactant flooding in the fields located in the Peninsular Malaysia [8]. Later in 1986, a screening study was carried out by Shell to look into the potential of thermal EOR method in Miri field East Malaysia. However, this process was ruled out due to the operational, properties of reservoir fluid, safety and commercial limitations of the method for Malaysian reservoirs [8], [9].

Recognizing the potential of EOR in the fields, PETRONAS endorsed a comprehensive screening study in 2000. The screening study on seventy two reservoirs has identified almost a billion barrels of additional reserves that can be achieved through EOR [8]. The outcome of this study revealed that 52 reservoirs are technically feasible for EOR processes. The screening study has also identified several key EOR technologies that are most applicable to Malaysian oil reservoirs; namely gas injection, chemical injection, and microbial**.** The hydrocarbon $CO_2$ gas flooding in miscible or immiscible mode was found to be the most suitable process [8,9]. These techniques have been successful in certain reservoirs where they have been applied but they are not suitable for all reservoirs due to poor sweep efficiency and reservoir heterogeneity. To further improve the sweep efficiency and mobility control during gas injection, water alternating gas (WAG) process has been implemented [9], [10]. However, this process is not sufficient for all reservoirs because it is greatly affected by several factors such as reservoir heterogeneity, rock wettability, and miscibility condition [10]. When a WAG has failed to control the sweep efficiency in such reservoirs, miscible gas injection techniques are not economically viable due to the unfavorable mobility ratio results in viscous fingering and poor sweep efficiency [10], ]11]. Therefore, other techniques such as chemical flooding can be used to improve the injection process. PETRONAS has conducted an experimental work to study the efficiency of chemical EOR processes for several fields in Malaysia [12]. The chemical EOR processes investigated include surfactant, surfactant-polymer, alkali-surfactant, and alkali-surfactant-polymer. This study has proven that there is potential for chemical EOR application in Malaysian fields [12].

## 1.2 Chemical Flooding for EOR

The chemical combination flooding, which has been developed in recent years, is an important method for enhanced oil recovery includes alkaline flooding, alkali-surfactant flooding, surfactant-polymer flooding, and alkali-surfactant-polymer flooding. Alkaline flooding and its variants are EOR processes that have been employed to recover the residual oil after primary and secondary recovery process.

The concept of recovering oil by alkaline flooding dated back to 1917 when Squires stated that displacement might be made more effective by introducing an alkali into the water [13]. The earliest known patent on alkaline flooding for enhancing oil recovery was issued to Flyeman in Canada in 1920 for developing a process to separate bitumen from tar sands using sodium carbonate [13]. Compared to other EOR methods, it does not require expensive surface equipment, and can be applied without the restriction to well depths and formation thickness.

In an alkaline flood process, the surfactants are generated in situ by chemical reaction between the alkali in the aqueous phase and the organic acids of the oil phase. However, for a low acidic oil reservoir, the amount of surfactants generated in situ is insufficient to produce an ultra-low interfacial tension [7]. A very useful technique for increasing oil recovery of alkaline flooding involves the incorporation of surfactants to the flood water in order to effectively lower the oil/water interfacial tension. Using a combination of alkaline and surfactant in the flood water for oil recovery is referred to as alkali-surfactant flooding.

The theory of combining surfactants and alkalis was first proposed by Reisberg and Doscher in 1956 [14]. They added non-ionic surfactants to the alkali solution to improve oil recovery in laboratory scale. Recent work has shown that the addition of alkali to the surfactant solution would not only decrease the interfacial tension (IFT), but also reduces the surfactant adsorption on the negatively charged sand surface [15]. An inexpensive alkali could be used with expensive surfactants in chemical flooding to achieve both a technically successful and economically feasible flood.

Alkali-surfactant flooding is a promising method for enhanced oil recovery. With the combination of alkali and a small amount of surfactant, oil-water IFT could be reduced much more than with either alkali or surfactant alone [16]. However, the recovery factor of this process is usually insufficient due to the unfavourable mobility ratio. Hence, a polymer is added to the surfactant solution to improve the sweep efficiency. Daging oil field in China is one of the successful fields to apply this process on a field scale with good technological results [17]. However, because of the high cost of surfactants, this process has not been expanded. In order to reduce the cost of the surfactant and to enlarge the swept volume, this technology was upgraded to alkali-surfactant-polymer flooding [17]. The combination of alkali-surfactant-polymer process was expected to cause the residual oil to be economically recovered from the reservoir.

Alkali-surfactant-polymer (ASP) is considered to be the most promising and cost-effective chemical method in recent years. The new technique of ASP flooding has been developed on the basis of alkali, surfactant, and polymer flooding research in 1970s and 1980s [18]. ASP flooding uses the benefits of the three flooding methods simultaneously, and oil recovery is greatly enhanced by decreasing interfacial tension, increasing the capillary number, enhancing microscopic displacing efficiency, and improving the mobility ratio [19].

ASP flooding has been evaluated in the laboratory and used widely in the field application with great success. In 2006, Ibrahim and co-workers conducted the first laboratory study to assess the suitability of ASP flooding for Angsi field in Malaysia [12]. The experimental results showed a tertiary oil recovery of 28.6% of OOIP was obtained using ASP flooding. They concluded that chemical flooding had great potential in recovering residual oil. In contrast, gas flooding techniques were not suitable because of the unfavorable mobility ratio resulted in a poor sweep efficiency [12]. Field performance of ASP process has also been demonstrated with great success in USA [20], India [21], Venezuela [22] and China [23, 24, 25]. Daqing oil field in China is probably one of the earliest fields to apply ASP on a field scale with an increase in oil recovery of 18-25% OOIP.

Despite the existence of a substantial amount of prior art describing the use and benefits of chemical flooding as enhanced oil recovery method, little interest in chemical flooding has been recognized by the oil companies [26]. The main shortcoming involves the high cost of chemicals particularly the surfactant manufacture and raw materials. The recovered oil by this process was not economical or the economical and technical risk was too high compared with the oil price [26]. However, a lot of work has been conducted to develop an economical surfactant in the recent years when the crude oil prices remained high. To reduce the cost of surfactant production, much attention was focused toward agriculturally derived oleochemicals as alternative feedstocks [27]. Many surfactants have been produced from the natural oils to satisfy EOR requirements [28], [29], [30]. Soybean and coconut oils are the most popular raw materials used to derive oleochemical feedstocks such as fatty alcohol and esters [31].

Paradoxically, these surfactants use edible vegetable oils for its synthesis and it will compete with the food supply in the long-term. As the demand of vegetable oils for food increases annually in recent years, the surfactant becomes more expensive as the cost of these oils increase [27]. According to United States Department of Agriculture Oilseeds 2009 [32], the average cost of soybean oil was approximately $ 395 per tonne during the last six months. Meanwhile, the cost of non-edible oils such as Jatropha oil is about $ 250 per tonne. However, the typical cost of the major petrochemical feedstock such as ethylene is $ 595 per tonne. This makes the study and production of Jatropha oil based surfactant an attractive pursuit for chemical EOR.

In 2000s, the chemical combination flooding or ASP flooding has proven as a cost-effective EOR method [19] [22] [25]. Many new chemicals formula and injection strategy have been developed but the process is not without some disadvantages. A process that eliminates or reduces some of the existing problems associated with ASP flooding is needed and this research work is proposing such a process.

### 1.3 Description of the Problem

The major problems associated with the chemical flooding are 1) the high cost of surfactant manufacturing in which the recovered oil is insufficient to offset the cost of surfactants [26] [29], 2) scale and precipitation problems caused by divalent metal cations such as calcium ($Ca^{2+}$) and magnesium ($Mg^{2+}$) that may present in the injection and reservoir waters [20] [22] [25]. In order to reduce the cost of surfactant, various surfactants have been produced from different renewable resources such as vegetable oils and fats. However, as the surfactants is produced from these sources, there are concerns that surfactant feedstock may compete with food supply in the long-term. Hence, renewable resources that will not compete with food must be discovered.

The second problem is associated with the divalent metal cations such as $Ca^{2+}$ and $Mg^{2+}$ present in the injection water and the reservoir brine. These ions react with the alkali such as sodium hydroxide or sodium carbonate in the chemical slug and then precipitate. In this case, the ASP slug will not proceed effectively due to the extensive consumption of the alkali. The alkali concentration will not be sufficient to provide the alkalinity that is used to generate in-situ surfactant. Also, the alkali will not be able to modify the active site on the surface of the porous media which help to reduce the loss of surfactant, and polymer through adsorption.

In order to make the ASP project feasible and economical, it is often desirable to use the produced water or the seawater to prepare the chemical slug. Unfortunately most produced water or seawater contains high quantities of divalent cations. Therefore, softened water is used to prepare the ASP slug and also to preflush the reservoir before ASP injection. A general rule of thumb for applying the ASP process is that the divalent cations concentration needs to be less than 10 ppm [33]. The water should be treated using ion-exchange or some other preferred technique to remove the undesired ions. This increases the limitations of the chemical flooding methods practically for offshore operations where the space is limited. The up-front equipment cost, the operation cost and the space limitation on the offshore platform could be appreciable and often becomes the stopper for the ASP project. Therefore, in order to facilitate the design of effective ASP systems, more fundamental and applied research must be carried out to eliminate or reduce some of the existing problems.

## 1.4 The Proposed AAPS Flooding Formulation Design

The proposed Acid-Alkali-Polymeric Surfactant (AAPS) flooding design aims at developing a new and effective chemical formula as an enhanced oil recovery method. The purpose of this method is to make an economical chemical flooding project using any convenient water source without the need for softening the injection water or preflushing the reservoir before injection. To further reduce the cost of the developed formula, a new polymeric surfactant based on non-edible Jatropha oil was produced. The polymeric surfactant is the main component used in the new formula.

The polymeric surfactant was designed to provide an ultra low interfacial tension and viscosity control as one component system. However, this surfactant would not act effectively with the use of any water source due to the presence of divalent metal cations. In order to use any water source such as seawater or formation water, acrylic acid or the sodium salt of acrylic acid was used to prevent the reaction between divalent metal cations and the polymeric surfactant. The sodium salt of acrylic acid is a super absorbent polymer and is used widely as a precipitation inhibitor for divalent metal cation such as calcium and magnesium [34], [35]. The inhibitory effect of the sodium acrylate is due to the adsorption of the molecules on the surfaces of the divalent metal crystals. The sodium acrylate is usually prepared by converting the free acrylic acid to sodium salt form by an admixture of a water solution of the acid with the alkaline material [34].

In the AAPS formula, the precipitation inhibitor (sodium acrylate) was produced in-situ with the added alkali before introducing the polymeric surfactant to the system. The AAPS formula was introduced to the seawater in the following order, acid, alkali, and polymeric surfactant. The expected reactions that may occur during the preparation are shown below. As shown in Equations 1.1 and 1.2, when the acid is added to the seawater that contains large quantities of divalent metal cations, mostly sodium, calcium, and magnesium, the acrylic acid will be reacted with the sodium ion to form sodium acrylate with an excess amount of acrylic acid. When the alkali (sodium carbonate) is then added to the mixture, more sodium acrylate and divalent metal cations, e.g., calcium, magnesium, and potassium will be formed. The sodium acrylate adsorbs at the active growth sites of the metal cations to prevent them from precipitating. Therefore, if enough acid concentration was used at the beginning, a sufficient precipitation inhibitor will be generated to prevent the precipitations of divalent metal cations as follows:

$$C_3H_4O_2 + Na \longrightarrow C_3H_3NaO_2 + H_2O \qquad (1.1)$$

$$C_3H_4O_2 + Na_2CO_3 \longrightarrow C_3H_3NaO_2 + CO_2 + H_2O \qquad (1.2)$$

When there are no $Ca^{2+}$ and $Mg^{2+}$ ions in the solution, then the surfactant is introduced to the system without any precipitation problems. The influence of the inhibitor on precipitation reaction may be explained in terms of three effects, (a) direct complexation of sodium acrylate with crystal lattice ions in solution; (b) adsorption of sodium acrylate on the crystal surface either generally or at the active growth sites; (c) sodium acrylate may change the ionic strength of the solution and hence increasing the effective solubilities of the $Ca^{2+}$ and $Mg^{2+}$ ions [36].

## 1.5 Objectives of the Study

1. To develop new and low-cost conventional and polymeric surfactants from Jatropha oil for enhanced oil recovery application.

2. To develop a new Acid-Alkali-Polymeric Surfactant flooding formulation that improves the conventional ASP flooding system.

3. To determine the optimum chemicals concentration and the best injection strategy for the new Acid-Alkali-Polymeric Surfactant (AAPS) slug with seawater and Alkali-Polymeric Surfactant (APS) slug for softened water.

## 1.6 Scope of the Study

To achieve the objectives mentioned above, the scope of this study was divided into two main parts. The first part focused on the synthesis and characterization of new conventional and polymeric surfactants based on non-edible Jatropha oil. The second part concerns the development of the new Acid-Alkali-Polymeric Surfactant flooding formulation and its efficiency in enhanced oil recovery. The detailed scope is as follows:

**Part I**

1. Production of Fatty Acid Methyl Ester from Jatropha oil by a two-step transesterification process.
2. Identification of the fatty acid contents of the produced Fatty Acid Methyl Ester by GC-MS.
3. Synthesis of the conventional surfactant (Fatty Acid Methyl Ester sulfonate) by sulfonation process.
4. Synthesis of different types pf polymeric surfactants (Polymeric Methyl Ester sulfonate) by polymerization process.
5. Characterization of the conventional and polymeric surfactants by FTIR, TGA, IFT, and viscosity.
6. Selection of the best polymeric surfactant type and concentration for the AAPS solution with the seawater and APS solution with the softened water.

**Part II**

7. Determination of the optimum alkali to acid ratio for generating sufficient in-situ inhibitor amount for preventing $Ca^{2+}$ and $Mg^{2+}$ precipitations.
8. Examination of the compatibility of the generated in-situ inhibitor with the polymeric surfactant using natural seawater.
9. Examination the effect of the in-situ inhibitor on the viscosity performance of Acid-Alkali-Polymeric Surfactant system using natural seawater.
10. Examination of the effect of in-situ inhibitor and alkali on the interfacial tension performance of Acid-Alkali-Polymeric Surfactant system and Alkali-Polymeric Surfactant system respectively.
11. Investigation of the phase behaviour of the Acid-Alkali-Polymeric Surfactant system and Alkali-Polymeric Surfactant system with Angsi crude oil using seawater and softened water respectively.

12. Determination of the surfactant adsorption onto sandstone surface in the presence and absence of Acid-Alkali and only Alkali using sea and softened water.
13. Studying the effect of alkali concentration, and polymeric urfactant concentration on oil recovery performance of the Acid-Alkali-Polymeric Surfactant system and Alkali-Polymeric Surfactant system.
14. Studying the effect of slug size on oil recovery performance of the Acid-Alkali-Polymeric Surfactant system and Alkali-Polymeric Surfactant system.
15. Identification of the optimum chemicals concentration and the suitable injection strategy for Acid-Alkali-Polymeric Surfactant system with seawater and Alkali-Polymeric Surfactant system for softened water.

## 1.7 Research Benefits

❖ *Jatropha oil as raw material for surfactant synthesis:*

- It is a non-edible oil so it will not compete with food supply.
- It is not a petroleum derivative.

❖ *Acid-Alkali-Polymeric Surfactant flooding formulation as a new chemical EOR method:*

- Polymeric surfactant: One component system for IFT reduction and viscosity control.
- Using any water sources such as formation water or seawater.
- No water treatment is required: it is not required to remove the calcium and Magnesium ions from the injection water. This can be made using appropriate concentration of acid and alkali. Further, this eliminates the cost of water treatment equipment.
- Minimal surface equipment required for the water treatment equipment.
- New, effective, and economic chemical enhanced oil recovery method.

## 1.8 Thesis Organization

This research work was organized into six chapters. The first chapter provides a brief introduction to EOR, fundamentals of chemical EOR and the roles of alkali, surfactant, and polymer in oil recovery process. It also provides the problems prevalent in an ASP process and the mechanism of a new method to overcome some of the existing problems associated with conventional ASP flooding.

Chapter 2 describes an extensive background on this thesis and the preferred EOR methods for Malaysian oil reservoirs. The EOR process and the chemical recovery mechanisms are reviewed. The general considerations of ASP flooding are presented, and different surfactant raw materials and synthesis methods are introduced.

Chapter 3 lays out the research methodology employed to accomplish the objectives of this study. Two parts are described in this chapter. The first part deals with the surfactant synthesis and characterization and the second part presents the design process for the new AAPS formula.

Chapter 4 deals with the characterization results of the conventional and polymeric surfactants produced based on Jatropha oil. The performance of the polymeric surfactant for IFT reduction and viscosity control using sea and softened water are also presented.

Chapter 5 discusses the performance of the generated in-situ inhibitor in preventing divalent metal cations precipitations with the use of seawater. The effects of the in-situ inhibitor on the IFT, phase behavior, and surfactant adsorption were discussed and the optimum chemicals concentration for each system was defined. It also shows the oil recovery performance of the formulated slugs using sea and softened water. Chapter 6 summarizes the main conclusions of this study and provides recommendations for future work.

# CHAPTER 2

# LITERATURE REVIEW

This chapter provides a full background about enhanced oil recovery methods and reviews the previous work related to alkali-surfactant-polymer (ASP) process. It begins with general information on enhanced oil recovery in Malaysia and the concepts of ASP process. The general mechanisms and properties of alkali, surfactant, and polymer flooding are also discussed. Various surfactant raw materials and synthesis methods are described. Finally, the general considerations of ASP flooding, which are essential to designing a new chemical flooding formulation are presented.

## 2.1 Enhanced Oil Recovery in Malaysia

Malaysia has large deposits of hydrocarbon resource remaining in the reservoir of on operating fields. According to the estimates by PETRONAS, on an average, less than one-third of the original oil in place is recoverable with current recovery technologies [8]. A lot of research and field tests and applications with respect to the unrecoverable oil were conducted. It has been identified that almost a billion barrels of additional reserves can be achieved through enhanced oil recovery (EOR) [8]. EOR methods hold promise for recovering a significant portion of the oil that is left in the ground after conventional recovery process. Of the various EOR methods that have been researched and applied, miscible and immiscible gas injection, chemical flooding and microbial have been used for oil recovery [8], [9].

Currently, the $CO_2$ gas flooding in miscible or immiscible mode accounts for the most EOR method that is successfully applied in certain reservoirs with high pressure and low permeability [8], [9]. However, gas methods are not suitable for all reservoirs due to reservoir pressures depletion, reservoir heterogeneity and in such reservoirs, gas techniques are not economical due to unfavorable mobility ratio resulting in poor sweep efficiency [9], [10]. In order to improve the sweep efficiency from depleted reservoir, chemical recovery techniques are required.

Chemical recovery methods include alkaline flooding, surfactant flooding, polymer flooding, and alkali-surfactant-polymer flooding have been investigated and good technological results were observed. However, because of the high cost of these processes, little attention has been paid to chemical methods in past decades. Although chemical methods are slightly expensive as compared to gas methods, these methods become more attractive with the current oil price. The mechanisms of chemical methods vary, depending on the chemical materials added into the reservoir.

The efficiency of this process is a function of liquid viscosities, relative permeabilities, interfacial tensions, wettabilities and capillary pressures [37]. Even if all the oil were contacted with injected chemicals, some oil would still remain in the reservoir. This is due to the trapping of oil droplets by capillary forces due to the high interfacial tension (IFT) between water and oil [37]. The capillary number (*Nc*) is used to express the forces acting on an entrapped droplet of oil within a porous media. *Nc* is a function of the Darcy velocity (*v*), the viscosity ($\mu$) of the mobile phase, and the IFT ($\sigma$) between the mobile and the trapped oil phase [33]. Equation 2.1 below shows the relationship of Darcy velocity, viscosity and IFT to the capillary number.

$$N_C = v\mu / \sigma \qquad (2.1)$$

Figure 2.1 shows capillary desaturation curves that plot residual saturation of oil versus a capillary number on a logarithmic x-axis. From this figure, increasing capillary number reduces the residual oil saturation. The residual oil saturations for both nonwetting and wetting cases are roughly constant at low capillary numbers. Above a certain capillary number, the residual saturation begins to decease. This phenomenon indicates that large capillary number is beneficial to high recovery efficiency because the residual oil fraction becomes smaller. Capillary number must be increased in order to reduce the residual oil saturation. The most logical way to increase the capillary number is to reduce the IFT [33], [37]. Therefore, the principal objective of the chemical process is to lower the interfacial tension so that the recovery performance will be improved.

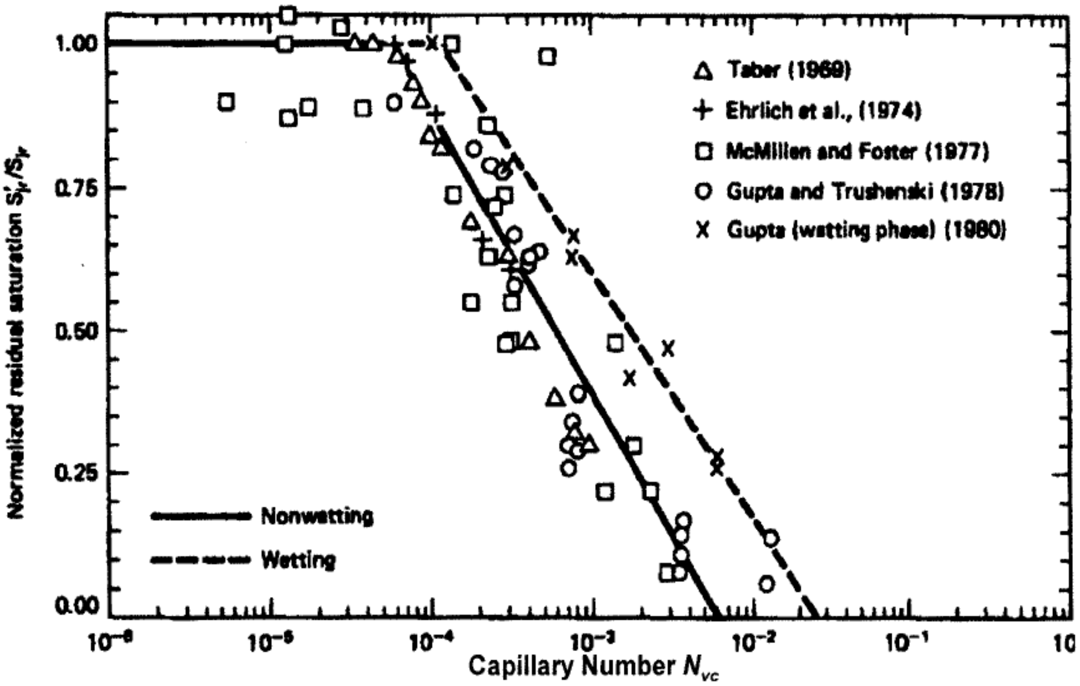


**Figure 2.1:** capillary pressure curves for sandstone cores [37]

## 2.2 Alkaline Enhanced Oil Recovery

Alkaline flooding and its variants are enhanced oil recovery processes that have, for many years, been employed to recover the residual oil after the conventional methods. The concept of recovering oil by alkaline flooding dated back to 1917 when Squires stated that displacement might be made more effective by introducing an alkali into the water [13].

Oil recovery mechanisms by alkaline flooding are complicated and there is a divergence of opinion on the governing principles. There are different proposed mechanisms by which alkaline flooding may improve oil recovery. These include emulsification with entrainment, emulsification with entrapment, emulsification with coalescence, wettability reversal, wettability gradients, oil-phase swelling, disruption of rigid films, and low interfacial tensions [38], [39]. The existence of different mechanisms should be attributed to the chemical character of the crude oil and the reservoir rock. Different crude oils can lead to a widely disparate behavior when they contact with alkali under dissimilar environments such as temperature, salinity, hardness concentration, and pH [39].

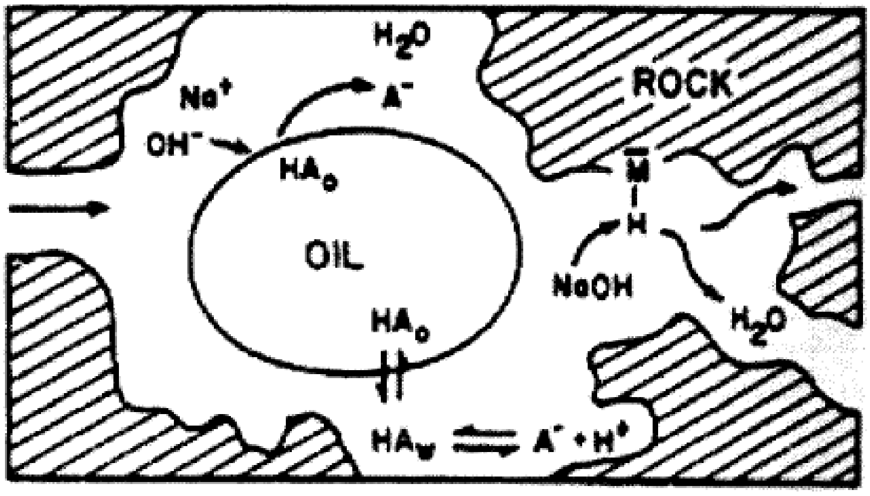


**Figure 2.2:** Schematic of alkali recovery process [39]

The alkali technique can be distinguished from other recovery methods on the basis that the chemicals promoting oil recovery are generated in situ by saponification. The acid number of a crude oil is one of the most important quantities in the alkaline flooding. It characterizes the amount of natural soap that can be generated by the addition of alkali. Acid number is defined as the milligrams of potassium hydroxide (KOH) that is required to neutralize one gram of crude oil [39]. Several investigators have proposed chemical models for the alkali-oil-rock chemistry. Figure 2.2 demonstrates one model by DeZabala et al. [39]. In this figure, $HA_O$ denotes the acid in oil phase, and $HA_W$ the acid in aqueous phase. A condition is created whereby hydrogen ($H^+$) becomes deficient as they are consumed by the hydroxyl ions ($OH^-$) in the aqueous phase. Under this condition, soap is generated and it will adsorb at oil-water interfaces and can lower interfacial tension.

Wettability also plays an important role in alkaline flooding, which controls the initial distribution of residual oil in the pore spaces [40]. The main idea of wettability alteration is to reduce the capillary forces holding the oil in the reservoir rock. In the original wetting state of the medium, the nonwetting phase occupies large pores, and the wetting phase occupies the small pores. If the wettability of a medium is reversed, the wettability of large pores changes from oil wet to water wet. Depending on the rock mineralogy, alkali can interact with reservoir rock in several ways, which include surface exchange and hydrolysis, and with hardness ions in the fluid and those exchanged with the rock surface [41].

Leach et al. [42] reported that the use of alkaline water could cause wettability alteration and improve oil recovery in some naturally oil-wet reservoirs. In 1974, Jennings and co-workers presented an experimental study on the potential of using alkaline flooding in improving oil recovery for an acidic crude oil [43]. The experimental results showed that sodium hydroxide was very reactive with the acidic components in crude oil. The generated in-situ emulsification tended to plug growing water fingers and channels, diverting flow to give improved volumetric coverage or sweep efficiency.

There are many alkali candidates for enhanced oil recovery, which include sodium hydroxide, sodium orthophosphate, sodium carbonate, and sodium silicate. Nutting [44] investigated the use sodium carbonate and sodium silicate for improving waterflood performance. He predicted that stronger alkalis, for instance sodium hydroxide or potassium hydroxide, would be too reactive with the crude and would be used up before they could be effective. Thomas [45] performed an experimental study to determine the role of alkaline chemicals in the recovery of low gravity crude oils. He compared the properties of these chemicals with emphasis on sodium orthosilicate and sodium hydroxide. His laboratory results indicated that significant incremental oil recovery can be obtained by using sodium orthosilicate.

Cheng [46] made a comparative evaluation of chemical consumption during alkaline flooding. The outcome of these comparisons indicated that sodium carbonate is a good candidate for the alkaline flooding. Because of its buffering effect, sodium carbonate had a reduced consumption and has less permeability damage compared to sodium hydroxide and sodium silicate. Burk [47] found that sodium carbonate is much less corrosive for sandstone.

In the alkaline flood process with low acidic crude oils, the generated *in situ* surfactant is insufficient to produce ultra-low interfacial tensions. Nelson et al. [48] presented the concept of using a commercial surfactant to augment the in *situ* surfactant. They found that a properly chosen co-surfactant could significantly reduce the IFT between oil trapped in small capillary pores and the water surrounding those pores. Besides improving oil production by IFT reduction, surfactant can also solubilize oil, forming an emulsion of oil and water.

In order to design an effective alkali-surfactant flooding formulation, it is important to utilize the synergistic effect between the surfactant and alkali. Surfactants tend to accumulate at the oil and water interfaces where the hydrophilic and hydrophobic ends of the molecules can be in a minimal energy state. This increases the surface pressure and decreases both the interfacial energy and the IFT. Rudin and Wasan [49] concluded that the dominant mechanism of the synergistic effect was the formation of mixed micelles of the surfactants and the generated *in situ* surfactant. The mixed micelles caused the IFT to drop lower than it can with either surfactant or alkali alone [48], [16]. At the same time, surfactant adsorption on sand is reduced by the presence of alkali. The sand surface will become increasingly negatively charged with an increase in pH and will thereby retard the adsorption of the anionic surfactant.

A number of alkaline and alkali-surfactant flooding field tests have been described in the literature [50], [51]. Success of these processes in an actual reservoir will depend on how well and for how long the internally-generated surfactant and the externally-added surfactant work together as intended. Mayer et al. [50] summarized based on known field tests the amount of alkali injected and the performance results for early alkaline flooding processes. Most of the projects were not as profitable as expected. Falls et al. [52] reported successful field tests using alkaline-surfactant flooding in recovering waterflood residual oil from sandstone reservoirs in the White Castle Field, USA. The process recovered at least 38% of the residual oil after waterflooding.

### 2.3 Surfactant Enhanced Oil Recovery

Surfactant use for oil recovery is not a recent development in petroleum field. De Groot was granted a patent in 1929 claiming water-soluble surfactants as an aid to improve oil recovery [53]. The success of the surfactant flooding depends on many factors such as formulation, cost of surfactants, availability of chemicals, environmental impact and oil prices in the market. In enhanced oil recovery, surfactants could be used in several formulations to enhance oil production. Some of these formulations are surfactant-alkali flooding, surfactant-polymer flooding, micellar polymer flooding, and alkali-surfactant-polymer flooding.

From a technical point of view, surfactant flooding and its variants is one of the most successful methods to enhance oil recovery from depleted reservoirs. However, it is well documented that surfactant flooding is only marginally economical, or in most cases directly uneconomical [26]. It was concluded by the oil companies at the end of 1980s that the method was not economical, or the economical and technical risks were too high compared with the oil price [26]. The research declined drastically during the 1990s. However, there are still some researchers who are trying to improve the technique by simplifying the flooding process, improving the efficiency of the surfactants and developing new surfactants.

Surfactant and polymer are the principal components used in chemical flooding. The surfactant lowers the IFT between the crude oil and injected water, while the polymer lowers water mobility to create good mobility control. A lot of work have been reported on surfactant flooding and surfactant-polymer flooding since the first work by Gogarty and Olson in the early 1960s [54]. They reported the first patent for field trial using petroleum sulfonates with chemical slug containing hydrocarbons, water, electrolyte and co-surfactants.

In the 1970s and 1980s, few large-scale field tests of surfactant flooding and surfactant-polymer flooding were carried out for enhanced oil recovery. A large-scale application of the Maraflood oil recovery process was applied at the Henry Unit in Crawford Country, Illinois [55]. The oil recovery was about 25% of residual oil in place (ROIP). Gilliland and Conley [56] reported the performance of surfactant flooding in Big Muddy reservoir. The oil recovery was 36% of ROIP. The injected chemical slug was 0.25 PV containing 2.5% petroleum sulfonate, 3% isobutyl alcohol, 0-2% sodium hydroxide and 200 ppm xanthan. The chemical slug was then followed by 0.5 PV polymer drive.

Widmyer et al. [57] reported the performance of surfactant flooding on the Salem unit LTPF project. This project used a surfactant slug containing 2% petroleum sulfonate in softened water. The chemical slug was followed by xanthan polymer slug. The oil recovery was in between 37% and 43% ROIP. Holm [58] presented the micellar/polymer project in Bell Creek field in Montana. This project was a technical success, but an economic failure. 10% OOIP was produced and the chemical cost was estimated to be $12/bbl.

Reppert et al. [59] and Maerker and Gale [60] reported pilot test for the Loudon field. Approximately 68% of water flooded residual oil was recovered by injecting a 0.3PV chemical slug containing 2.3% of surfactant with xanthan coinjection without cosolvent, followed by 1PV of higher polymer viscosity drive. Wang and co-workers reported a successful surfactant-polymer and micellar-polymer flooding pilot tests in Daging field, China [17]. However, this process has been discontinued due to the high cost of surfactants.

Most pilots reported in 1990s accomplished a higher oil recovery than those in 1970s and 1980s. The improvements in chemicals and understanding of process mechanisms were the causes for these successes. These field tests indicated that surfactant flooding and its variants can be technically successful. However, the main factor which can be manipulated for EOR is the cost of the surfactant and the selection of surfactant, the other factors that might affect the surfactant performance are being determined by reservoir conditions [61].

The selection of surfactants for enhanced oil recovery application requires laboratory testing with crude oil and other chemical components such as polymer, alkaline, co-surfactant and co-solvent. Wangqi and Dave [62] conducted screening studied by interfacial tension experiments using different types of surfactants and validated by core flood tests. The IFT results showed wide range of IFT reduction, depends on the surfactant concentration and type and also on the water used to prepare the surfactant solutions. Core flood results indicated that 11.2% OOIP could be recovered when the selected surfactant concentration and type was combined with alkali and polymer. Flaaten et al. [63] started the screening and optimization of surfactant formulations by microemulsion phase behavior using various combinations of surfactants, co-solvents and alkalis. Branched alcohol propoxy sulfates and internal olefin sulfonates demonstrated a superior performance when mixed with conventional alkali. The recovery performance indicated that nearly 100% of residual oil was recovered with very low surfactant adsorption.

### 2.4 Surfactant

Surfactant/surface active agents are amphitpathic substances with at least one hydrophilic and at least one hydrophobic group in the same molecule [64]. This character makes them capable of adsorbing at the interfaces between liquids, solids, and gases. The hydrophilic portion is usually called the head and the hydrophobic portion (usually hydrocarbon chain) is named the 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 the chain, and the functional groups [64]. According to the charge of the head group, surfactants are categorized into four groups: anionic, nonionic, cationic, and zwitterionic surfactants

*Anionic surfactants,* which include soap, are negatively charged and the counter ions are usually small cations such as sodium, potassium, and ammonium ions. 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 [64].

*Nonionic surfactants* do not form ionic bonds. The ether groups of nonionic surfactants will form hydrogen bonds with water so that nonionic surfactants exhibit surfactant properties. As a consequence, they are compatible with other types and are excellent candidates to enter complex mixtures. They are much less sensitive to electrolytes, particularly divalent cations, than ionic surfactants, and can be used with high salinity or hard water [64].

*Cationic surfactants* are positively charged and dissociated in water into an amphiphilic cation and an anion. A very large proportion of this class possesses nitrogen atom as seen in fatty amine salts and quaternary ammoniums, with one or several long chains of the alkyl type. These surfactants are not popular choices for oil recovery as they are more expensive than anionic, and are highly adsorbed by the anionic surfaces of clays and sand [64].

*Zwitterionic surfactants* exhibit both anionic and cationic dissociations. These surfactants display positive and negative charges and are truly amphoteric, often with a minimum of interfacial activity and a concomitant maximum of water solubility. These surfactants have not been used in oil recovery [64].

The past decade has seen the introduction of a new class of surface active substance, so-called polymeric surfactants or surface active polymers, which are produced from the association of one or several macromolecular structures [64]. These structures exhibit hydrophilic and lipophilic characters, either as separated blocks or as grafts. These are illustrated in Figure 2.3, where H and L represent hydrophilic and lipophilic monomer units, respectively. In Figure 2.3, the hydrophilic monomer units H are linked together to form a hydrophilic group and lipophilic units L form a lipophilic group. The result is a macromolecular surfactant with well defined and separated hydrophilic and lipophilic parts, which is much bigger than a conventional surfactant molecule. Associative polymers are the most used polymers in the polymeric surfactant synthesis [65].

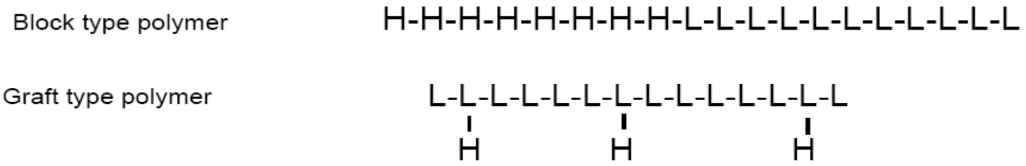


**Figure 2.3:** Configurations of one or several macromolecular structures [64]

Associative polymers are macromolecules with attractive groups that form an interesting class of polymeric systems with numerous applications. The association of their attractive groups leads to the formation of physical bonds. This class of polymers includes charged polymers, block copolymers in strongly selective solvents, and polymers with hydrogen bonding [66]. Block copolymers consist of either blocks of one type of homopolymer attached sequentially to blocks of another type or grafted onto the main chain of a different polymer [67]. Examples of block copolymers in selective solvents are amphiphilic copolymers, such as poly(ethylene-oxides) poly(propylene-oxides) poly(ethylene oxide) copolymers, and hydrophobically modified polymers [68], [69].

Hydrophobically modified associative polymers are synthetically derived, water soluble polymers that contain a small numbers of hydrophobic groups. These hydrophobic groups aggregate in order to minimize their exposure to water, in a fashion analogous to surfactants [70]. Several hydrophobically modified polymers are currently available commercially and utilized in a wide range of applications. Examples of those polymers are: hydrohpobically modified (hydroxyethyl) cellulose [71], hydrophobically modified ethoxylate urethane [72], hydrophobically modified polyacrylamide and hydrophobically modified alkali soluble emulsion (HASE) polymers [73]. These hydrophobically modified polymers have either a telechelic structure in which the chains are end-capped with the hydrophobic groups, or more complicated comb-like structures in which the hydrophobic groups are randomly grafted to the polymer backbone [65].

The hydrophobically modified alkali soluble emulsion (HASE) polymers have several advantages over other associative polymers in terms of cost and wide formulation latitude [74]. Compared to other hydrophobically modified polymers, HASE polymers have a unique ability to dramatically modify the solution properties. In particular, a few percent of the polymer can increase the solution zero-shear viscosity up to several decades. On the other hand, their shear thinning property and the high shear rate viscosity are very low. A viscosity profile which possesses a large zero-shear viscosity and a low high-shear viscosity is ideal for many applications [65]. Therefore, this type of polymer was used in this study to synthesis the polymeric surfactant.

### 2.4.1 Surfactants Raw Materials

Many kinds of surfactant structures are available today on the market and their price range from 1 $/lb to 20 times more [64]. The raw materials are extremely varied and come from diverse origins, involving transformation ranging from a simple hydrolysis to multistep high pressure synthesis processes. The main raw materials for surfactant production are petrochemical feedstocks such as ethylene and propylene oxides, and/or agricultural materials such as vegetable oils, animal fats, and starches [64].

For the time being, vegetable oils are the most favourite oleochemical raw materials. The principal raw materials from which the natural fatty acids are derived are soybean, palm, coconut, rapeseed and sunflower oil. Because these oils are considered as edible oils, 101 million tonnes of fats and oils were produced worldwide in 1998 which is used in human foodstuffs [31]. In recent years, the amounts produced have continuously increased by approximately 3% per year because of their high share of fatty acids. The composition of the fatty acids contained in the oil determines the further use of the oils. These oils are particularly suitable for further processing to surfactants for washing and cleansing agents as well as cosmetics [31].

The oils and fats are triglycerides which typically consist of glycerine and saturated and unsaturated fatty acids. From a chemical point of view, triglycerides offer two reactive sites, the double bond in the unsaturated fatty acid chain and the acid group of the fatty acid chain. With regards to surfactant production based on triglycerides, the majority of derivatization reactions are carried out at the carboxylic group, whereas oleochemical reactions are performed on the alkyl chain or double bond [31]. For most of the uses, oils and fats must be split into the so-called oleochemical base materials: fatty acid methyl esters, fatty acids, and glycerol.

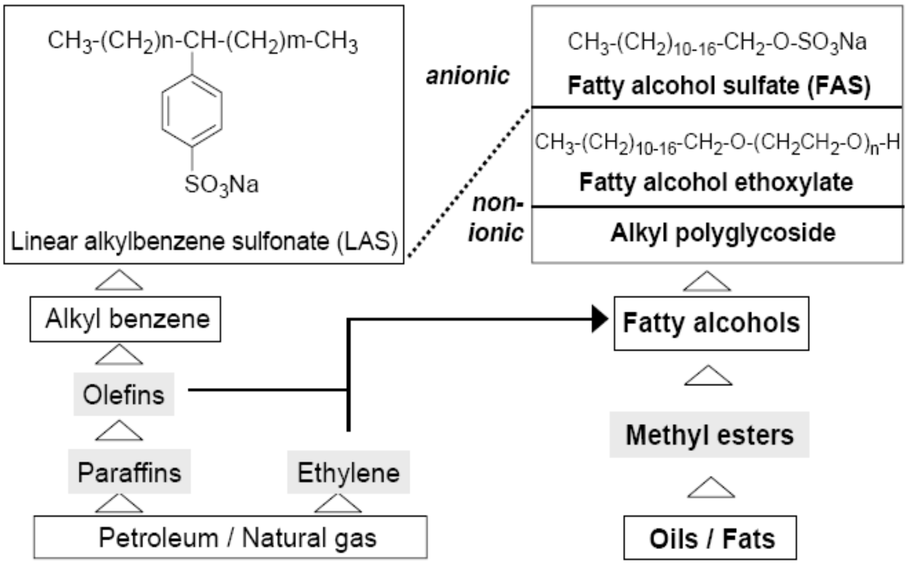


**Figure 2.4:** Production of Surfactants and Examples of Products [31]

Currently, fats and oils are one of the most important raw materials for the oleochemical industry. Figure 2.4 shows some of the major processes by which various oleochemicals and their derivatives can be obtained from fats and oils [31].

As can be seen from Figure 2.4, fatty acid and their various fractions are the building blocks that, with proper selection and application of oleochemistry, are converted to higher value products. Their range of application covers a broad spectrum in the oleochemical industry. Fatty acid can undergo different processes in the manufacture of various oleochemical derivatives.

### 2.4.2 Surfactant Production from Natural Oils and Fats

Many types of surfactants have been produced from the natural oils and fats and the selection of surfactant is dependent on the conditions in the reservoir as well as the cost and availability of the surfactants. Several types of the surfactants that can be made by the fatty acids or its derivation are listed below.

***a. Anionic Surfactants***

1. Soaps and other Carboxylate surfactants
2. Sulfonation and Sulfatation surfactant
3. Alkyl sulfates and alkyl ethoxy sulfates
4. Other Anionic Surfactants

***b. Nonionic Surfactants***

1. Ethoxylated Alcohols
2. Fatty acid Esters
3. Other nonionic Surfactants

A wide variety of carboxylate surfactants or salts have been investigated to evaluate their potential for enhanced oil recovery. The major carboxylate surfactants derived from the fatty acid are isostearate, stearate, oleate, neutralized tall oils and tall oil fatty acids [75]. These surfactants are used for a highly specific purpose, such as in high salinity and/or high brine environments [75], [76]. The carboxylate surfactants can be prepared by extracting carboxylic acids from crude oil or certain oil fractions and using the salts thereof for IFT reduction [75], [76].

Shaw [76] conducted a series of experiments to investigate the applicability of different carboxylate surfactants in reducing the IFT. The results showed that carboxylates with alcohols as cosurfactants produced excellent phase behavior with ndecane. The interfacial tensions between the phases at the optimal salinity were 0.001 dyne/cm.

A series of core flood tests were also performed to investigate the performance of various types of carboxylate surfactants for oil recovery [76]. These tests were conducted using 0.1 PV surfactant slug containing 3% sodium carboxylates, 3% cosurfactant and 0.6% sodium carbonate base. The results showed excellent displacement efficiency. He concluded that sodium oleate is a potential low-cost surfactant for enhanced oil recovery because oleic acid is available in large quantities and can be extracted from vegetable oils [76].

Li et al. [29] developed a new series of surfactants whose major composition is naturally mixed carboxylate from saponificating leftover bits and pieces of cotton seed oil, soybean oil, and animal oil. These surfactants are very cheaply priced as compared to commercial surfactants. They used these surfactants in alkali-surfactant-polymer flooding with a concentration of 1% alkali, 0.5% surfactant, and 1000 ppm polymer. The results showed that the oil recovery is increased by 26.8% OOIP [29].

Other anionic surfactants have also been produced from natural oils to satisfy various requirements and mainly to reduce IFT to a considerable extent. These surfactants are very stable under reservoir conditions and do not form any deposits in the flood water or formation water. Some of these surfactants are ether sulfates, ether carboxylates, ether sulfonates and ether phosphates in particular have been proposed as surfactants for use in a high-salinity environment. Ether sulfates and ether phosphates are readily obtainable on an industrial scale, but lack stability to hydrolysis. Ether sulfonates and, more particularly, alkyl ether sulfonates have shown particularly interesting properties in screening tests. They combine high electrolyte compatibility with high stability to hydrolysis at high temperatures. They also showed the appearance of the desired three-phase states in the oil/water/surfactant systems with a broad middle phase micro-emulsion range and a pronounced reduction in interfacial tension [28].

Numerous synthesis methods have been proposed for the preparation of these surfactants. Ando et al. [77] synthesized fatty alcohol ether sulfates or alkyl ether sulfate by adding ethylene oxide to a synthetic or natural alcohol to form alcohol ethoxylate. This alcohol ethoxylate was then sulfated with sulfur trioxide diluted with inert gas by means of a thin film type sulfation device. This type of surfactants have unlimited water solubility and possess superior skin compatibility. Accordingly, they are used in liquid shampoos and bath preparations. One characteristic of this surfactant is its ability to increase its viscosity by the addition of an electrolyte such as salt [27].

Liu et al. [30] conducted a series of sandpack flood tests to evaluate the performance of alkali-surfactant flooding. Alkyl ether sulfate was selected to reduce interfacial tension and to emulsify the oil in the formation brine. The interfacial tensions decreased significantly due to the addition of alkyl ether sulfate and reached $10^{-3}$ dyne/cm at 50 mg/L surfactant. The results of sandpack flood tests showed that the tertiary oil recovery could reach 24% OOIP by injecting a 0.5PV of the formulated chemical slug [30].

Piorr and Meffert [78] disclosed a new process for the production of ether sulfonate surfactants which enables those surfactants to be produced from readily obtainable starting materials. They synthesized the ether sulfonate by a continuous sulfonation process. According to this process, ether sulfonates were produced by reaction of sulfur trioxide and either an unsaturated fatty alky lower alkyl ether or an unsaturated fatty alkyl polyoxyalkyl lower alkyl ether.

Wuest et al. [28] disclosed a new process for the production of surfactant and surfactant mixture for use in enhanced oil recovery. The surfactant mixture consists of an alkyl ether sulfonic acid or salt as principal constituent and nonionic fatty alcohol ethers. This surfactant mixture is mainly based on fatty alcohol ether sulfonate which enables this industrially interesting class of surfactants to be economically obtained. The alkyl ether sulfonic acid is obtained by the reaction of alkyl ether sulfate with an aqueous alkali metal sulfite solution in a nucleophilic substitution with sulfite at temperatures of 160 to 220°C.

Another class of anionic surfactant is named fatty acid methyl esters sulfonate. This surfactant is considered a material with a great potential. Its superior sequestering effect on water hardness gives it an advantage over fatty alcohol sulfate [27]. Various techniques have been used for preparing different types of sulfonated fatty acid esters where the falling film reactor is the most popular technique [79], [80]. In this technique, the sulfonation takes place at temperature range from 50 to 85 $^{o}$C using sulfur trioxide as sulfonation agent. The produced surfactant is very dark in color and need to be bleached at 60 $^{o}$C for one hour [81]. However, the produced surfactant by this process is very costly and it is not desirable for EOR project.

For the nonionic surfactants, alkyl polyglycosides (APGs) is one of the most important nonionic surfactant. This type of surfactants is prepared with renewable raw materials, such as starch and fat or their components, namely glucose and fatty alcohols. McCurry et al. [82] and Beaulieu [83] produced the alkyl polyglycosides by a process which involves reacting a reducing sugar with an alcohol to obtain an alkyl polyglycosides product containing unreacted alcohol. APGs are usually used in a number of household detergents, cosmetics, and agricultural products.

Tang et al. [84] developed a new chemical formula for chemical flooding system using the alkyl polyglycosides (APGs). The surfactant compositions comprising one or more APGs and one or more aromatic alcohols. In this study, APGs have been considered for the first time for EOR application. They reported that APGs are very effective at mobilizing oil trapped in porous rock and the use of additional cosurfactants may significantly increase the usefulness of surfactant flooding. Moreover, a useful property for APG formulations is the phase behavior and IFT reduction that are largely independent of temperature and salinity. This may be due to the fact that APGs are nonionic and generally have a large head group [84].

All the previous studies indicated that fatty acid and its variations make up one of the major basic oleochemicals enjoying a continuing growth rate. Fatty acid methyl esters and fatty alcohols are increasingly gaining favor as the surfactant raw materials of choice because of their biodegradability as well as availability from renewable resources. However, Gregorio [27] reported that fatty acid methyl esters found more interest as starting materials compared to fatty acids. The use of methyl esters instead of fatty acids is rapidly gaining ground because of the following advantages [27]:

1. Lower energy consumption. The production of methyl esters requires much lower reactor temperatures and pressures than the splitting of fats and oils to obtain fatty acids.
2. Less expensive equipment. Methyl esters are non-corrosive, hence they can be processed in carbon steel equipment while fatty acids are corrosive and require heavy-duty stainless steel equipment.
3. More concentrated glycerine byproduct. Transesterification is a dry reaction and yields concentrated glycerine, while fat splitting produces glycerine water.

Based on the previous discussion, the use of vegetable oils for oleochemical feedstocks has recently been given much attention. However, as the demand for vegetable oils for food has increased tremendously in recent years, it is becoming more difficult to justify the use of these oils for oleochemical industry purposes such as surfactant production [27]. Also, these oils could be more expensive to use as surfactant raw material. Hence, the contribution of non-edible oils such as Jatropha oil will be significant as a non-edible oil source for surfactant production. According to United States Department of Agriculture Oilseeds, 2009 [32], the average cost of soybean oil was approximately $395 per tonne during the last six months. Meanwhile, the cost of non-edible oils such as Jatropha oil is about $250 per tonne. However, the typical cost of the major petrochemical feedstock such as ethylene is $595 per tonne. This makes the study and production of Jatropha oil based surfactant an attractive pursuit for chemical EOR.

### 2.4.3 Jatropha Tree

Jatropha curcas L. is a plant belonging to Euphorbiaceae family that produces a significant amount of oil from its seeds. This is a non-edible oil-bearing plant widespread in arid, semi-arid and tropical regions of the world. Jatropha is a drought resistant perennial tree that grows in marginal lands and can live over 50 years [85]. Pant et al. [86] reported that Jatropha oil content varies depending on the types of species and climatic conditions, but mainly on the altitude where it is grown. The oil content in Jatropha seed is reported to be in the ranges from 30 to 50% by weight of the seed and ranges from 45% to 60% weight of the kernel itself [87]. The Jatropha tree has several beneficial properties such as its stem is being used as a natural tooth paste and brush, latex from stem is being used as natural pesticides and wound healing, its leaf as feed for silkworms among other uses [88]. It is a rapidly growing tree and easily propagated. Figure 2.5 shows the Jatropha plant as a living fence to protect crops, its fruits and the oil-bearing seed.

**Figure 2.5:** Jatropha planted as living fence, its fruit and seed

Jatropha usually grows below 1400 meters elevation from the sea level and requires a minimum rainfall of 250mm, with an optimum rainfall between 900-1200mm [85]. This plant is not even browsed by animals for its leaves. Recently Jatropha curcas is being considered as one of the most promising potential oil source to produce biodiesel in Asia, Europe and Africa. Chhetri et al. [88] discussed the multiple use of Jatropha for different purposes. Among other parts of the Jatropha tree, the seed has so far been found appropriate for numerous uses. The analysis of the fatty acids of Jatropha oil shows that oleic acid is the main one and followed by linoleic acid as presented in Table 2.1.

**Table 2.1:** Comparison between fatty acid composition of Jatropha oil and other oils [89], [90]

| Fatty acid | | Jatropha oil | Coconut oil | Soya oil | Palm oil |
|---|---|---|---|---|---|
| Lauric | C12:0 | - | 48 | - | - |
| Myristic | C14:0 | 0 – 0.1 | 17 | 0.1 | 0.9 - 1.5 |
| Palmitic | C16:0 | 14.1 – 15.3 | 9 | 11 | 39.2 -45.8 |
| Palmitoleic | C16:1 | 0 – 1.3 | - | 0.1 | 0 - 0.4 |
| Stearic | C18:0 | 3.7 – 9.8 | 2 | 4 | 3.7 - 5.1 |
| Oleic | C18:1 | 34.3 – 45.8 | 6 | 23.4 | 37.4 - 44.1 |
| Linoleic | C18:2 | 29.0 – 44.2 | 3 | 53.2 | 8.7 - 12.5 |

In view of the foregoing discussions, many new surfactants have been produced using different raw materials to satisfy EOR requirements. The recent literatures have paid more attention to the development of new candidates for EOR that are able to create low IFT conditions. The goal of research was to develop a new chemical design that can recover additional oil in a cost-effective manner. There are surfactants that have emerged from the literature search as being newer, intriguing ideas for EOR applications. However, the choice of surfactant is dependent on the conditions in the reservoir, as well as the cost and availability of the surfactants. In order to make a cost-effective chemical slug system, a combination Alkali-surfactant-polymer (ASP) slug has been proven as an effective system. The purpose of the alkali is to form an in-situ surfactant and also to reduce the surfactant adsorption by increasing the pH of the flooding material. The function of polymer is to reduce the mobility of the aqueous phase, thus improving the sweep efficiency. A polymer also increases the capillary number, by increasing the viscosity of the displacing phase. This will, in addition, improve the microscopic displacement efficiency.

## 2.5 Alkali-Surfactant-Polymer Flooding

Alkali-surfactant-polymer (ASP) flooding has been found to be one of the major EOR techniques that can be successfully used in producing light and medium oils after conventional methods. The advantage of ASP flooding over conventional alkaline flooding is that ASP can be used for low acid number crudes while alkaline flooding can only be applied for medium to high acid number crudes. In the ASP process, alkali can be used to make an in-situ surfactant with acidic oils and increases the pH to lower surfactant adsorption. Surfactants are used to lower the IFT between oil and water while polymer is used to improve the sweep efficiency by providing mobility control [18]. ASP process uses the benefits of the three flooding methods, and oil recovery is greatly enhanced by decreasing interfacial tension (IFT), increasing the capillary number, enhancing microscopic displacing efficiency, and improving the mobility ratio [19].

In recent years, there have been many field pilot tests using ASP in USA [20], India [21], Venezuela [22] and China [23], [24], [25], [91], [92]. One of the biggest differences between ASP process and surfactant process is that ASP has two surfactants, synthetic surfactant that is injected and the natural soap created by the alkali in situ. However, the mechanism of the alkali-surfactant flooding is still not fully understood. Most investigators agreed that the key issues for the alkali-surfactant-polymer flooding are IFT reduction at low surfactant concentration, wettability alteration, low adsorption of surfactant by alkali, and mobility control.

## 2.6 Design Parameters for ASP Process

### 2.6.1 Interfacial Tension Mechanism

Interfacial tension (IFT) reduction is one of the most important factors in alkali-surfactant-polymer flooding. Krumrine et al. [93] found that low IFT could be achieved with several alkaline chemicals and dilute surfactant systems. With the addition of a small amount of surfactant to the alkali-solution, the IFT become lower than with either surfactant or alkali alone [94]. Nasr-El-Din et al. [95] found the alkali-surfactant mass ratio changes the time to achieve minimum IFT by using dynamic IFT measurement. Hirasaki and Zhang [96] found that there were optimum conditions for the IFT reduction by changing the concentration of alkali and surfactant.

Rudin and Wasan [97] claimed that the organic acid amount in the oil has significant effect on the IFT reduction of an alkali-surfactant-oil system. They found that at low crude oil acid concentrations, the addition of an alkali to the added surfactant solution would only make interfacial tension increase. But in medium to high acid concentrations, the addition of an alkali can produce ultralow interfacial tension. On the other hand, several investigators reported that the conventional screening criteria for an alkaline flood such as the acid number are no longer as critical to success as was thought in the past [24, 97, 98]. Furthermore, Mayer et al. [50] in their summary of field tests pointed out that there is no single definitive criterion for crude oil properties needed for alkaline flooding, and no direct correlation has been observed between the acid number and the magnitude of the enhanced oil recovery. French and Burchfield [100] reported that oil acid number is important for achieving low IFT in alkaline floods that do not include added synthetic surfactant in the alkaline flooding formulations.

Injection of a combination of alkali with synthetic surfactant and polymer is a much cost-effective method than the conventional alkaline flooding technique. Krumrine and Falcone [101] and Campbell [102] presented comparisons of important properties of various alkalis in order of increasing benefits. It can be observed from those comparisons that alkalis producing low IFT do not necessarily yield better oil recovery. This is because the IFT is a function of the type of crude, brine composition, pH, temperature and the concentration of surfactant and co-surfactant used. This aside, alkalis producing low IFT may have low adsorption reduction capabilities and might not be compatible with the injected and reservoir brines.

Shenawi [103] investigated the effect of alkalinity, salinity and divalent ions on the IFT with different crude oils. He concluded that temperature has no strong effect on minimum IFT and the presence of divalent ions reduced the effectiveness of alkali solutions in reducing the IFT. It was also observed that minimum IFT increased with increase in sodium chloride concentration. Cooke et al. [104] observed that divalent ions such as calcium and magnesium increase the interfacial tension between acidic oil and alkaline water. This is because calcium and magnesium ions react with organic acids to form the corresponding calcium or magnesium soaps which possess a reduced surface activity.

Sharma et al. [105] investigated transient interfacial tension behavior of crude oil caustic interfaces. They showed the existence of a maximum in dynamic IFT curve, at higher pH. Such a trend was not observed at low pH. The absolute value of IFT was found to be higher at higher sodium chloride concentration and divalent ions dramatically increase IFT. Burk [47] showed that high pH is not a necessary condition for low IFT in an alkali-surfactant-polymer flooding. Sodium carbonate was found to maintain its pH over a wide range despite alkali depletion in the reservoir.

In addition to low interfacial tension, wettability alteration is also considered as an important factor for ASP recovery mechanism. The addition of alkali to the dilute surfactant solution can change the wettability. Many researchers have found that the ultra low IFT and wettability alteration existed in the ASP process would be the main reason for enhanced oil recovery [48, 96, 100, 106]. In this thesis, the wettability alteration will not be further discussed, but we still should keep in mind that wettability alteration is very important for alkali-surfactant process. The purpose of this research work was to design a cost-effective method by mitigating the negative effects of the undesired divalent metal cations. The complex interaction between the combined chemicals will be the first issue to be resolved in this study.

### 2.6.2 Fluid-Fluid Interaction

Although Alkali-surfactant-polymer (ASP) flooding has been recognized to be the most cost-effective techniques in EOR, the success of this process depends on the way they are combined to produce compatible and effective slug with reservoir fluids. Several mechanisms have been proposed for this technique, but they are still not well understood. This is because of the high dependence of this process on reactions between the injected fluid and minerals on the surface of the reservoir rocks, which are not chemically inert. Several investigators reported that reservoir rock minerals, brine composition, and oil properties have been recognized to be the most important parameters for determining the feasibility of alkaline flooding and its variants [98], [100], [107]. The design of an effective alkaline containing chemical slug requires an understanding of the interaction mechanisms between the above parameters and the reaction mechanisms that deplete the alkalis.

In an ASP flooding process, the complex interactions between the various injected chemicals and reservoir fluids and rocks can be classified as fluid/fluid interaction and fluid/rock interaction [108]. Lorenz and Peru [109] presented a review of 50 alkaline flooding field projects in the United States. Despite this extensive field testing, about one fourth of these projects reported problems with scale formation due to alkali consumption. This problem is caused by the reaction between the alkali and the divalent metal cations present in the reservoir brine. The presence of divalent metal cations such as calcium and magnesium ions in the brine will result in the consumption of the alkalis causing the calcium and magnesium salts to precipitate [35].

The effect of the divalent metal cations either on the injection brine or on the reservoir brine in ASP process has been examined by many researchers. Many suggestions have been made to remove the divalent metal cations from the injection brine. The first and the most used suggestion is to soften the injection water through ion exchange to remove the divalent metal cations thereby preventing precipitation within the injection well. Jennings et al. [43] concluded that water hardness in the form of calcium ions can inactivate the in situ surfactant so the calcium had to be removed from the injection water. Clara et al. [22] studied the performance of ASP process for La Salina field using lake water. Their results showed that all the chemicals were not compatible with the lake water where precipitations were formed with very low chemical concentration. For this reason, it was necessary to soften the lake water to dissolve the chemicals. Wang et al. [17] described the performance of ASP flooding for Daqing field in China. They concluded that the ASP slug must be prepared by fresh water.

While these suggestions can eliminate plugging of the injection well, it may not be sufficient to prevent plugging within the reservoir in the vicinity of the injection well. This is because the formation water (connate water) contains significant levels of dissolved divalent metal cations. Therefore, still another suggestion has been to inject a preflush of water substantially free of divalent metal cations into the reservoir in order to condition the reservoir and reduce or prevent plugging in the vicinity of the injection well [110]. Al-Hashim et al. [108] conducted a series of compatibility tests for ASP flooding and they concluded that the ASP slug has to be prepared by softened brine and protected by pre-and after flush softening brine slugs.

Another suggestion has been to remove precipitated hydroxides or carbonates from the injection water by filtration before the ASP flood water is injected into the reservoir. Pratap and Gauma [21] presented the results of field implementation of ASP flooding in India. In this project, formation water was used to prepare the ASP slug. However, the ASP slug was passed though a sand filter and then through micron filter to remove the undissolved particles. Ibrahim et al. [12] conducted an experimental study to evaluate the performance of ASP process for Malaysian oil field using nanofiltered seawater. It was found that essentially any alkaline solution in nanofiltered seawater showed some precipitation. At that point, it was determined that the plugging was probably due to precipitation of residual calcium as calcium carbonate from the synthetic nanofiltered seawater. Therefore, it was concluded that the nanofiltered seawater must be softened in order to keep the solution clear.

Bunge and Radke [111] investigated the divalent ion exchange mechanism in causing precipitation between alkali and reservoir brine. They concluded that continuous alkali injection removes calcium most efficiently. In addition, it was observed that an alkaline preflush for hardness cation removal is not attractive if calcium hydroxide is precipitated. This is because the solubility of calcium hydroxide permits large concentrations of calcium ions to occur when low-pH solutions contact the precipitated material. This will be detrimental to the surfactant slug. French and Burchfield [100] showed that an alkaline preflush protects synthetic surfactants from precipitation by removal of divalent ions. A low-pH alkaline (such as sodium bicarbonate and sodium carbonate) was effective in reducing alkali consumption and scaling in production wells.

Shawn and Lorenz [112] investigated mineral-alkaline reaction under dynamic conditions. They pointed out that carbon dioxide in the reservoir constitutes an acid capacity that must be naturalized by the injected alkali. It was also observed that all alkalis reduce divalent ion content of brine which leads to a reduction in degradation of co-injected surfactant.

The alkali-polymer interaction is another key factor in the project design. Alkaline agents significantly increase the ionic strength of ASP formulation. The viscosity of a given polymer concentration is much lower in saline solutions than in fresh water. Wang et al. [113] showed that when the polymer solutions are exposed either to high temperature or high pH values, the polymer amide groups can hydrolyze. However, the carbon-carbon backbone of the polymer is quite stable as long as oxygen and free redials are absent. Thus, the concentration and expense of polymer may be unusually high when saline water is used for the ASP flooding. It was also observed that viscosity increased with the increase of polymer concentration and was significantly lower with 1.4% - 1.5% alkali than without alkali. Shiyi et al. [114] mentioned that the injected alkali has both side effects, the favorable one is to decrease the IFT and the unfavorable one is to decrease the solution viscosity.

Nasr-El-Din et al. [95] conducted an experimental study to examine the effectiveness of alkali concentration on ASP performance. Their experiments also confirmed an exponential decrease in viscosity of the combined ASP slug with the increase in alkali concentration. Wang et al. [115] pointed out that the effectiveness of a polymer in ASP flooding is directly determined by the magnitude of the polymer viscosity. The viscosity depends on the quality of the water used for dilution. It was also observed that the increased salinity and hardness in the reservoir water decrease solution viscosity for anionic polymers. French and Josephson [116] showed that the interaction between polymer and surfactant is affected by pH, ionic strength, crude oil, and the properties of the polymer and the surfactant. They observed that polymer-surfactant interaction had an adverse effect on polymer rheology and the magnitude of the interaction was least for non-ionic surfactant and biopolymer.

Due to divalent metal cation problems, several investigators have developed new techniques to prevent calcium and magnesium precipitations. Bunge and Radke [117] concluded the weak-acid calcium/hydrogen ion exchange causes a hardness concentration dependence of hydroxide uptake isotherms. Therefore, alkaline uptake should be measured in the presence of field brine. Novosad [118] suggested to inject lignosulfonate as a sacrificial agent to reduce the divalent metal cations present in the reservoir brine. The purpose of this agent was to reduce the adsorptive capacity of reservoir surfaces by pre-adsorbing chemicals on active surface sites of reservoir rocks. Usually these chemicals are waste materials or some inexpensive chemicals.

Bernard [34] and Mohnot and Chakrabarti [35] developed a new method for enhancing oil recovery by injecting an aqueous solution containing an alkali material and a water soluble precipitation inhibitor. The purpose of the precipitation inhibitor was to prevent the divalent metal cations from precipitating within the injection fluid or within the reservoir water. The injection water used in this invention can come from any convenient source, and does not need to be free of divalent ions. They suggested that any other additives such as surfactant and polymer could be added to the solution to optimize the effectiveness of the alkaline flooding. The shortcoming of this proposal is that, the water-soluble precipitation inhibitors will provide a reduced protection against the precipitation of the divalent metal cations with time.

Barger and Lee [33] disclosed a new type of organic alkali that replaces and improves the performance of traditional inorganic alkalis commonly used in the industry. The new organic alkali was evaluated in ASP formulations containing commonly used surfactant and polymer and compared to that conventional inorganic alkali. The organic alkali was found to be compatible with brines containing high divalent cations concentration without any precipitations. For surfactant adsorption, the results indicate that the adsorption rate for surfactant using organic alkali is the same as that obtained using inorganic alkali. However, the cost of this type of organic alkali is high compared to the conventional alkali such as sodium hydroxide or sodium carbonate.

### 2.6.3 Surfactant Adsorption

Research on surfactant adsorption is of interest in EOR because it relates to the efficiency of surfactant in displacing residual oil. Too much loss of surfactant on reservoir rocks would quickly diminish the life of a surfactant in the displacement process. It has been shown that the nature of the adsorption isotherm depends to a large extent on the type of surfactant used, the morphological and mineralogical characteristics of the rock, the type of electrolytes present in the solution, and the nature of the forces of the interaction between the surfactant species and the solid surface [119].

The most important cause of ionic surfactants adsorbing onto a solid is often the electrical interaction between the charged solid surface and surfactant ions, which can be explained by electrical double layer theory [61]. The forces of adsorption due to electrostatic attraction or repulsion between a charged solid surface and the charged surfactant can play a governing role in the system with oppositely charged solid and surfactant. The occurrence of surface charge on the mineral particles is considered to be due either to preferential dissolution or hydrolysis of surface species followed by pH dependent dissociation of surface hydroxyl groups [120].

The amount of adsorbed surfactant depends on the surfactant character, the rock properties, pH, potential determining ion in solution and salinity [120]. The pH may alter the surface charge to change the adsorption amount and the salinity may change the electrical potential of surface sites for the adsorption [120]. For example, a change in the pH of the aqueous phase usually indicates changes in the adsorption of ionic surfactants on charged solid surfaces. The sand surface will be positively charged under a low pH conditions and negatively charged under high pH conditions. Adsorption of anionic surfactant on sandstone would decrease with an increase of pH because the increasing OH- makes the sand surface more negative and electrostatic repulsive force will drive more anionic surfactants to solution [120].

It is well known that surfactant adsorption increases with the increase of surfactant concentration in solution until surfactant concentration reaches a certain level. After that concentration level is reached, surfactant adsorption will no longer change with surfactant concentration. Austad et al. [121] showed that the surfactant adsorption would remain constant after the surfactant concentration reached a critical micelle concentration. The surfactant, especially for a multi-component surfactant mixture, often contains a second or even a third layer of molecular adsorption on a solid surface. This will increase the adsorption to a greater degree than that required for the formation of a monolayer [121].

Berea core is one of most commonly used sandstone cores used in lab investigation of the effect of minerals on surfactant adsorption. Berea sandstone is composed of quartz, kaolinite, illite, and other minerals [119]. Trogus et al. [122] conducted adsorption experiments on Berea cores using nonionic surfactants and anionic surfactants for static and dynamic systems. They reported increased level of adsorption with increasing chain length of anionic surfactants and the opposite was true for nonionic surfactants. Ziegler [123] investigated the temperature effects on adsorption for nonionic surfactants onto Berea sandstone under static and dynamic conditions. They found that at low concentrations, the adsorption of nonionic surfactant decreased with increase in temperature, whereas the opposite was true for high concentrations. On the other hand Hanna and Somasundaran [124] have found increased adsorption with increase in temperature for Mahogany sulfonate/Berea sandstone system.

Glover et a1. [125] observed severe retention of surfactants in a system containing considerable amount of divalent ions, most probably due to the precipitation of surfactants. Celik et al. [126] also pointed out that while monovalent cations caused the precipitation of sulfonates upon increasing the sulfonate concentration, the multivalent cations exhibited redissolution of the precipitates upon further increase of sulfonate concentration. Lawson et al. [127] observed that multivalent cations increased the adsorption of anionic surfactant, whereas salts of larger anions reduced the adsorption of anionic surfactant.

Fernandez et al. [128] studied the effect of alcohol on surfactant adsorption. They reported that adding small quantities of alcohol appeared to decrease adsorption. Their experiments showed that the heavier alcohols were somewhat more effective in reducing the adsorption plateau. Gilliland and Conley [55] reported in their study that retention (adsorption + physical entrapment) of sulfonate, on Berea sandstone core, would increase linearly with salinity. They reported decreased sulfonate retention in sandstone core with increase in alcohol to sulfonate ratio. Their results showed that the presence of crude oil in the core would decrease the sulfonate retention. The decrease in adsorption of sulfonate with increasing salinity of the system was also reported by Celik et al. [126].

Adsorption of surfactants in the presence of crude oil is different from that in the absence of crude oil. The literature contains many conflicting reports on the effect of reservoir parameter on surfactant loss in the presence of crude oil. These conflicting results exist due to a lack of understanding of phase behaviour of the system studied. Malmberg and Smith [129] reported that smaller slug and residual oil decrease the adsorption.

Glover et al. [125] studied the retention behaviour of lower, middle and upper phase microemulsions on Berea sandstone core bearing residual oil. Their results indicated highest retention from upper phase microemulsion and lowest retention from lower phase microemulsion. They found that a linear relationship of retention increase with salinity exists at lower salt concentration. The onset of phase trapping with small-bank microemulsion-flooding occurred at higher brine concentration. They attributed the linear trend to adsorption and retention levels in excess of this trend to phase trapping [125].

Mayers and Salter [130] conducted static adsorption experiments on crushed Berea in which the active surfactant concentration and surfactant/alcohol ratio was kept constant and brine/oil mass ratio was varied. Surfactant adsorption was found to be independent of the structural and compositional differences between the micellar fluids injected. The rate of adsorption of surfactant was found to increase with decreasing brine/oil ratio. Surfactant retention for dynamic system using middle phase microemulsion was found to be independent of brine/oil mass ratio, and phase trapping was not the dominant mechanism for surfactant retention in a divalent-ion-free system [130].

## 2.7 Injection Strategy and Field Performance

Alkali-surfactant-polymer (ASP) flooding is more appealing and favorable compared to conventional EOR methods. ASP flooding has been evaluated in the laboratory and used widely in the field with great success. Adding a synthetic surfactant to alkali solution has been proven to be an effective countermeasure to both alkali loss and low acid content of oil, while co-injection of polymer with alkali or alkali/surfactant slugs significantly improves oil recovery.

Hawkins et al. [131] studied the effect of slug composition on oil recovery response. They concluded that simultaneous injection of alkali and polymer is more effective than the same chemicals injected sequentially with no contact between the alkali and polymer. They also indicated that the synergism of alkali and polymer (AP) results from a combination of improved sweep and mobilization of residual oil due to reduced interfacial tension. Improved recovery by combined ASP slugs was explained by the same mechanisms as AP slugs. Adding surfactant to AP slugs further reduces interfacial tension, and achieves significantly higher recovery than AP slugs [131].

French [132] conducted several coreflood tests to investigate the best injection strategies for field application. It is shown that the highest recovery was accomplished when the alkali and surfactant was followed by polymer. However, a slight decrease was observed when the alkali-surfactant-polymer was simultaneously injected as a single slug, but oil production occurred faster. His experiments also showed that although polymer alone does not mobilize much residual oil after waterflooding, injection of small slugs of alkali and surfactant during an ongoing polymer-flood improves oil recovery significantly. It was also shown that the alkaline preflush before the main slug increased oil production in all cases, but the effect was most pronounced when the cores were saturated with brine that contained divalent ions [132].

When a polymer is used in an alkali-surfactant flooding, it can also provide the mobility control at the low IFT front. Otherwise, the front is not stable and will finger and dissipate. Meyers et al. [133] reported an ASP flood in the West Kiehl Minnelusa Unit, where co-injection of alkali, low surfactant concentration, and polymer was applied as 0.8% sodium bicarbonate, 0.1% Petrostep B-100, 0.105% Pusher 700 respectively. The estimated recovery of ASP flooding was 20.7 % OOIP over waterflood recovery.

Vargo et al. [134] presented the field performance for ASP flooding in Cambridge Field, USA. The laboratory formulated slug was injected immediately after primary production which consisted of 1.25% sodium carbonate, 0.1% active Petrostep B-100, and 1450 mg/L Alcoflood 1275A. The ASP injection sequence was 30.7% PV of alkali-surfactant-polymer solution followed by 25% PV of polymer drive solution followed by water. A 25 micron filter was used to filter the ASP slug before injection. Estimated ultimate incremental oil production from the swept area was 26.8% OOIP [134].

Clara et al. [22] evaluated the potential application of ASP flooding process for an offshore application in the La Salina Field, Venezuela. The feasibility of applying the ASP technology was based on a series of experiments including fluid compatibility, chemical thermal stability, interfacial tension between crude oil and ASP solution, and physical simulation using reservoir core samples. The injection sequence was 0.3PV of ASP slug followed by 0.3PV of polymer solution and followed by at least 5PV of chase water. In this study, softened lake water was used for both ASP slug preparation and the chase water. The coreflood results indicate that oil cut responded significantly due to ASP injection. Average oil recovery of ASP injection was 24.6% OOIP. Average oil recovery from the EOR process (water + ASP) was 70.2% OOIP [22].

Pratap and Gauma [21] presented the performance of ASP flooding in Viraj oil field, India. The fluid injection sequence during the pilot was preflush, 20%PV of ASP slug, 30% PV of mobility buffer, and 60% PV of chase water. The optimized ASP slug consisted of 1.5% sodium carbonate, 0.2% surfactant, and 800 ppm polymer. The mobility buffer consisted of a series of different polymer solutions. The first slug was 10% PV of 600 ppm polymer which is followed by 10% PV of 400 ppm and 200 ppm concentrations each. All the chemical solutions were passed through a sand filter and then through micron filter to remove the undissolved particles. The results of laboratory displacement studies and performance prediction indicated that ASP flood in Viraj field could produce incremental oil in the range of 18-24% OOIP over waterflooding [21].

Al-Hashim et al. [107] conducted a systematic study to test the applicability of ASP processes as an enhanced oil recovery method to Saudi Arabian carbonate reservoirs. Compatibility tests showed that the ASP slug has to be prepared by softened brine and protected by pre- and afterflush softening brine slugs. Using reservoir core sample, 60% PV of the formulated ASP slug was proceeded and followed by 30% PV of softened water followed by formation water as chase water. The coreflood result showed that 39.5% OOIP was recovered over waterflooding and 18.2% OOIP was recovered after injecting the ASP slug followed by 5.66 PV chase water [107]. Ibrahim et al. [12] conducted different injection schemes and strategies to determine the optimum ASP flooding process for Angsi field, Malaysian. Based on the fluid-fluid compatibility tests, the nanofiltered seawater was softened to keep the solution clear. The core flood results indicated that 13.9% OOIP was recovered when the ASP slug was followed by chase water, while 28.8% OOIP was produced when a higher concentrations of ASP slug was protected by pre- and afterflush slugs [12].

Chang et al. [24] reported two ASP pilot tests conducted in China. In the western part of Gudao reservoir, the injection process was conducted in a three slugs system consisted of 0.1 PV polymer preflush, 0.3 PV ASP slug and 0.05 PV polymer drive followed by chase water. As a result, the oil rate increased from 360 to 1490 barrel per day, and with a corresponding to watercut reduction from 96 to 83%. The total oil recovery was 15.5% OOIP. In Karamay field, the ASP scheme was designed as a 0.4

PV water preflush, 0.34 PV ASP slug, and 0.15 PV polymer drive followed with continued waterdrive. The recovery incremental was 25% OOIP [24].

Recently, few large scale successes with these processes have been reported in china. Daqing oil field in China is one of the earliest and successful fields to apply ASP on a field scale application. Based on enormous laboratory experimental studies, three ASP pilot tests were conducted in western part of central Saertu, central part of Xing 5 area utilizing small well spacing pilot at Daqing oil field. The pilot tests showed that the oil recoveries were increased by 21.4% OOIP, 25% OOIP, and 23.24% OOIP using ASP flooding over water flooding. As a result of the successes of these tests, two extended ASP flooding tests were conducted in West Xing 2 area and West part of North 1 zone, and the oil recoveries were 19.6% OOIP and 21.04% OOIP respectively [23], [25], [135], [136], [137].

Hui and Qinglong [25] provided a review of a recent development of pilot tests conducted in Daqing field. A summary of these tests is given in Table 2.2. Performance of ASP pilot tests showed a pronounced response due to chemical injection. As shown in Table 2, using different injection strategies and schemes, oil recovery can be further increased. The ASP flooding in Daqing field recovered more than 20% OOIP additional oil beyond waterflooding recovery.

**Table 2.2:** Design and performance of ASP processes in Daqing field [25]

| Slug name | | | ASP 1 | ASP 2 | ASP 3 | ASP 4 | ASP 5 |
|---|---|---|---|---|---|---|---|
| Polymer preflush | PV injected | | - | - | - | 0.376 | - |
| | Concentration | | - | - | - | 1500 ppm | - |
| Primary ASP slug | PV injected | | 0.32 | 0.37 | 0.33 | 0.351 | 0.30 |
| | Formulation | | A: 1.25% | A: 1.2% | A: 1.2% | A: 1.2% | A: 1.2% |
| | | | S:0.3% | S:0.3% | S:0.15+0.2% | S:0.3% | S:0.1% |
| | | | P:1200ppm | P:1200ppm | P:1800ppm | P:2300ppm | P:1400ppm |
| Secondary ASP slug | PV injected | | - | - | 0.158 | 0.1 | |
| | Formulation | | - | - | A: 1.2% | A: 1.2% | A: 1.2% |
| | | | - | - | S:0.11% | S:0.11% | S:0.11% |
| | | | - | - | P:1800ppm | P:1800ppm | P:1800ppm |
| Protective polymer slug | 1 | PV | 0.28 | 0.183 | 0.253 | 0.05 | 0.05 |
| | | concentration | 600 ppm | 1200ppm | 800 ppm | 1000 ppm | 900 ppm |
| | 2 | PV | - | 0.094 | - | 0.1 | 0.05 |
| | | concentration | - | 800 ppm | - | 700 ppm | 700 ppm |
| | 3 | PV | - | 0.031 | - | 0.05 | 0.1 |
| | | concentration | - | 400 ppm | - | 500 ppm | 600 ppm |
| Successive waterflood | | | Flood until watercut reached 98% | | | | |
| Recovery, % OOIP | | | 21.4% | 25% | 23.24% | 19.4% | 20.63% |

## 2.8 Summary

In Malaysia and many other countries, a significant amount of crude oil is suspected to remain in the ground after conventional recovery processes. In Malaysian producing fields, an average of 63% of the discovered recourses would not be produced with the use of current production strategies. This made EOR methods attractive techniques for the unrecovered oil. Of the various EOR methods that have been researched and applied, chemical flooding showed a promising performance to recover the residual oil after conventional methods.

The main factor which can be manipulated for chemical EOR is the cost and the availability of surfactant. Recently, many new surfactants were produced using various raw materials to satisfy different EOR requirements. The goal of the recent research was mainly to develop new surfactants that can recover additional oil in a cost-effective manner using vegetable oils as a surfactant raw material. Fatty acid methyl esters and fatty alcohols are the most important raw materials because of their biodegradability as well as availability from renewable resources.

Alkali-surfactant-polymer (ASP) is considered to be the most promising and cost-effective chemical method in recent years. In the ASP process, alkali is used to make an in-situ surfactant with acidic components of the crude oil and increases the pH to lower surfactant adsorption. Surfactants are used to decrease the IFT between oil and water while polymer is used to improve the sweep efficiency by providing mobility control.

The success of ASP process is highly depending on the way that they are combined to produce compatible and effective slug with reservoir fluids. It was reported that the injection water quality has a significant effect in ASP performance. Several mechanisms have been proposed for this technique, but they are still not well understood. In most cases, softened water must be used to avoid the calcium and magnesium precipitation problems. It was also found that the key issue for the ASP flooding is the IFT reduction at low surfactant concentration. With the addition of a small amount of surfactant to the alkali-solution, the IFT become lower than with either surfactant or alkali alone. Adding polymer to the surfactant and alkali, further improves the sweep efficiency, and achieves significantly higher recovery than surfactant and alkali.

# CHAPTER 3

# MATERIALS AND METHODOLOGY

In order to achieve the objectives mentioned in the first Chapter, the research methodology was carried out in two main parts. The purpose of the first part was to develop new surfactants based on Jatropha oil. Five types of polymeric methyl ester sulfonate were produced based on sodium methyl ester sulfonate. In the second part, the selected synthesized polymeric surfactant was introduced to develop a new Acid-Alkali- Polymeric Surfactant (AAPS) flooding formulation. This formulation is aimed at developing an enhanced oil recovery process for Malaysian oil reservoirs by mitigating the undesired effects of divalent metal cations. A comprehensive approach was conducted to test the applicability of the new AAPS flooding design with the new synthesized surfactant as an enhanced oil recovery method.

## 3.1 Materials

### 3.1.1 Jatropha oil

In the first part of this study, non-edible Jatropha oil was used as a starting raw material to produce different types of surfactants for EOR application. Crude Jatropha oil was purchased from a local oil industry (Bionas) in Kuala Lumpur, Malaysia, and used as received. The Jatropha oil properties obtained from the same company are given in Table 3.1. Jatropha oil was selected because it is a non-edible oil so it will not compete with food supply. In addition, it is not a petroleum derivative. Finally, it is a drought resistant perennial tree that grows in marginal lands and can live over 50 years. Under these conditions, it is expected that the supply ability and availability of Jatropha oil will not be a major concern.

**Table 3.1:** Jatropha oil properties (obtained from oil supplier)

| | |
|---|---|
| Density, g/cm$^3$ | 0.92 |
| Flash point, C$^o$ | 236 |
| Cloud point, C$^o$ | 8 |
| Iodine value | 95-107 |
| Acid value (mgKOH/g) | 0.92-10 |
| Sulfur content, ppm | 0.13 |
| Phosphate content ppm | 290 |

### 3.1.2 Crude oil

Throughout this study, Angsi crude oil (I-68) was used as an oil medium. This crude was obtained from Angsi field which is located in the offshore Malay Basin, Malaysia. General characteristics of Angsi crude are presented in Table 3.2. Angsi crude with an acid number of 0.478 mgKOH/g was selected as a good candidate for the AAPS process because of its low wax content and low viscosity.

**Table 3.2:** Angsi crude oil and reservoir properties [138]

| | |
|---|---|
| Carbonate content | 110 ppm |
| API gravity | 40.1 |
| Wax content | 14.1% |
| Asphaltenes | 0.5% |
| Oil viscosity @ reservoir condition | 0.3 cp |
| Oil density @ ambient temperature | 0.827gm/cm$^3$ |
| Reservoir temperature | 119 $^o$C |
| Reservoir pressure | 2199 psi |
| Reservoir lithology | Sandstone |
| Average porosity | 22% |
| Permeability | 200 md |
| Formation water salinity | 10000 ppm |

### 3.1.3 Chemicals

All chemicals used in this study were purchased from different trade companies and used as received. A full list of chemicals and details are listed in Appendix A.

## 3.2 Experiments-Part I

The purpose of this part was to develop new surfactants for enhanced oil recovery application. Several experiments have been conducted to synthesis different surfactants based on fatty acid methyl ester derived from Jatropha oil. The experiments started from the production of methyl ester to surfactant synthesis and characterizations. Figure 3.1 shows the production processes used in this part.

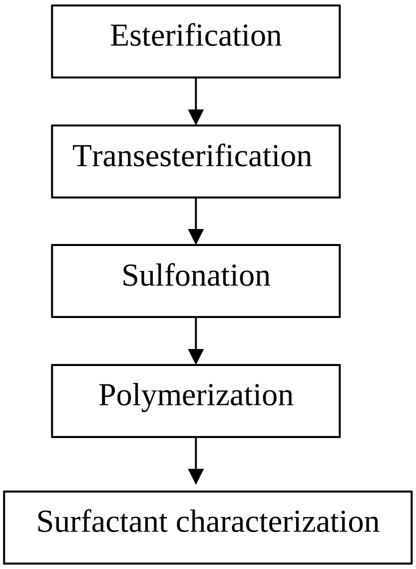


**Figure 3.1:** Flow chart of surfactant production processes

### 3.2.1 Fatty Acid Methyl Ester Production

Fatty acid methyl ester is a renewable and environmentally friendly energy source. The most commonly used technique to produce methyl esters involve transesterification reaction in which triglycerides are reacted with methanol in the presence of a catalyst to produce mono alkyl esters. However, this process is greatly affected by the free fatty acid (FFA) content of the raw material. The presence of high FFA (i.e. high acid value) in the raw material results in soap formation that could decrease the methyl ester yield and complicate the separation and purification of product [139]. This problem can be avoided by pre-treating the oil with an acid catalyst esterification to convert the FFAs into esters before the alkali catalyst is used. Hence, fatty acid methyl ester was produced via a two-step transesterification as described below:

- *First step: Acid-catalysed esterification*

The main purpose of acid-catalyzed esterification was to reduce the acid value of Jatropha oil. This oil had an initial acid value of 10.54 mg KOH/ g-oil corresponding to a free fatty acid (FFA) of 3.75%. Therefore, the effect of different methanol to oil volume ratios of 0.17, 0.25, and 0.30 on the reduction of acid value was studied using 1.14% v/w sulfuric acid as a catalyst. In this step, the reaction was carried out at $60^o$ C for 120 minutes using 250 ml round bottom flask. After the reaction, the mixture was allowed to settle for three hours and the methanol – water fraction at the top was removed by a separating funnel. The effectiveness of this step was evaluated by determining the acid value of the product separated at the bottom using American Oil Chemists' Society method [140]. The product having an acid value of less than 1 mg KOH/g was subsequently used for the main transesterification reaction in the next step.

- *Second step: Alkaline-catalysed transesterification*

The transesterification reaction was conducted to produce the methyl esters from the treated Jatropha oil. Different methanol to oil ratios with a constant potassium hydroxide (KOH) to oil ratio (0.5%w/w) were used to determine the optimum condition. The methanol to oil volume ratios used in this reaction were 0.16, 0.22, and 0.26. The reaction was carried out at $60^o$ C for 35 minutes. Similar methanol to oil ratios and KOH were also applied by Tiwari et al. [140] during methyl esters production from Jatropha oil.

In this step, the reaction was carried out using 250 ml round bottom flask. At the end of the reaction, the product was allowed to settle overnight before removing the glycerol layer from the bottom in a separating funnel to recover the ester layer on the top. The top layer was washed with water to remove residual KOH and methanol. Then the washed esters were heated at $105^o$ C for 10 min to remove residual water. The final product was then analyzed by gas chromatography-mass spectrometry (GC-MS) to determine the fatty acid methyl ester composition. Once the optimum methanol to oil ratio was determined, additional runs were done to collect the needed amount. The experimental setup used in this step is shown in Figure 3.2.

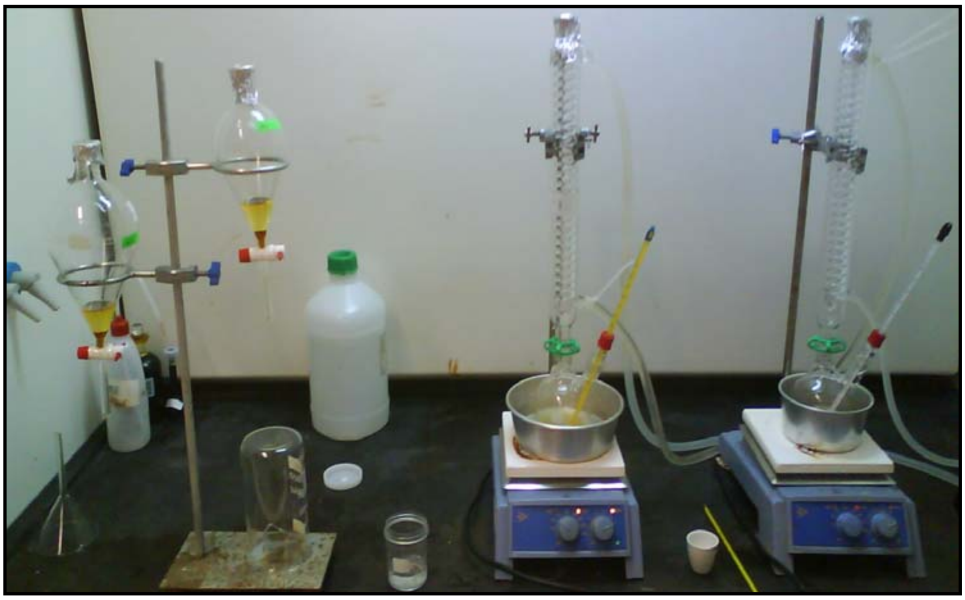


**Figure 3.2:** Experimental setup for transesterification process

### 3.2.2 Sulfonation Process

The sulfonation method used in this study was according to Chonlin et al. [142] but without purification process. The purpose of the sulfonation process was to synthesis sodium methyl ester sulfonate (SMES) based on fatty acid methyl ester as feedstocks. The sulfonation reaction was carried out in a laboratory scale using 250 ml round bottom flask (Figure 3.3).

In a typical run, chlorosulfonic acid (10.5 g) was added very slowly and with stirring to pyridine solution (45 ml) in an ice cooled 250 ml round bottom flask. A solution of fatty acid methyl ester (7.76 g) in 45 ml pyridine was introduced gradually to the above mixture over 30 minutes. The reactor and contents were subsequently warmed in a steam bath until the solution became clear. The reaction was quenched and the product converted to the sodium salt by pouring the contents into an ice-cooled aqueous sodium carbonate solution (90 g in 300 ml water) and sufficient solid sodium bicarbonate to keep the solution saturated with inorganic sodium salts. The product was extracted twice using n-butanol (40 ml each) in a separating funnel. Solvent was removed from the crude product using a rotary evaporator and the product redissolved in water. Organic impurities were removed from the aqueous solution of methyl ester sulfonate by extraction with ether. The crude product was then concentrated, isolated, and dried under vacuum for 24 hours for further characterization. The sodium methyl ester sulfonate (SMES) was used in subsequent reaction involving grafting and polymerization of SMES.

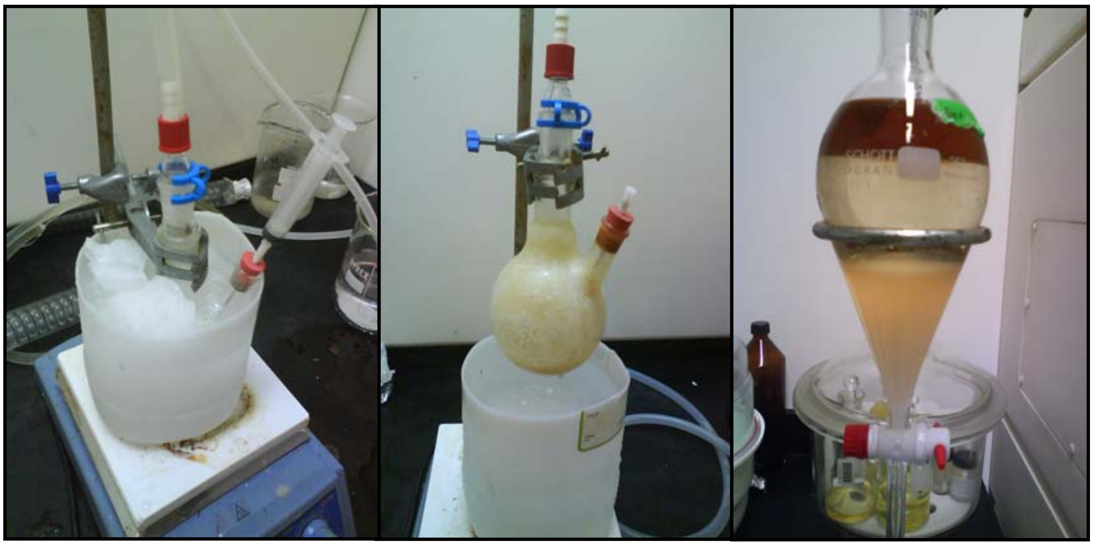


**Figure 3.3:** Experimental setup for the sulfonation process

### 3.2.3 Polymerization Process

A single step route similar to Ye et al. [143] was used to produce polymeric methyl ester sulfonate (PMES) via polymerization process. The purpose of this process is to attach the sulfonate group of SMES to the polymer backbone (polyacrylamide) as a one component system for ITF reduction and viscosity control. For this purpose, different surfactant (SMES) to acrylamide weight ratios were used in the polymerization reaction.

The polymerization process was conducted using a 250 ml-three necked flask (Figure 3.4). In a typical run, the polymerization was conducted using the methyl ester sulfonate (SMES) as surfactant and potassium persulfate as an initiator. The initiator solution was prepared by dissolving 0.123 g in 10 ml deionized water and the pH was adjusted to 9-10 with sodium hydroxide. The surfactant solution was prepared by dissolving appropriate amount of SMES in 100 ml deionized water. An appropriate amount of acrylamide monomer was dissolved in 70 ml deionized water and purged with nitrogen to remove residual oxygen. Afterward, the surfactant solution was added to the acrylamide solution and stirred under nitrogen until a clear solution was observed. The solution was then heated to 60 $^{o}$C, and the initiator was added. The polymerization reaction was conducted at 60 $^{o}$C for 1.5 hours using auto shaker water bath. The crude product was then extracted with acetone and dried in an oven for 12 hours.

The experiment showed above was conducted for the production of several polymeric methyl ester sulfonates using different SMES to acrylamide weight ratios. Table 3.3 summarizes the total runs conducted for these experiments, and Figure 3.4 shows the experimental setup and the final product after the polymerization process.

**Table 3.3:** Experiment details for polymerization reaction

| Experiment No. | Surfactant to acrylamide ratio | Polymeric surfactant name |
|---|---|---|
| 1 | 1:0.50 | SURF 1 |
| 2 | 1:0.60 | SURF 2 |
| 3 | 1:0.80 | SURF 3 |
| 4 | 1:1.16 | SURF 4 |
| 5 | 1:1.33 | SURF 5 |

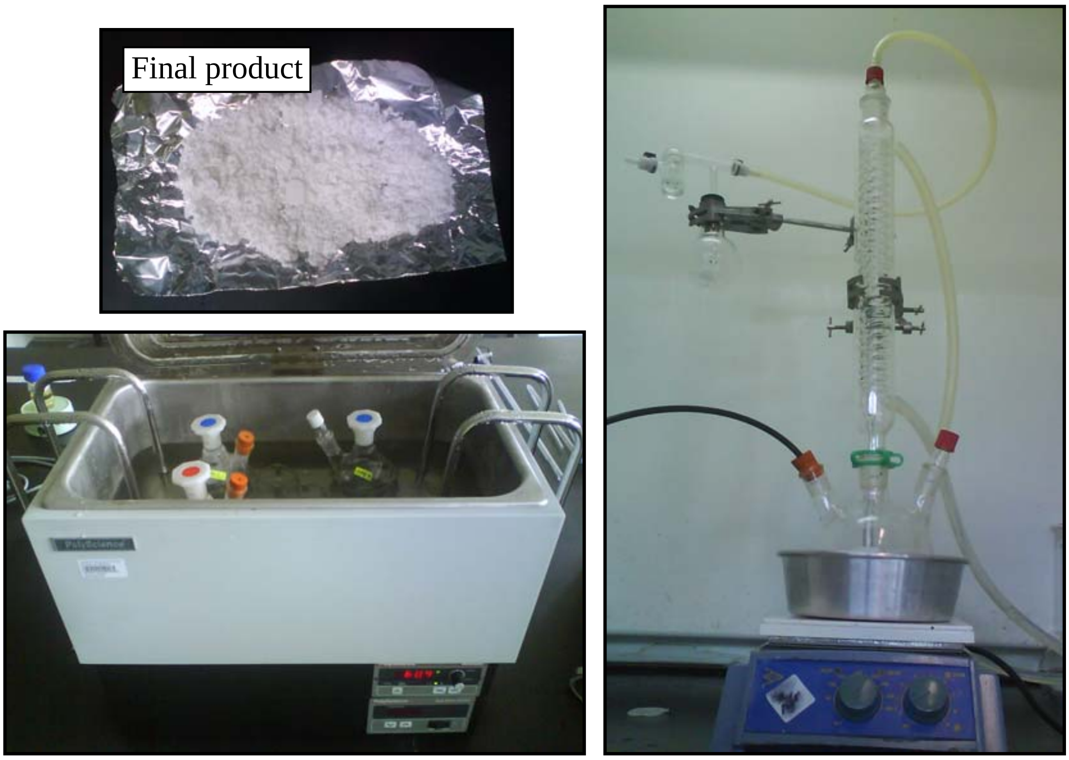


**Figure 3.4:** Experimental setup and the final product after polymerization process

## 3.3 Surfactant Characterization

### 3.3.1 Fourier Transform Infra-Red (FTIR)

FTIR spectrophotometer was used to determine the chemical functional groups present in the surfactant. Different functional groups are susceptible to absorb characteristic frequencies of IR radiation. FTIR spectra of sodium methyl ester sulfonate and polymeric methyl ester sulfonates were recorded by preparing the transmission KBr disk of the relevant sample. Approximately, 0.5 gram of the respective sample was mixed with 1.5 gram of analytical reagent grade KBr. A small quantity of the resulting mixture was pressed under pressure to form a thin KBr disc that was then scanned on the FTIR apparatus.

### 3.3.2 Thermal Stability Test

The thermal stability of each sample of the produced surfactants was measured using Perkin Elmer TGA7 bench model thermogravimeter analyzer (TGA) (Figure 3.5). The TGA determines changes of weight loss of a substance against temperature. For each run, about 10 mg of sample was placed in a platinum crucible inside a temperature programmable furnace and held for 1 minute at 30 $^{o}$C with continuous purging using nitrogen. Then, the TGA was conducted for temperature range from 30 $^{o}$C to 500 $^{o}$C with increments of 30 $^{o}$C/min.

**Figure 3.5**: Perkin Elmer TGA7 bench model thermogravimeter analyzer

### 3.3.3 Interfacial Tension Test

Interfacial tension (IFT) between Angsi crude oil and various surfactant solutions were measured by spinning drop method. Model SVT 20 spinning drop tensiometer equipped with video camera was used to determine the surface activity at ambient temperature. For each sample, the fluids whose IFT was to be measured were introduced into a capillary tube. The tube was first filled with the denser fluid and then closed with teflon cap having a rubber septum. Then, a drop of the less dense fluid (oil) was injected into the tube through the rubber septum using a syringe.

The tube-cap assembly was inserted into the tensiometer slot and screwed firmly in place. Appropriate rotation speed was then adjusted so that the oil droplet can be suitably elongated. Lastly, the IFT between the two fluids were calculated with a built-in software system according to the following equation:

$$\sigma = 3.42694 * 10^{-7} (\rho^h - \rho^d)\omega^2 D^3 \tag{3.1}$$

Where, $\sigma$ is interfacial tension (dyne/cm), $\rho^h$ the density of dense (outer) phase (g/cm$^3$), $\rho^d$ the density of the light (drop) phase (g/cm$^3$), $\omega$ the rotational velocity (rpm), and D the measured drop diameter (mm). Prior to the IFT measurements, densities and refractive indices of both of the phases should be known. The densities of the two fluids were measured using density meter model DMA 35N. All the measurements were conducted at room temperature.

### 3.3.4 Refractive Index Measurement

The refractive index for each sample was measured by a digital refractometer model ATAGO RX-5000. All the measurements were conducted at ambient temperature. Before starting the measurement, the glass surface was cleaned with distilled water and dried with tissue paper. A drop of sample was then introduced into the glass surface and the glass prism was placed over it. After a while, digital display was used to obtain the value of the refractive index for that sample.

### 3.3.5 Kinematic Viscosity Test

The kinematic viscosity of various solutions was measured according to ASTM D 445. Tamson viscometer model TVB445 was used to measure the viscosity at test temperature (Figure 3.6). In this method, the viscosity was measured as a function of time for a fixed volume of liquid to flow under gravity through a calibrated capillary tube. For a typical run, the calibrated capillary tube was filled with a sample and allowed to remain 15 minutes in the kinematic viscosity bath to reach the test temperature. The head level of the test sample was adjusted by using a suction to a position in the capillary arm of the instrument above the first timing mark. The time required for the sample to pass from the first to a lower second timing mark was measured in seconds. The viscosity of the sample was then calculated by multiplying the measured time by the viscometer constant.

**Figure 3.6:** Tamson viscometer model TVB445

### 3.4 Experiments-Part II

In this study, two chemical flooding formulations were developed for seawater and softened water. The first formula consists of acid-alkali-polymeric surfactant (AAPS) and second formula consists of alkali and polymeric surfactant (APS). The AAPS formula was aimed to overcome the precipitation problems when seawater was used to prepare the chemical slug. The second formula (APS) was developed to simulate the conventional ASP flooding and also to examine the performance of the polymeric surfactant with alkali using softened water. Various experiments have been conducted to determine the optimum conditions for each chemicals system. The experiments began with a comprehensive screening study and ended with an optimization process for the new acid-alkali-polymeric surfactant formula and alkali-polymeric surfactant system. Figure 3.7 shows the experiments tasks performed in this part.

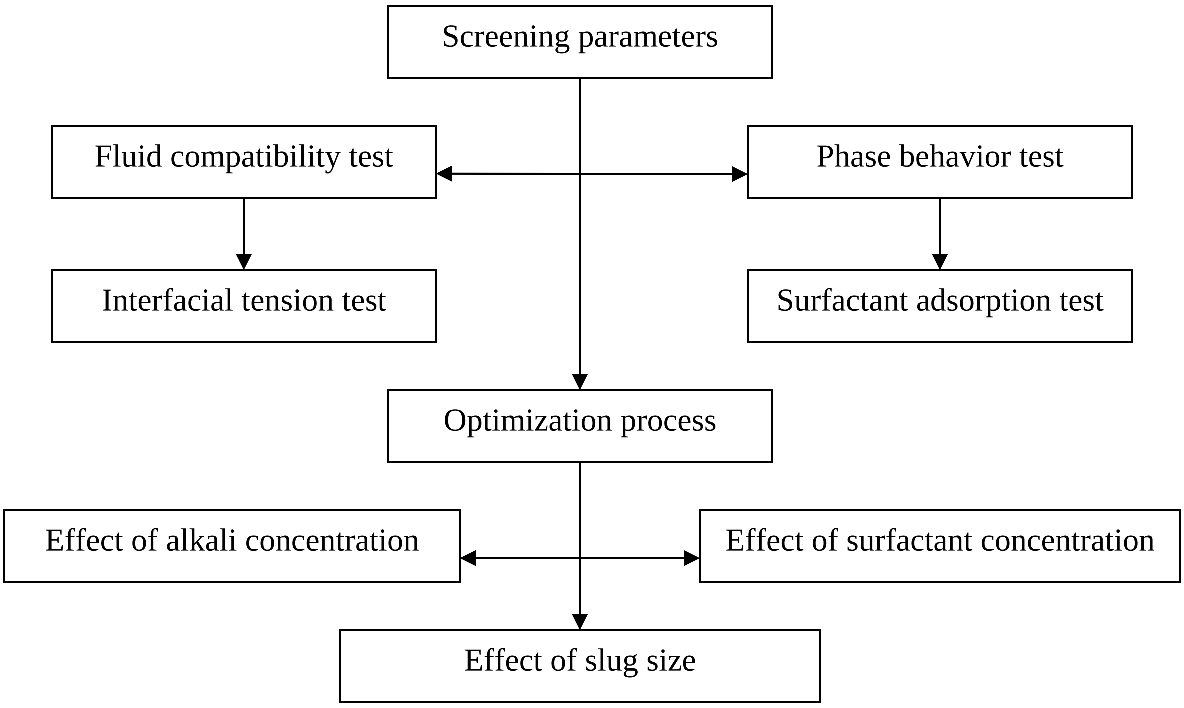


**Figure 3.7:** Flow chart of AAPS and APS design process

### 3.5 Screening Criteria for AAPS and APS Flooding

Before applying enhanced oil recovery to any reservoir, it is essential that a screening protocol is first performed. In this study, a comprehensive approach has been taken to evaluate the feasibility of the new AAPS and APS formulas incorporating the produced polymeric surfactant using sea and softened water for comparison purposes. The approach included fluid-fluid interactions tests, interfacial tension measurements, phase behavior (emulsification) tests and surfactant adsorption tests. The purpose of this approach was to understand the mechanism of the developed formulas and to determine the technical feasibility of each formula using softened water and natural seawater.

## 3.6 Fluid-Fluid Interactions Test

Since one of challenges of this study is to use natural seawater rather than softened water for chemical preparation, much attention has been given to study the effectiveness of acrylic acid on forming in-situ inhibitor to prevent calcium and magnesium precipitations. In order to design an effective AAPS slug that is capable of producing low IFT, and has a favorable mobility ratio, the acid-alkali-polymeric surfactant must be compatible with each other and with the injection water. For this reason, various fluid-fluid compatibility tests were conducted using natural seawater and softened water for comparison purposes. The fluid-fluid interactions involved in this study are as follows:

### 3.6.1 Acid-Alkali Interaction

Because the alkali is greatly affected by the presence of divalent metal cations such as calcium ($Ca^{2+}$) and magnesium ($Mg^{2+}$), two experiments were conducted in this section. The purpose of the first experiment was to study the effect of the metal cations on alkali performance using softened and natural seawater. The second experiment was aimed at investigating the performance of the generated in-situ precipitation inhibitor in preventing $Ca^{2+}$ and $Mg^{2+}$ precipitations over time. Different acid to alkali weight ratios were used to define the optimum ratio. Natural seawater having a large quantity of divalent metal cations was used to prepare the alkali-acid solutions. Three types of alkalis, namely, sodium hydroxide, sodium carbonate, and sodium bicarbonate were screened to define the suitable candidate.

In carrying out this experiment, samples of different acid to alkali weight ratios were prepared. These samples were placed under different temperatures 26°C, 60°C, and 90°C for ninety days. Then, observation was made by visual evaluation for the formation of solids as being indicative of incompatible fluid.

### 3.6.2 Acid-Polymeric Surfactant Interaction

The purpose of this test was to investigate the compatibility of the polymeric surfactant with the inhibitor. As the role of the polymeric surfactant is to provide a good viscosity, so the effect of the in-situ inhibitor on polymeric surfactant viscosity and pH were investigated using natural seawater. Two experiments were conducted in this section. In the first experiment, different samples were prepared using 0.6% acrylic acid concentration and various surfactant concentrations. Then, all the solutions were maintained at 90°C for 62 days, and observation was made over time for any phase separation. In the second experiment, the effect of various acid concentrations on surfactant viscosity was investigated using 0.6% surfactant concentration. Then, the kinematic viscosity of each sample was measured using Tamson viscometer model TVB44 at 90°C.

### 3.6.3 Acid-Alkali-Polymeric Surfactant Interaction

The aim of this test was not only to investigate the compatibility of the combined chemicals with the seawater, but also to study the effect of the added alkali on the generated in-situ inhibitor and on the system viscosity. For this reason, two experiments were also conducted in this section. In the first experiment, different AAPS samples were prepared using the selected surfactant concentration with different concentrations of the selected alkaline candidate. The acid concentration used here was based on the optimum acid to alkali ratio obtained from the first interaction test. Consequently, all the samples were kept at 90 °C for 63 days, and observation was made for any precipitations over 63 days. In the second experiment, other samples were prepared with the same concentrations as in the first experiment for viscosity and pH measurements. The kinematic viscosity of each sample was measured using Tamson viscometer model TVB44 at 90°C, and the pH was measured using OAKTON pH meter at ambient temperature.

## 3.7 Interfacial Tension Measurements

The interfacial tension (IFT) measurements were made between Angsi crude oil and polymeric surfactant-water system, alkali-polymeric surfactant system, acid-polymeric surfactant system, acid-alkali-polymeric surfactant system. The purpose of these measurements was to investigate the effect of the acid or the inhibitor on the IFT performance and to determine the optimum alkali concentration for softened and seawater. Therefore, the selected polymeric surfactant concentrations obtained from the first part with different concentrations of the selected alkali were used in this experiment. The optimum acid to alkali ratio was utilized to keep the solutions clear when seawater was used to prepare the solutions. All the measurements were conducted at ambient temperature using the spinning drop method outlined in section 3.3.3.

## 3.8 Phase Behavior Test (Spontaneous Emulsification)

In order to confirm which system has the potential to reduce IFT to an ultralow level, emulsification tests between alkali-polymeric surfactant/crude oil system and acid-alkali-polymeric surfactant/crude oil system were conducted. Different alkali concentrations were used to study the effect of alkali and the generated in-situ inhibitor on the emulsification behavior. These tests were carried out in test tubes at a fixed oil phase/water phase ratio using the same chemical concentrations used in the IFT test. The test tubes were then placed in an oven at 90$^{o}$C and mixed by tumbling every week. Evaluation was made by discoloration of the aqueous phase kept over 24 days.

## 3.9 Static Surfactant Adsorption

Static adsorption studies were made in the absence and presence of different alkali concentrations using softened and seawater. The aim of this test was to compare the polymeric surfactant adsorption of a pure polymeric surfactant solution with the adsorption of an alkali-polymeric surfactant solution and acid-alkali-polymeric surfactant solutions. In carrying out this test, a constant weight ratio of polymeric surfactant solution and sand was kept at 1:1. Ground sandstone collected from Lumut beach was used in this experiment.

The static adsorption experiments were performed as the following. Known concentrations of polymeric surfactant and acid-alkali-polymeric surfactant solutions were prepared individually. Calibration curves between polymeric surfactant and acid-alkali-polymeric surfactant concentrations and refractive indices were plotted.

After mixing these samples with the sand, the mixtures were then mixed together using a magnetic stirrer for one hour. Consequently, the samples were placed in an oven at 90 $^{o}$C for five days to establish the adsorption equilibrium. After the equilibrium period, the polymeric surfactant concentration in each sample was determined by the comparing the obtained refractive index values with the initially plotted calibration curves. The polymeric surfactant adsorption for each sample was calculated by the following equation:

$$\Gamma = \frac{M_{tot.solution} * (C^{0} - C)}{M_{sand}} * 10^{-3} \qquad (3.2)$$

Where

$\Gamma$ = polymeric surfactant adsorption on sand, mg/g-sand

M $_{tot.solutio}$ = total mass of solution in original bulk solution, g.

$C^{0}$ = polymeric surfactant concentration in initial solution before being equilibrated with sand, ppm.

C = polymeric surfactant concentration in aqueous solution after being equilibrated with sand, ppm.

M $_{sand}$ = total mass of sand, g.

### 3.10 Optimization Process for AAPS and APS Formulas

The purpose of this process was to assess the effectiveness of the developed flooding formulations for enhanced oil recovery using softened and natural seawater. However, in order to design a cost-effective chemical slug, a series of core flood tests were conducted to identify the optimum chemicals concentration along with a suitable injection strategy. Based on the screened study performed in the previous sections, the best chemicals concentrations were selected as a starting point in the optimization process. This is because the selected concentrations might not be optimum for core flood test. The effects of surfactant concentration, alkali concentration, and slug size on oil recovery performance were investigated using Berea core samples. A total of 15 core flood tests were conducted to determine the optimum conditions for acid-alkali-polymeric surfactant (AAPS) system and alkali-polymeric surfactant (APS) system.

In the optimization process, seven core flood runs were conducted to study the effect of surfactant concentration on oil recovery performance for softened and seawater. In these tests, different surfactant concentrations for each system were employed using the same alkali concentration and slug size. The optimum surfactant concentrations for both cases obtained from this step were then used in the second experiment. In the second experiment, the effect of alkali concentration for both cases was examined using four core samples. The same slug size was used to identify the optimum alkali concentrations. According to the optimum surfactant and alkali concentrations determined from these experiments, another four runs were performed to study the effect of the slug size on recovery performance for each system. On the basis of the above core flood tests, the recovery incremental as a function of surfactant concentration, alkali concentration, and slug size were investigated and the optimum conditions for the AAPS and ASP systems were determined.

### 3.10.1 Experimental Setup and Core Flooding Procedure

All core flood experiments were conducted using relative permeability system (RPS) equipment. The setup used for the core flood tests is depicted as in Figure 3.8. In this study, additional three valves were added to the system to control the flow of the injected chemicals through the tubing line. A schematic diagram of the RPS after adding the valves is shown in Figure 3.9. It consists of a core holder, pumps for fluid injection, two digital pressure gauges to measure the inlet and outlet pressure during the experiment, three accumulators, and nine valves to control the flow. The stainless steel core holder used was 3 inch in diameter and 12 inch in length. Throughout this study, the accumulators A, B, and C were used for chemical slug, brine, and crude oil respectively.

In this study, fifteen core flood tests were conducted to test the performance of the developed chemical formulas. The first formula which consists of acid-alkali-polymeric surfactant was prepared by seawater, while the second formula which consists of alkali-polymeric surfactant was prepared using softened water. A synthetic brine solution similar to Angsi formation water was used to displace the crude oil before and after the chemical flood was initiated. For each run, the injection rate during water flood and oil flood was 2 ml/min, whereas an injection rate of 0.5 ml/min was used during chemical slug injection.

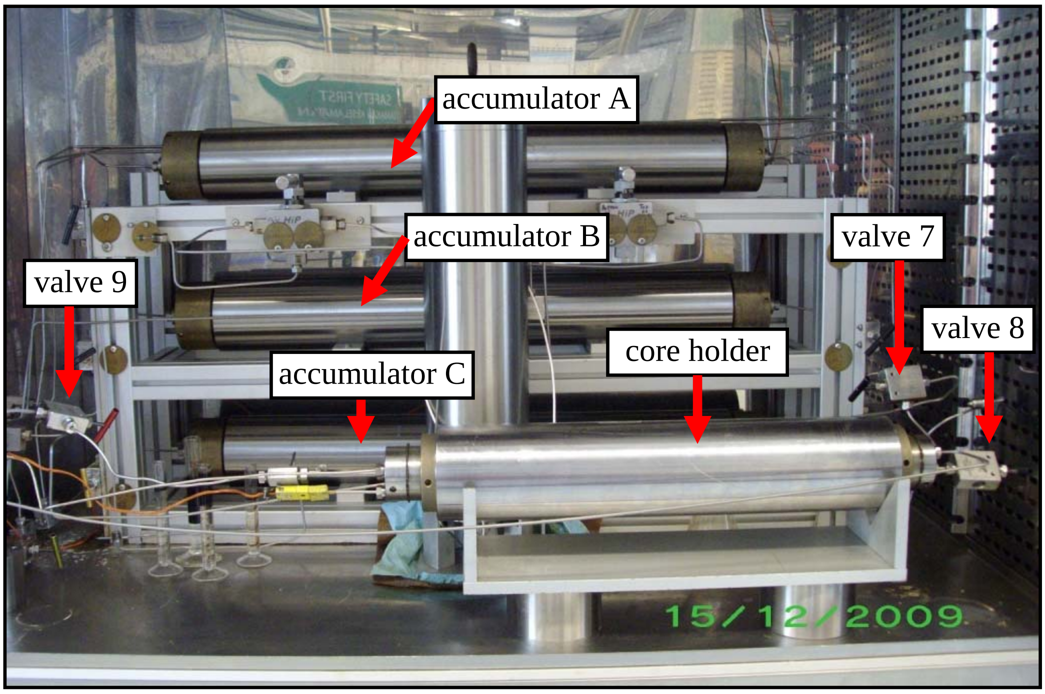


**Figure 3.8:** Relative permeability system used for core flood test

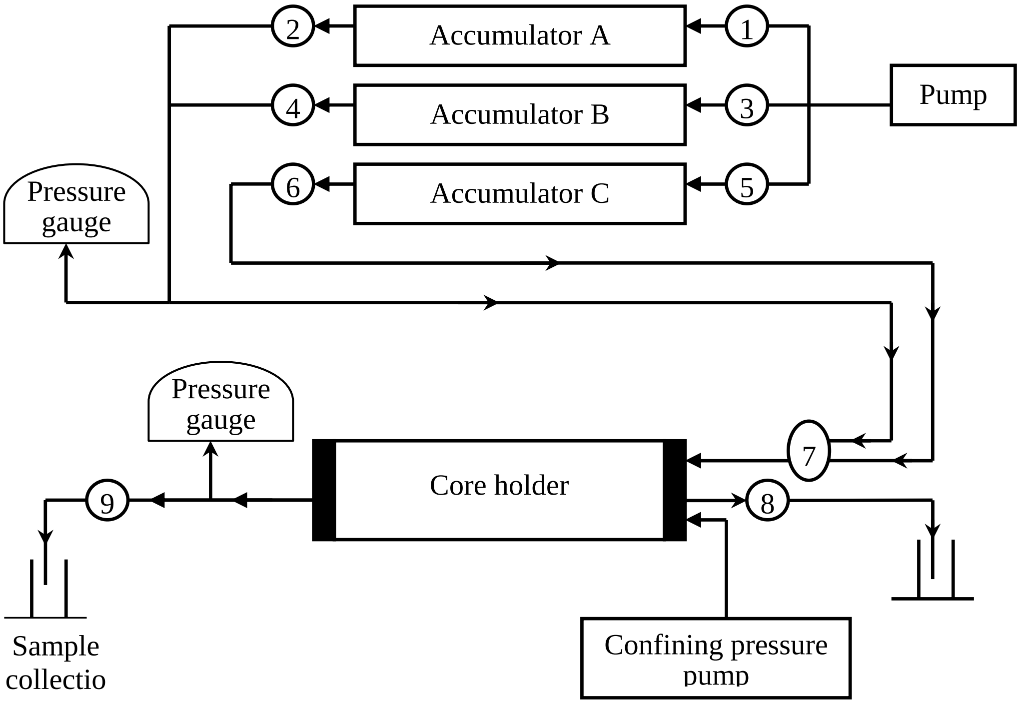


**Figure 3.9:** Schematic diagram of the relative permeability system after adding the valve number 7, 8, and 9

In carrying out these experiments, it was planned to do all the measurements at a temperature of 90 $^{o}$C, but it was difficult to maintain this temperature during the run, and therefore a temperature of 80 $^{o}$C was applied for the tests. The production pressure during the experiments was set at atmospheric pressure. Prior to core flood test, all core samples were saturated with a synthetic brine solution similar to Angsi formation water. For each run, a saturated core sample with known pore volume was placed in the core holder, and a confining pressure of 2000 psi was applied. After this, the core sample was continuously flooded with brine at an injection rate of 2 ml/min to ensure that there is no air in the system.

Following this process, the valves were adjusted and the injection of crude oil was started to displace out the remaining brine in the tubing before the core holder. After cleaning the tubing, the oil injection continued at an injection rate of 2 ml/min until water production ceased. Original oil in place was then calculated based on the total water volume displaced from the core at the outlet. Following the oil injection, same process used during oil injection was used to remove the remaining crude oil in the tubing. The core sample was then waterflooded with synthetic formation brine using the same injection rate. The injection of the brine was continued until the oil production became negligible (oil cut < 1%). Residual oil was then calculated based on the total volume of the produced oil.

After the second waterflooding, the core sample was flooded with chemical slug using an injection rate of 0.5 ml/min. The injection of chemical slug was continued until 0.5 PV was collected at the outlet. Consequently, the core was flushed with an extended waterflooding until the oil production became negligible. Valves 8 and 9 were also used in these stages to displace the undesired fluids. During each run, the effluent was collected using a fraction collector in 5 min increments.

### 3.10.2 Core Samples Preparation

A total of eight Berea core samples with 1.5 inch in diameter and 3 inch in length were used in this study (Figure 3.10). However, due to the availability of the core samples, all the cores were reused again after they were cleaned and aged to restore their original wettability. The cleaning process was performed by extracting all the remaining fluids with Soxhlet extractor using toluene as a solvent (Figure 3.11). In the extraction process, the used core sample was placed in the thimble for 12 hours at 60 $^{o}$C to remove all the remaining fluids. The core sample was then dried in an oven for 24 hours before measuring the porosity and permeability of that sample. After measuring the porosity and permeability, the cleaned and dried core was saturated with a synthetic brine solution similar to Angsi formation water. The synthetic brine properties are given in Table 3.4. Saturation was performed by loading the core sample in a container filled with the synthetic brine under vacuum. Vacuum pump was used for at least 24 hours before conducting the core flood experiment.

**Table 3.4:** Synthetic brine properties

| | |
|---|---|
| Sodium | 3810 ppm |
| Calcium | 30 ppm |
| Magnesium | 25 ppm |
| Potassium | 55 ppm |
| Chloride | 6070 ppm |
| Total salinity | 9990 ppm |

The core properties such as, air permeability, porosity, pore volume were measured by PoroPerm instrument. The PoroPerm is a permeameter and porosimeter used to determine properties of dried core sample using helium gas. All the measurement was based on the unsteady state method (pressure falloff) whereas the pore volume is determined using the Boyle's law technique.

**Figure 3.10:** Berea sandstone core samples

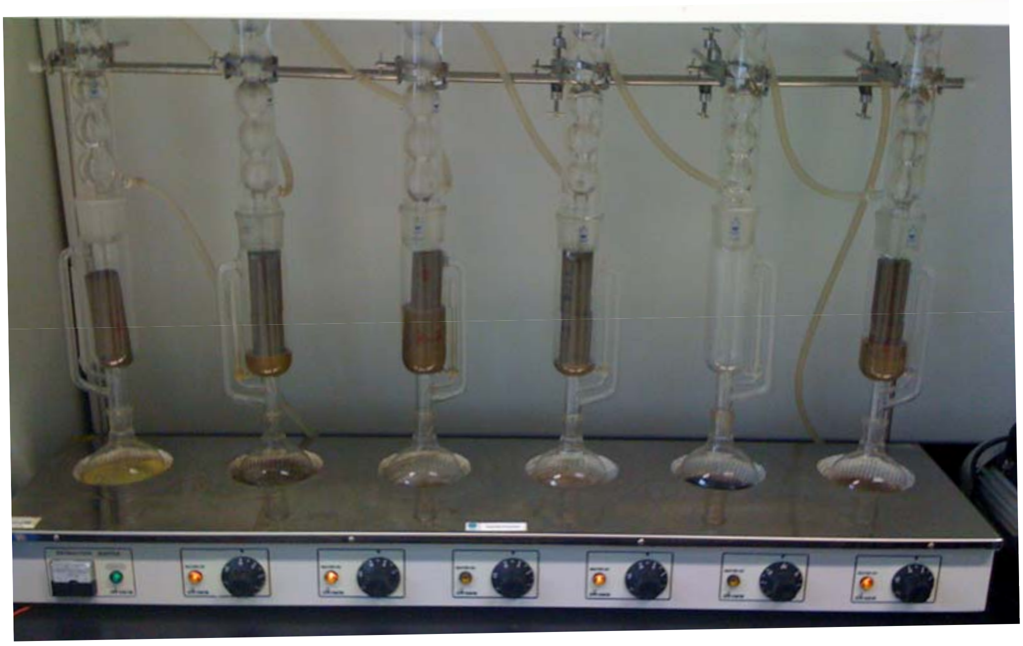


**Figure 3.11:** Core cleaning process using Soxhlet extractors

# CHAPTER 4

# SURFACTANT SYNTHESIS AND CHARACTERIZATION

This chapter presents the results for methyl ester production from Jatropha oil and its fatty acid compositions. The results of the characterization analyses of the sodium methyl ester sulfonate and different types of polymeric methyl ester sulfonate are discussed. This chapter also describes the performance of the polymeric surfactant for IFT reduction and viscosity control using softened water and seawater. The best polymeric surfactant type and concentration for softened and seawater are determined.

## 4.1 Methyl Ester Production

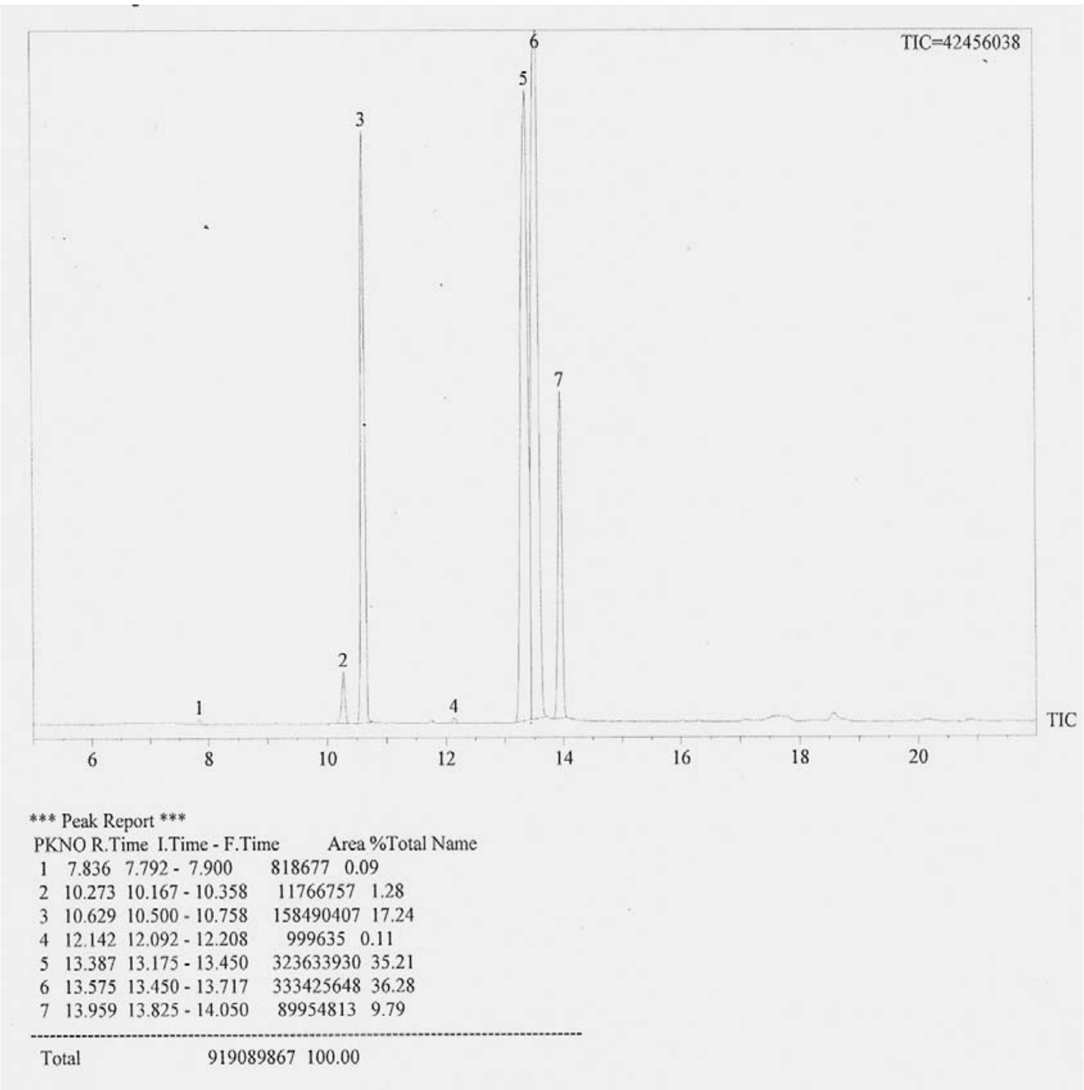
The fatty acid methyl ester from Jatropha oil was produced via a two-step transesterification process. In the first step which involved a pre-treatment step, three methanol to oil volume ratios were used to reduce the acid value of the crude Jatropha oil. The acid value of the crude Jatropha oil was greatly influenced by methanol-oil ratio over the 120 minutes reaction time. The pre-treatment of the Jatropha oil with a methanol to oil ratio of 0.17v/v reduced the acid value from 10.5 to 0.221 mg KOH/g-oil. With methanol to oil ratios of 0.25v/v and 0.30v/v, the acid value decreased to 0.156 and 0.056 mg KOH / g oil, respectively. As a result, all the ratios gave very low acid value even though they were much lower than the recommended value of 1 mg KOH/g-oil [140]. Therefore, the lowest methanol-oil ratio of 0.17 v/v was selected as the optimum ratio to be used for the transesterification step. Based on the weight of oil used in this step, an average yield of about 90% could be derived. This is similar to the yield obtained by Tiwari et al. [141] who conducted the pre-treatment of Jatropha oil that contained 28 mg KOH/g-oil using a methanol-oil volume ratio of 0.28 over 88 minutes reaction time.

In the second step, the pre-treated oil was used as feedstock for the alkaline-catalyzed transesterification. In the transesterification reaction, three different methanol to oil volume ratios were studied to identify the optimum ratio. As a result of the 35 minutes reaction time, there were no significant differences in the methyl ester yield between the methanol to oil ratios of 0.22v/v, and 0.26v/v as compared to 0.16v/v. For instance, a maximum yield of 99.8% and 99.3% were obtained with the methanol to oil ratios of 0.22v/v, and 0.26v/v respectively, while a yield of 96.4% was obtained when the lowest ratio of 0.16v/v was used. It can be seen that the methyl ester yield is significantly affected by the methanol to oil ratio. Therefore, the methanol to oil ratio of 0.22v/v was selected as the optimum ratio for this study. According to Tiwari et al. [141] a maximum yield of 99% was obtained with a methanol to oil ratio of 0.16 v/v and 24 min reaction time. As compared to other oils, a maximum yield of 95% was obtained with a methanol to oil molar ratio of 12:1 and 3 hours reaction time from soybean oil [144]. This makes Jatropha oil a promising source for methyl ester production.

**Table 4.1:** Analysis of the fatty acid methyl ester

| | Jatropha oil | Soybean oil [90] |
|---|---|---|
| Palmitic acid methyl ester | 17.24 | 11.0 |
| Stearic acid methyl ester | 9.79 | 4.0 |
| Margaric acid methyl ester | 0.11 | - |
| Myristate methyl ester | 0.09 | 0.1 |
| Palmitoleic acid methyl ester | 1.28 | 0.1 |
| Linoleic acid methyl ester | 35.21 | 53.2 |
| Oleic acid methyl ester | 36.28 | 23.4 |

After selecting the optimum methanol to oil ratio, the final product of the methyl ester was characterized by Gas Chromatography-Mass Spectrometry (GC-MS) to confirm the presence of fatty acid methyl esters. The composition of the fatty acid methyl esters produced from Jatropha oil is summarized in Table 4.1 and the raw chromatography results are presented in Figure 4.1. The presence of methyl esters were assessed from the library which was provided with the equipment. As can be seen in Table 4.1, Jatropha oil methyl ester was found to contain 27.23% saturated fatty acid and 72.77% unsaturated fatty acid. It was also found that Jatropha oil has a high quantity of linoleic acid methyl ester and oleic acid methyl ester. As compared to soybean oil, Jatropha oil has a potential as a fatty acid source.



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*** Peak Report ***
PKNO R.Time  I.Time - F.Time        Area %Total Name
 1   7.836   7.792 -  7.900       818677   0.09
 2  10.273  10.167 - 10.358     11766757   1.28
 3  10.629  10.500 - 10.758    158490407  17.24
 4  12.142  12.092 - 12.208       999635   0.11
 5  13.387  13.175 - 13.450    323633930  35.21
 6  13.575  13.450 - 13.717    333425648  36.28
 7  13.959  13.825 - 14.050     89954813   9.79
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 Total                         919089867 100.00
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**Figure 4.1:** Chromatography results for fatty acid methyl ester

## 4.2 Sulfonation and Polymerization of the Produced Methyl Ester

The fatty acid methyl ester produced from Jatropha oil was sulfonated according to Chonlin et al. [142]. Since n-butanol and sodium carbonate are already used in chemical EOR as cosolvent and alkali respectively, the sulfonated methyl ester obtained was used in subsequent experiment without any purification so as to minimize the cost of manufacturing. Five types of polymeric methyl ester sulfonate were produced using different methyl ester sulfonate to acrylamide ratio. These surfactants are shown in Table 4.2.

**Table 4.2:** Different types of polymeric methyl ester sulfonate

| Polymeric surfactant name | Surfactant to acrylamide weight ratio |
|---|---|
| SURF 1 | 1:0.50 |
| SURF 2 | 1:0.60 |
| SURF 3 | 1:0.80 |
| SURF 4 | 1:1.16 |
| SURF 5 | 1:1.33 |

## 4.3 FTIR Spectroscopy Analyses of the Produced Surfactants

The FTIR spectrum of sodium methyl ester sulfonate is shown in Figure 4.2. In this study, all the IR absorption bands were analyzed with reference to the Spectrometric identification of organic compounds by Silverstein et al. [145]. The broad absorbance peaks between 3300-2500 $cm^{-1}$ represented the O–H stretching of carboxylic acid. The presence of esters was indicated by the absorbance peak of C=O stretching vibration between 1730-1715 $cm^{-1}$. The presence of the significant peaks at 1450 $cm^{-1}$ corresponded to the asymmetrical bending vibration band of methyl group (C-H). Peaks between 1160 - 1120 $cm^{-1}$ indicated the presence of sulfonate groups due to S=O stretching [145, 146]. The peaks at 1410 and 1068 $cm^{-1}$ were another indication of the presence of sulfonate groups due to the S=O stretching vibration. These results indicate that this compound must be sodium methyl ester sulfonate.

The polymeric surfactants produced based on sodium methyl ester sulfonate were also characterized using FTIR. The IR spectrums recorded of the five produced surfactants showed similar pattern but the percentage of transmission was different due to the variation in their molecular weights. The results indicated the chemical compounds for these five surfactants were the same. The spectrum recorded after scanning on the FTIR of surfactant SURF 1 is shown Figure 4.3. The IR spectra of the other four types of surfactant (SURF 2, SURF 3, SURF 4, and SURF 5) are given in Figure 4.4.

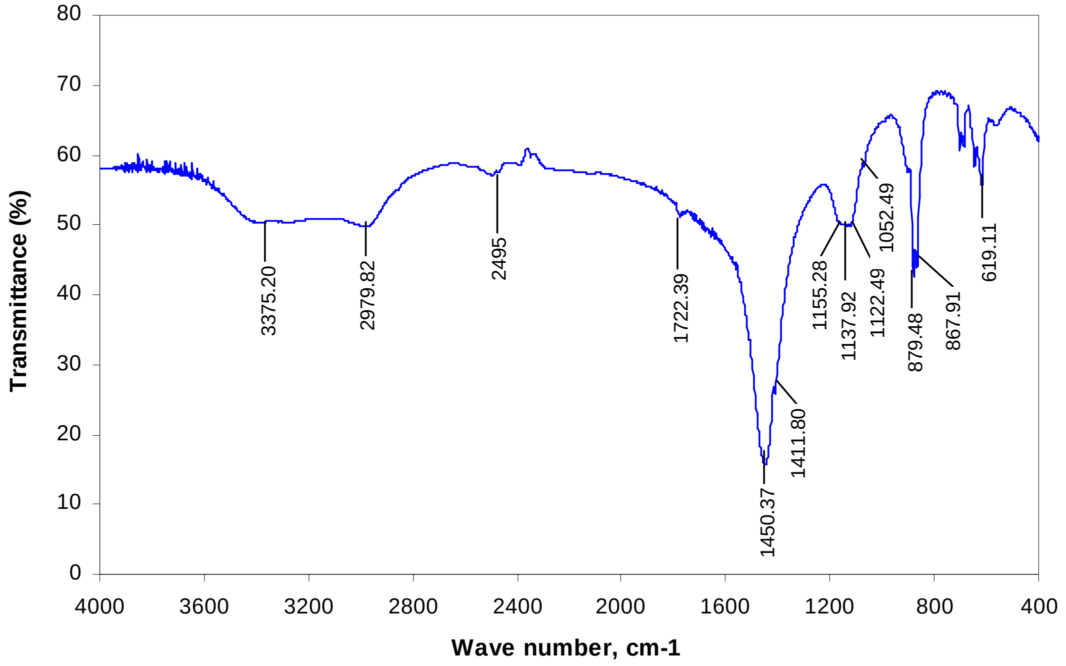


**Figure 4.2:** FTIR spectrum of sodium methyl ester sulfonate

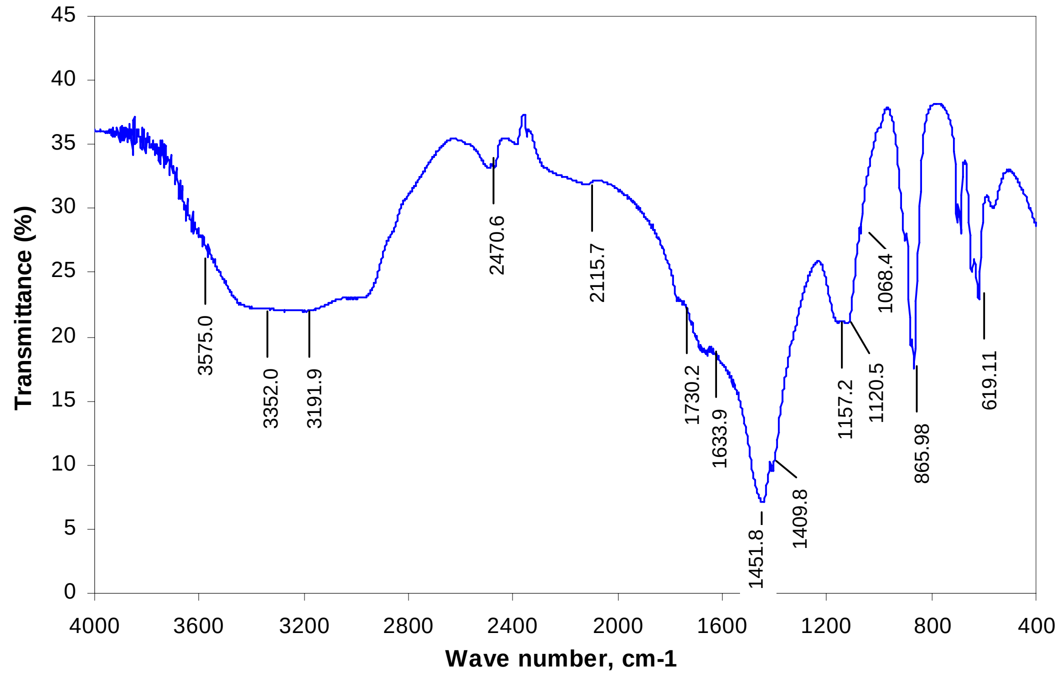


**Figure 4.3:** FTIR spectrum of polymeric SURF 1

As shown in Figure 4.3, the peaks between 1160 - 1120 cm$^{-1}$ and 1409 and 1068 cm$^{-1}$ indicated the presence of sulfonate groups due to C=O stretching. The absorbance peaks between1730-1715 cm$^{-1}$ represented the S=O stretching vibration indicated the presence of esters. The presence of the significant peaks at 1450 cm$^{-1}$ corresponded to the asymmetrical bending vibration band of methyl group (C-H).

Changes in the absorbance peaks between 2975-3352 $cm^{-1}$ were due to the introduction of acrylamide to the surfactant. The peaks between 3350-3180 $cm^{-1}$ were indication of the presence of primary and secondary amides due to N-H stretching. The peaks between 1680-1630 $cm^{-1}$ were another indication of the presence of amide groups due to the C=O stretching vibration [145].

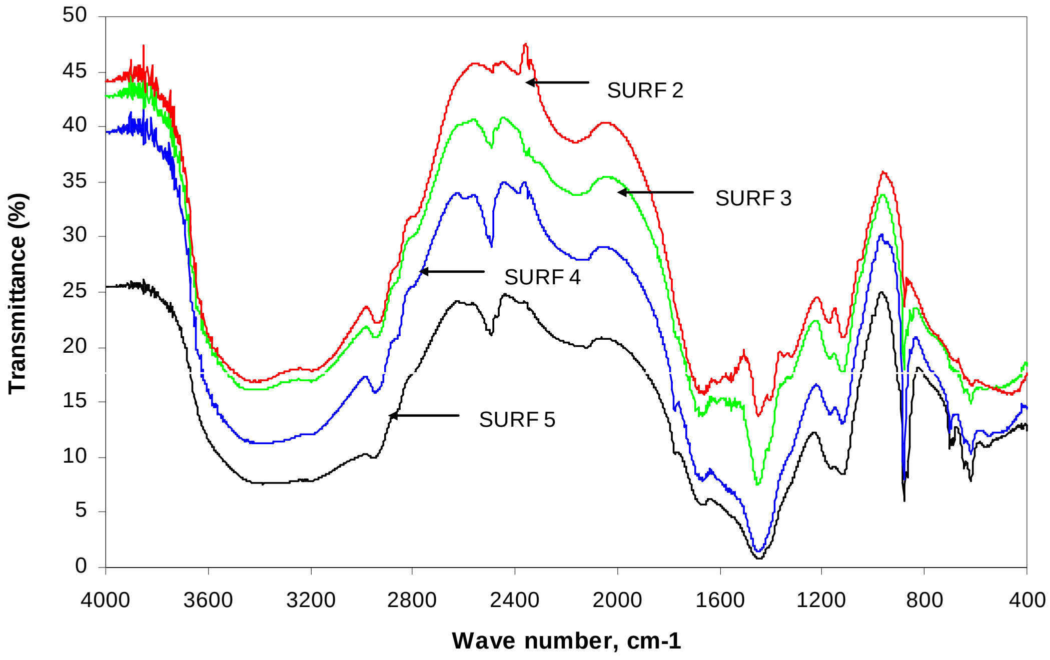


**Figure 4.4:** FTIR spectrum of polymeric surfactants (SURF 2- SURF 5)

## 4.4 Thermal Stability Analyses of the Surfactants

The thermal degradation of the sodium methyl ester sulfonate (SMES) and the polymeric surfactants were examined by thermogravimeter analyses (TGA) between 30 °C and 500 °C. The thermal behavior of the SMES and polymeric methyl ester sulfonates are compared with each other and the TGA curve for each surfactant is illustrated in Figure 4.5.

As shown in Figure 4.5, the TGA profile of SMES showed that 3.4 % weight loss was observed at 100 °C due to the loss of bound water. However, 45% weight loss occurred sharply from 100 °C to 180 °C, revealing that SMES molecules start to decompose at temperature exceeding 100 °C. Beyond this temperature, thermal stability of SMES was completely steady up to 500 °C. On the other hand, all polymeric surfactants show different degradation behavior as compared to SMES. All five polymeric surfactants showed similar trends with 3 distinctive degradation regions. The first degradation near 100 °C is attributed to the loss of water bound where an average of 6% weight loss was observed. The second region from 100 to 300 °C corresponds to the degradation of amide groups. The third region from 300 to 500 °C represents a complex degradation process which may result from the condensation of the residual amide groups and cyclic amide rings [147].

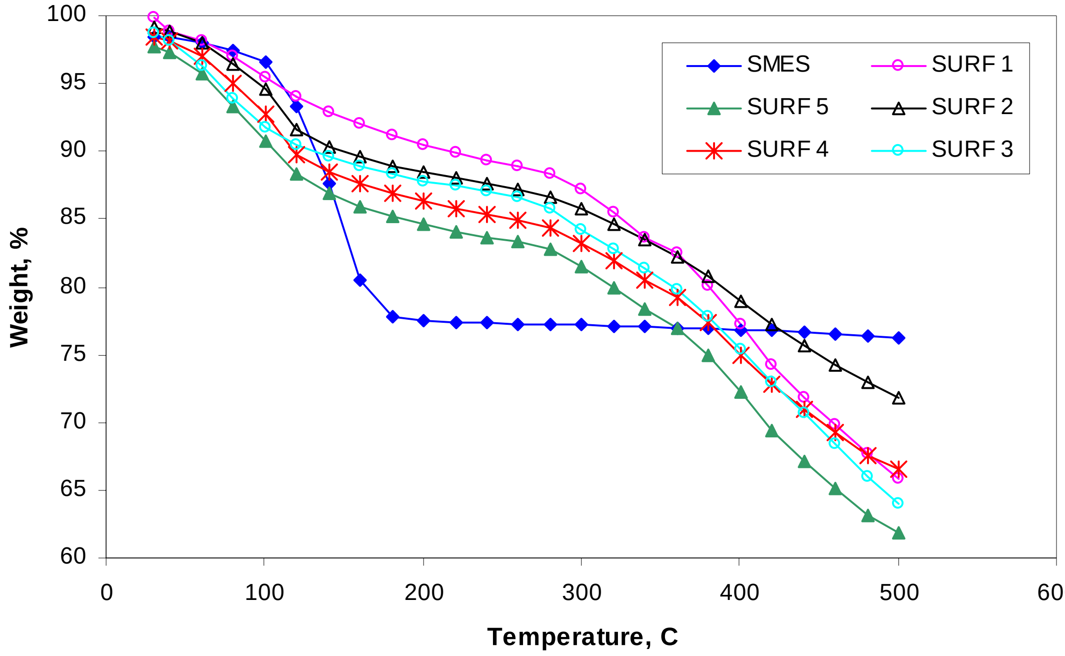


**Figure 4.5:** TGA curves for SMES and different types of polymeric surfactants

From all the TGA curves presented in Figure 4.5, the SMES showed less mass loss as compared to the polymeric surfactants at about 100 °C, while the polymeric surfactants demonstrated much less mass loss when the temperature exceeded 100 °C. It was also shown that the degradation increased as the surfactant to acrylamide ratio was decreased. For instance, in case of SURF 1 where the surfactant to acrylamide ratio was 1:0.5, the TGA showed 4% weight loss at 100 °C, while about 9% weight loss was recorded for lowest ratio of 1:1.33 in the case of SURF 5. As the reservoir temperature used in this study is 90 °C, all the polymeric surfactants retain an average of 95% of their original structure and mass. It could be concluded that these polymeric surfactants are thermally stable under the desired reservoir temperature.

## 4.5 Interfacial Tension Measurements

Interfacial tension (IFT) measurements between Angsi crude oil and sodium methyl ester sulfonate (SMES) and polymeric methyl ester sulfonates were performed using various surfactant concentrations. All the measurements were conducted at ambient temperature by spinning drop method.

Figure 4.6 shows the interfacial tension performance between Angsi crude oil and SMES at different surfactant concentrations. All the surfactant solutions were prepared by softened water on weight basis. As shown in Figure 4.6, the SMES showed good IFT reduction as compared to a commercial surfactant, sodium dodecyl sulfate (SDS). At 0.2% loading, SMES reduced the interfacial tension between softened water and crude oil from about 13.6 mN/m to 0.82 mN/m. This demonstrates the surface adsorption and aggregative properties of the new surface-active compound. It can be seen that the interfacial tension of SMES solution reduced drastically with surfactant concentration increments. For instance, when the surfactant concentration was increased to 0.4% and 0.6%, the IFT dropped continuously to an optimum value of 0.56 mN/m and 0.45 mN/m respectively.

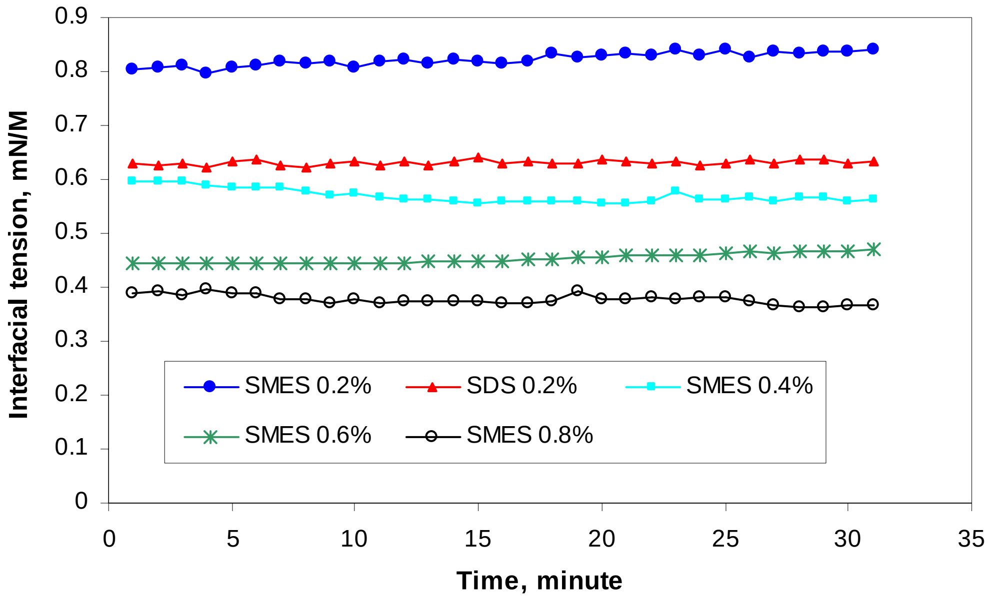


**Figure 4.6:** IFT between crude oil and various SMES concentrations

The surface activity of the SMES was also compared with a commercial surfactant (SDS), and is depicted graphically in Figure 4.6. Using the same concentration of 0.2% for both surfactants, the SMES and SDS reduced the interfacial tension with crude oil to 0.82 mN/m and 0.63 mN/m respectively. These results indicate that there is no much difference in the interfacial tension reduction while the cost of the produced surfactant is very much lower than the commercial SDS.

Figure 4.7 shows the IFT performance of different types polymeric methyl ester sulfonate (PMES) using 0.2 % surfactant concentration. During these measurements, softened water and seawater were used to prepare each type of PMES for comparison purpose. All polymeric surfactants showed a significant reduction of the IFT with the use of softened water. However, a slight increase of the IFT values were observed with the seawater due to the high salinity. Further, more IFT reduction was observed when the surfactant to acrylamide ratio was increased for all cases. As shown in Figure 4.7 with the lowest ratio (SURF 5), the IFT between crude oil the surfactant solution was reduced from 13.6 mN/m to 0.66 mN/m and 0.9 mN/m for softened and seawater respectively, and reached 0.32 mN/m and 0.48 mN/m at the highest surfactant to acrylamide ratio as seen with SURF 1. This explains the surface adsorption and aggregative properties of the attached sulfonated group to the polymer chains. As the surfactant to acrylamide ratio increased, there are more surfactant and sulfonate groups available on the polymer backbone diminishing the IFT values.

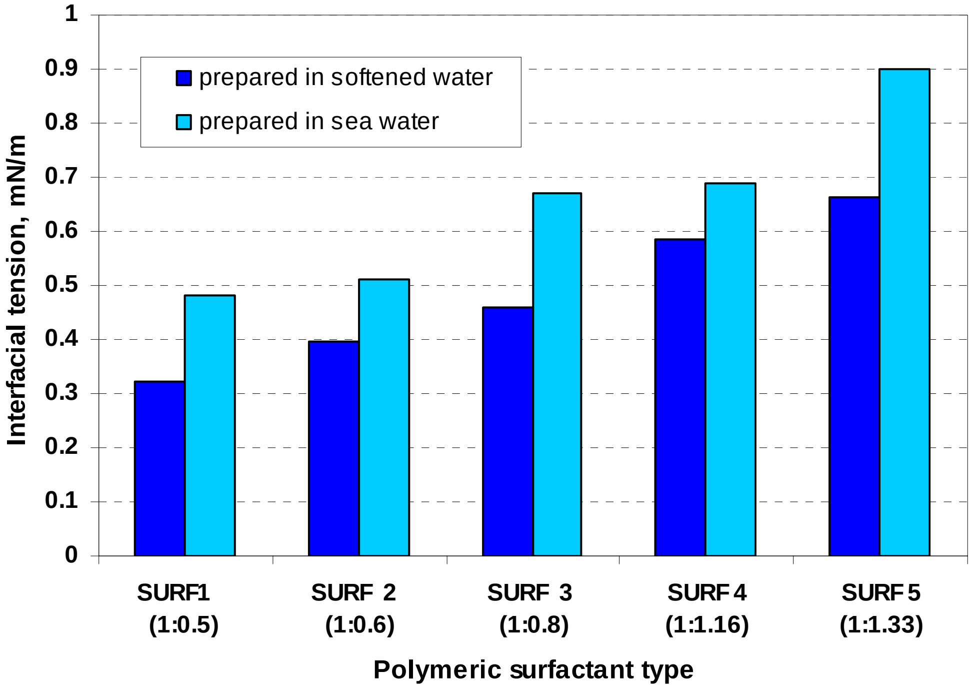


**Figure 4.7:** IFT between crude oil and various polymeric surfactants

### 4.6 Viscosity Measurements

The kinematic viscosity of each polymeric surfactant (SURF 1 - SURF 5) was measured using Tamson viscometer. All surfactant solutions were prepared in softened water and seawater using 0.2% surfactant concentration. The purpose of this test was to ascertain the best surfactant type and concentration to be used in the second part of this study. All the measurements were conducted at 90 °C as a reservoir temperature.

Figure 4.8, shows the viscosity performance of each polymeric surfactant using 0.2% surfactant concentration in softened water at 90°C. As can be seen from Figure 4.8, the viscosity performance increased significantly as the surfactant to acrylamide ratio was decreased. This is due to the increasing amount of polymer chains attached with the surfactant. The more acrylamide used in the polymerization process results in a higher viscosity. Hence, the highest viscosity was achieved with the lowest surfactant to acrylamide ratio as seen in SURF 5. There is however a trade off. SURF 5 despite possessing the highest viscosity has also the highest IFT.

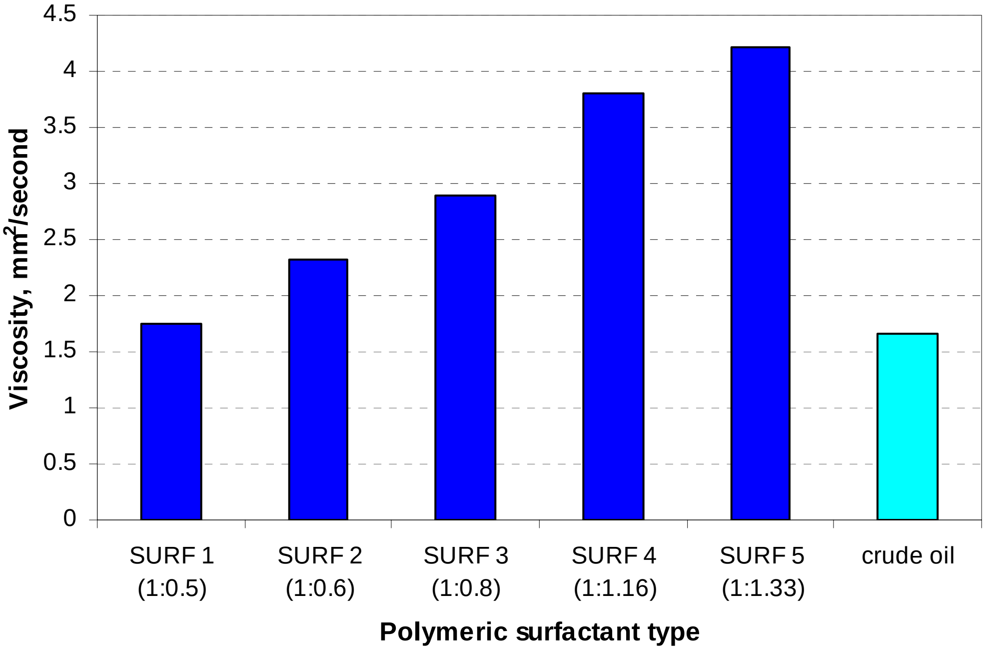


**Figure 4.8:** Viscosity performance of different polymeric surfactants using softened water at 90°C

Based on crude oil viscosity (1.654 mm$^2$/sec), SURF 1 with the ratio of 1:0.5 was selected as the best surfactant when softened water was used as the aqueous phase. Using SURF 1, the viscosity of the chemical slug can be adjusted by increasing the surfactant concentration to yield good viscosity and an ultra low IFT. Unlike SURF 2 and SURF 3 for example, the viscosities are much higher as compared to the crude oil. If a higher surfactant concentration is used for IFT purpose, the viscosity disparity will be further exacerbated and may cause other problem in the injection process.

In order to determine the best surfactant concentration for the selected surfactant (SURF 1), the viscosity of different surfactant concentrations were investigated using softened water. As demonstrated in Figure 4.9, SURF 1 shows a significant increment in the viscosity as the polymeric surfactant concentration was increased. Using 0.2% surfactant concentration, the viscosity was almost the same as with crude oil viscosity of 1.654 mm$^2$/sec. When the concentration of SURF 1 was increased to 0.6%, the viscosity was about two times the crude oil viscosity, which is quite high as compared to the crude oil. Therefore, it may be concluded that for achieving an effective chemical slug using softened water, SURF 1 with 0.4% concentration was selected as the best surfactant for IFT reduction and viscosity control.

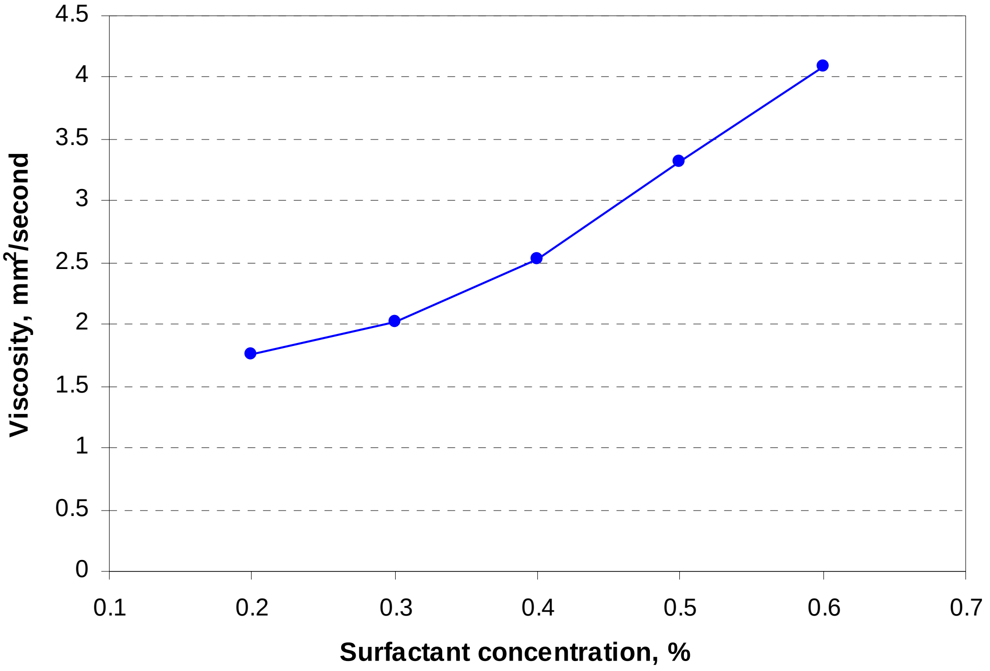


**Figure 4.9:** Viscosity performance of SURF 1 using different surfactant concentrations at 90$^o$C

The effect of seawater on the viscosity performance of the polymeric surfactant was also investigated. All the measurements were conducted at 90 $^o$C using 0.2% surfactant concentration. As shown in Figure 4.10, the viscosity of all surfactants was greatly influenced in seawater as compared to softened water. In all cases, the viscosities diminished a value even lesser than crude oil viscosity. The main reason for the viscosity reduction is probably due to the high salinity and hardness of the seawater. Seawater has a large quantity of divalent metal cations which can significantly reduce the polymeric surfactant viscosity [135]. The polymeric surfactant being negatively charged has an affinity for the divalent metal cations, forcing the polymer to coil up. The viscosity becomes diminished. In softened water, the negatively charged polymeric surfactant remains extended and has a higher viscosity feature as the side chain grafts offer points of attachment resisting the polymeric chains slide past others. Based on the results plotted in Figure 4.10, a higher concentration of surfactants must be used to obtain the best surfactant type and concentration for seawater application.

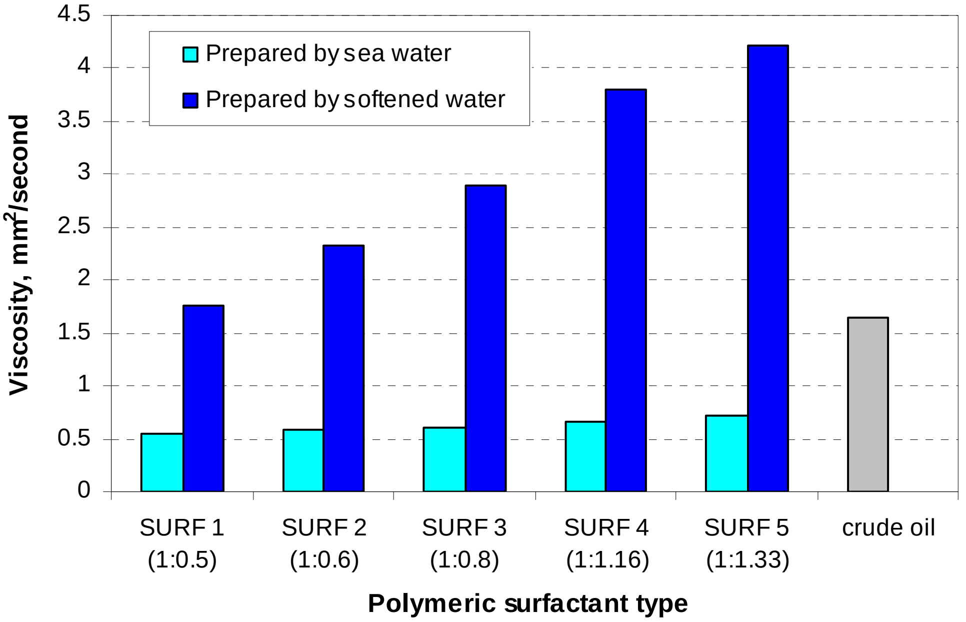


**Figure 4.10:** Viscosity performance of different polymeric surfactants using seawater and softened water at 90°C

In order to ascertain the best surfactant for seawater environment, the viscosity of varying concentration of each polymeric surfactant was investigated at 90°C. As can be seen from Figure 4.11, the viscosity increased significantly as the surfactant concentration was increased. However, in order to design a cost-effective chemical slug, SURF 1, SURF 2, and SURF 3 were not considered for selection. This is because a high concentration is required if these surfactant is selected. The selection of the most favorable surfactant was based on several factors: economy, ultra low IFT and suitable viscosity, even at the expense of a high concentration requirement.

Hence, SURF 4 with the concentration of 0.6% was selected as the candidate surfactant for IFT reduction and viscosity control when seawater was used as the media.

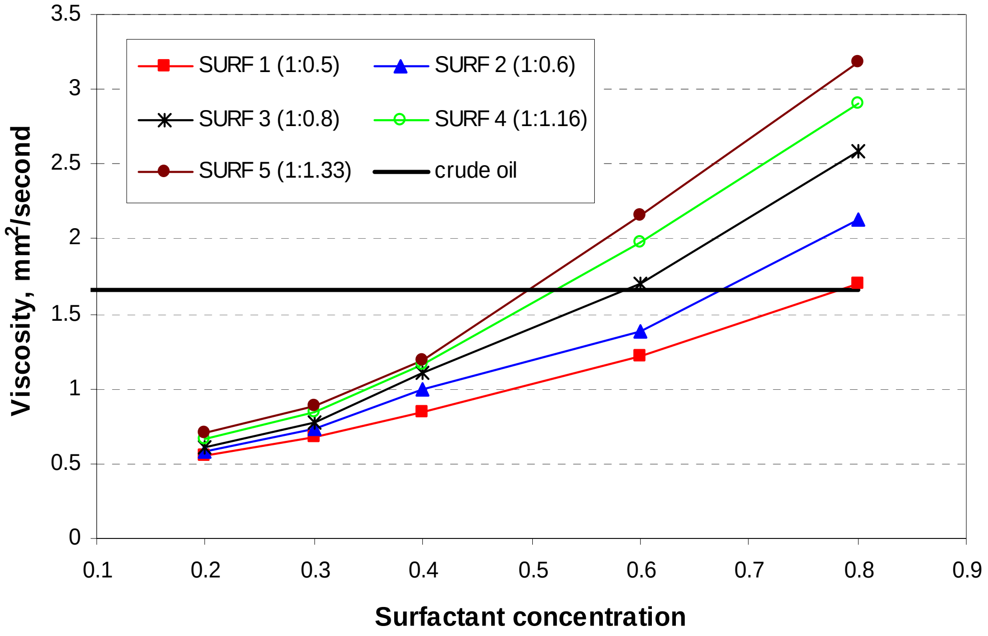


**Figure 4.11:** Viscosity performance of different polymeric surfactants at various concentrations at 90°C

## 4.7 Summary

The experimental results showed that the non-edible Jatropha oil is a suitable raw material for surfactant production. Production of sodium methyl ester sulfonate (SMES) and polymeric methyl ester sulfonate (PMES) based on non-edible Jatropha oil can satisfy EOR requirements. Its non edibility and low free fatty acid content make it cost-effective compared to other vegetable oils and petrochemical feedstocks. FTIR spectra of SMES and PMES have confirmed the presence of the desired components. Thermal decomposition profiles of SMES and PMES have demonstrated that they posses the needful thermal stabilities under reservoir temperature of 90 °C.

Interfacial tension and viscosity performances of the polymeric methyl ester sulfonate (PMES) indicated that this surfactant was an excellent candidate for chemical enhanced oil recovery. The high surfactant to acrylamide ratio provides good IFT reduction, while the low surfactant to acrylamide ratio results in a high viscous solution. Seawater has a significant effect on the IFT and viscosity performance as compared to softened water. High surfactant concentration should be used to attain suitable viscosity and ultra low IFT when seawater was used to prepare the surfactant solution.

In the case of softened water, SURF 1 with a concentration of 0.4% was selected as the best condition for IFT reduction and viscosity control, while SURF 4 with a concentration of 0.6% was chosen for seawater application.

# CHAPTER 5

# ACID-ALKALI-SURFACTANT FLOODING DESIGN

In this chapter, a new Acid-Alkali-Polymeric Surfactant (AAPS) flooding formulation has been developed to overcome the precipitation problems caused by the divalent metal cations. Also, the performance of alkali and polymeric surfactant (APS) in the absence of acid was evaluated using softened water. In order to find the optimum chemical solution for Angsi crude oil, a comprehensive screening study was organized to understand the mechanism for each formula with the use of seawater and softened water. This included fluid-fluid interactions tests, interfacial tension measurements, phase behavior tests, and surfactant adsorption tests. To further assess the technical feasibility of the proposed formulas, a series of core flood tests were conducted to determine the optimum chemicals concentration and the suitable injection strategy. The effects of surfactant concentration, alkali concentration, and slug size on oil recovery performance are also discussed in this chapter.

## 5.1 Characterization of Seawater and Softened Water

The properties of seawater and softened water used in this study are presented in Table 5.1. The seawater used throughout this study was collected from Lumut sea, Malaysia. As can be seen from this table that seawater has a large quantity of divalent metal cations as compared to the softened water. In this study, seawater was used for acid-alkali-polymeric surfactant preparation and softened water for alkali-polymeric surfactant system.

**Table 5.1:** Seawater and softened water properties

| | Seawater | Softened water |
|---|---|---|
| Salinity | 33,400 ppm | < 2 ppm |
| Sodium, $Na^+$ | 11,908 ppm | 43.9 ppm |
| Chloride, $Cl^-$ | 14,010 ppm | 48 ppm |
| Calcium, $Ca^{2+}$ | 790 ppm | 0.9 ppm |
| Magnesium, $Mg^{2+}$ | 6720 ppm | 13.6 ppm |
| Potassium, $K^+$ | 373 ppm | 0.6 ppm |
| Sulfates, $SO_4$ | 1977 ppm | - |

## 5.2 Fluid/Fluid Compatibility Test

### 5.2.1 Alkali-Water Interaction Test

The compatibility of alkali with seawater and softened water was evaluated using 0.3% of different alkalis. Sodium hydroxide, sodium carbonate, and sodium bicarbonate were used to study the effect of divalent metal cations. The alkali-water interaction was monitored by observation of the onset of precipitation at 90°C.

As can be seen from Table 5.2, all the alkalis employed were significantly affected by the type of water used to prepare the solutions. In case of seawater, sodium hydroxide and sodium carbonate were immediately consumed by the calcium ($Ca^{2+}$) and magnesium ($Mg^{2+}$) ions to form their corresponding insoluble hydroxides and carbonates precipitates. However, sodium bicarbonate showed a higher resistance to $Ca^{2+}$ and $Mg^{2+}$ ions where the precipitation was formed after seven days of mixing. On the other hand, precipitations were also observed when softened water was used to prepare sodium hydroxide and sodium carbonate solutions maintained at 90°C. The strong alkali such as sodium hydroxide started to precipitate after 12 days at 90°C while 40 days was recorded for sodium carbonate to form its insoluble salts. This is because sodium hydroxide is more reactive with divalent metal cations which result in loss of alkalinity and excessive precipitation. However, no precipitations were formed when sodium bicarbonate was prepared by softened water maintained for 90 days at 90°C. This is because the bicarbonate has a higher solubility than carbonate and hydroxide and therefore, no precipitations were generated for 90 days.

### 5.2.2 Acid-Alkali Interaction Test

Based on the previous compatibility test, all alkalis were not compatible with any water contains even small quantities of the divalent metal cations. It is essential that calcium and magnesium ions must be removed from water. In this study, alkali and acrylic acid were used together with seawater to form an in-situ inhibitor to mitigate precipitation tendencies of the divalent ions and alkali. However, the generated in-situ inhibitor greatly depends on the acrylic acid to alkali ratio and the divalent metal cations present in the seawater. Hence, it is imperative to evaluate the performance of the in-situ precipitation inhibitor using different acrylic acid to alkali weight ratios. The three common alkalis i.e. sodium hydroxide, sodium carbonate, and sodium bicarbonate were screened to define the suitable candidate. All the results for compatibility tests are presented in Appendix B. Table 5.2 summarizes the results for each acid to alkali ratio over 90 days at 90°C. Figure 5.1 shows the performance of the in-situ inhibitor in preventing $Ca^{2+}$ and $Mg^{2+}$ precipitations over time.

Based on the results presented in Table 5.2, the in-situ inhibitor was very effective in preventing $Ca^{2+}$ and $Mg^{2+}$ precipitations over 90 days at reservoir temperature of 90°C. It was also observed that the efficiency of the inhibitor increased as the acid to alkali ratio was increased. With a small acid to alkali ratio, the produced inhibitor (sodium acrylate) was insufficient to prevent the precipitation. All the acid was neutralized by the added alkali and sodium ions present in the seawater. However, when a high acid to alkali ratio was used, only the required amount of acid was neutralized by the added alkali. The inhibitor concentration was increased as a result of the reaction of the alkali and sodium ions with the acrylic acid. The inhibitor and excess free acid were able to react with $Ca^{2+}$ and $Mg^{2+}$ ions to form soluble divalent metal acrylates. As a result, the highest acid to alkali ratio was observed with the strong pH alkali (sodium hydroxide). The acid to alkali ratio of 2.33:1 was found to be the optimum ratio for sodium hydroxide to prevent any precipitations, while the ratio of 1.66:1 and 1:1 were the optimum ratios for sodium carbonate and sodium bicarbonate respectively.

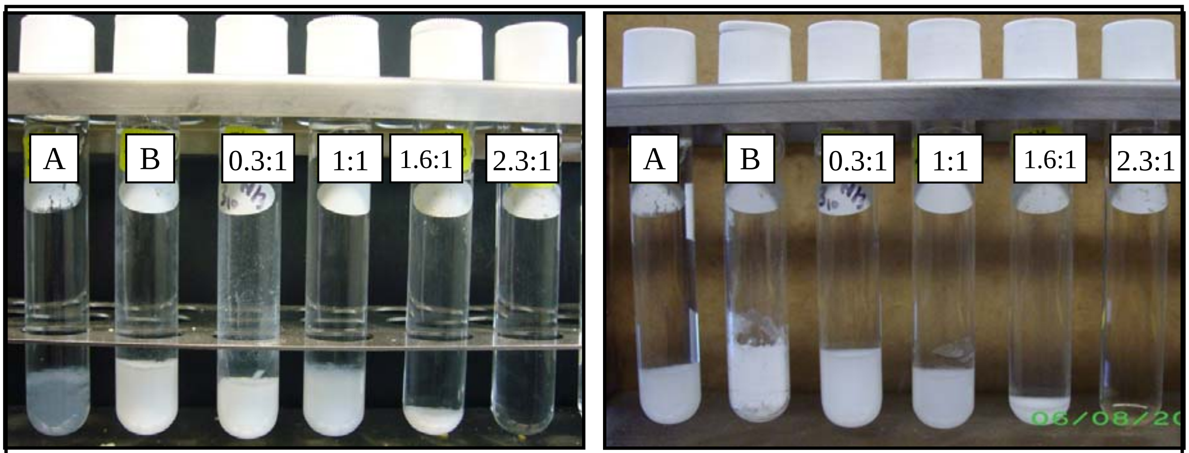
In the case of sodium hydroxide, a high acid to alkali ratio was required to provide adequate inhibitor (sodium acrylate) as compared to the other alkalis. With an acid to alkali ratio of 1.66:1, the acid was fully consumed by the alkali and the generated inhibitor was inadequate to prevent the $Ca^{2+}$ and $Mg^{2+}$ precipitations. As the acid to alkali ratio was increased to 2.33:1, $Ca^{2+}$ and $Mg^{2+}$ ions became more soluble due to the presence of inhibitor and excess acrylic acid. The inhibitor adsorbs on the active growth sites of the $Ca^{2+}$ and $Mg^{2+}$ surfaces to prevent them from precipitating. The presence of acid makes the solution more acidic which increases the solubilities of these ions.

**Table 5.2:** Summary of the acid-alkali compatibility test after 90 days at 90 $^{o}$C

| Sodium hydroxide | | | | | | |
|---|---|---|---|---|---|---|
| | 0.3% in seawater | 0.3:1 | 1:1 | 1.66:1 | 2.33:1 | 0.3% in softened water |
| pH | 10.9 | 11.1 | 11.06 | 11 | 5.73 | 11.63 |
| days | compatibility | | | | | |
| 0 | ppt | ppt | ppt | Cloud | clr | clr |
| 4 | ppt | ppt | ppt | ppt | clr | clr |
| 12 | ppt | ppt | ppt | ppt | clr | ppt |
| 90 | ppt | ppt | ppt | ppt | clr | ppt |
| Sodium carbonate | | | | | | |
| pH | 10.64 | 10.4 | 10.22 | 5.7 | 5.02 | 12.24 |
| days | compatibility | | | | | |
| 0 | ppt | Cloud | clr | clr | clr | clr |
| 4 | ppt | ppt | clr | clr | clr | clr |
| 26 | ppt | ppt | ppt | clr | clr | clr |
| 40 | ppt | ppt | ppt | clr | clr | ppt |
| 90 | ppt | ppt | ppt | clr | clr | ppt |
| Sodium bicarbonate | | | | | | |
| pH | 9.63 | 9.31 | 5.63 | 4.86 | 4.33 | - |
| days | compatibility | | | | | |
| 0 | clr | clr | clr | clr | clr | clr |
| 7 | ppt | clr | clr | clr | clr | clr |
| 19 | ppt | ppt | clr | clr | clr | clr |
| 90 | ppt | ppt | clr | clr | clr | clr |

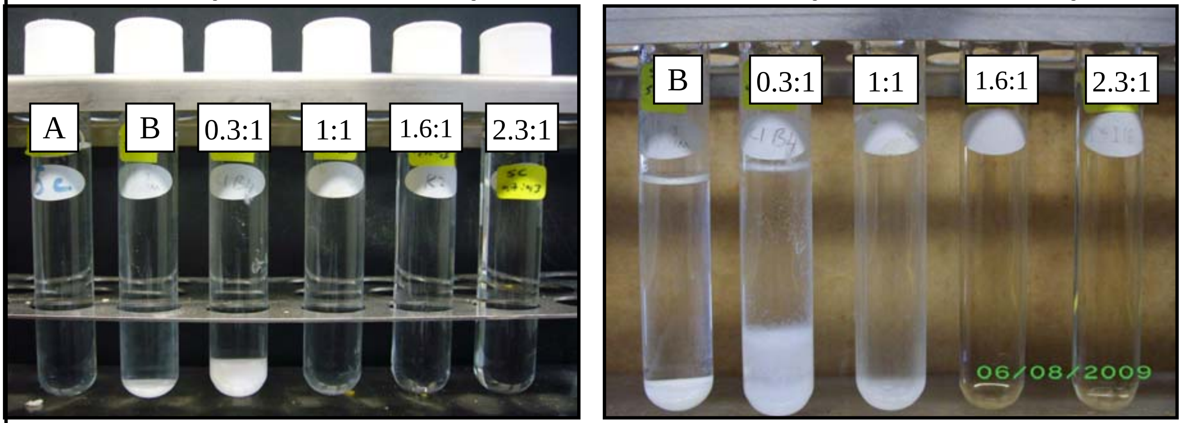
*ppt denotes precipitation, clr denotes clear solution*

When the alkali was changed from sodium hydroxide to sodium carbonate, a similar pattern was emerged. A 0.3% solution of sodium carbonate formed an immediate precipitation with the used of seawater (Table 5.2). However, the precipitation was mitigated when acrylic acid was incorporated. In contrast to sodium hydroxide, the critical ratio for precipitation retardation for sodium carbonate is lower as seen with the acid to alkali ratio of 1:1.66. The precipitation retardation for sodium bicarbonate occurs at an even lower acid to alkali ratio of 1:1. This is because the sodium bicarbonate is a weak base, so more acid is expected to remain in solution. Therefore, the formed $Ca^{2+}$ and $Mg^{2+}$ ions were in a soluble phase as a result of the low pH of the solution.



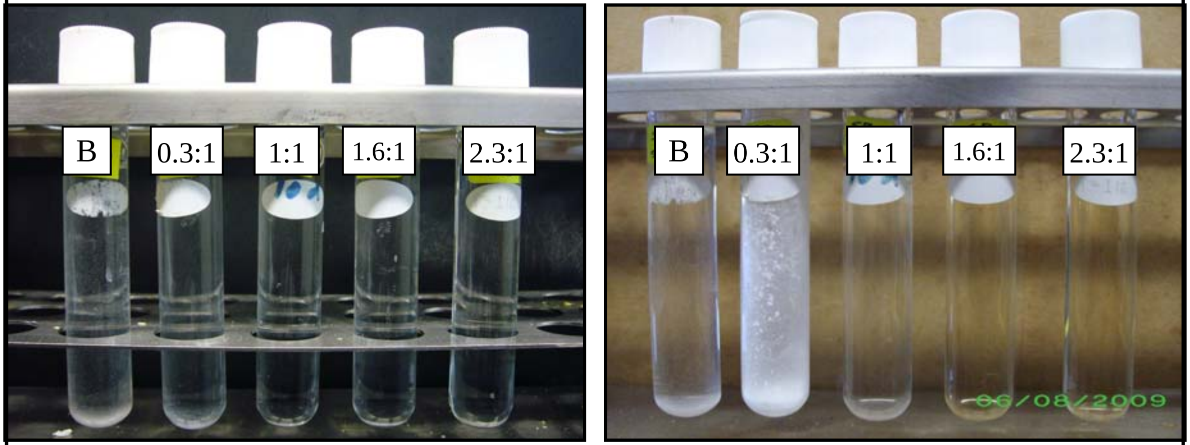
Sodium hydroxide after 22 days

Sodium hydroxide after 90 days



Sodium carbonate after 22 days

Sodium carbonate after 90 days



Sodium bicarbonate after 22 days

Sodium bicarbonate after 22 days

A = 0.3% alkali prepared in softened water.   B = 0.3% alkali prepared in seawater

**Figure 5.1:** Performance of the in-situ inhibitor on preventing $Ca^{2+}$ and $Mg^{2+}$ precipitations over time

From the foregoing, sodium hydroxide was not considered for selection because of its detrimental reaction with the acrylic acid and $Ca^{2+}$ and $Mg^{2+}$ ions. On the other hand, the weak pH alkali (sodium bicarbonate) showed the lowest acid to alkali ratio required to maintain the solution without precipitation. However, because the high pH is also needed in this system, so the sodium carbonate was selected as the best candidate for this study.

**Table 5.3:** The effect of temperature on the precipitation inhibitor performance

<table>
<tr><th colspan="7">26$^{o}$C</th></tr>
<tr><th>days</th><th>0.3% in seawater</th><th>0.3:1</th><th>1:1</th><th>1.66:1</th><th>2.33:1</th><th>0.3% in softened water</th></tr>
<tr><td>0</td><td>ppt</td><td>Cloud</td><td>clr</td><td>clr</td><td>clr</td><td>clr</td></tr>
<tr><td>5</td><td>ppt</td><td>Cloud</td><td>clr</td><td>clr</td><td>clr</td><td>clr</td></tr>
<tr><td>6</td><td>ppt</td><td>ppt</td><td>clr</td><td>clr</td><td>clr</td><td>clr</td></tr>
<tr><td>54</td><td>ppt</td><td>ppt</td><td>clr</td><td>clr</td><td>clr</td><td>clr</td></tr>
<tr><th colspan="7">60$^{o}$C</th></tr>
<tr><td>0</td><td>ppt</td><td>Cloud</td><td>clr</td><td>clr</td><td>clr</td><td>clr</td></tr>
<tr><td>3</td><td>ppt</td><td>ppt</td><td>clr</td><td>clr</td><td>clr</td><td>clr</td></tr>
<tr><td>36</td><td>ppt</td><td>ppt</td><td>ppt</td><td>clr</td><td>clr</td><td>clr</td></tr>
<tr><td>47</td><td>ppt</td><td>ppt</td><td>ppt</td><td>clr</td><td>clr</td><td>ppt</td></tr>
<tr><td>54</td><td>ppt</td><td>ppt</td><td>ppt</td><td>clr</td><td>clr</td><td>ppt</td></tr>
<tr><th colspan="7">90$^{o}$C</th></tr>
<tr><td>0</td><td>ppt</td><td>Cloud</td><td>clr</td><td>clr</td><td>clr</td><td>clr</td></tr>
<tr><td>4</td><td>ppt</td><td>ppt</td><td>clr</td><td>clr</td><td>clr</td><td>clr</td></tr>
<tr><td>26</td><td>ppt</td><td>ppt</td><td>ppt</td><td>clr</td><td>clr</td><td>clr</td></tr>
<tr><td>40</td><td>ppt</td><td>ppt</td><td>ppt</td><td>clr</td><td>clr</td><td>ppt</td></tr>
<tr><td>54</td><td>ppt</td><td>ppt</td><td>ppt</td><td>clr</td><td>clr</td><td>ppt</td></tr>
</table>

*ppt denotes precipitation, clr denotes clear solution*

The effect of temperature on the precipitation inhibitor performance was also investigated at different temperatures (26 $^{o}$C, 60 $^{o}$C, and 90$^{o}$C) for 54 days. Different acid to alkali ratios were utilized using sodium carbonate as an alkali. As can be seen from Table 5.3, the temperature has no effect on the inhibitor performance when the optimum acid to alkali ratio was used. However, when the acid to alkali ratio was less than optimum, the inhibitor was significantly affected when the temperature exceeded 60$^{o}$C. Beyond 60$^{o}$C, temperature has little affect on the inhibitor performance. For instance, with an acid to alkali ratio of 1:1, no precipitation was formed at 26$^{o}$C, while the $Ca^{2+}$ and $Mg^{2+}$ precipitations were generated after 36 and 26 days at 60 $^{o}$C and 90$^{o}$C respectively due to the elevated temperature. The phenomenon of markedly decreasing inhibitor efficiency over time may be due to the degrees of adsorption of inhibitor molecules on the precipitating $Ca^{2+}$ and $Mg^{2+}$ particles. The generated in-situ inhibitor is insufficient when the acid to alkali ratio was 1:1.

Based on the above results, it may be concluded that to achieve an effective chemical slug that is capable to prevent divalent ions precipitations, the acid to sodium carbonate ratio of 1.66:1 was selected as the optimum ratio for the usage with seawater environment. Hence, whenever alkali is used with seawater, the acid concentration must be proportional to alkali concentration using the optimum acid to alkali ratio of 1.66:1. This ratio is expected to provide sufficient inhibitor to keep the solution free of precipitations.

### 5.2.3 Acid-Polymeric Surfactant Interaction Test

The compatibility of different polymeric surfactant concentrations was investigated using softened and seawater. In the case of seawater, the compatibility of the polymeric surfactant was investigated in the presence and absence of acrylic acid. As shown in Figure 5.2, all the solutions remained clear for 62 days at 90°C when softened water was used to prepare the polymeric surfactant solutions. However, the polymeric surfactant was incompatible with seawater whereby precipitations were generated from the first day. This is attributed to the high salinity of the seawater along with the increased tendency of interaction between the divalent cations and the sulfonate group of the polymeric surfactant.

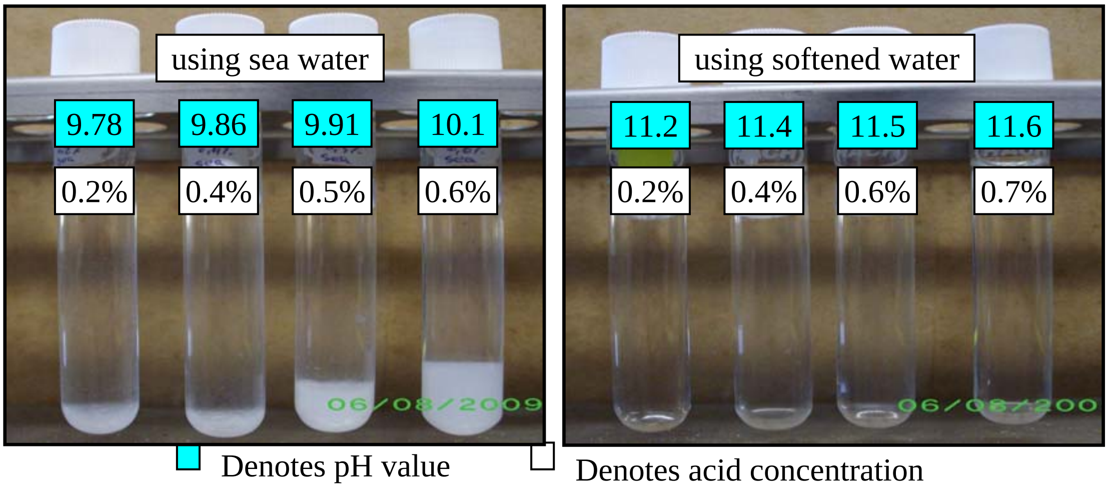
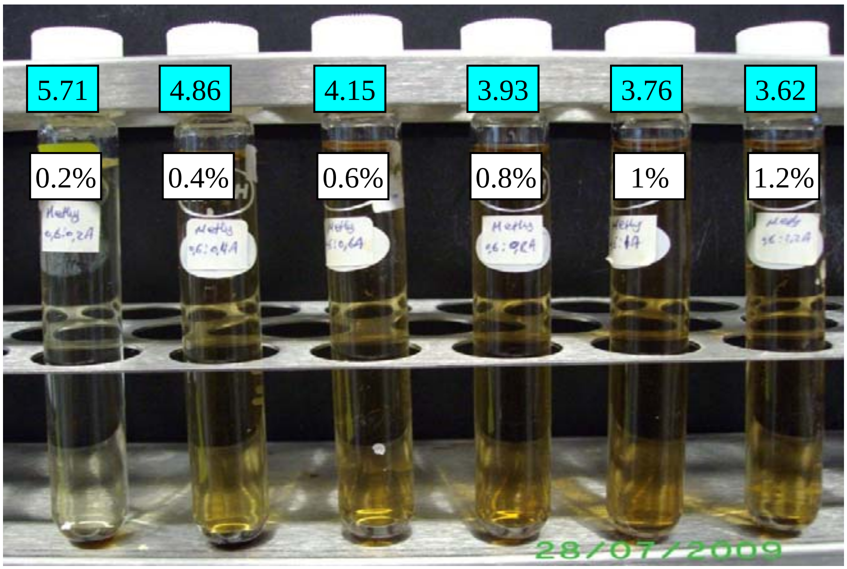


**Figure 5.2:** Compatibility of polymeric surfactant with softened water and seawater after 62 days at 90°C

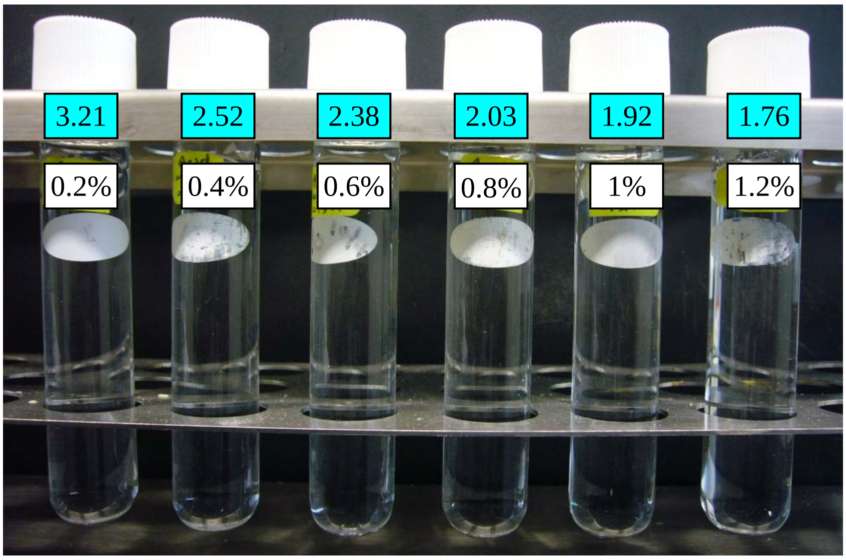
In order to use seawater for surfactant preparation, the acrylic acid was used to generate an in-situ inhibitor. The effect of different acid concentrations on preventing precipitation was studied using 0.6% polymeric surfactant concentration of SURF 4. As a result, the acrylic acid was very effective in keeping the solutions clear without any precipitations. Even with 0.2% acid concentration, no precipitation was observed when the solutions were maintained at 90°C for 62 days. This is probably due to the presence of the acid which reduces the pH of the surfactant solution from 10.1 to 5.71 in case of 0.2% acid concentration. The low pH made the $Ca^{2+}$ and $Mg^{2+}$ ions more soluble in the solution.



🟦 Denotes pH value ☐ Denotes acid concentration

**Figure 5.3:** The effect of different acid concentrations on surfactant compatibility after 62 days at 90°C (0.6% surfactant)

On the other hand, some changes in the colour were observed after 26 days when the surfactant solutions were kept at 90°C. As shown in Figure 5.3, the yellow solutions may be associated with surfactant degradation caused by the reaction between the surfactant molecule and $Ca^{2+}$ and $Mg^{2+}$ ions. An explanation for the surfactant degradation is that when the acid was added to the seawater, the sodium ion present in the seawater is not sufficient to react with all the acid and therefore, excess of amount of acid is still remaining in the solution. At the same time, the generated in-situ inhibitor is not sufficient to prevent $Ca^{2+}$ and $Mg^{2+}$ precipitations, but because there is some acid in the solution, so these ions will be in a soluble phase. When the surfactant is introduced to the solution, the $Ca^{2+}$ and $Mg^{2+}$ react with the surfactant molecule to cause the surfactant to loss its weigh in a degradation form. Another indication is that when different acid concentrations were prepared by seawater without surfactant, no colour change and no precipitation were observed for 90 days at 90°C (Figure 5.4).



🟦 Denotes pH value ☐ Denotes acid concentration

**Figure 5.4:** The effect of different acid concentrations with the seawater for 90 days at 90°C (no surfactant)

The effect of different acid concentrations on the selected surfactant viscosity was studied using 0.6% surfactant concentration of SURF 4. As can be seen in Figure 5.5, there was no significant difference in the viscosity when the acid was used in the system at 90°C. For instance, when there was no acid on the system, the viscosity of the surfactant solution was 1.97 $mm^2$/sec which is almost the same as the viscosity obtained when 0.4% acid concentration was used. Nevertheless, a little change in the viscosity was observed when the acid concentration was increased from 0.4% to 0.8% and remained constant when the acid concentration was as high as 1.2%. The reduction in the viscosity at higher acid concentration could be attributed to acrylic acid repulsion. The negatively charged polymeric surfactant will tent to coil up and its volume remained small to offer any resistance to chain sliding past each other. From the results, it could be concluded that when the acid concentration is higher than the surfactant concentration, some changes in the viscosity should be considered.

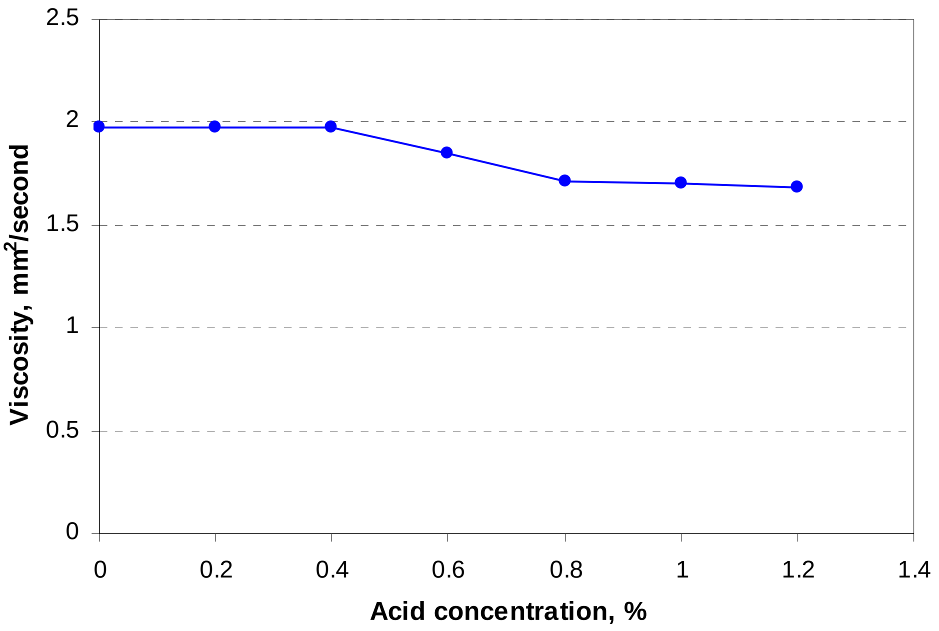


**Figure 5.5:** The effect of various acid concentrations on surfactant viscosity using seawater (0.6% surfactant-90°C)

### 5.2.4 Acid-Alkali-Polymeric Surfactant Interaction Test

The compatibility of the acid-alkali-polymeric surfactant (AAPS) with seawater was investigated at different temperatures for 63 days. Different sodium carbonate concentrations were used to screen the optimum alkali concentration for generating sufficient amount of inhibitor in the presence of surfactant. In this test, the surfactant concentration of SURF 4 was maintained at 0.6% and the acid concentration was set proportional to the alkali concentration using 1.66:1acid to alkali ratio. The summary of the compatibility tests are presented in Table 5.4 and the performance of the inhibitor is shown in Figure 5.6.

As shown in Table 5.4, all the AAPS solutions remained clear for 63 days when these solutions were kept at the room temperature. However, precipitations were formed when AAPS solutions were maintained at 90°C. As can be seen from Table 5.4, precipitations were generated when the alkali concentration was 0.6% or less, while clear solutions were obtained when the alkali concentration exceeded 0.6%. It was also observed that the pH was decreased as the alkali and acid concentrations were increased. An explanation is that when the alkali concentration was 0.6% or less, the acid amount is not sufficient to generate the required amount of in-situ inhibitor in the presence of surfactant. The acid was fully neutralized by the, sodium ion, alkali and the surfactant. For this reason, high pH was observed when the alkali concentration was low. However, when the alkali concentration exceeded 0.6%, the generated in-situ inhibitor is capable of preventing any precipitations. Under this condition, the marked reduction in the $Ca^{2+}$ and $Mg^{2+}$ precipitations must be attributed to surface adsorption factor and the concomitant increase in ionic strength of the solution in the presence of inhibitor.

**Table 5.4:** Effect of different alkali-acid concentrations on the inhibitor performance

| days | Alkali concentration @ 90°C | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 0.2% | 0.4% | 0.6% | 0.8% | 1% | 1.2% | 1.4% | 1.6% |
| | Acid concentration | | | | | | | |
| | 0.33% | 0.66% | 0.99% | 1.32% | 1.66% | 1.99% | 2.32% | 2.65% |
| | pH | | | | | | | |
| | 9.54 | 9.36 | 9.17 | 9.09 | 9.05 | 8.74 | 8.69 | 8.01 |
| 1 | clr | clr | clr | clr | clr | clr | clr | clr |
| 26 | clr | clr | clr | clr | clr | clr | clr | clr |
| 36 | ppt | clr | clr | clr | clr | clr | clr | clr |
| 40 | ppt | clr | clr | clr | clr | clr | clr | clr |
| 49 | ppt | ppt | ppt | clr | clr | clr | clr | clr |
| 63 | ppt | ppt | ppt | clr | clr | clr | clr | clr |
| At 26°C | | | | | | | | |
| 1 | clr | clr | clr | clr | clr | clr | clr | clr |
| 36 | clr | clr | clr | clr | clr | clr | clr | clr |
| 63 | clr | clr | clr | clr | clr | clr | clr | clr |

*ppt denotes precipitation, clr denotes clear solution*

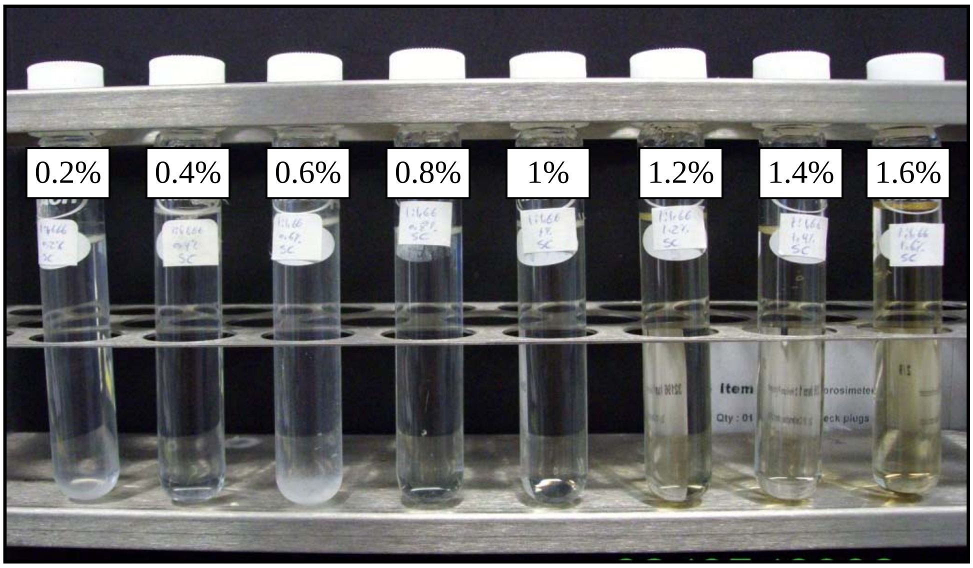


**Figure 5.6:** Effect of different alkali concentrations on the inhibitor performance

The effect of the inhibitor in viscosity performance was investigated using different alkali and acid concentrations and 0.6% surfactant concentration of SURF 4. All viscosity measurements were conducted at 90°C. The most interesting and important finding shown in Figure 5.7 is the large increment in the viscosity of acid-alkali-polymeric surfactant (AAPS) as compared to the acid-polymeric surfactant (AS) solution. For instance, when the AS solution was prepared without alkali, the viscosity of the solution was about 1.85 $mm^2$/sec which is 1.12 times the crude oil viscosity. However, when the alkali was added to the system to simulate AAPS slug, the viscosity of the AAPS system increased sharply and kept on increasing as the alkali concentration was increased. At 1.6% alkali concentration, the viscosity of the AAPS solution was found to be 2.935 $mm^2$/sec which is about 1.8 times the crude oil viscosity.

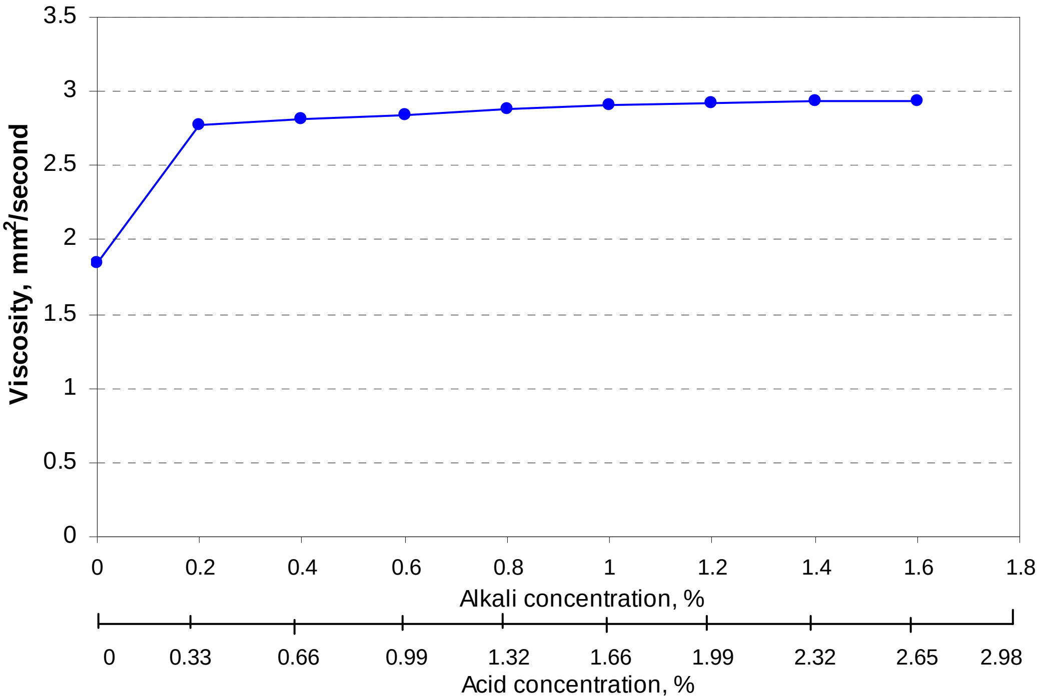


**Figure 5.7:** The effect of different alkali-acid concentrations on the viscosity performance using seawater (0.6% surfactant - 90°C)

The increase in the viscosity shown in Figure 5.7 is mainly due to the presence of the inhibitor and the excess amount of acrylic acid in the solution. The inhibitor is a compound that adsorbs on the metals surfaces, thereby providing a protective film bound around the cations. This film is thought to provide the resistance to sliding between the cationic bundles. The remaining free acrylic acid may also react with more cations to form more bound film complex. Further, the acrylic acid molecule is bigger compared to the metals molecules, and it is plausible that the bound effect may contribute to the increase in viscosity. This increase in the viscosity is essential to improve the sweep efficiency by preventing fingering due to reservoir heterogeneities. This feature makes the new AAPS slug a superior compared to the conventional ASP where the polymer is greatly affected by the alkali [94].

The effect of alkali concentration on viscosity performance of the polymeric surfactant with softened water was also investigated in this section. Figure 5.8 shows the viscosity performance in the absence and presence of different alkali concentrations using 0.4% surfactant concentration of SURF 1. It can be seen from this figure that the presence of the alkali with concentrations ranging from 0.2% to 1% did not affect the viscosity of the system. This figure also shows that the viscosity values for the range of sodium carbonate concentration investigated is basically the same (2.533 $mm^2/sec$). Unlike the conventional ASP formula, the viscosity of the polymeric surfactant is not affected by alkali incorporation.

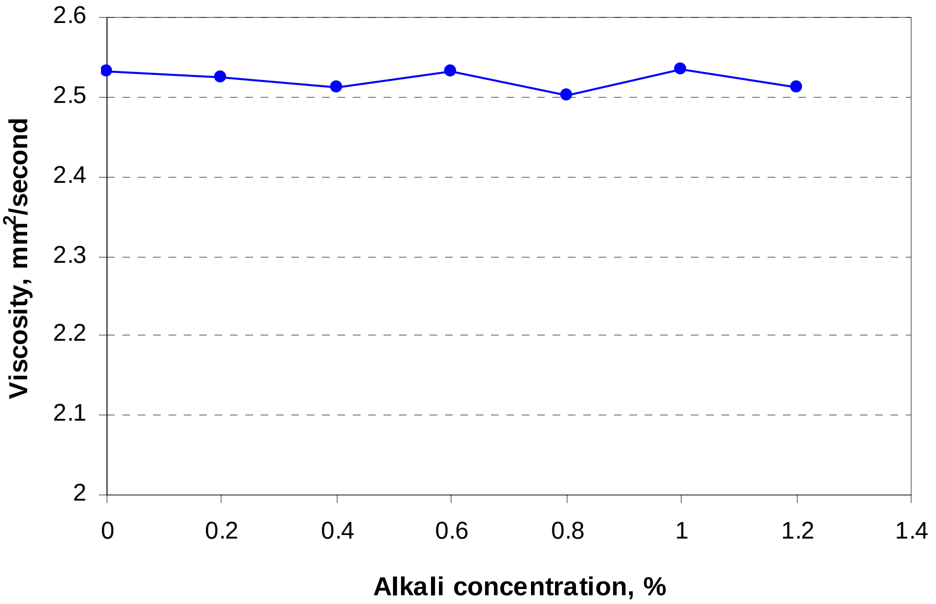


**Figure 5.8:** The effect of different alkali concentrations on the viscosity performance using softened water (0.4% surfactant - 90°C)

### 5.3 Interfacial Tension Measurements

The attainment of a low interfacial tension (IFT) is crucial in the immiscible displacement process in the porous media. Extensive IFT measurements were conducted to screen the best chemical formula for the usage of softened water and seawater. The IFT measurements were made between polymeric surfactant-water system, alkali-polymeric surfactant system, acid-polymeric surfactant system, acid-alkali-polymeric surfactant system, and Angsi crude oil. The surfactant concentrations of 0.4% and 0.6% were used for the softened water and seawater respectively. It should be noted that SURF 1 and SURF 4 were used for softened and seawater respectively.

Figure 5.9 shows the IFT between Angsi crude oil and various surfactant concentrations using softened water. The surfactant showed good results in terms of IFT reduction where the IFT between the crude oil and surfactant solution was reduced from 13.6 mN/m to 0.323 mN/m using 0.2% surfactant concentration. As can be seen in Figure 5.9, the IFT reduced drastically upon the addition of surfactant concentration which explains the surface adsorption and aggregative properties of the surfactant. Using 0.4% surfactant concentration of SURF 1, the IFT decreased to 0.192 mN/m where the interfacial tension was stabilized.

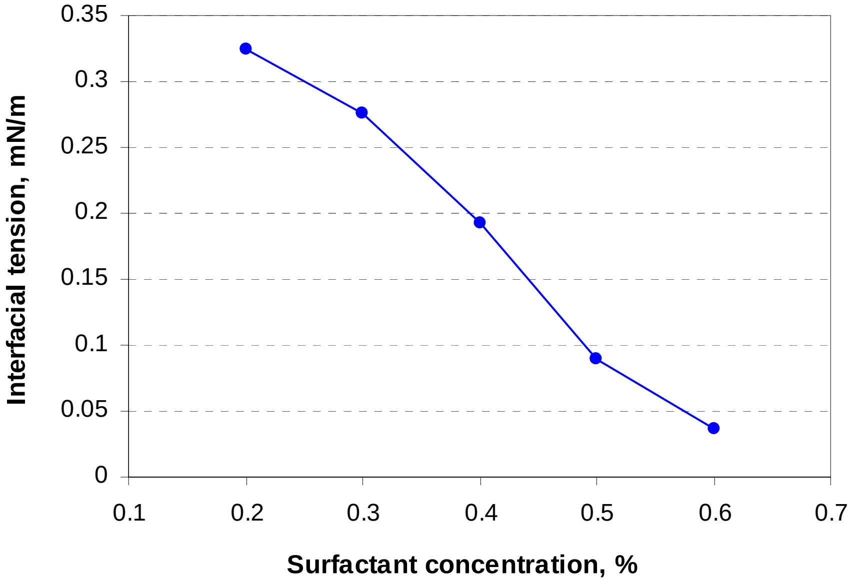


**Figure 5.9:** IFT between crude oil and various surfactant concentrations using softened water

Figure 5.10 shows the effect of different alkali concentrations on IFT performance using 0.4% surfactant with softened water. As can be seen in Figure 5.10, the IFT decreased significantly due to the addition of alkali concentration and reached 0.024 mN/m at 0.8% alkali. When the alkali concentration was 0.2%, IFT did not change much. However, significant reduction in the IFT was observed when the alkali concentration was increased from 0.2% to 0.8%. This rapid decrease in the IFT value is associated with the production of in-situ surfactants with the added surfactant to produce synergistic mixtures at the oil/brine interface. As a result, 0.8% alkali concentration was seen as the optimum concentration in the presence of 0.4% surfactant concentration of SURF 1.

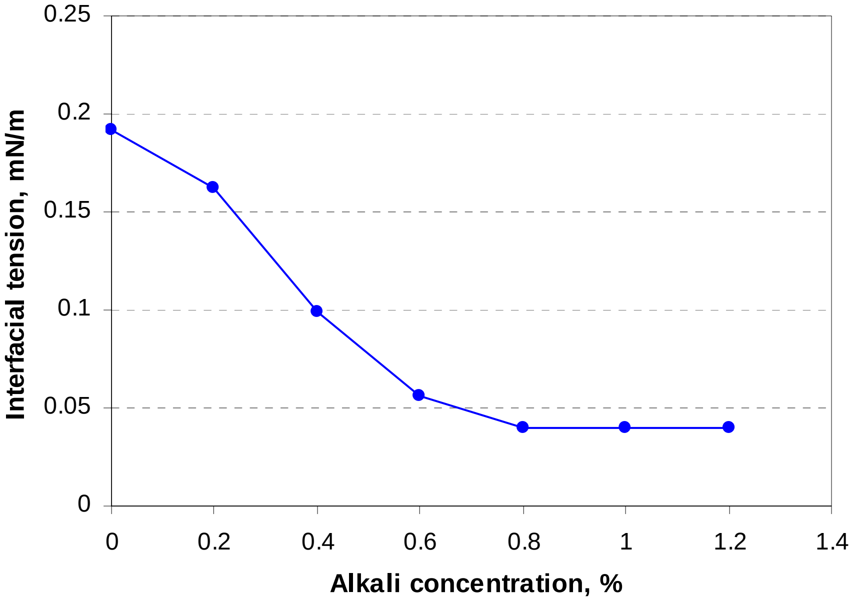


**Figure 5.10:** IFT between crude oil and various alkali concentrations in the presence of 0.4% surfactant using softened water

In the case of seawater, the effect of the acid on the surface activity of the polymeric surfactant was investigated using different acid concentrations and 0.6% surfactant concentration of SURF 4. No alkali was used in this test. As shown in Figure 5.11, the IFT between Angsi crude oil and surfactant solution was significantly affected by the presence of acid in the system. When there was no acid in the system, 0.6% surfactant concentration reduced the IFT from about 13.6 mN/m to 0.154 mN/m. However, a significant increase of the IFT was observed when the acid was introduced to the system. It was also observed that the IFT increases as the acid concentration was increased to 0.6%. This corresponds to the results obtained from the compatibility test when the surfactant and acid were combined. The increment in the IFT is mainly due to surfactant degradation caused by the reaction between the surfactant and the soluble $Ca^{2+}$ and $Mg^{2+}$ ions. The excess amount of the acid increases the solubility of the $Ca^{2+}$ and $Mg^{2+}$ ions. These ions then react with the surfactant molecule to form their salts that are less surface active.

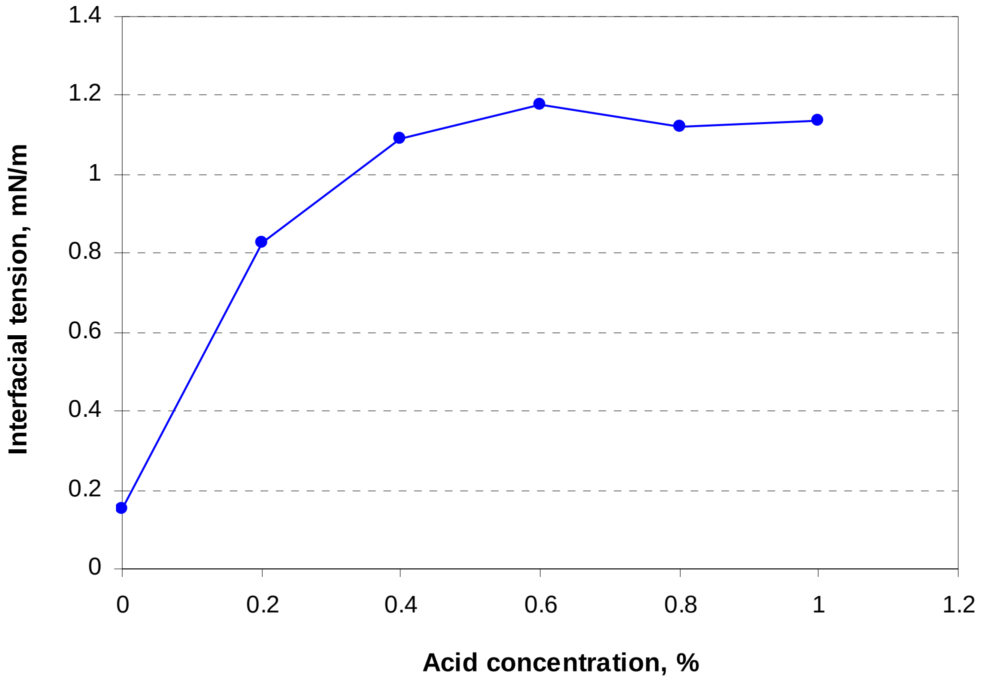


**Figure 5.11:** IFT between crude oil and various acid concentrations in the presence of 0.6% surfactant using seawater

Figure 5.12 shows the IFT measurements between the crude oil and full system of acid-alkali-polymeric surfactant. The effect of precipitation inhibitor in the IFT between crude oil and AAPS solution was investigated using different alkali-acid concentrations and 0.6% surfactant concentration. The acid concentration was set proportional to alkali concentration using the ratio 1.66:1. As can be seen from Figure 5.12, the IFT increased drastically with the addition of alkali and acid concentrations and remained constant as the alkali and acid concentrations were as high as 0.6% and 0.99% respectively. It was also observed that the IFT obtained from the combination of acid-alkali-polymeric surfactant is much lower than only acid and polymeric surfactant. This is associated with the change on salinity of system caused by the generated in-situ inhibitor and excess amount of acrylic acid. When the acid and alkali are used together with the polymeric surfactant, the generated inhibitor can block the active sits of the $Ca^{2+}$ and $Mg^{2+}$ ions resulting in a decrease on the salinity of the system. At a critical acid and alkali concentrations, the surfactant will be able to play its role of reducing the IFT. As shown in Figure 5.12, the critical acid and alkali concentrations were seen to be 0.99% and 0.6% respectively.

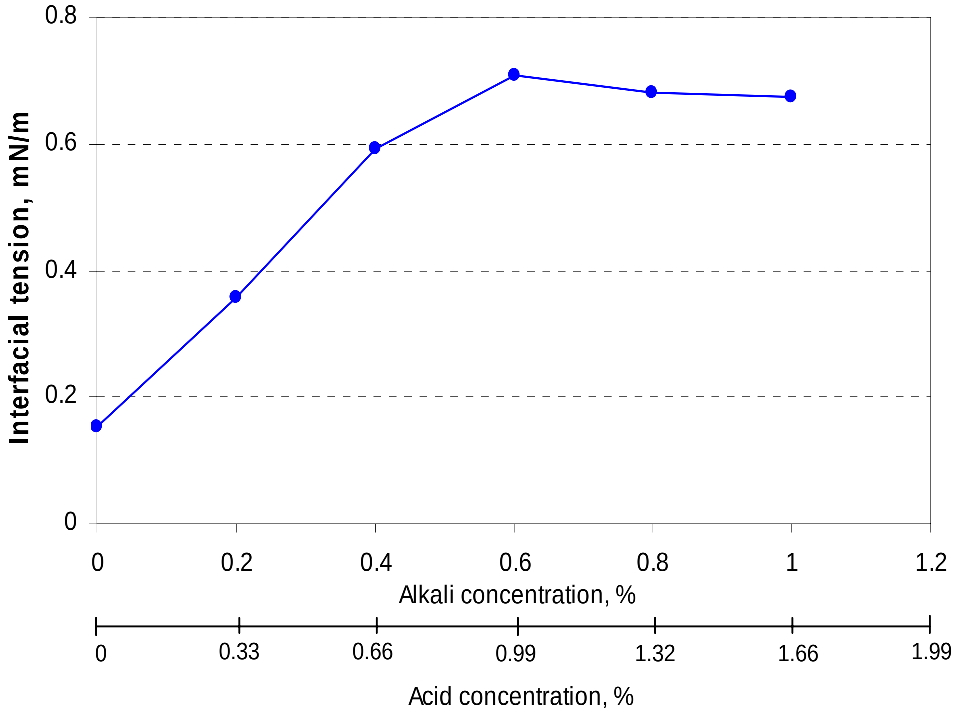


**Figure 5.12:** IFT between crude oil and various alkali-acid concentrations in the presence of 0.6% surfactant using seawater

## 5.4 Phase Behavior Test

The microemulsion behavior has been used to describe a micellar phase containing surfactant, brine, and oil in thermodynamic equilibrium. Winsor first described microemulsion phase behavior as type I (oil-in-water emulsion), type II (water-in-oil emulsion), and type III (a bicontinuous oil/water phase also known as a middle phase microemulsion) [148]. In the oil-in-water emulsion, oil molecules are solubilized within the micelle and water is the continuous phase. In water-in-oil, the reverse is the case and oil is the continuous phase. Previous investigators reported that the type of emulsion formed is dependent on the salinity of brine. At salinities less than optimal, most of the surfactant partition in the aqueous phase and consequently oil-in-water emulsion is formed (Type I). At salinities greater than optimal, most of the surfactant partition in the oil phase which results in the formation of water-in-oil emulsion (Type II). At optimal salinity, equal amount of oil and water are solubilized in the middle phase (Type III) microemulsion [63].

To help understand which chemical formula has the best potential to recover additional oil beyond water flooding, emulsification evaluations were performed at reservoir temperature for 24 days. The microemulsion test was conducted between alkali-polymeric surfactant (APS)/crude oil system and acid-alkali-polymeric surfactant (AAPS)/ crude oil system. The surfactant concentrations for softened and seawater were maintained at 0.4% and 0.6% respectively. Different sodium carbonate concentrations were applied to study the effect of alkali and inhibitor on the emulsion behavior. The formation of microemulsion for APS system and AAPS system is shown in Figure 5.13.

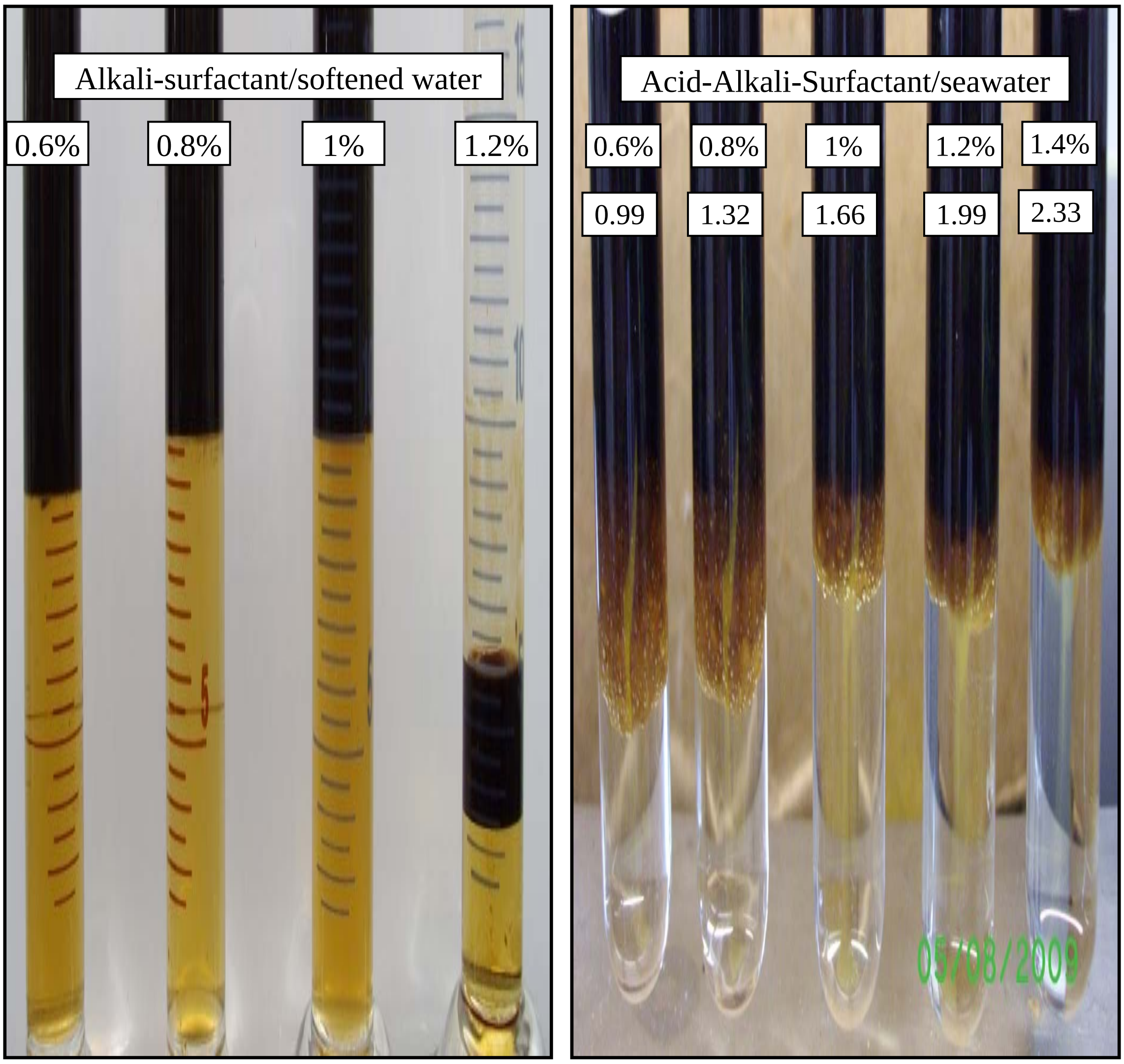


**Figure 5.13:** Phase behavior of APS/crude oil system and AAPS/crude oil system after 24 days at 90°C

Figure 5.13 shows the formation of oil-in-water microemulsion when softened water was used. This result is expected due to the low salinity of the softened water. It was also observed that the oil-in-water (Type I) emulsion increased over time, which suggests the interfacial tension between crude oil and chemical mixture remained low throughout the test period. On the other hand, alkali had not much influence on the formed microemulsion due to the low acid number of Angsi crude oil and also because of the low salinity. Almost the same microemulsion was observed with 0.6% and 1.2% alkali concentration. This indicates that the emulsification action was mostly due to the presence of the 0.4% surfactant concentration of SURF 1.

In the case of the AAPS system, all the AAPS solutions possess a middle phase microemulsion (type III). Type III microemulsion is unique and favorable because both interfaces have equal volumes and low IFT. However, as the alkali and acid concentrations increased, the middle phase microemulsion volume was decreased due to the reduction of the salinity. This decreases the surfactant concentration in the middle phase, resulting in an increase of IFT in the middle phase microemulsion [63]. This is corresponding with results obtained from IFT measurement as illustrated in Figure 5.12. The IFT was increased as the alkali-acid concentrations were increased.

## 5.5 Static Surfactant Adsorption

Surfactant adsorption is detrimental for an enhanced oil recovery process as it results in surfactant loss and reduces surfactant activity. The adsorption of surfactant from aqueous solution in the absence and presence of different alkali concentrations were investigated using softened and seawater. It should be noted that when the surfactant solution was prepared using seawater, 0.6% acid was used to keep the solution free from precipitation. The adsorption of surfactant for each case was determined by comparing the obtained refractive index after equilibrium with an initially plotted calibration curve. The calibration curve represents a plot of refractive index for varying of surfactants. All the calibration curves and refractive index readings are given in Appendix C.

Figure 5.14 presents the adsorption isotherms of different surfactant concentrations in softened water. The surfactant adsorption was increased as the surfactant concentration was increased. At low surfactant concentration, the surfactant adsorption occurred mainly due to ion exchange. When the surfactant concentration exceed 0.3%, the adsorption increment progressed at a lower rate with the increase of surfactant concentration. This indicates that the adsorption has to overcome the electrostatic repulsive force between surfactant and the similarly charged solid in these surfactant concentrations. This figure also shows that when the surfactant concentration was 0.6%, the saturation adsorption of the surfactant on sand was almost reached. The saturation adsorption was estimated to be 1.31 mg/g-sand. From these results, it could be concluded that the adsorption of the surfactant on sand is a function of surfactant concentration. When a dilute surfactant concentration is used, the corresponding loss of the surfactant will be lower than the saturation adsorption of the surfactant.

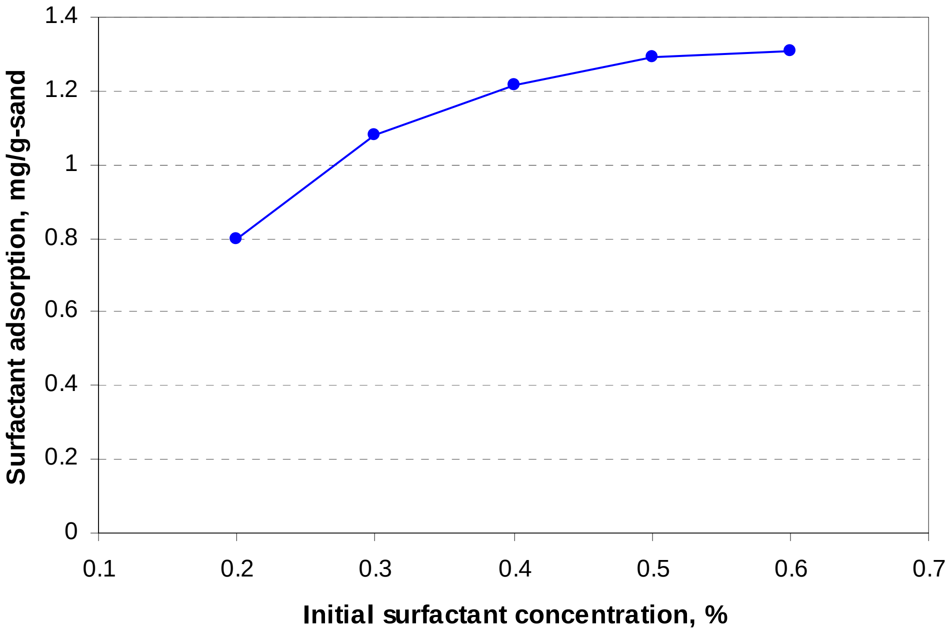


**Figure 5.14:** Adsorption isotherm of different surfactant concentrations using softened water at 90$^o$C

In the case of seawater, more surfactant adsorption was observed as compared to the usage of softened water (Figure 5.15). For instance, at 0.6% surfactant concentration, the adsorption was 1.31 mg/g-sand in the case of softened water where the saturation adsorption was reached while 2.59 mg/g-sand was observed with the use of seawater. There are two main reasons for this behavior. The first is the presence of acid in the system which decreased the pH of the surfactant concentration from about 10 to 4.5. The low pH increases the electrostatic attraction between the surfactant and the negatively charged sand, driving more surfactant to the sand surface. The second reason is the high salinity of the seawater which increases the ionic strength in solution. Moreover, the increase of the adsorption with increase of surfactant concentration could be due to presence of multi-component surfactant mixture as stated by Austad et al. [121]. This makes multi layers of the surfactant to be adsorbed on the solid surface, which causes adsorption to a greater degree than that required for the formation of a monolayer.

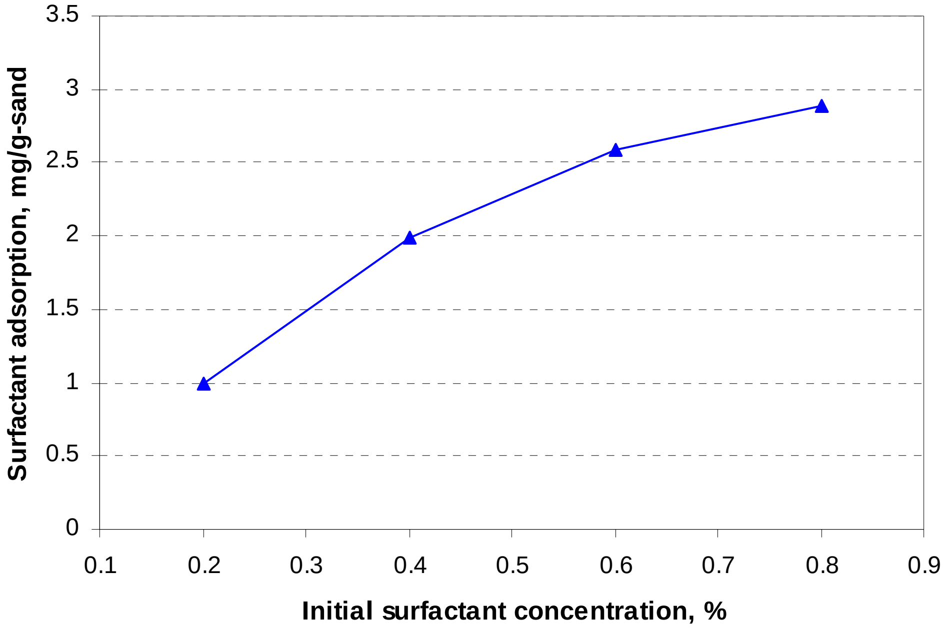


**Figure 5.15:** Adsorption isotherm of different surfactant concentrations using seawater at 90°C

Figure 5.16 shows the effect of alkali on surfactant adsorption with the use of softened water. Different sodium carbonate concentrations with 0.4% surfactant concentrations were used in this test. The surfactant adsorption decreased considerably with the addition of alkali to the surfactant solution. This is because high pH makes the sand surface more negative, and the electrostatic repulsive force drives more surfactant to solution. As shown in Figure 5.16, when the alkali was introduced to the system, the surfactant adsorption was reduced from 1.21 mg/g-sand to 0.79 mg/g-sand due to the introduction of 0.2% alkali to the solution. When the alkali concentration was over 0.6%, the saturation adsorption of the surfactant on sand was optimal, as shown by the adsorption isotherm. The saturation adsorption was estimated to be about 0.4 mg/g-sand.

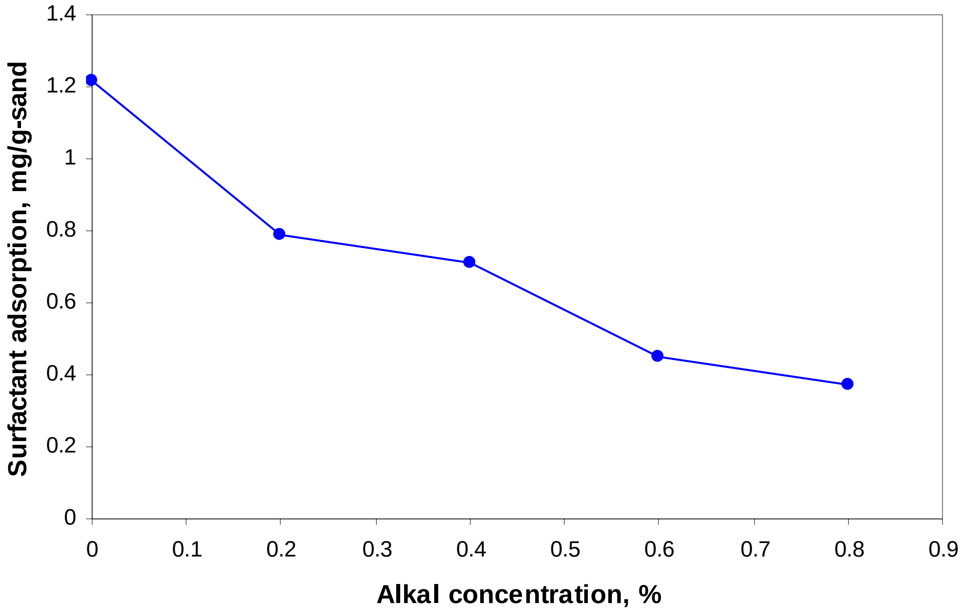


**Figure 5.16:** The effect of different alkali concentration on surfactant adsorption isotherms at 90°C

Figure 5.17 shows the surfactant adsorption isotherm when the three components are combined using natural seawater. The effect of alkali-acid concentrations on surfactant adsorption was investigated using 0.6% surfactant. The acid concentration was proportional to the alkali concentration using the ratio of 1.66:1. As shown in Figure 5.17, the surfactant adsorption decreased significantly when small alkali and acid concentrations were added to the system, while considerable increase was observed when the alkali and acid concentrations were increased. When the alkali and acid concentrations were 0.2% and 0.33% respectively, surfactant adsorption reduced from 2.59 mg/g-sand to 1.12 mg/g-sand due to the increase in the pH from 4.1 to 9.45. However, with further increases of alkali-acid concentrations, the surfactant adsorption increased gradually but it is still lower than that in the systems without alkali and acid. The increase of surfactant adsorption corresponds to the decline in the pH caused by presence of acid in the solution. As the alkali and acid concentrations increase, more in-situ inhibitor and free acid would be present in the system. The multi-component surfactant mixture may also increase the surfactant adsorption amount as stated by as stated by Austad et al. [121].

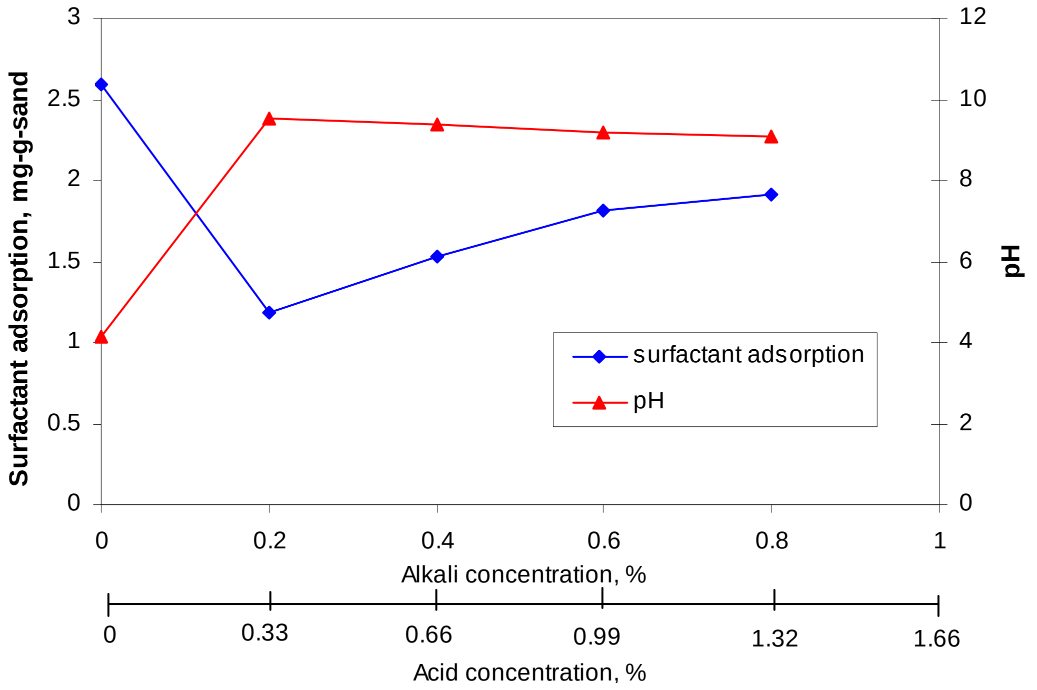


**Figure 5.17:** The effect of different alkali-acid concentrations on surfactant adsorption isotherms at 90$^o$C.

## 5.6 Optimization Process for AAPS and APS Formulas

Although the proposed Acid-Alkali-Polymeric Surfactant and Alkali-Polymeric Surfactant formulations have shown promising potential in the screening tests, it is a relatively new technology for chemical EOR, and is not a technically well developed. Therefore, core flood experiments are essential to evaluate the influential parameters in order to design a cost-effective injection strategy for the target oil residual oil remains. In this study, 15 core flood tests were conducted to determine the optimum conditions for the developed formulas. With these tests, the incremental in oil recoveries of different chemical injections were obtained, and the achievable synergy of AAPS and APS were examined. The effects of chemical concentrations and slug size on oil recovery performance were also investigated for the usage of softened water and seawater. The cores properties and core flood results for the AAPS system and APS system are summarized in Table 5.5 and Table 5.6 respectively. For all the displacement processes, similar injection strategy was used for all the experiments including acid-alkali-polymeric surfactant and alkali-polymeric surfactant systems.

**Table 5.5:** Summary of core flood tests for acid-alkali-polymeric surfactant system using seawater

| | Surfactant affect | | | | Alkali affect | | | Slug size affect | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Run 1 | Run 2 | Run 3 | Run 4 | Run 5 | Run 2 | Run 6 | Run 7 | Run 2 | Run 8 |
| ***Chemical data*** | | | | | | | | | | |
| Acid concentration. % | 0.99 | 0.99 | 0.99 | 0.99 | 0.33 | 0.99 | 1.66 | 0.99 | 0.99 | 0.99 |
| Alkali concentration. % | 0.6 | 0.6 | 0.6 | 0.6 | **0.2** | **0.6** | **1** | 0.6 | 0.6 | 0.6 |
| Surfactant concentration. % | **0.2** | **0.6** | **1** | **1.2** | 0.6 | 0.6 | 0.6 | 0.6 | 0.6 | 0.6 |
| ***Core data*** | | | | | | | | | | |
| Permeability, md | 102 | 105 | 104 | 86 | 100 | 105 | 78 | 64.1 | 105 | 86.9 |
| Porosity, % | 16.8 | 17.27 | 16.8 | 16.4 | 17.4 | 17.27 | 15.9 | 15.2 | 17.27 | 16.2 |
| Pore volume, ml | 14.4 | 13.9 | 14.2 | 13.9 | 14.6 | 13.9 | 13.4 | 12.8 | 13.9 | 13.1 |
| OOIP, ml | 9 | 7 | 8 | 8.3 | 9.5 | 7 | 9 | 7.5 | 7 | 8 |
| ***Slugs size*** | | | | | | | | | | |
| Initial waterflood slug (PV) | 3.74 | 3.87 | 4.21 | 3.58 | 3.54 | 3.87 | 3.28 | 4.04 | 3.87 | 3.50 |
| Chemical flood slug (PV) | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | **0.3** | **0.5** | **1** |
| Extended waterflood slug (PV) | 4.66 | 5.38 | 4.94 | 5.09 | 4.31 | 5.38 | 4.37 | 4.18 | 5.38 | 5.07 |
| ***Recovery data*** | | | | | | | | | | |
| waterflood recovery (% OOIP) | 57.7 | 58.5 | 61.2 | 63.8 | 48.4 | 58.5 | 48.1 | 52.9 | 58.5 | 55.1 |
| AAS recovery (% OOIP) | **7.2** | **18.8** | **20.0** | **21.3** | **12.2** | **18.8** | **8.2** | **8.6** | **18.8** | **20.0** |
| AAS recovery (% ROIP) | 17.1 | 45.5 | 51.6 | 59.0 | 23.6 | 45.5 | 15.8 | 18.4 | 45.5 | 44.5 |
| Total recovery (% OOIP) | 65.0 | 77.4 | 81.2 | 85.1 | 60.6 | 77.4 | 56.3 | 61.6 | 77.4 | 75.1 |

**Table 5.6:** Summary of core flood tests for alkali-polymeric surfactant system using softened water

| | Surfactant affect | | | Alkali affect | | | Slug size affect | | |
|---|---|---|---|---|---|---|---|---|---|
| | Run 1 | Run 2 | Run 3 | Run 4 | Run 2 | Run 5 | Run 6 | Run 2 | Run 7 |
| ***Chemical data*** | | | | | | | | | |
| Alkali concentration. % | 0.8 | 0.8 | 0.8 | **0.2** | **0.8** | **1** | 0.8 | 0.8 | 0.8 |
| Surfactant concentration. % | **0.4** | **0.6** | **1** | 0.6 | 0.6 | 0.6 | 0.6 | 0.6 | 0.6 |
| ***Core data*** | | | | | | | | | |
| Permeability, md | 88.4 | 113 | 84.9 | 82 | 113 | 94 | 76 | 113 | 71 |
| Porosity, % | 15.7 | 16.4 | 16.9 | 16.5 | 16.4 | 16.4 | 15.9 | 16.4 | 15.7 |
| Pore volume, ml | 13.3 | 13.2 | 14.5 | 13.9 | 13.2 | 13.2 | 13.2 | 13.2 | 13.4 |
| OOIP, ml | 7.9 | 8 | 8 | 8.2 | 8 | 8.3 | 9 | 8 | 8.9 |
| ***Slugs size*** | | | | | | | | | |
| Initial waterflood slug (PV) | 3.59 | 3.47 | 2.76 | 2.86 | 3.47 | 3.33 | 5.43 | 3.47 | 4.47 |
| Chemical flood slug (PV) | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | **0.3** | **0.5** | **1** |
| Extended waterflood slug (PV) | 4.09 | 4.11 | 3.54 | 3.64 | 4.11 | 5.04 | 4.70 | 4.11 | 4.72 |
| ***Recovery data*** | | | | | | | | | |
| waterflood recovery (% OOIP) | 48.1 | 53.7 | 56.2 | 50.0 | 53.7 | 54.2 | 49.8 | 53.7 | 49.4 |
| AS recovery (% OOIP) | **12.6** | **16.2** | **20.7** | **12.8** | **16.2** | **9.0** | **11.4** | **16.2** | **17.1** |
| AS recovery (% ROIP) | 24.3 | 35.1 | 47.4 | 25.6 | 35.1 | 19.7 | 22.8 | 35.1 | 3.8 |
| Total recovery (% OOIP) | 60.7 | 70.0 | 77.0 | 62.8 | 70.0 | 63.2 | 61.3 | 70.0 | 66.6 |

### 5.6.1 Effect of Surfactant Concentration

Based on a series of tests: from compatibility tests, IFT measurements, phase behaviour tests, and surfactant adsorption tests, the chemical formulas of 0.99% acid, 0.6% alkali, 0.6% polymeric surfactant and 0.8% alkali, 0.4% polymeric surfactant were determined as the best formulas for the seawater and softened water respectively. However, in order to examine the effectiveness of the new polymeric surfactant for enhanced oil recovery application, four runs with different surfactant concentrations (0.2%, 0.6%, 1%, and 1.2%) were conducted to confirm the optimum concentration for the AAPS system. For each run, alkali and acid concentrations were kept constant at 0.6% and 0.99% respectively.

Table 5.5 presents the results of these runs and Figure 5.18 shows the recovery performance as a function of pore volume injected. The recovery increased as the surfactant concentration was increased in the surfactant concentration tested. However, the oil recovery significantly increased when the surfactant concentration was increased from 0.2 to 0.6%. In run 1 with 0.2% surfactant concentration, only 7.2% OOIP was recovered after the injection of 0.5PV of AAPS slug followed by 4.66PV chase water. This is due to the unfavourable mobility ratio caused by the low surfactant concentration. However, with 0.6% surfactant in Run 2, 18.8% OOIP was produced over water flooding when 0.5 PV of AAS slug was injected and followed by 5.38 PV chase water. This indicates that the mobility control between the AAPS and crude oil was essential for the new system. By using 0.6% surfactant concentration, an ultra low IFT and improved sweep efficiency could be achieved as compared to a lower surfactant concentration. Though Run 3 and Run 4 had a higher injected surfactant concentration, the incremental oil recovery was not significant as compared with Run 2. This could be attributed to the high adsorption when the surfactant concentration exceeds 0.6% as discussed earlier in section 5.5. From these results, it could be concluded that 0.6% surfactant is the optimum surfactant concentration for the AAPS system.

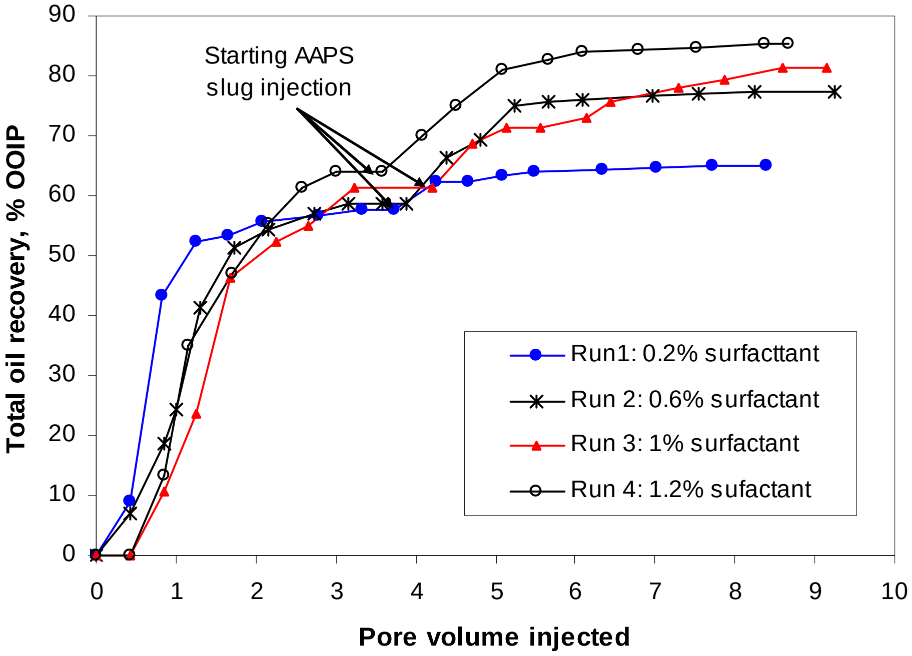


**Figure 5.18:** Effect of surfactant concentration on oil recovery in acid-alkali polymeric surfactant flooding system

For APS system, three core flood runs were conducted to investigate the effect of the polymeric surfactant concentration. The alkali concentration used was the same for all runs. Figure 5.19 shows that Run 3 with the highest surfactant concentration (1%) had accomplished a better performance in enhanced oil recovery than Run 2 (0.6%) and Run 1 (0.4%). Run 2 and Run 3 recovered 16.2% OOIP and 20.7% OOIP when 0.5% PV of APS slug was followed by chase water respectively. In Run 1 with the lowest surfactant concentration produced only 12.6 % OOIP after the injection of 0.5 PV of APS slug followed by extend waterflood. Base on the IFT and phase behaviour tests, the high oil recovery from Run 2 and Run 3 were due to the synergistic effect between surfactant and alkali to emulsify and mobilize the crude oil. However, with 0.4% surfactant concentration (Run 1), the recovery mechanism was only due to the formed microemulsion as a result of the low IFT observed during IFT test. The surfactant viscosity was not sufficient to mobilize the emulsified crude oil. Based on these results, the screened surfactant concentration from the screening study conducted prior to the core flood test was not effective in core flood test. Therefore, in order to design a cost and effective slug, 0.6% surfactant is selected as the optimum surfactant concentration for the APS system.

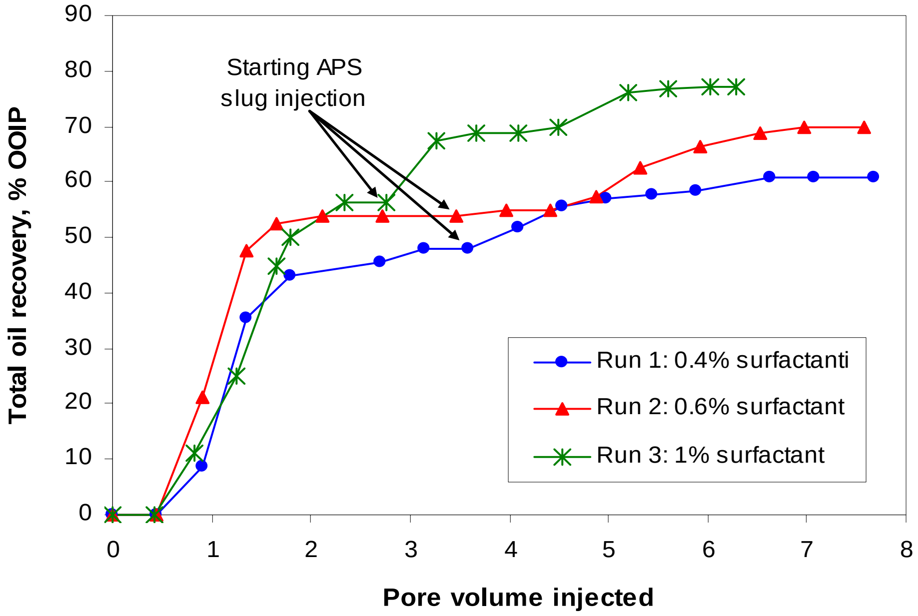


**Figure 5.19:** Effect of surfactant concentration on oil recovery in alkali-polymeric surfactant flooding system

### 5.6.2 Effect of Alkali Concentration

To evaluate the effect of alkali-acid concentration (generated in situ inhibitor) on residual oil recovery in the proposed AAPS formula, two runs (Run 5 and Run 6) with different alkali concentrations were conducted to compare them with run 2 using 0.6% alkali concentration. The concentration of surfactant in these runs was kept constant at 0.6% and the acid concentration was proportional to alkali concentration using the ratio of 1.66:1. A comparison of recoveries for different alkali-acid concentrations is plotted in Figure 5.20. From this figure, Run 2 with 0.6% alkali concentration showed higher oil recovery than Run 5 with 0.2% alkali and Run 6 with 1% alkali. Run 2 yielded 18.8 % OOIP while Run 6 had recovered only 8.2% OOIP, despite Run 6 possessing a higher alkali concentration. The reason for the low oil recovery in Run 6 is probably that the surfactant adsorption and the IFT were too high due to the presence of acid. On the other hand, the reason for the low oil recovery in Run 5 corresponding to the results obtained from compatibility test. At low alkali concentration, the in situ generated inhibitor is not sufficient to prevent precipitations. Hence, some precipitation may be occurred due to the reaction between the AAPS slug and brine presented in the core. Based on these results, 0.99% acid, 0.6% alkali and 0.6% polymeric surfactant were selected as the optimum concentrations for the AAPS system.

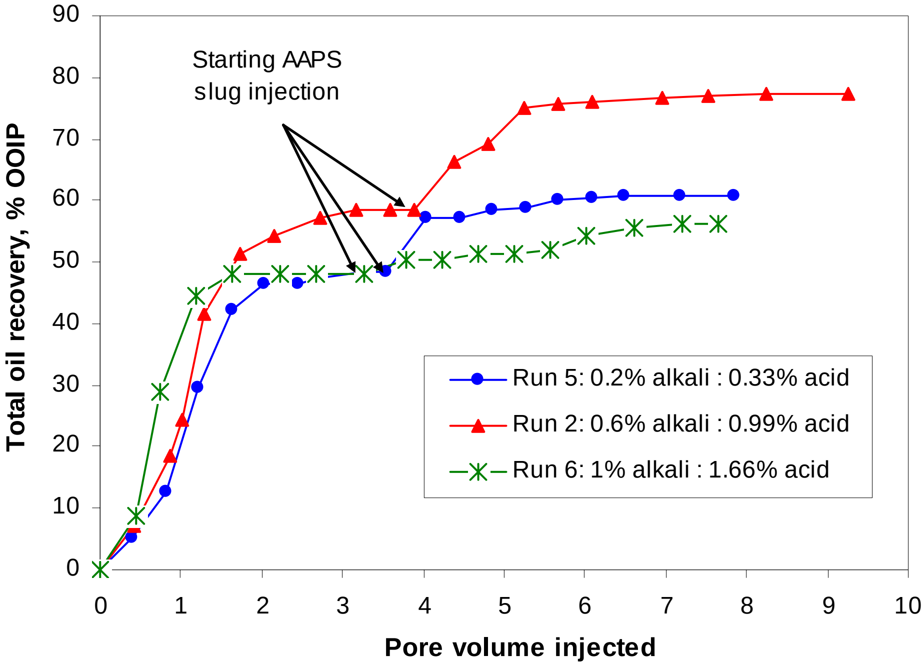


**Figure 5.20:** Effect of alkali concentration on oil recovery in acid-alkali-polymeric surfactant flooding system

In the case of APS, two runs (Run 4 and Run 5) were conducted using 0.2% and 1% alkali concentration. The surfactant concentration was kept constant at 0.6% as the optimum concentration. Figure 5.21 shows the recovery comparison between Run 4 and Run 5 with Run 2 which uses different alkali concentration but same surfactant concentration. The oil recovery profile in Figure 5.21 shows that Run 2 with 0.8% alkali had the highest oil recovery. APS slug recovered 16.2% OOIP in Run 2, which was higher than the 12.8% OOIP of Run 4 and 9% OOIP of Run 5. Though Run 5 had the highest alkali concentration, the oil recovery achieved was lower than in Run 2 and Run 5. This is because of the large amount of oil-in-emulsion caused by the high alkali concentration used during this run. Figure 5.22 shows the amount of the oil-in-water emulsion formed during Run 5 and Run 4. When a high alkali concentration was used in Run 5, more oil-in-water emulsion was observed due to the low salinity. Most of the surfactant remained in the aqueous phase, resulting in a very low water-microemulsion IFT and increasing oil-microemulsion IFT [63]. This type of emulsion makes the aqueous phase more viscous. The extend water flood would bypass this viscous phase, resulting in a poor sweep efficiency. On the other hand, Run 2 with 0.8% alkali had better synergistic effect with crude in forming emulsion, with a suitable emulsion viscosity. The chase water could flow simultaneously with the APS slug, displacing more oil. As a result, 0.8% alkali and 0.6% polymeric surfactant were selected as the optimum concentrations for the APS system.

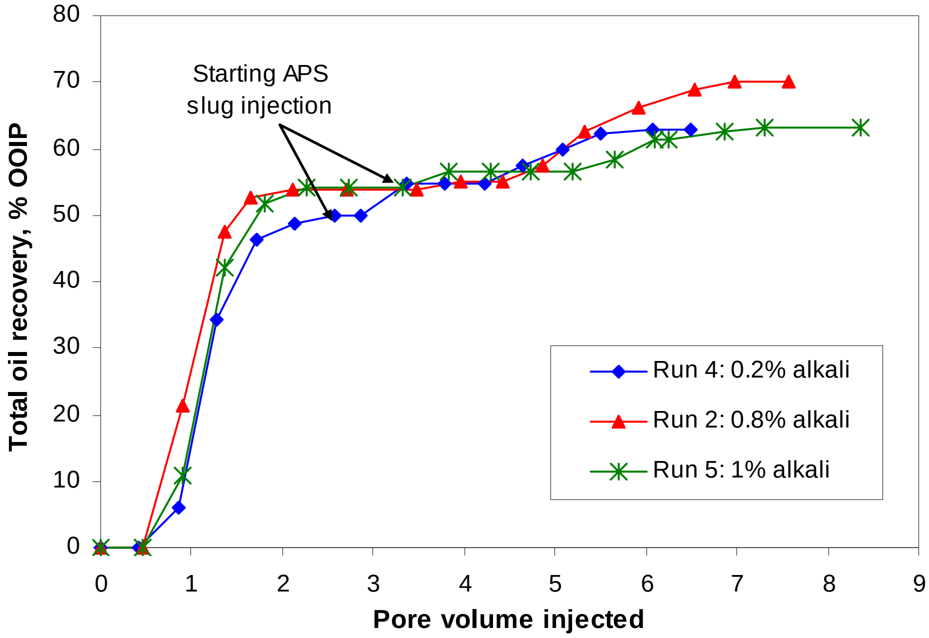


**Figure 5.21:** Effect of alkali concentration on oil recovery in alkali-polymeric surfactant flooding system

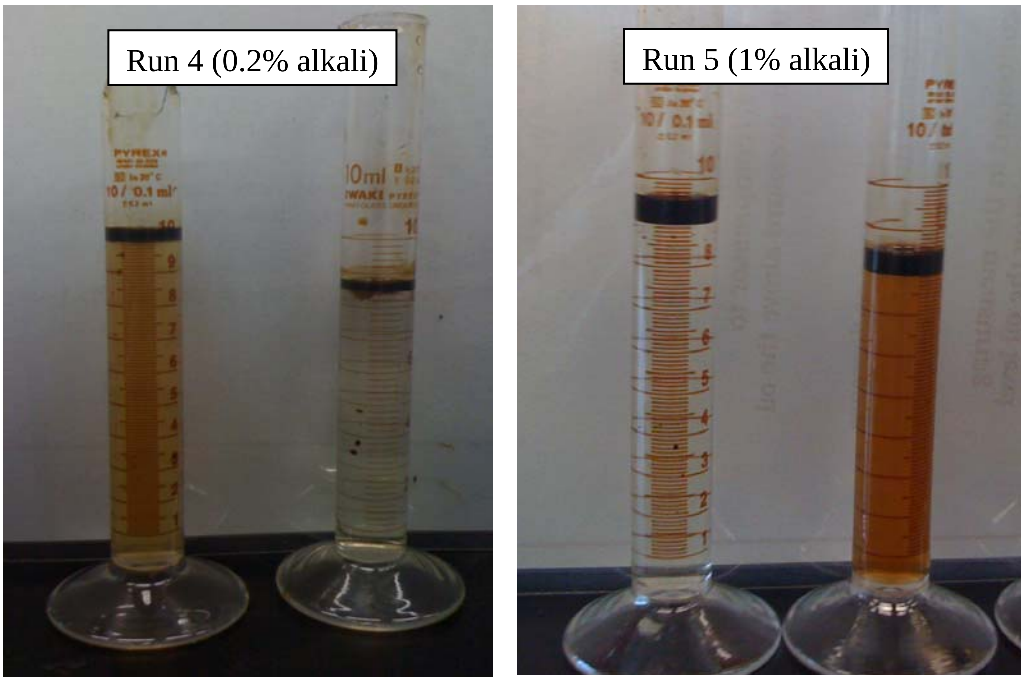


**Figure 5.22:** Oil-in-water emulsion formed during Run 4 and Run 5

On the basis of the above core flood results, 0.99% acid, 0.6% alkali, and 0.6% polymeric surfactant were selected as the optimum concentrations for the AAPS formulation, while 0.8% alkali and 0.6% polymeric surfactant were chosen as the optimum concentrations for APS formulation. These concentrations were used in the later core flood tests to investigate the effect of slug size on the recovery performance.

### 5.6.3 Effect of slug size

Determining the smallest effective chemical slug size to minimize chemical consumption and recover maximum residual oil is one of the most important criteria in the optimization process. To investigate the effect of slug size, the optimum alkali and surfactant concentrations for the AAPS system and APS system were used. Keeping these chemical concentrations constant, a series of experiments was performed using different chemical slug size.

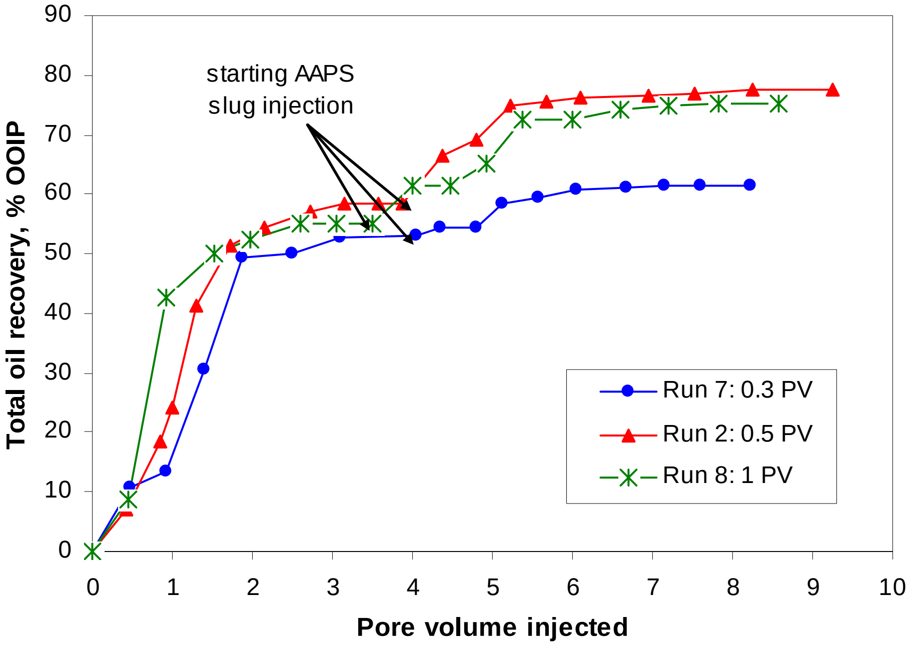


**Figure 5.23:** Effect of slug size on oil recovery in acid-alkali-surfactant flooding system

For the AAPS system, the AAPS slug size was varied from 0.3 PV in Run 7, 0.5 PV in Run 2, and 1 PV in Run 8. The tertiary oil recoveries as a function of injected pore volume are plotted in Figure 5.23. The tertiary oil recovery is significantly improved as the slug size was increased up to 0.5 PV in Run 2. Only 8.6% OOIP was recovered when 0.3 PV of AAPS slug was injected and followed by chase water, while 18.8% OOIP and 20% OOIP were produced when the AAPS slug was increased to 0.5 PV in Run 2 and 1 PV in Run 8 respectively. Obviously, 0.3 PV of AAPS slug was not effective in forming an oil bank for recovering waterflooded residual oil as compared to Run 2 and Run 8. However, only a small incremental recovery was observed when the AAS slug size was increased from 0.5 PV to 1 PV. This means that the injection of 0.5PV of AAPS slug is effective and therefore more economical than other relatively larger slug size.

Figure 5.24 shows the oil recovery performance as a function of different slug sizes for APS system. The APS slug size was varied from 0.3 PV in Run 6, 0.5 PV in Run 2, and 1 PV in Run 7. As shown in Figure 5.24, the same trend was observed with the APS system as compared to AAPS system. The recovery performance was much improved as the slug size was enlarged from 0.3 PV to 0.5 PV. However, when the slug size of APS system was increased to 1 PV in Run 7, tertiary oil recovery produced 17.1% OOIP which was higher than 16.2% OOIP of Run 2 using 0.5 PV. Therefore, 0.5 PV is considered as the optimum slug size for the APS system.

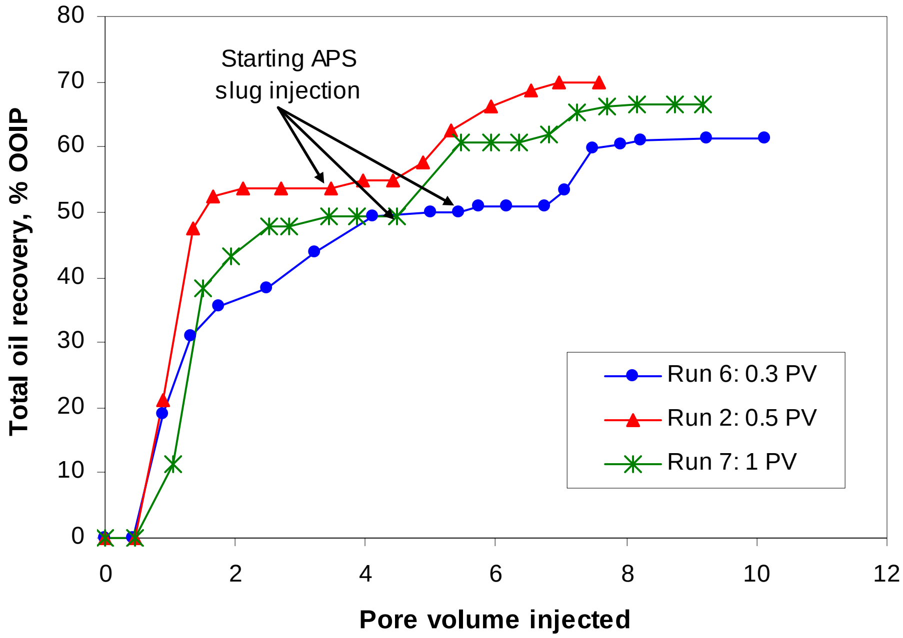


**Figure 5.24:** Effect of slug size on oil recovery in alkali-polymeric surfactant flooding system

## 5.7 Summary

Divalent metal cations are one of the main factors limiting the application of chemical flooding in enhanced oil recovery process. The AAPS flooding formulation was developed to overcome the precipitation problems caused by calcium and magnesium ions. The APS formulation was also developed to simulate the conventional ASP flooding. The experimental results showed that the generated in-situ inhibitor was very effective in preventing calcium and magnesium precipitations. Sodium carbonate was found to be the best alkali candidate for the new system. The acid to sodium carbonate ratio of 1.66:1 was found to be the optimum ratio to keep the solution free from precipitations for 90 days at 90°C. The high alkali concentration generated more in-situ inhibitor and thus the pH of the solution was decreased. The presence of the alkali with concentrations ranging from 0.2% to 1% did not affect the viscosity of APS system. Whereas, viscosity of AAPS system was increased with the increase of alkali and acid concentrations.

Interfacial tension measurements indicated that the addition of alkali would significantly reduce the IFT between Angsi crude oil and aqueous solution in the APS system. However, an increase In the IFT was observed as the alkali acid concentrations were increased in the AAPS system.

Middle phase microemulsion was observed with the combination of AAPS system while a large oil-in-water emulsion was observed in case of APS system. Surfactant adsorption on sand has also been discussed, along with the effects of alkali concentration, inhibitor and salinity. It was found that adsorption would decrease in the presence of alkali and acid, despite a slight increase on the surfactant adsorption with the increase of alkali and acid concentrations in the case of AAPS system.

Acid-alkali-polymeric surfactant and alkali-polymeric surfactant flooding in Berea cores were discussed in this chapter. Fifteen core flood tests were carried out to determine the optimum conditions for enhanced oil recovery. The optimum chemicals concentration for the AAPS system was determined as 0.99% acid, 0.6% alkali, 0.6% polymeric surfactant. The optimum concentration for the APS system was found to be 0.8% alkali and 0.6% polymeric surfactant. These concentrations had the best performance in mobilizing and driving the crude oil after waterflooding. Injection of 0.5PV of the formulated slugs of AAPS and APS followed by chase water produced an additional 18.8% OOIP and 16.2% OOIP over water flooding respectively. Inspection of the recovery performance during the core flood tests also revealed that the high alkali concentration could increase the microemulsion formation and the in-situ inhibitor, but could not improve the oil recovery. The large microemulsion increased the viscosity of the APS slug while the high amount of in-situ inhibitor increased both the IFT and the surfactant adsorption.

# CHAPTER 6

# CONCLUSIONS AND RECOMMENDATIONS

## 6.1 Conclusions

In this study, the objectives mentioned in the first chapter were accomplished in two main parts. In the first part, new conventional and polymeric surfactants based on Jatropha oil were successfully synthesized. In the second part, new chemical formulation that takes care of the divalent metal cations was developed and its effectiveness in enhanced oil recovery was investigated. The optimum chemicals concentration and the suitable injection strategy for the Acid-Alkali-Polymeric Surfactant (AAPS) system were determined. The biggest benefit of the new system is its use of seawater rather than softened water while maintaining the desired slug properties. This makes the new AAPS formula an attractive and cost-effective agent for chemical EOR particularly for offshore field application.

Based on the findings and results obtained from the first part, it can be concluded that the non-edible Jatropha oil can potentially be used as surfactant raw material. Production of sodium methyl ester sulfonate (SMES) based on non-edible Jatropha oil can satisfy EOR requirements. This is because the non-edible Jatropha oil is an inexpensive, natural and renewable raw material. SMES provides good surfactant properties at low cost, and therefore a strong economic incentive to substitute SDS and other commercial surfactants in EOR applications.

On the basis of the results obtained from IFT and viscosity measurements, the polymeric methyl ester sulfonate (PMES) showed excellent properties for IFT reduction and viscosity control. The grafting of SMES onto a polymer to produce PMES offers many benefits compared to the existing chemical EOR methods. The presence of both the surfactant and polymer as one component system makes the PMES easier to handle especially in offshore application. Based on Angsi crude oil viscosity, SURF 1 with a concentration of 0.4% was the best for the usage of softened water, while SURF 4 with a concentration of 0.6% was found to be the optimum for seawater application.

Based on the analysis of a comprehensive screening study, the optimum chemicals concentration for the new formulations of AAPS and APS have been determined. The in-situ inhibitor was very effective in preventing the $Ca^{2+}$ and $Mg^{2+}$ precipitations over 90 days at 90°C. Sodium carbonate to acid weight ratio of 1.66:1 was found to be the optimum ratio to keep the solution clear without any precipitations. The most interesting and important feature of the AAPS system is the large increment in the viscosity of AAPS solution. This feature makes the new formula superior to the conventional ASP process.

Results from the optimization process in coreflood tests indicated that 0.99% acid with 0.6% alkali and 0.6% polymeric surfactant had the best performance for enhanced oil recovery, while 0.8% alkali and 0.6% polymeric surfactant was found to be the optimum condition for APS system. These concentrations had the best performance in mobilizing and driving the crude oil after waterflooding. Using the optimum concentrations, only a small incremental oil recovery was obtained with slugs higher than 0.5 PV for both cases. Injection of 0.5 PV of the formulated slugs followed by chase water produced an additional 18.8% and 16.2% OOIP over water flood for AAPS system and APS system respectively.

## 6.2 Recommendations and future work

Several recommendations are made for future work:

1. The surfactant to acrylamide ratio of 1:1.6 was selected as the optimum ratio for IFT reduction and viscosity control with the use of seawater. Lower surfactant to acrylamide ratio should be tested in the polymerization reaction. This allows the use of low polymeric surfactant concentration for viscosity control.

2. Acid-alkali-seawater compatibility should be investigated using a combination of sodium carbonate and sodium bicarbonate. This combination is expected to provide a lower acid to alkali ratio.

3. The phase behavior tests used in this study were performed using seawater and softened water. More phase behavior tests should be conducted using different brine salinities to determine the optimum salinity for the polymeric surfactant and alkali.

4. More core flood experiments should be conducted to the study the performance of only the polymeric surfactant with brine. Injection of polymeric surfactant slug followed by alkali slug should also be investigated.

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147. S. Laishun, “An approach to the flam retardation and smoke suppression of ethylene-vinyl acetate copolymer by plasma grafting of Acrylamide,” *Reactive and Functional Polymers*, vol. 45, pp. 85-93, 2000.

148. P.A. Winsor, “Solvent Properties of Amphiphilic Compounds” *Butterworth Scientific Publications*, London, 1954.

# Appendix A

## List of Chemicals

| Chemicals | Brand |
|---|---|
| Methanol (99.5%) | Analytical reagent (AR) grade |
| Sulfuric acid (99%) | Analytical reagent (AR) grade |
| Potassium hydroxide | Merck |
| Chlorosulfonic acid (97%) | For synthesis, Merck |
| Pyridine (99.5%) | Analytical reagent (AR) grade, Merck |
| Ether (99.7) | Merck |
| N-butanol (99.5%) | Merck |
| Acrylamide (≥99%) | For synthesis, Merck |
| Potassium persulfate (99%) | Systerm, ChemAR |
| Acetone | Merck |
| Acrylic acid | Aldrich |
| Sodium bicarbonate | Sigma-Aldrich |
| Sodium carbonate | Systerm, ChemAR |
| Sodium hydroxide | Systerm, ChemAR |
| Sodium chloride | Systerm, ChemAR |
| Calcium chloride | Systerm, ChemAR |
| Magnesium chloride | Systerm, ChemAR |
| Potassium chloride | Systerm, ChemAR |

## Appendix B

## Fluid-Fluid Compatibility Tests

**Table B-1:** Sodium hydroxide-acid compatibility test after 90 days at 90 $^oC$

| days | 0.3% in sea water | 1:0.3 | 1:1 | 1:1.66 | 1:2.33 | 0.3% in softened water |
|---|---|---|---|---|---|---|
| | pH | | | | | |
| | 10.9 | 11.1 | 11.06 | 11 | 5.73 | 11.63 |
| 0 | ppt | ppt | ppt | Cloud | clear | clear |
| 1 | ppt | ppt | ppt | Cloud | clear | clear |
| 2 | ppt | ppt | ppt | Cloud | clear | clear |
| 3 | ppt | ppt | ppt | Cloud | clear | clear |
| 4 | ppt | ppt | ppt | ppt | clear | clear |
| 8 | ppt | ppt | ppt | ppt | clear | clear |
| 12 | ppt | ppt | ppt | ppt | clear | ppt |
| 19 | ppt | ppt | ppt | ppt | clear | ppt |
| 22 | ppt | ppt | ppt | ppt | clear | ppt |
| 33 | ppt | ppt | ppt | ppt | clear | ppt |
| 36 | ppt | ppt | ppt | ppt | clear | ppt |
| 40 | ppt | ppt | ppt | ppt | clear | ppt |
| 43 | ppt | ppt | ppt | ppt | clear | ppt |
| 54 | ppt | ppt | ppt | ppt | clear | ppt |
| 76 | ppt | ppt | ppt | ppt | clear | ppt |
| 90 | ppt | ppt | ppt | ppt | clear | ppt |
| pH | 7.85 | 8.51 | 8.01 | 7.68 | 5.81 | 12.19 |

**Table B-2:** Sodium bicarbonate-acid compatibility test after 90 days at 90 $^oC$

| days | 0.3% in sea water | 1:0.3 | 1:1 | 1:1.66 | 1:2.33 | 0.3% in softened water |
|---|---|---|---|---|---|---|
| | pH | | | | | |
| | 9.63 | 9.31 | 5.63 | 4.86 | 4.33 | - |
| 0 | clear | clear | clear | clear | clear | clear |
| 1 | clear | clear | clear | clear | clear | clear |
| 6 | clear | clear | clear | clear | clear | clear |
| 7 | ppt | clear | clear | clear | clear | clear |
| 15 | ppt | clear | clear | clear | clear | clear |
| 19 | ppt | ppt | clear | clear | clear | clear |
| 22 | ppt | ppt | clear | clear | clear | clear |
| 36 | ppt | ppt | clear | clear | clear | clear |
| 40 | ppt | ppt | clear | clear | clear | clear |
| 43 | ppt | ppt | clear | clear | clear | clear |
| 47 | ppt | ppt | clear | clear | clear | clear |
| 54 | ppt | ppt | clear | clear | clear | clear |
| 76 | ppt | ppt | clear | clear | clear | clear |
| 90 | ppt | ppt | clear | clear | clear | clear |
| pH | 8.13 | 6.73 | 7.19 | 5.05 | 4.51 | - |

**Table B-3:** Sodium carbonate-acid compatibility test after 90 days at 90 °C

| days | 0.3% in sea water | 1:0.3 | 1:1 | 1:1.66 | 1:2.33 | 0.3% in softened water |
|---|---|---|---|---|---|---|
| | pH | | | | | |
| | 10.64 | 10.4 | 10.22 | 5.7 | 5.02 | 12.24 |
| 0 | ppt | Cloud | clear | clear | clear | clear |
| 1 | ppt | Cloud | clear | clear | clear | clear |
| 2 | ppt | Cloud | clear | clear | clear | clear |
| 3 | ppt | Cloud | clear | clear | clear | clear |
| 4 | ppt | ppt | clear | clear | clear | clear |
| 5 | ppt | ppt | clear | clear | clear | clear |
| 6 | ppt | ppt | clear | clear | clear | clear |
| 7 | ppt | ppt | clear | clear | clear | clear |
| 8 | ppt | ppt | clear | clear | clear | clear |
| 12 | ppt | ppt | clear | clear | clear | clear |
| 15 | ppt | ppt | clear | clear | clear | clear |
| 19 | ppt | ppt | clear | clear | clear | clear |
| 22 | ppt | ppt | clear | clear | clear | clear |
| 26 | ppt | ppt | ppt | clear | clear | clear |
| 29 | ppt | ppt | ppt | clear | clear | clear |
| 33 | ppt | ppt | ppt | clear | clear | clear |
| 36 | ppt | ppt | ppt | clear | clear | clear |
| 40 | ppt | ppt | ppt | clear | clear | ppt |
| 43 | ppt | ppt | ppt | clear | clear | ppt |
| 47 | ppt | ppt | ppt | clear | clear | ppt |
| 54 | ppt | ppt | ppt | clear | clear | ppt |
| 76 | ppt | ppt | ppt | clear | clear | ppt |
| 90 | ppt | ppt | ppt | clear | clear | ppt |
| pH | 7.95 | 9.6 | 7.44 | 6.64 | 5.5 | 11.03 |

# Appendix C

## Surfactant Adsorption Measurements

**Table C-1:** Surfactant adsorption measurement in the absence of alkali using sea water

| 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|
| Initial Surfactant conc. % | RI after equilibrium | RI before equilibrium | Surfactant conc. After equilibrium % | Surfactant adsorption after equilibrium mg/g-sand |
| 0.2 | 1.34092 | 1.34110 | 0.101 | 0.99 |
| 0.4 | 1.34110 | 1.34150 | 0.201 | 1.99 |
| **0.6** | **1.34138** | **1.34168** | **0.341** | **2.59** |
| 0.8 | 1.34160 | 1.34195 | 0.511 | 2.89 |

(2) and (3) refractive index before and after equilibrium
(4) surfactant concentration after equilibrium obtained from calibration curve
(5) surfactant adsorption calculated by Equation 3.2

Experimental conditions

Total mass of surfactant solution = 10 grams
Total mass of sand = 10 grams
Equilibrium time = 5 days
Test temperature = 90$^o$C

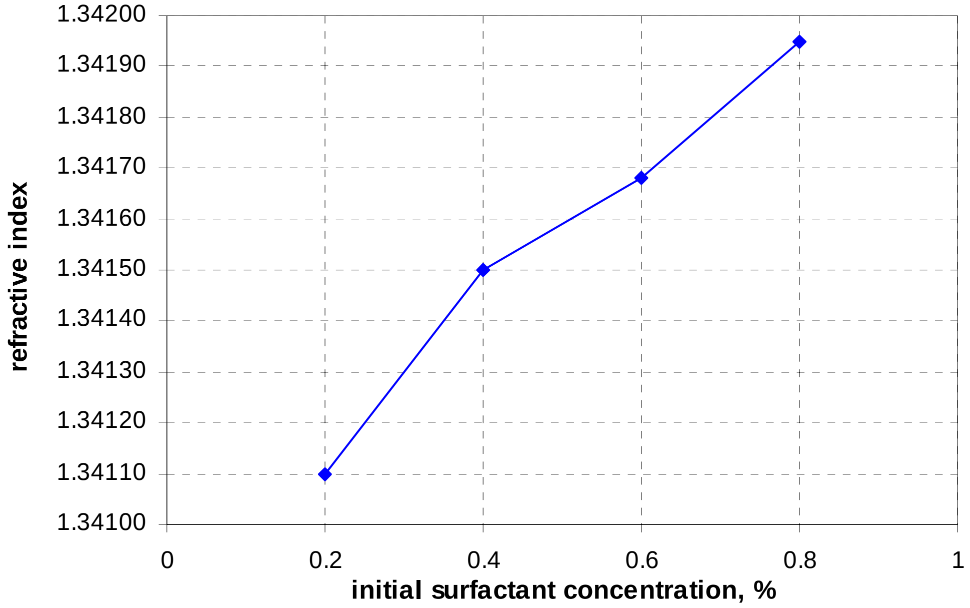


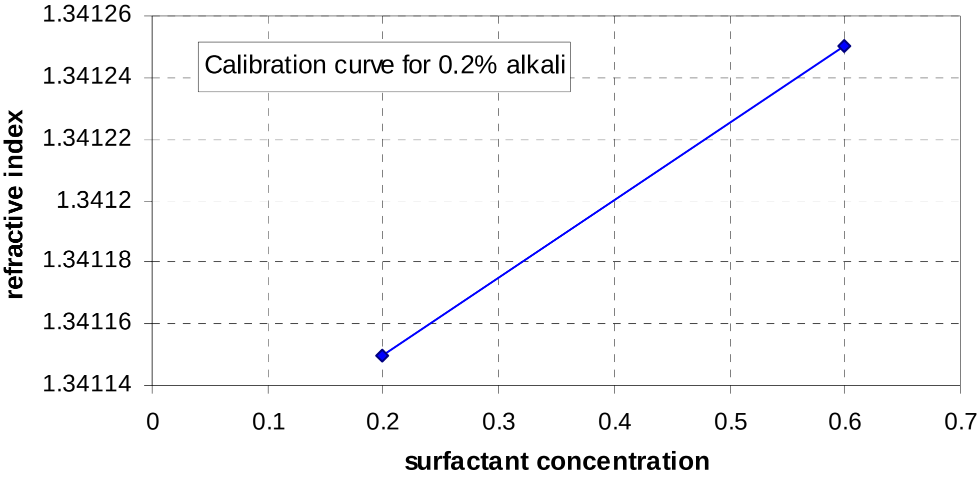
Figure C-1: calibration curve for determining surfactant concentration after equilibrium

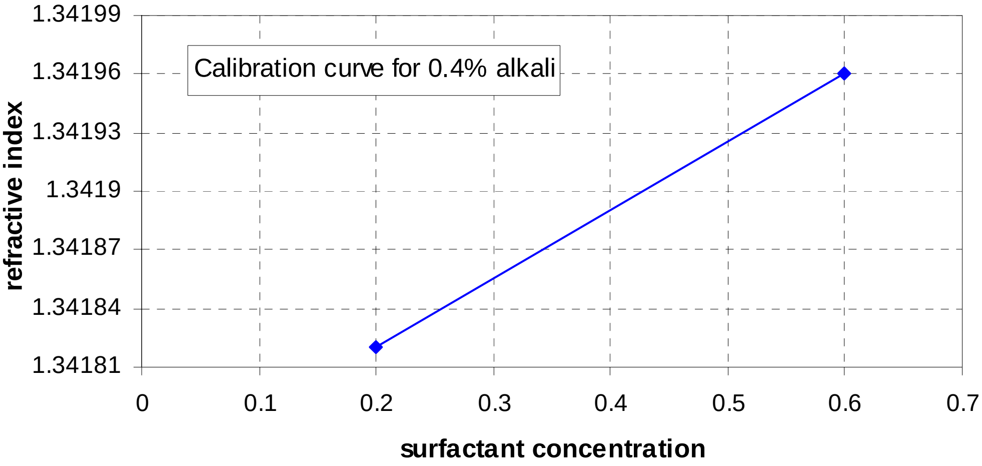
**Table C-2:** Surfactant adsorption measurement in the presence of 0.6% surfactant and various alkali-acid concentrations using sea water

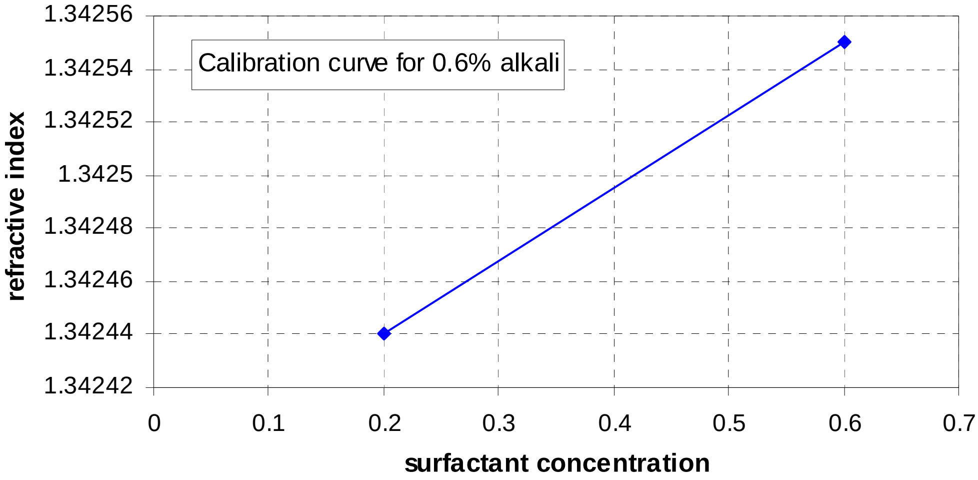
| Alkali conc. % | RI after equilibrium | RI before equilibrium | Surfactant conc. After equilibrium % | Surfactant adsorption after equilibrium mg/g-sand |
|---|---|---|---|---|
| 0.2 | 1.34122 | 1.34125 | 0.481 | 1.19 |
| 0.4 | 1.34191 | 1.34196 | 0.447 | 1.53 |
| **0.6** | **1.34250** | **1.34255** | **0.418** | **1.82** |
| 0.8 | 1.34312 | 1.34321 | 0.409 | 1.91 |

Experimental conditions

Total mass of surfactant solution = 10 grams
Total mass of sand = 10 grams
Equilibrium time = 5 days
Test temperature = 90°C






Calibration curve for 0.6% alkali
refractive index
1.34256
1.34254
1.34252
1.3425
1.34248
1.34246
1.34244
1.34242
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
surfactant concentration

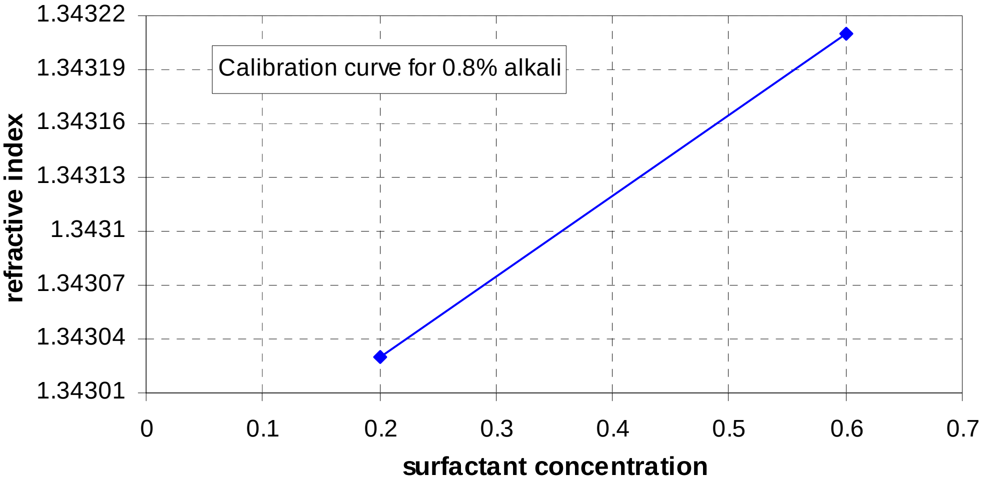

Calibration curve for 0.8% alkali
refractive index
1.34322
1.34319
1.34316
1.34313
1.3431
1.34307
1.34304
1.34301
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
surfactant concentration

**Table C-3:** Surfactant adsorption measurement in the absence of alkali using softened water

| Initial Surfactant conc. % | RI after equilibrium | RI before equilibrium | Surfactant conc. After equilibrium % | Surfactant adsorption after equilibrium mg/g-sand |
|---|---|---|---|---|
| 0.2 | 1.33527 | 1.33534 | 0.147 | 0.795 |
| 0.3 | 1.33537 | 1.33546 | 0.228 | 1.08 |
| **0.4** | **1.33549** | **1.33562** | **0.319** | **1.215** |
| 0.5 | 1.33563 | 1.33574 | 0.414 | 1.29 |
| 0.6 | 1.33569 | 1.33580 | 0.525 | 1.3125 |

Experimental conditions

Total mass of surfactant solution = 6 grams
Total mass of sand = 4 grams
Equilibrium time = 5 days
Test temperature = 90°C

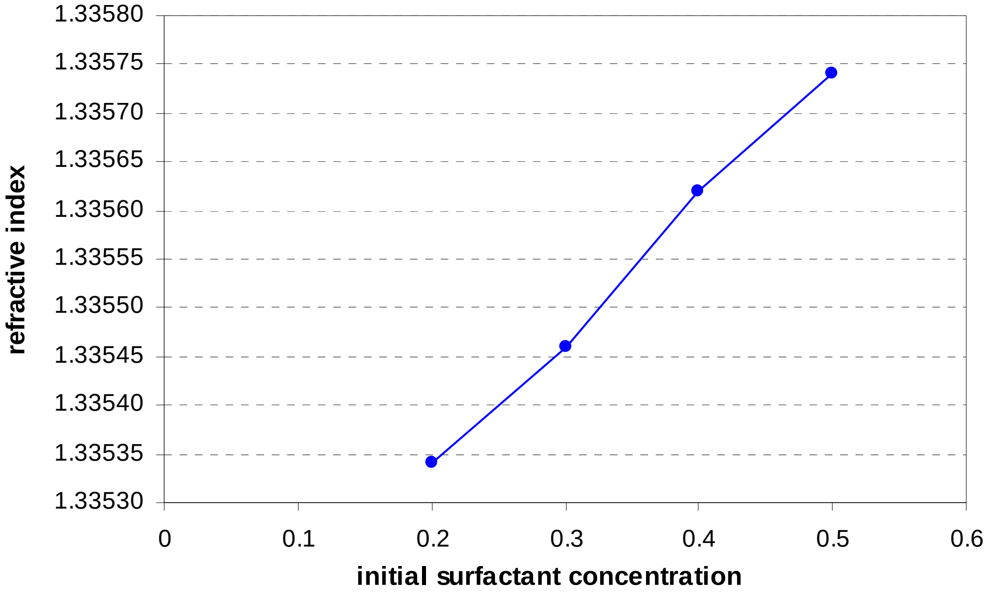


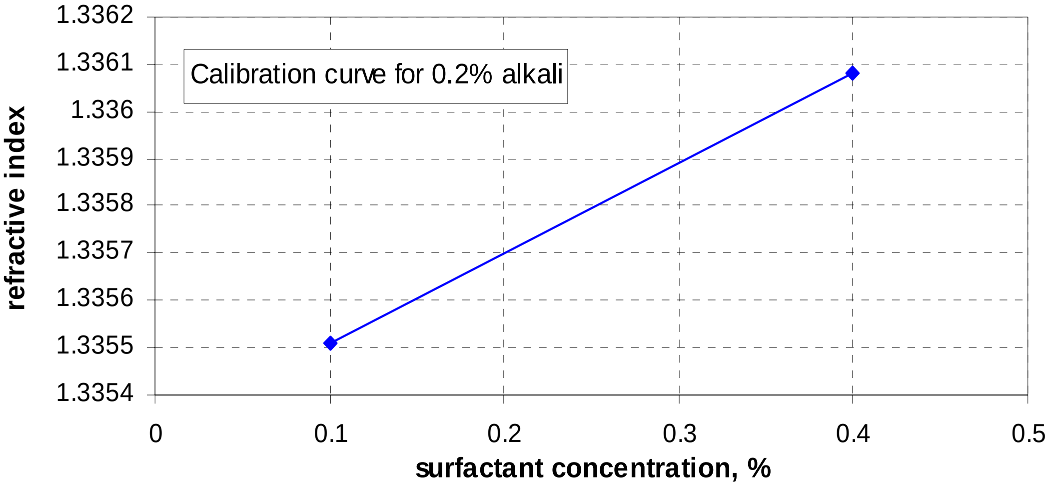
Figure C-2: calibration curve for determining surfactant concentration after equilibrium

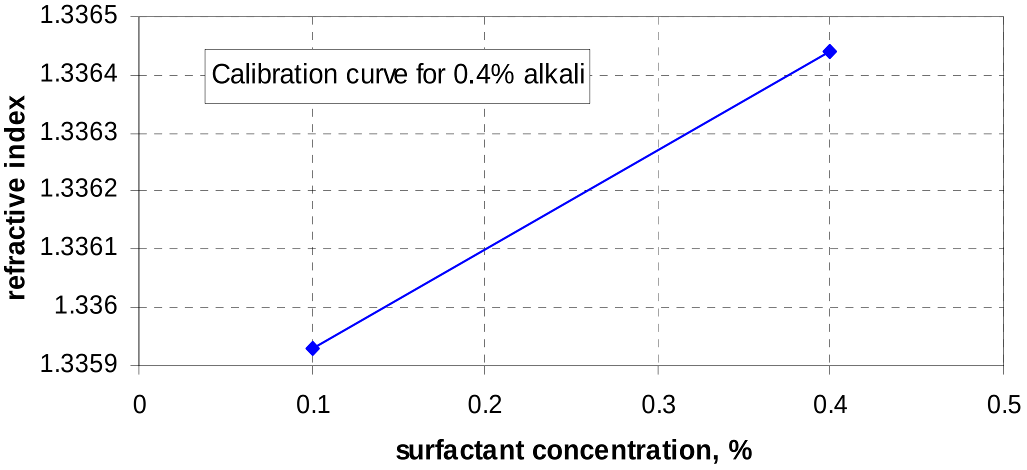
**Table C-4:** Surfactant adsorption measurement in the presence of 0.4% surfactant and various alkali concentrations using softened water

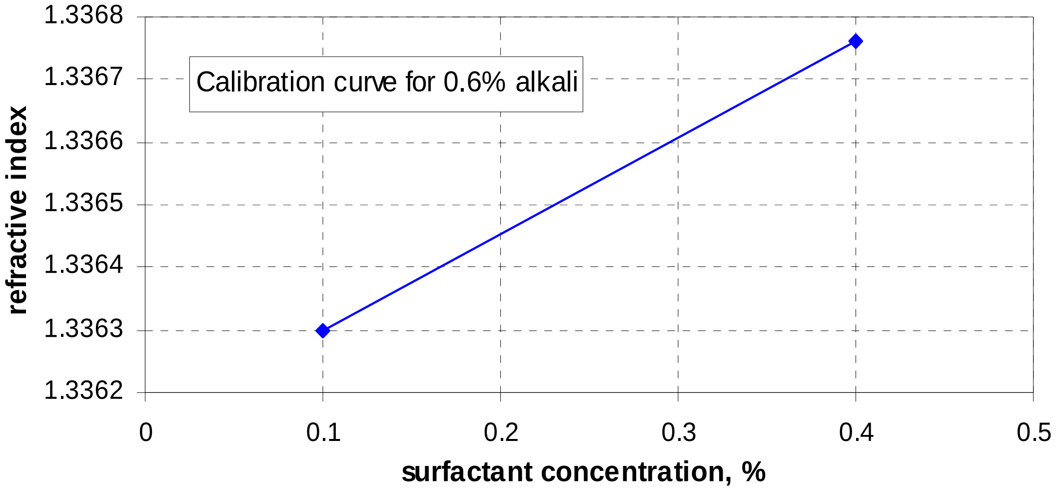
| Alkali conc. % | RI after equilibrium | RI before equilibrium | Surfactant conc. After equilibrium % | Surfactant adsorption after equilibrium mg/g-sand |
|---|---|---|---|---|
| 0.2 | 1.33593 | 1.33608 | 0.321 | 0.79 |
| 0.4 | 1.33632 | 1.33644 | 0.329 | 0.71 |
| 0.6 | 1.33669 | 1.33676 | 0.355 | 0.45 |
| 0.8 | 1.33717 | 1.33722 | 0.363 | 0.37 |

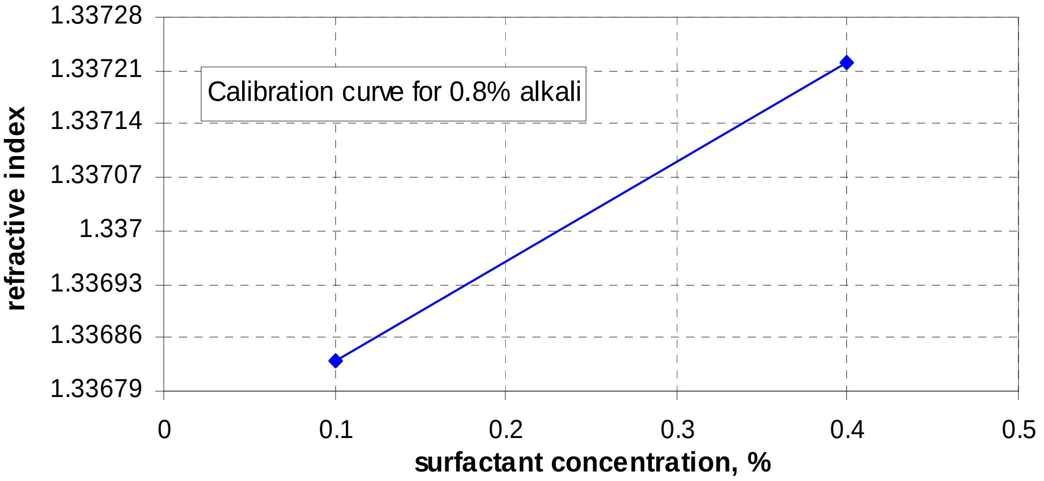
Experimental conditions

Total mass of surfactant solution = 6 grams
Total mass of sand = 6 grams
Equilibrium time = 5 days
Test temperature = 90$^{o}$C






Calibration curve for 0.6% alkali
refractive index
1.3368
1.3367
1.3366
1.3365
1.3364
1.3363
1.3362
0
0.1
0.2
0.3
0.4
0.5
surfactant concentration, %


Calibration curve for 0.8% alkali
refractive index
1.33728
1.33721
1.33714
1.33707
1.337
1.33693
1.33686
1.33679
0
0.1
0.2
0.3
0.4
0.5
surfactant concentration, %

# Appendix D

## List of Publications

1. Elraies, K. A. Tan, I. Saaid, I. (2009). Synthesis and Performance of a New Surfactant for Enhanced Oil Recovery. *International Journal of Petroleum Science and Technology*, India. ISSN 0973-6328, Volume 3, (1), pp. 1–9.

2. Elraies, K. A. Tan, I. Awang, M., and Saaid, I. (2009). Synthesis and Performance of Sodium Methyl Ester Sulfonate for Enhanced Oil Recovery. *Petroleum Science and Technology*, UK. Paper ID, LPET-2009-0120. R1. In press.

3. Elraies, K. A. Tan, I. Fathaddin, M., and Abo-jabal, A. (2009). Development of a New Polymeric Surfactant for Chemical Enhanced Oil Recovery. *Petroleum Science and Technology*, UK. Paper ID, LPET-2009-0342. R1. In press.

4. Elraies, K. A., and Tan, I. (2010). Design and Application of a New Chemicals Combination System for Chemical EOR. *BIT's 1st Annual World Congress of Well Stimulation and EOR* (WSEOR). April 12-14, Chengdu, China.

5. Elraies, K. A., Tan, I., and Fathaddin, T. M. (2010). Improved ASP Process Using a New Chemicals Combination System. International Conference on Integrated Petroleum Engineering and Geosciences, June 15-17. Kuala Lumpur, Malaysia.

6. Tan, I., Elraies, K. A., Saaid, I. (2010). Design of a New Polymeric Surfactant for Enhanced Oil Recovery Application. International Conference on Integrated Petroleum Engineering and Geosciences, June 15-17. Kuala Lumpur, Malaysia.

7. Elraies, K. A., Tan, I., and Fathaddin, M. (2010). A New Approach to Low-Cost, High Performance Chemical Flooding System. *SPE 133004, presented at SPE Production and Operations Conference and Exhibition,* June 8-10, Tunis, Tunisia.

8. Elraies, K. A., Tan, I., and Fathaddin, M. (2010). Design and Application of a New Acid-Alkali-Surfactant Flooding Formulation for Malaysian reservoirs. SPE 133005, *to be presented at the SPE Asia Pacific Oil & Gas Conference and Exhibition*, October, 18-20, Brisbane, Australia.