REDUCTION OF SURFACTANT ADSORPTION BY ALKALINE SUBSTANCES IN CARBONATE RESERVOIR

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Field of Study	Georesources and Petroleum Engineering
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ยศนันท์ วัฒน์พานิช : การลดการดูดซับสารลดแรงตึงผิวด้วยสารอัลคาไลน์ในแหล่งกักเก็บคาร์บอเนต (REDUCTION OF SURFACTANT ADSORPTION BY ALKALINE SUBSTANCES IN CARBONATE RESERVOIR) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: อ. ดร.ฟ้าลั่น ศรีสุริยชัย, 70 หน้า.

การฉีดอัดสารลดแรงตึงผิวเป็นการเพิ่มการผลิตน้ำมันด้วยสารเคมีประเภทหนึ่ง โดยมีวัตถุประสงค์เพื่อลดแรงตึงระหว่างผิวน้ำมันและน้ำให้อยู่ในระดับที่ต่ำมาก ทำให้น้ำมันสามารถไหลไปพร้อมกับน้ำในรูปแบบของอิมัลชัน น้ำมันที่ค้างอยู่ในรูพรุนของหินจึงลดลงจนแทบไม่หลงเหลือในสภาวะที่เหมาะสม อย่างไรก็ดีปัญหาที่สำคัญอย่างหนึ่งของวิธีนี้คือสารลดแรงตึงผิวสามารถที่จะถูกดูดซับไว้บนพื้นผิวของหินเนื่องจากประจุที่ตรงกันข้ามกันส่งผลให้ประสิทธิภาพของสารลดแรงตึงผิวที่ฉีดอัดลงไปลดลงและก่อให้เกิดความไม่มีประสิทธิภาพในเชิงเศรษฐศาสตร์ อย่างไรก็ดีมีรายงานวิจัยพบว่าการดูดซับของสารลดแรงตึงผิวบนพื้นผิวหินสามารถทำให้ลดลงได้ โดยใช้สารอัลคาไลน์ผสมกับสารลดแรงตึงผิว เพื่อให้สารอัลคาไลน์ซึ่งสามารถให้ประจุลบได้มากถูกดูดซับไว้ก่อนแทนสารลดแรงตึงผิว รวมถึงการดูดซับสารลดแรงตึงผิวสามารถย้อนกลับได้ในสภาวะที่เหมาะสม จึงทำให้จำนวนของสารลดแรงตึงผิวที่คงเหลือในน้ำมีอยู่มากและการดูดซับบนพื้นผิวหินลดลง

จากการศึกษาการดูดซับและการย้อนกลับของสารลดแรงตึงผิวแบบสถิตย์พบว่า โซเดียมคาร์บอเนต ซึ่งเป็นสารอัลคาไลน์ที่มีความเป็นด่างในระดับกลางสามารถใช้ผสมไปพร้อมกับโซเดียมโดเดคซิลเบนซีนซัลโฟเนตที่เป็นสารลดแรงตึงผิวประจุลบได้ในหินตัวอย่างโดโลไมต์ เนื่องจากโซเดียมคาร์บอเนตสามารถให้ประจุที่เพียงพอที่จะแย่งชิงและถูกดูดซับบนพื้นผิวของหินได้ดีกว่าสารลดแรงตึงผิว ในขณะเดียวกันประจุของอัลคาไลน์ประเภทนี้ยังไม่รุนแรงพอที่จะผลักให้โมเลกุลของสารลดแรงตึงผิวถูกดูดซับบนพื้นผิวของหิน จากการศึกษายังพบว่าการย้อนกลับการดูดซับของสารลดแรงตึงผิวไม่ขึ้นกับปริมาณที่ถูกดูดซับแต่ขึ้นตรงกับความเข้มข้นของทั้งสารอัลคาไลน์และสารลดแรงตึงผิว จากการทดลองในส่วนนี้พบว่าความเข้มข้นที่เหมาะสมของสารอัลคาไลน์และสารลดแรงตึงผิวอยู่ที่ 0.6 และ 0.8 เปอร์เซ็นต์โดยน้ำหนักตามลำดับ

จากการศึกษาการดูดซับและการย้อนกลับของสารลดแรงตึงผิวแบบจลน์ที่ศึกษาควบคู่ไปพร้อมกับตัวแปร ได้แก่ ค่าความเค็มของน้ำในแหล่งกักเก็บ อัตราการฉีดอัด และ อุณหภูมิ พบว่า ที่ค่าความเค็มของน้ำในแหล่งกักเก็บต่ำสุด 10,000 ส่วนในล้านให้ผลดีที่สุด เนื่องจากผลของประจุลบในน้ำที่มีน้อยไม่ทำให้เกิดการผลักสารลดแรงตึงผิวและยังส่งผลให้การดูดซับต่ำและเกิดการย้อนกลับได้ดี อัตราการไหลสูงที่สุดที่ 0.8 ลูกบาศก์เซนติเมตรต่อนาทีสามารถลดค่าการดูดซับและเพิ่มค่าการย้อนกลับของสารลดแรงตึงผิว เนื่องจากที่ค่าการฉีดอัดที่อัตราเร็วสูงสามารถลดระยะเวลาสัมผัสระหว่างโมเลกุลของสารลดแรงตึงผิวกับพื้นผิวของหินได้มากกว่าที่ค่าการฉีดอัดต่ำ ที่อุณหภูมิ 70 องศาเซลเซียส โมเลกุลของสารลดแรงตึงผิวคงเหลืออยู่ในสารละลายได้มากกว่าที่อุณหภูมิต่ำกว่าตามพลังงานของโมเลกุลที่ขึ้นกับอุณหภูมิ ทั้งนี้การรวมทุกสภาวะเอื้ออำนวยทั้งหมดยิ่งช่วยส่งผลให้ค่าการดูดซับของสารลดแรงตึงผิวลดลงถึง 0.43 มิลลิกรัมต่อกรัมของหิน ค่าการย้อนกลับของสารลดแรงตึงผิว 0.39 มิลลิกรัมต่อกรัมของหิน และคงเหลือสารลดแรงตึงผิวอยู่บนพื้นผิวของหิน 0.04 มิลลิกรัมต่อกรัมของหิน

ภาควิชา	วิศวกรรมเหมืองแร่และปิโตรเลียม	ลายมือชื่อนิสิต	....
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YOSNUN VATHANAPANICH: REDUCTION OF SURFACTANT ADSORPTION BY ALKALINE SUBSTANCES IN CARBONATE RESERVOIR. ADVISOR: FALAN SRISURIYACHAI, Ph.D., 70 pp.

Surfactant flooding is a chemical enhanced oil recovery process in which small amount of surfactant is added to injected water. The technique is performed to reduce interfacial tension between oil and water to ultra-low condition where oil and water phases are linked together as surfactant molecule composes of both hydrophilic and hydrophobic parts. Oil is then liberated in flowing water in a form of emulsion and residual oil saturation can be further reduced to nearly zero in appropriate conditions. However, surfactant loss due to adsorption onto rock surface is one of the major concerns as surfactant compounds are generally expensive chemical. A polar part of surfactant is attracted by opposite charge of rock. This problem weakens the effectiveness of the injected surfactant slug in reducing interfacial tension between oil-water phases and consecutively causes the process to be uneconomical. However, surfactant adsorption can be minimized. From several studies, alkaline substance can be added in surfactant solution. Alkali which provides strong negative charge will function as a sacrificial agent, competing surfactant in adsorption process and reducing the amount of surfactant adsorption. It is also discovered that surfactant is not permanently adsorbed onto rock surface. Desorption may occur, yielding number of active surfactant monomer to increase.

From this study, static adsorption and desorption tests show that sodium carbonate(Na_2CO_3), which is moderately strong base is recommended to co-inject with sodium dodecyl benzene sulfonate representing surfactant in dolomite sample. Sodium carbonate provides adequately strong charge to compete adsorbing with surfactant onto carbonate surface. At the same time, this base is not too strong to reinforce adsorption of surfactant. It is also found that desorption of surfactant is not a function of adsorbed amount but it is still a function of alkali and surfactant concentrations. Alkali and surfactant concentrations of 0.6% and 0.8% by weight, respectively are discovered to be optimal concentrations.

In dynamic adsorption and desorption tests, several parameters related to alkali-surfactant flooding is investigated. The smallest salinity of 10,000 ppm yields the best result as amount of anionic ion is small in the system. The highest injection rate of 0.8 cm^3/min, helps preventing adsorption and desorption by reducing retention time between surfactant molecule and rock surface. High temperature of $70^{o}C$ is more favorable than lower temperature as surfactant is more active and prefers to remain in aqueous phase. Combing the best conditions results in surfactant adsorption of 0.43 mg/g, surfactant desorption of 0.39 mg/g, and surfactant retaining just 0.04 mg/g.

Department: Mining and Petroleum Engineering Student's Signature ....
Field of Study: Georesources and Petroleum Engineering Advisor's Signature ....
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LIST OF ABBREVIATIONS

$CaCO_3$	Calcium Carbonate
$CaCl_2$	Calcium Chloride
$CaMg(CO_3)_2$	Calcium Magnesium Carbonate
CO_2	Carbon Dioxide
CPC	Catalpyidinium Chloride
CEOR	Chemical Enhanced Oil Recovery
Cl^-	Chloride ion
CAC	Critical Admicelle Concentration
CMC	Critical Micelle Concentration
DF	Dilution Factor
DPC	Dodecyl Pyridinium Chloride
OH^-	Hydroxide ion
IFT	Interfacial Tension
$MgCl_2$	Magnesium Chloride
PV	Pore Volume
P.Z.C.	Point of Zero Charge
pH	Potential of Hydrogen
Na_2CO_3	Sodium Carbonate
SDBS	Sodium Dodecyl Benzene Sulfonate
SDS	Sodium Dodecyl Sulfonate
$NaHCO_3$	Sodium Hydrogen Carbonate
NaOH	Sodium Hydroxide
SL	Sodium Lignosulfonate
SO_4^{2-}	Sulfate ion
SPR	Surfactant Per Rock ratio

LIST OF NOMENCLATURES

ΔP	Pressure different across core
μ	Viscosity
ϕ	Porosity
k	Absolute permeability
A	Cross-sectional area of core sample
ρ_{Grain}	Density of grain
ρ_{Water}	Density of water
$\rho_{Formation\ brine}$	Density of formation brine
d	Diameter of core sample
$Dry\ weight$	Dry weight of core sample
q	Flow rate
L	Length of core sample
M_{Grain}	Mass of grain
$M_{Pycnometer}$	Mass of pycnometer
M_{Water}	Mass of water
V_{Grain}	Volume of grain
$V_{Hyamine}$	Volume of hyamine
$V_{Pycnometer}$	Volume of pycnometer
V_{Water}	Volume of water
$Wet\ weight$	Weight of saturated core sample with formation brine

CHAPTER 1

INTRODUCTION

1.1 Background

Chemical Enhanced Oil Recovery (CEOR) is one of tertiary recovery techniques implemented in oilfields to achieve an increment of oil production beyond physical displacement mechanism. The process is mainly based on injection of fluids containing chemical that are absent in the reservoir. The injected fluids may interact with reservoir rock and fluids in both physical and chemical manners to generate favorable conditions for oil production. In the present time, CEOR can be sub-categorized into surfactant flooding, alkaline flooding, polymer flooding, and combinations of the three techniques are also possible as long as they are compatible to each other. All the mentioned techniques may be costly but they could yield extremely high benefits to specific type of reservoir.

Surfactant flooding, a CEOR process in which a small amount of surfactant is added to injected water, is chosen to perform in this study. The presence of surfactant reduces the interfacial tension (IFT) between oil and water to ultra-low condition by linking oil and water phases together as surfactant molecule composes of both hydrophilic and hydrophobic parts. Oil is then liberated in a form of emulsion and residual oil saturation can be reduced to nearly zero in an appropriate condition. However, there is also a problem occurred during surfactant flooding which is surfactant loss due to adsorption onto the rock surface. A polar part of surfactant is attracted by opposite charge that can be observed on the rock surface. This problem weakens the effectiveness of the injected surfactant slug in reducing IFT between oil-water phases and consecutively causes the process to be uneconomical. Prevention of surfactant loss during the process of surfactant flooding could therefore reduce the field operation cost. In order to prevent the adsorption and also to favor desorption of surfactant, injection of alkaline substances as a sacrificial agent is performed.

As alkali substance highly ionizes in water, providing hydroxide ion, neutralization of surface charge can rapidly occur especially surface that possesses positive charges such as Limestone and Dolostone. Moreover, hydroxide ion may cause the ion exchange with previously adsorbed surfactant, facilitating desorption of surfactant and hence, more active monomers are liberated to reduce IFT.

Since surfactant loss is one of the major concerns in surfactant flooding, many experiments on adsorption and desorption of surfactant were performed to understand these mechanisms. Nonetheless, the comparison of periods to inject alkali substance to enhance effectiveness of surfactant is not yet performed. Hence, this study will focus on the combination of alkali and surfactant flooding by indicating the effectiveness of adding alkali substance into surfactant slug in different periods including pre-injection of surfactant slug and co-injecting with surfactant slug and also some combinations of these two periods. Understanding adsorption/desorption mechanisms of surfactant in a presence of alkaline substance will provide practical guidelines to prevent surfactant adsorption in implementation of surfactant flooding.

1.2 Objectives

1. To study effects of surfactant concentration, alkali concentration, type of alkaline substance and time to inject alkali on surfactant adsorption onto carbonate formation.
2. To indicate the most effective way of using alkaline substance in surfactant flooding to prevent surfactant adsorption in carbonate reservoir.

1.3 Outline of Methodology

1. Prepare chemical substances which are: sodium dodecyl benzene sulfonate (SDBS) as surfactant, sodium hydroxide (NaOH), sodium carbonate (Na_2CO_3), and sodium hydrogen carbonate ($NaHCO_3$) are as alkali.

2. Prepare carbonate rock samples in two forms as grain size and core samples in order to perform the experiment in both static and dynamic adsorption and desorption tests.
3. Perform static adsorption test for pre-screening the alkali and indicating the time to inject the alkali by stirring grinded rock samples with alkali/surfactant solution for six hours. The supernatant is collected to identify the adsorption value. The filtrated samples are collected to identify desorption value by stirring with distilled water for six hours and colleting supernatant.
4. The conditions selected from previous section are studied in dynamic adsorption test by using coreflood apparatus. The variation of salinity, injection rate, and temperature are performed in order to indicate the most effective way of using alkali substance in surfactant flooding.

1.4 Outline of Thesis

There are six chapters in this thesis as the following outline:

1. CHAPTER 1 introduces background and basic concepts of surfactant flooding and some concepts of using alkali as sacrificial agent in surfactant flooding, short methodology of this thesis, and outline of this thesis.
2. CHAPTER 2 reviews previous studies which are related to adsorption/desorption of surfactant active monomers onto rock surface in surfactant flooding in different conditions. The presence of alkali as sacrificial agent is also mentioned.
3. CHAPTER 3 determines relevant theories which are related to surfactant flooding, type of surfactants, adsorption and desorption of surfactant, application of alkaline substances in surfactant flooding, carbonate formation and its surface properties.
4. CHAPTER 4 explains the methodology in details of this thesis thoroughly.

5. CHAPTER 5 provides the results and discussion of laboratory experiment.
6. CHAPTER 6 concludes results and new findings and gives the recommendations of performing surfactant flooding.

CHAPTER 2
LITERATURE REVIEW

Adsorption and desorption of surfactant play important roles in the chemical enhanced oil recovery specifically on surfactant flooding. Adsorption at early stage and desorption at late time could affect the effectiveness of surfactant and operation cost of field. Many researchers proved that surfactant can be adsorbed onto rock surface but not permanently, it can be desorbed by injecting surfactant slug at lower concentrations or even pure water. On the other hand, various researches also proved that pre-injection of alkali as the sacrificial agent and co-injection of alkali together with surfactant can reduce adsorption of surfactant onto rock surface.

2.1 The Study of Adsorption and Desorption of Surfactant in Different Conditions

Somasundaran and Hanna [1] studied the adsorption and desorption of anionic surfactant which was sodium dodecyl benzene sulfonate (SDBS) onto rock surface which was sodium kaolinite with different concentrations. In this research, the terms abstraction and deabstraction were used to describe adsorption and desorption of SDBS onto rock surface. The laboratory test was conducted, when the surfactant slug advanced to rock surface, the higher adsorption would occur with the higher surfactant concentrations and lower with lower surfactant concentrations. On the other hand, desorption occurred when surfactant slug with lower concentrations is injected after the higher one. In other words, flushing core with water subsequently to the advance of a surfactant slug can remove abstracted sulfonate from rock surface. Apart from surfactant concentrations, pH value also showed as an impact on the adsorption, for instance, at pH 6.6 (nearly neutral), the desorption isotherm was similar to adsorption isotherm as less hysteresis. However, the test also conducted at pH in acidic range of 4.6, the result indicated that the more acidic of pH, the more precipitation and hysteresis was yielded. In conclusion, the higher adsorption of the surfactant occurs at lower pH value.

Hamid and Onur [2] studied the adsorption of surfactant with different concentrations, reservoir temperatures, and pH values. In this study, an anionic surfactant, which is sodium dodecyl sulfonate, was tested on Berea sandstone with various concentrations, temperatures, and pH values. The result indicated that, increase of concentration yielded an increase of adsorption. However, no more adsorption taken place when the isotherm curve reached plateau concentration (or Critical Micelle Concentration (CMC)) which indicated that no more space for surfactant molecules to adhere to the rock surface. The result of various temperatures effect indicated that the adsorption dropped substantially when increasing temperature of the system. The effect of temperature can be explained in term of solubility as the higher temperature the higher on solubility, therefore, surfactant tended to accommodate in solution more than on rock surface. The effect of pH showed that the adsorption decreased as pH increased in the case of anionic surfactant.

2.2 The Study of Adsorption and Desorption of Surfactant in the Presence of Alkali Substances

Tabatabal and Gonzalez [3] studied intensively on the adsorption of anionic and cationic surfactants on pure carbonate rock surface (synthetic calcite of 99.95 % $CaCO_3$ and natural dolomite [$CaMg(CO_3)_2$] in the presence of added electrolytes which are Na_2CO_3, $MgCl_2$, and $CaCl_2$. The cationic surfactants used in this research are catalpyridinium chloride (CPC) and dodecyl pyridinium chloride (DPC), and sodium dodecyl sulfate (SDS) for anionic surfactant. The laboratory test was conducted with varying of surfactant and electrolyte concentrations. The results indicated that SDS in the presence of 0.05 or 0.2 M $MgCl_2$, the adsorption was higher than SDS without added electrolyte, and for adding Na_2CO_3 of 0.05 or 0.2 M, the adsorption was somewhat lower than without added electrolyte, whereas the effect of 10^{-5} M of $CaCl_2$ appeared to be negligible. Moreover, the addition of excess Na_2CO_3 also increased the pH which tends to make the surface more negative. However, the adsorption isotherms for CPC and DPC in the presence of added electrolyte was somewhat lower than SDS as the additional of salts of multivalent cations can increase the adsorption of anionic surfactant, whereas decreased for cationic surfactant. Therefore, the use of cationic surfactant in the presence of added electrolyte was preferable for carbonate reservoir due to less in surfactant loss compared to anionic surfactant.

Azam et al. [4] investigated adsorption of a novel synthesized anionic surfactant which contained 16-18 carbons in a chain with branch in the middle and a sulfonate head group at various conditions on Berea sandstone rock sample. The CMC of surfactant and Point of Zero Charge (P.Z.C.) of Berea sandstone were qualified in this study. In addition, static adsorption tests were performed to observe the effect of pH, salinity, and temperature on surfactant adsorption. From the experiments, the result of CMC was found to be at 1,790 ppm (0.179 %wt) and therefore, the increasing of surfactant concentration above the mentioned point did not increase surfactant adsorption, but only increased micellization in solution. According to P.Z.C. of Berea sandstone, it was found to be 8.0. This result can be explained that at pH beyond 8.0, Berea rock sample carries negative charge on its surface, therefore, the adsorption of anionic surfactants will lower compares to the case of pH below 8.0, adsorption values due to repulsion forces between each other. Moreover, in order to evaluate this effect, two different type of alkalis, which are sodium metaborate (pH 9.5) and sodium teraborate (pH 10.5), were used to adjust the pH of the rock sample. The results found that, surfactant appears to adsorb lesser onto Berea sandstone in the presence of sodium tetraborate which provided the adsorption value of 0.28 mg/g, while in case of sodium metaborate, the adsorption value of 0.36 mg/g. For the effect of salinity on adsorption, the experimental results show that adsorption of anionic surfactant increases with an increase of salt concentration until reached 20,000 ppm (2 %wt). After this concentration, any increase in salinity did not significantly affect surfactant adsorption. Surfactant adsorption was increased to 1.29 and 1.56 mg/g by the addition of 1 and 2 wt.% NaCl, respectively. The addition of NaCl decreases the functional group electrostatic repulsion in the adsorbed layer. In case of temperature, the adsorption is reversed to the salinity as the adsorption of surfactant is reduced with the increment of temperature. This is due to the higher kinetic energy, leading to weaker force of interaction between surfactant and Berea sandstone.

Shamsijazeyi and Hirasaki [5] investigated the application of adding alkali as sacrificial agent for reducing the adsorption of anionic surfactant on sandstone and carbonate rock surface. In this research, sodium polyacrylate was used as a sacrificial agent. The laboratory test was conducted for both dynamic and static adsorptions. The dynamic test showed that adding of sodium polyacrylate can reduce the adsorption as well as static test. However, the decrease of adsorption in dynamic test and static test did not match since the much higher divalent ions concentration and polyacrylate in dynamic test. The conclusion was that if the right molecular weight and concentration of sodium polyacrylatea are chosen, the effective sacrificial agent for both sandstone and carbonate reservoirs would be existed.

Bortolotti and Srisuriyachai [6] investigated the application of alkali flooding and alkali-surfactant-polymer flooding techniques combined with intermittent flow. The experiment was conducted in coreflooding. This study focused on the mixture of alkali/surfactant which was fixed for alkali concentration of 2.0 M according to the lowest interacial tension (IFT). The result indicated that the mixture of alkali/surfactant yields much lower IFT and increased significantly amount of producible oil compared to the solely cases. Moreover, alkalines substance can also prevent the surfactant loss due to the adsorption on the rock surface.

Gogoi [7] examined the effects of surfactant and alkali desorption concentration in the extended waterflood on oil-water IFT reduction and oil recovery. The experiments were conducted using coreflood apparatus to observe the adsorption and desorption behavior of anionic surfactant which was Sodium Lignosulfonate (SL) on core samples during enhanced oil recovery process (EOR) of oil with medium viscosity. Results from the experiment found that surfactant and NaOH were presented in the extended waterflood as the desorption process took place during flooding the extended water. This released the surfactant active monomers from adsorbed on the rock surface to the aqueous again. The desorbed surfactant helped reducing oil-water IFT and thus releasing producible oil. Moveover, this desorbed surfactant lasted for a long period of waterflood. The concentration of desorbed surfactant in the extended waterflood was found to be very low but an ultra-low IFT still achieved by using suitable alkali. Coreflood results showed an additional recovery of around 10% of the initial oil in place was obtained by desorbed surfactant and alkali. Results indicated that by utilizing desorbed surfactant during the extended waterflood operation, the efficiency and economics of surfactant flooding can be improved significantly.

Respect to literature reviews, it can be seen that adsorption and desorption of surfactant onto the rock surface has been performed in several criterions by many researchers. However, the reduction of surfactant loss by alkali injection in optimum conditions by the adjustment of operating parameters has not yet performed and this remains as major goal for this study.

CHAPTER 3

THEORY AND CONCEPT

In order to understand adsorption and desorption mechanisms of surfactant in a presence of alkaline substance in different periods including pre-injection and co-injection in carbonate rocks, there are several relevant theories and concepts required to be thoroughly understood including surfactant flooding, types of surfactant, adsorption and desorption of surfactant, measurement of surfactant loss, alkaline flooding, alkaline/surfactant flooding. Moreover, there are some important petrophysical properties of rock including wettability and point of zero charge involved in this study as they control effectiveness of the chosen techniques.

3.1 Surfactant Flooding

Surfactant flooding is the method performed to improve oil recovery by adding surfactant into injected water. Surfactant, which is a substance possessing ability to link water and oil together, reduces the interfacial tension or IFT at the interphase. As a result, oil can be liberated in a small droplet or as an emulsion which is a stable form of oil-in-water. At very favorable conditions, residual oil saturation is further reduced compared to saturation obtained from waterflooding or from natural depletion process. Sometimes, residual oil can be reduced to nearly zero in appropriate conditions. Even though surfactant can reduce residual oil saturation to almost zero, number of oil produced from surfactant flooding around the globe is still quite small compared to other techniques such as steamflooding, hydrocarbon injection and carbon dioxide (CO_2) flooding due to many requirements of the technique.

Surfactants are usually organic compounds that are amphiphilic since the molecule generally composes of hydrophilic head and hydrophobic tail. Hydrophilic head refers to the polar part of surfactant which strongly interacts with other polar molecules such as water, whereas, hydrophobic tail (so-called lipophilic tail) refers to the non-polar part which prefers to stick with other non-polar molecules such as oil or other hydrocarbon compounds. As a result, surfactants are soluble in both aqueous and organic solvents. According to the ionic nature of hydrophilic head, surfactants can be classified into four types including anionic, cationic, nonionic, and zwitterionic or amphoteric surfactants as shown in the figure 3.1.

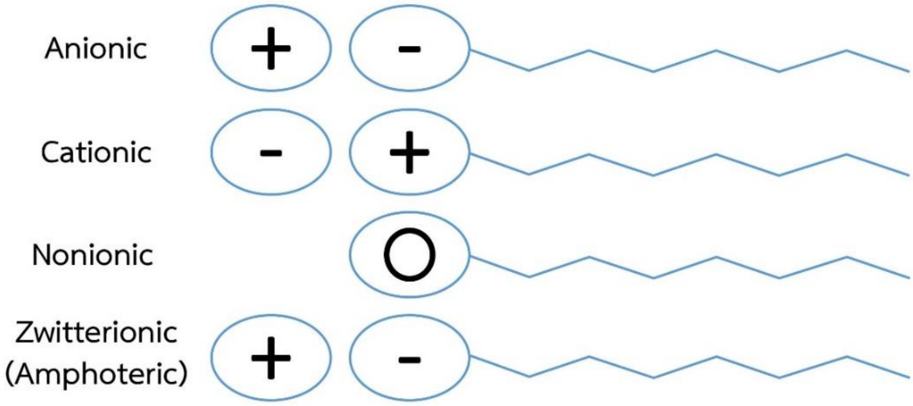

Figure 3.1 Four types of surfactant active monomer agent [8]

Anionic surfactant, is chosen to represent surfactant agent in this study. This type of surfactant is characterized by the negative charge in polar part. Anionic surfactant exhibits low adsorption on negatively charged surface such as sandstone surface. According to this, anionic surfactant is considered as an effective agent for surfactant flooding especially for sandstone reservoirs since it is capable to reduce interfacial tension between oil and water to the ultra-low condition where additional oil recovery can be obtained from further reduction of residual oil saturation in a form of fine emulsion. However, carbonate reservoirs, which are positively charged at usual reservoir conditions, are not suitable for this type of surfactant due to high depletion rate from adsorption onto rock surface.

Cationic surfactant is characterized by the positive charge on the polar part which is opposite from anionic surfactant. This type of surfactant exhibits low adsorption rate on the positively charged surface such as carbonate surface. Moreover, cationic surfactant is the only type of surfactant that is capable to alter wetting condition of reservoir rock from oil-wet to water-wet which is a more favorable condition for oil production. As a consequence, cationic surfactant is the best suited for carbonate reservoirs. On the other hand, sandstone reservoirs, which are negatively charged by nature, are not candidates for this type surfactant type due adsorption problem. Nevertheless, the cost of cationic surfactant is much higher compared anionic surfactant. Cationic surfactant is therefore, not commonly used even carbonate reservoir as there are other techniques to help reducing adsorption of anionic surfactants which is less expensive one.

Nonionic surfactant is a type of surfactant that does not possess actual charge on its structure as it does not ionize in aqueous phase. Due to composition of different elements inside the structure, the molecule exhibits different electronegativity within the molecule and this makes nonionic surfactant to possess function as other surfactants. However, as the charge property is not well pronounced, this type of surfactant is not preferable in terms of interfacial tension reduction compared to anionic and cationic surfactant due to its characteristic. However, it exhibits a good tolerance to a high salinity environment. Nowadays, nonionic surfactant is used as co-surfactant. Co-surfactant will assist major surfactant which can be anionic or cationic to partition in both oil and aqueous phases. In general, co-surfactant which is usually alcohol based surfactant will be used when water system is too high or too low in salinity.

Zwitterionic surfactant is a mixture of previously mentioned types of surfactant within the same molecule. Therefore, the combinations can be anionic-cationic, nonionic-anionic, and nonionic-cationic. This type of surfactant is strongly tolerant to high temperature and high salinity. However, this type of surfactant is very expensive compared to the other types and not widely used in petroleum industries [8].

3.2 Adsorption and Desorption of Surfactant

Adsorption and desorption of surfactant play important roles in effectiveness of surfactant in oil recovery mechanism. Adsorption and desorption directly affect amount of active surfactant monomer in injected fluid which consecutively affects interfacial tension as well as residual oil saturation. Hence, it could be said that these two terms partially make surfactant flooding process to be economically feasible. Several studies have indicated the benefits obtaining from desorbed active surfactant monomer to improve the efficiency in interfacial tension reduction and economics of surfactant flooding.

During surfactant flooding process, as surfactant slug comes into contact with reservoir rock and fluid, there would be a loss of surfactant due to adsorption onto solid as well as liquid interface. At the interface, the adsorption behavior can be either physical or chemical adsorptions. There are many different ways to differentiate physical and chemical adsorption such as the comparison of the reversibility of physical adsorption-desorption, typical lower rate of physical and chemical adsorption. However, the main criterion used to distinguish the adsorption type is charge transfer. If there is no the transferring of electrons during the adsorption, it is considered as physical adsorption. On the contrary, if the electrons are transferred during the adsorption, the adsorption becomes chemical adsorption or chemisorption [9].

The adsorption of surfactant from aqueous solution is mainly based on two factors: (i) the energy from changing a surface-water contact into surface-surfactant contact and (ii) the removal of surfactant hydrocarbon moiety from aqueous environment. The adsorption will reach the maximum when the solution concentration is above CMC. Above the CMC, the surfactant activity is constant and hence the adsorption of surfactant in no longer increase [10].

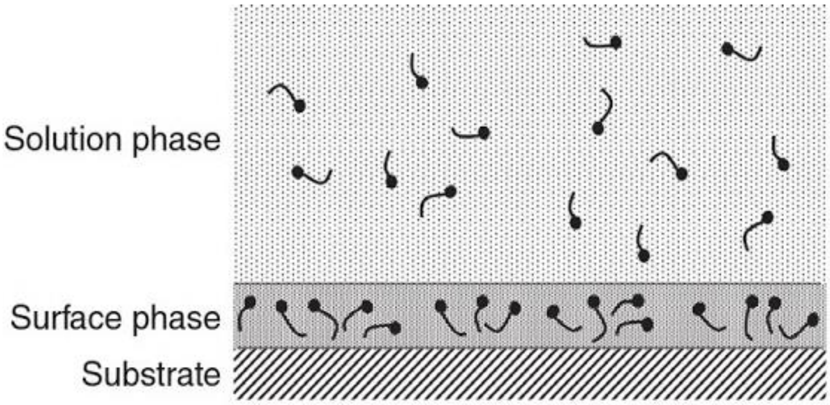

Figure 3.2 Adsorption onto surface regarded as a separate phase in equilibrium solution [10]

The adsorption mechanisms of surfactant are commonly described in terms of four-region isotherms with the different in surfactant concentrations shown in figure 3.3. In the region I: low surfactant concentrations, the surfactant monomers are adsorbed as individual ions with no interaction between the adsorbed molecules. In region II, for instance, the higher surfactant concentrations, the adsorption is higher as the surfactant concentration is increased. The changing of slope is steeper compared to region I, resulting in break line between region I and region II as the surfactant starts to aggregate from surface. This concentration is referred to the Critical Admicelle Concentration (CAC). The changing of slope between region II and region III can be described as the surfactant molecules are already filled in rock surface with further adsorption that is due to association between first and second layer hydrocarbon chains in region III. The reversal of surface charge also occurs as the surfactant ions were adsorbed. In region IV, the plateau adsorption is generally begun at or near CMC as the slope is horizontal [11].

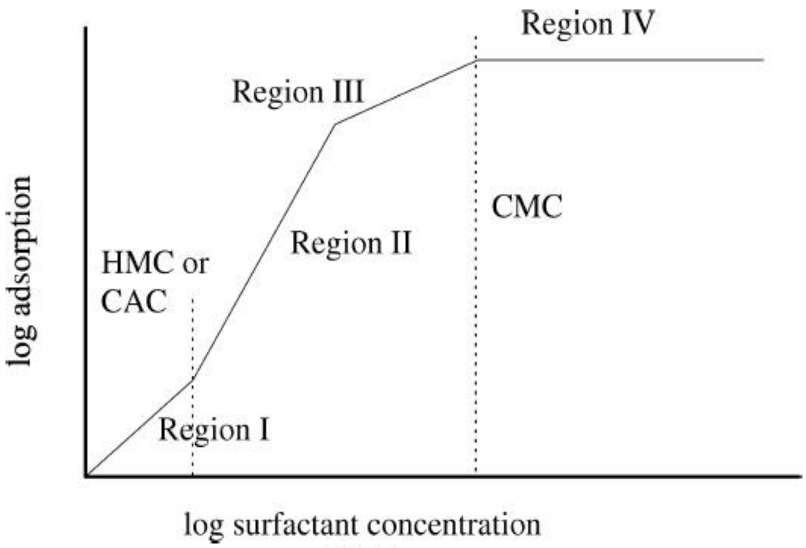

Figure 3.3 Typical four-region adsorption isotherm for monoisomeric surfactant [11]

After adsorption of surfactant onto rock surface, if concentration of surfactant is substantially reduced, previously adsorbed surfactant molecules may desorb from rock surface. Desorbed surfactant molecule will be reactive again and assist the remaining active surface molecule in injected fluid in reducing interfacial tension. Percentage of desorption depends on several factors. Many researches indicated that the surfactant can be adsorbed onto rock surface but not permanently, it can be desorbed. The surfactant can be desorbed from the rock surface at salinity and pH at reservoir conditions [12]. The salinity can lower the adsorption as salt ions come to interact with rock surface and then filled in rock surface. According to pH value in the reservoir, the value of pH is generally between 7 to 8 and sandstone is negatively charged, whereas carbonate is positively charged. The increasing of pH value above 9, anionic surfactant can be repulsed from carbonate due to similar charges of rock and surfactant.

Surfactant adsorption can be measured in different ways. Both static and dynamic tests are usually conducted. Static test is performed by separating compact rock into grains. Identifying surfactant concentration before and after adsorption will results in weight of surfactant retaining on rock surface. The unit of surfactant adsorption is usually expressed as milligram of surfactant per gram of rock sample. As grains are liberated and surface area is the maximum, surfactant adsorption would reach its maximum value. Dynamic adsorption is instead performed to identify actual quantity of surfactant to be adsorbed when direction of fluid movement is encounter. Moreover, rock surface is reduced in dynamic test as fluid-solid contact will occur through pore surface. However, results from dynamic test would represent actual adsorption-desorption phenomenon in porous medium. In order to quantify the amount of surfactant concentration (in this study, anionic surfactant is used), a two-phase system is created with surfactant/water solution and chloroform, to which methylene blue indicator is added. Methylene blue reacts with anionic surfactant to form chloroform soluble salts, causing it to concentrate in the chloroform phase. Cationic surfactant (Hyamine) is used as a titrant, as it preferentially forms a complex with the anionic surfactant, freeing methylene blue to migrate to the water phase. The end point is recorded when the two phases reach separate color intensity, the upper part turns to deep blue color as the color of methylene blue, whereas the lower liquid part is colorless as the original color of chloroform.

3.3 Application of Alkaline Substance in Surfactant Flooding

In alkaline flooding, an aqueous solution of alkaline substance such as sodium carbonate or sodium orthosilicate or sodium hydroxide is injected in a slug form into the reservoir to recover the residual oil that cannot be extracted by long term waterflooding process and natural depletion. Injected alkaline substance rapidly interacts with acid components in crude oil, generating in-situ anionic surfactant. This reaction is so-called saponification reaction and in order to achieve this reaction, formation oil should have adequate quantity of organic acid which is saponifiable substance. Generated surfactants are responsible for lowering interfacial tension between oil and water for improving oil recovery. Moreover, Alkali itself can change wetting conditions of rock surface especially carbonate reservoir from oil-wet to water-wet which is a favorable for oil production. Since alkaline substance can increase pH value easily with only small concentration, surface charge of carbonate surface can be switched to negative charge and previously adsorbed materials are expelled from the surface.

The surfactant and alkaline substances are combined, several benefits can be obtained. First, alkaline substances ionize in water, creating occupying ions in aqueous phase. These ions push surfactant toward oil-water interface and as a consequence, interfacial tension can be substantially reduced to ultra-low condition. In a presence of alkaline substance, ultra-low condition of surfactant solution can be achieved at much lower concentration compared to the case where alkaline substance is absent. Alkaline substance is also functioned as sacrificial material. As alkali ionizes and generates ions, these ions with strong charge property are quickly adsorbed onto rock surface. This prevents surfactant depletion and interfacial tension reduction can be maintained at longer period. In carbonate formation where rock surface possesses positive charges at normal reservoir condition, adding alkaline substance can switch the surface charge to negative side which results in the same charge property as anionic surfactant. Adsorbed oil through oil-wet induced material is easily liberated and at the same time, active surfactant monomers will not be depleted by rock surface due to the alteration of surface charge.

3.4 Carbonate Formation and Its Surface Properties

Carbonate rock is sedimentary rock that composes mainly of carbonate minerals and majority is oil-wet at normal pH condition, which is an unfavorable condition for oil production as the rock prefers to adhere by oil. According to this, the amount of producible oil after both primary and second recoveries is low. Hence, tertiary recovery should be performed to increase additional producible oil. Two important types of carbonate rocks are usually mentioned which are Limestone and Dolostone (so-called Dolomite).

Limestone composes mainly of either calcite or aragonite. These are both calcium carbonate ($CaCO_3$) but they are different in crystalline structures. Limestone can be formed in several ways. Some limestones are made up of organic materials, such as the bodies of marine organisms. When they were alive, these organisms absorbed calcium carbonate dissolved in water and used it to form their shells and skeletons. When they died, these shells and skeletons disintegrated to form a sediment that is consolidated into carbonate rock. Dolomite is formed when some or all of the calcium ions in limestone are replaced by magnesium ions. The compound formed in this process is known as calcium magnesium carbonate [$CaMg(CO_3)_2$]. This process is known as dolomitization. As magnesium ion is smaller in sized compared to calcium ion, dolomitization results in increment of porosity. In general, a complete replacement of magnesium ion would increase porosity by approximately 13 percent. Moreover, replacement of magnesium ion during dolomitization also increases matrix density from 2.71 to 2.87 g/cm^3. In case that the replacement of magnesium ion is not 100 percent, matrix density will be in between these two values. Both limestone and dolomite appear in a huge variety of forms. Each has different physical properties depending on the type and amount of impurities it contains (substances such as quartz, clay, pyrite, and silica). Carbonate rock usually contains natural fractures. This is a cause of many failures in oil production as flow is mostly conducted in fractures but not in matrix. Another unfavorable condition of carbonate rock is the surface property. This unfavorability can be explained by the P.Z.C.

Theoretically, P.Z.C. is the pH value at which the surface charge density changes from positive to negative or vice versa. For carbonate rock, P.Z.C. is about 9 [13]. At the ordinary reservoir conditions where pH value is in the range of 6-8, protonation of hydrogen ion is predominant and carbonate surface charge remains positive. As the amount of OH^- increases (increasing of pH), negative charges exceed in the solution and the protonation of hydrogen bond are broken. As a result, negatively charged remains on the carbonate rock surface. Exist of surface charge creates one important property which is wettability. Wettability, one of the petrophysical properties, is defined as a tendency of rock to preferentially adhere by particular fluid in a present of another immiscible fluid. Wettability is considered as an important factor controlling the location, flow, and the distribution of fluid in the reservoirs [13]. Basically, wettability of rock can be classified into three types: water-wet, oil-wet, and neutral-wet. In water-wet rock, continuous film of water covers rock surface and generally it is considered as a favorable condition for oil production whereas in an oil-wet reservoir, water is located in the centers of the larger pores and the surface tends to attach with oil which is an unfavorable condition for oil production. Neutral-wet (so called intermediate-wet), this term describes the surface of rocks having either water-wet and oil-wet characters or a surface without wettability preference. Several studies concluded that neutral-wet is the most favorable condition for oil production.

In carbonate formation where the surface is positively charged at normal reservoir condition, this attracts direct adsorption of organic acid compounds in oil such as carboxylic acid. After adsorption, carbonate surface is covered by R-group of carboxylic acid that tends to stick with oil phase. Eventually, the carbonate surface is oil-wet which is considered as unfavorable condition for oil production. However, in a presence of alkaline substance, negative charges can be raised and surface charge of carbonate can be switched to negative side.

CHAPTER 4
LABORATORY EXPERIMENT

The details of laboratory experiment are described in this chapter. In this study, outcrop Silurian dolomite sample is chosen to represent reservoir rock, sodium dodecyl benzene sulfonate as surfactant, and sodium hydroxide, sodium carbonate, and sodium hydrogen carbonate are as alkali substances. In order to investigate the adsorption and desorption behaviors of surfactant active monomers in the present of alkali substances. The laboratory experiments are designed in both static and dynamic adsorption tests.

As the chemicals loss onto rock surface play important roles in surfactant flooding, therefore; the focus of this thesis is mainly on adsorption and desorption of surfactant active monomers. The goal of this thesis is to find the optimum condition to perform surfactant flooding in the present of alkali substances.

4.1 Preparation of Rock Samples and Fluids

4.1.1 Preparation of Rock Samples

The rock sample is separated into two different types which are core samples (figure 4.1a) with the physical properties summarized in table 4.1 and grinded rock in grain size (figure 4.1b) for dynamic test and static test, respectively.

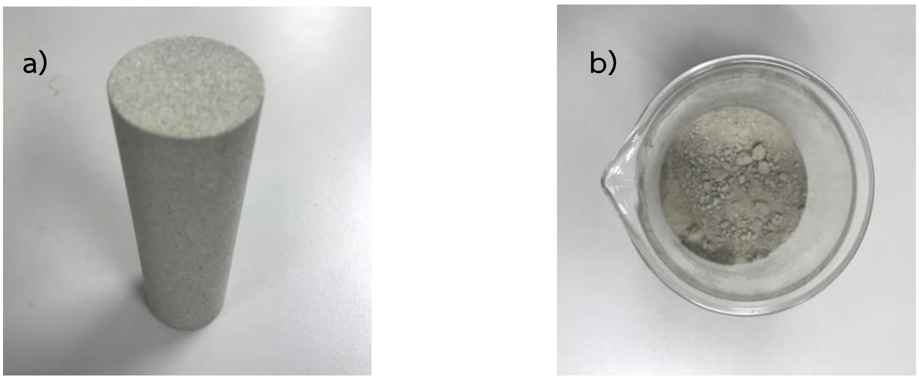

Figure 4.1 Silurian dolomite sample used in this study a) cylindrical core and b) grinded samples

Table 4.1 Physical Properties of Core Samples

Parameters	**Values**	**Units**
Length	62.50	mm
Diameter	37.80	mm
Dry Weight	165.17	Grams

In order to determine basic petrophysical properties and prepare samples for the experiment, all samples are cleaned by reflux extraction in Soxhlet apparatus as illustrated in figure 4.2 using toluene followed with methanol for eight hours each in order to ensure that the cores do not have wettability preference. The petrophysical properties of samples include pore volume, porosity, and permeability, and grain density.

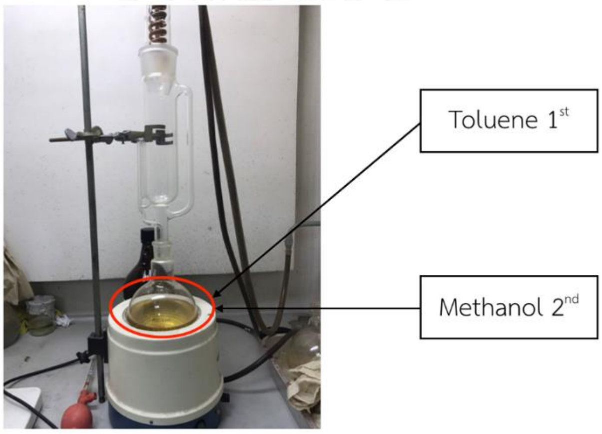

Figure 4.2 Soxhlet apparatus

After the core is cleaned by toluene and methanol, core is flooded by simulate formation brine with known value of density using coreflood apparatus until sample reaches 100% saturated, flow rate and pressure across core sample are recorded to calculate permeability using Darcy’s equation as shown in Equation 4.1.

$$q = \frac{kA\Delta P}{\mu L}$$ Equation 4.1,

where, q = flow rate (cm^3/min), k = absolute permeability (D), A = cross-sectional area of core sample (cm^2), ΔP = pressure different across core (atm), μ = viscosity (cp), and L = length of core sample (cm).

Then, core is removed from coreflood apparatus in order to measure saturated weight to determine pore volume and porosity as expressed in Equation 4.2 and 4.3, respectively.

$$PV = \frac{Wet\ weight\ \text{-}\ Dry\ weight}{\rho_{Formation\ brine}} \qquad \text{Equation 4.2,}$$

where, PV= pore volume (cm^3), $Wet\ weight$ = weight of saturated core sample with formation brine (g), $Dry\ weight$ = dry weight of core sample (g), and $\rho_{Formation\ brine}$ = density of formation brine (g/cm^3), and

$$\phi = \frac{PV}{\frac{\pi}{4} d^2 L} \qquad \text{Equation 4.3,}$$

where, ϕ = porosity (fraction) and d = diameter of core sample (cm).

For grinded sample, rock sample is grinded using mortar and pestle as illustrated in figure 4.3 into grain size. Nevertheless, for grain density, sample is further crushed into powder and the mentioned property is measured by pycnometer as depicted in figure 4.4.

Figure 4.3 Mortar and pestle used for grinding and crushing rock sample

Figure 4.4 Pycnometer used for measurement of grain density

In order to find grain density, the procedures are as followed. Firstly, dry pycnometer is weighted. Secondly, powder of samples is placed into pycnometer in a quantity about one fourth of volume of pycnometer and total weight is recorded. Then, slowly add water with known density into pycnometer and make sure that there is no gas bubble remained in pycnometer. Record total weight and calculate grain density by the following steps (Equations 4.4–4.8)

$$M_{Grain} = M_{Grain+Pycnometer} - M_{Pycnometer} \qquad \text{Equation 4.4,}$$

and then, the mass of grain is obtained. With a known density of water, volume of water can be calculated by:

$$M_{Water} = M_{Grain+Pycnometer+Water} - M_{Pycnometer} - M_{Grain} \qquad \text{Equation 4.5,}$$

from this equation, mass of water is obtained. And volume of water in pycnometer is

$$V_{Water} = \frac{M_{Water}}{\rho_{Water}} \qquad \text{Equation 4.6,}$$

and after volume of water is known, volume of grain can be identified by:

$$V_{Grain} = V_{Pycnometer} - V_{Water} \qquad \text{Equation 4.7,}$$

after obtained all of the above parameters, grain density can be calculated by:

$$\rho_{Grain} = \frac{M_{Grain}}{V_{Grain}} \qquad \text{Equation 4.8,}$$

where, M_{Grain} = mass of grain (g), $M_{Pycnometer}$ = mass of pycnometer, M_{Water} = mass of water (g), V_{Water} = volume of water (cm^3), ρ_{Water} = density of water (g/cm^3), V_{Grain} = volume of grain (cm^3), $V_{Pycnometer}$ = volume of pycnometer (g), and ρ_{Grain} = density of grain (g/cm^3).

4.1.2 Preparation of Fluids

4.1.2.1 Preparation of Alkali and Surfactant Solutions

To prepare alkali and surfactant or mixture of alkali-surfactant solutions, Sodium dodecylbenzene sulfonate is used to represent surfactant and three types of alkali are chosen including sodium hydroxide (NaOH), sodium carbonate (Na_2CO_3), and sodium hydrogen carbonate ($NaHCO_3$). The solutions are prepared in various concentrations from 0.2–1.0 %wt to study static adsorption test. Static adsorption test is performed in order to screen for appropriate alkali and period to inject alkali.

4.1.2.2 Preparation of Simulate Formation Brine

To prepare simulate formation brine, divalent ion including calcium and magnesium ions which can precipitate injected anionic surfactant are avoided, therefore, the formation brine is then prepared without calcium and magnesium ions (soften brine). The components of formation brine are shown in table 4.2. In this study, the formation brine is prepared at the concentrations of 10,000, 20,000, and 35,000 ppm in order to observe the effects of salinity on adsorption and desorption. Crude oil is absented in this study as surfactant adsorption is assumed to occur principally through aqueous phase and presence of crude oil may interfere the amount of adsorbed and desorbed surfactant as surfactant can partition in oil phase.

Table 4.2 Components of simulate formation brine

Chemicals	**%mol**	**%wt**
NaCl	99.86	99.71
Na_2SO_4	0.08	0.20
$NaHCO_3$	0.06	0.09

4.2 Static Adsorption and Desorption Test

Static adsorption is performed by stirring 5 grams of grain size samples with 50 grams of alkali/surfactant solution for 6 hours using magnetic stirrer. Supernatant is collected from stirring process by centrifuged with the rate of 5,000 rpm for 30 minutes and then filtered with 45-micron filter paper for one night to ensure that grains are completely separated from solution. Two-phase color titration is applied in order to determine the adsorption value. The filtered grains are collected and heated in oven with temperature of 70°C for 30 minutes. For static desorption, other 6 hours stirring process is performed using solution that surfactant is absent, filtered grains are weighted to identify the weight remaining from adsorption process. Supernatant is then collected again and determine the desorption value with the same procedures as adsorption process. The period of stirring processes of 6 hours for both adsorption and desorption tests are obtained from the adsorption and desorption values that remain stable or reach the equilibrium. The whole procedure is illustrated in figure 4.5.

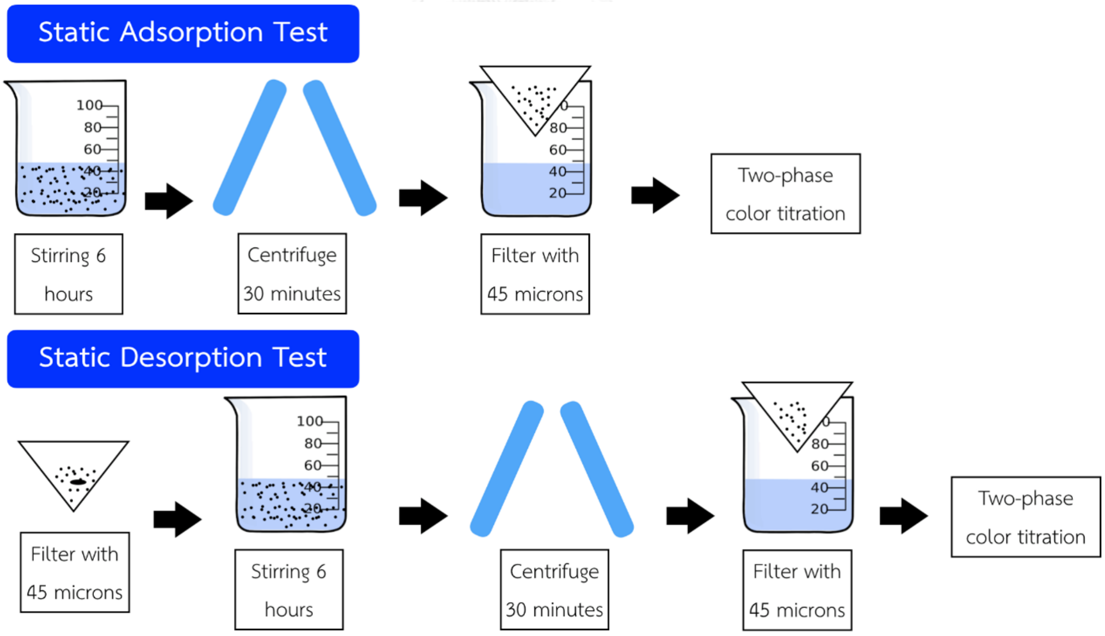

Figure 4.5 Static adsorption and desorption test procedures

As already mentioned, in order to quantify the amount of surfactant concentration in both adsorption and desorption processes, two-phase color titration is performed, a two-phase system is created with surfactant/water solution and chloroform, to which methylene blue which is an indicator is added (figure 4.6a). Methylene blue reacts with anionic surfactant to form chloroform soluble salts, causing it to concentrate in the chloroform phase (figure 4.6b). Hyamine, a cationic surfactant, is used as a titrant, as it preferentially forms a complex with the anionic surfactant, freeing methylene blue to migrate to aqueous phase. The end point is recorded when the two phases reach separated color intensity, the upper part turns to deep blue color as the color of methylene blue, whereas the lower liquid part is colorless as the original color of chloroform (figure 4.6c).

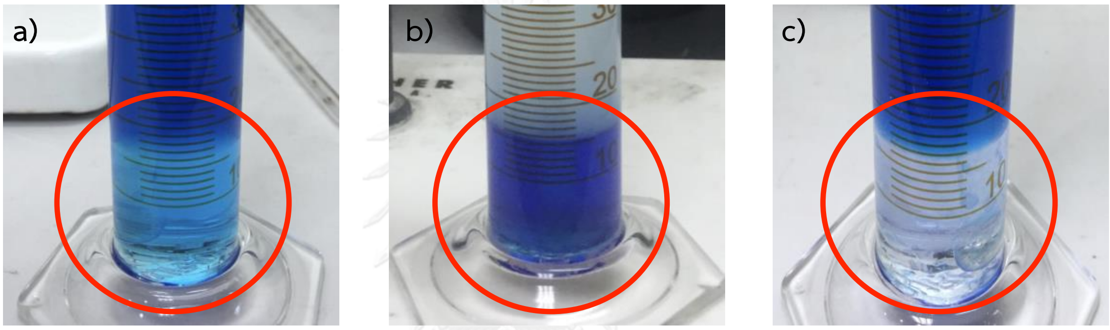

Figure 4.6 Color of solutions during color titration process of anionic surfactant a) start point, b) middle point, and c) end point

After performing two-phase color titration, in order to determine the adsorption and desorption values, the relationship of opposite charge property of surfactant is applied. As the titrant used for anionic surfactant titration in this study is 0.004 molar hyamine solution which is cationic with positive charge of 1 where its molecular structure is illustrated in figure 4.7a and anionic surfactant used in this study is sodium dodecyl benzene sulfonate composing of negative charge of 1 where its molecular structure is illustrated in figure 4.7b; therefore, 1 mole of hyamine will react with 1 mole of sodium dodecyl benzene sulfonate.

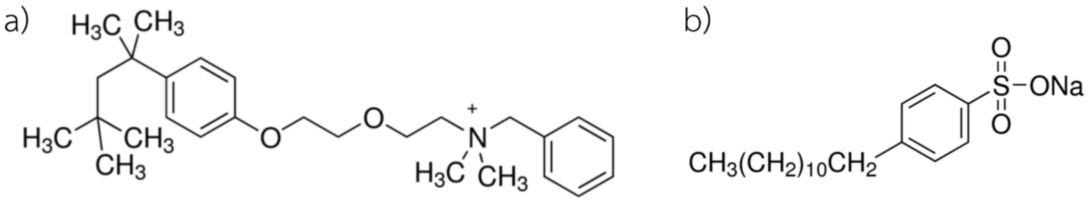

Figure 4.7 Molecular structure of a) hyamine b) sodium dodecyl benzene sulfonate

The selected amount of anionic surfactant solution used in titration is 10 ml from 100 ml mixture of 10 g anionic surfactant and distilled water. When the amount of hyamine solution used for reaching the end point of titration is determined, the concentration of remaining anionic surfactant from adsorption can be calculated by using the following equation:

$$n_{Sodium\,dodecylbenzenesulfonate} = n_{Hyamine} \quad \text{Equation 4.9,}$$

$$\frac{\%wt_{Remaining\ surfactant}}{100g_{Surfactant\ sol.}} \times \frac{\dfrac{Xg_{Surfactant\ sol.}}{348.48g_{Surfactant}}}{1\,mol_{Surfactant}} \times DF = \frac{\dfrac{0.004mol_{Hyamine}}{1L_{Hyamine}}}{\dfrac{1000ml_{Hyamine}}{1L_{Hyamine}}} \times V_{Hyamine} \quad \text{Equation 4.10,}$$

After calculating all of the constant values with X = 10 and 2 g, Equation 4.11 and 4.12 are obtained:

$$\%wt_{Remainingsurfactant} = 0.13939 \times V_{Hyamine} \quad \text{Equation 4.11,}$$

$$\%wt_{Remainingsurfactant} = 0.69696 \times V_{Hyamine} \quad \text{Equation 4.12,}$$

Therefore, the adsorption in case of static test is then calculated using Equation 4.13.

$$Adsorption = \frac{(\%wt_{Original\ surfactant} - \%wt_{Remaining\ surfactant})}{100} \times 1{,}000 \times SPR \quad \text{Equation 4.13}$$

where, $n_{Sodium\ dodecyl\ lbenzene\ sulfonate}$ = mole of sodium dodecyl benzene sulfonate, $n_{Hyamine}$ = mole of hyamine, X = 10 g solution for static and 2 g solution for dynamic test, DF = dilution factor, $V_{Hyamine}$ = volume of hyamine, 1000 = unit convertor from gram of surfactant to milligram of surfactant, SPR = surfactant per rock ratio.

The adsorption value obtained from the Equation 4.13 is in the unit of milligram of surfactant per 1 gram of rock (mg/g).

In case of desorption in the same unit as adsorption, Equation 4.11 is also applied to get $\%wt_{Remaining\ surfactant}$, the desorption is then calculated using Equation 4.14.

$$Desorption = \frac{\%wt_{Remaining\ surfactant}}{100} \times 1{,}000 \times SPR \qquad \text{Equation 4.14.}$$

4.3 Dynamic Adsorption and Desorption Test

Dynamic adsorption and desorption tests are performed by utilizing coreflood apparatus. The schematic of apparatus is illustrated in figure 4.8. From the figure, the simulate formation brine is filled in accumulator A, while the mixture of surfactant or alkali/surfactant is filled in accumulator B. There are two pressure detectors, inflow pressure is detected pressure in front of core holder, while outflow pressure is detected back pressure. To operate the system, simulate formation brine is injected into the core until the core is 100% saturated with formation brine. Then, formation brine is switched to surfactant slug. Effluent is collected from producing end every 2.0 cm^3 and titrated by two-phase color titration to quantify concentration of surfactant remained from flooding process. The flooding process is terminated when concentration of surfactant remained after passing through the core is constant or it is equal to the concentration of injected surfactant. Then, dynamic desorption is commenced. Formation brine is injected into core sample again to desorb the adsorbed surfactant. The effluent is collected every 2.0 cm^3 to identify concentration of surfactant from desorption process by two-phase color titration. For the case of desorption, flooding process is terminated when there is no more surfactant detected in the effluent or concentration of surfactant is zero.

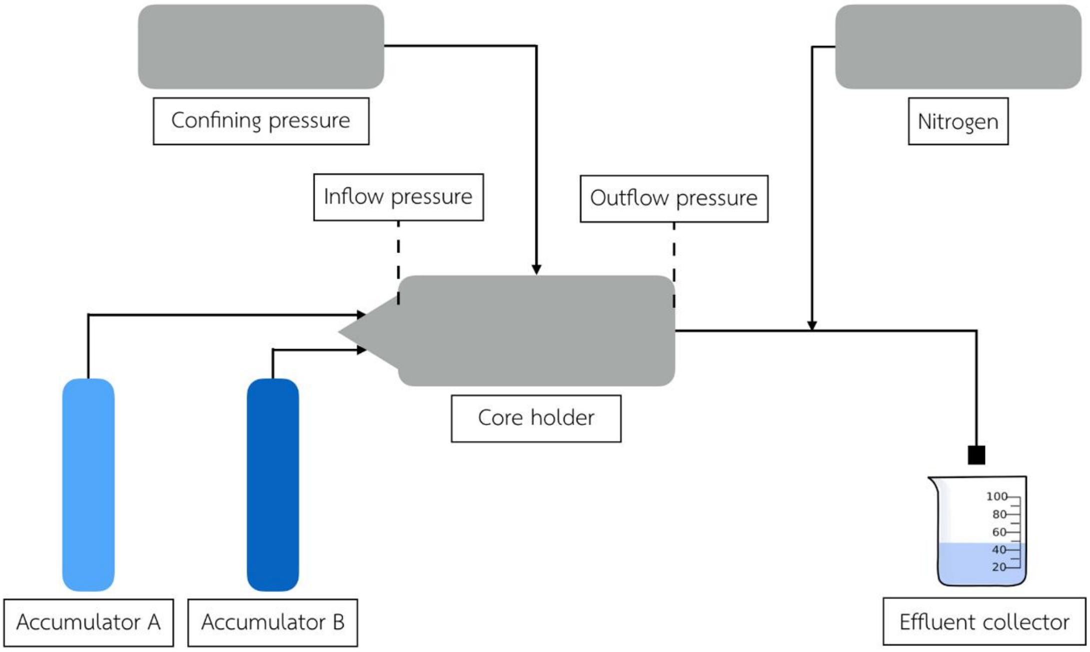

Figure 4.8 The schematic diagram of coreflood apparatus

The adsorption value is calculated by summation of surfactant remaining from flooding process compared to total amount of surfactant injected, whereas in the case of desorption, summation of desorbed amount is divided by total amount of adsorbed surfactant.

4.4 Thesis Methodology

1. Prepared the rock sample for both static and dynamic adsorption test. In this study, carbonate rock is used to represent reservoir rock as adsorption of anionic surfactant onto carbonate surface is generally higher compared to adsorption of anionic surfactant onto sandstone surface. For static test, the sample is grinded into grained size. The obtained data represent total adsorption from rock as rock surface is the maximum in spherical shape. Maximum adsorption is therefore applied to control amount of surfactant used in dynamic test. For dynamic test, core sample is cut into suitable cylindrical shape for performing in coreflood apparatus.

2. The samples are cleaned by using toluene and methanol, respectively in reflux glass apparatus (Soxhlet) followed by drying in the oven overnight.

3. Laboratory experiments are performed using anionic surfactant called sodium dodecyl benzene sulfonate on carbonate rock representing by Silurian dolomite.

   3.1 Static adsorption test

      3.1.1.Surfactant solution is prepared by distilled water and mixed with grinded carbonate sample until it reaches equilibrium stage in static condition. The mixture is then filtered and supernatant is collected by using fine paper filter to prevent the remaining carbonate particles in supernatant.

      3.1.2.Supernatant is diluted for titration using two-phase titration process in order to determine the remaining surfactant concentration. As a result, the adsorption can be calculated from differences between initial concentration and supernatant concentration.

      3.1.3.Surfactant-adsorbed carbonate grains are then mixed with distilled water until it reached the equilibrium to identify desorption of surfactant. After that, supernatant is collected again and used for the two-phase color titration process to determine concentration of surfactant from desorption.

      3.1.4.The blank test is conducted first in order to identify adsorption and desorption of anionic surfactant without presence of alkali by using value of surfactant concentration at 0.5 %wt.

      3.1.5.Pre-screening test for choosing type of alkali is performed in order to find the best suited alkali. In this section, three types of alkali are chosen including sodium hydroxide, sodium carbonate, and sodium hydrogen carbonate. The concentration of alkali and surfactant are fixed at 1.0 %wt and 0.5 %wt respectively. Both pre-injection and co-injection of alkali/surfactant are conducted.

3.1.6. The best alkali that results in the highest number of active monomer (the least adsorption and the highest desorption) from previous step is selected to perform static test with variation of alkali and surfactant concentrations. At this step, temperature is fixed at 30°C.

3.1.7. The conditions obtained from previous step are selected to perform dynamic test by using coreflood apparatus.

3.2. Dynamic adsorption test

3.2.1. Adsorption and desorption tests in dynamic mode are performed by using coreflood apparatus. Core sample is saturated using simulate formation brine. The reason why oil is not used in this study is because surfactant adsorption is adsorbed onto rock surface through aqueous phase not oil phase. Injection rate of 0.5 cm^3/min is initially applied as base injection rate.

3.2.2. Combination of surfactant and alkali is first injected to observe adsorption process. Effluent is collected at the producing end for every 2.0 cm^3 and titrated using two-phase color titration. Injection of surfactant-alkali formulation is ceased when concentration of surfactant at the producing end remains constant or the highest adsorption value is attained.

3.2.3. Brine that is used to prepare surfactant-alkali solution is injected instead of surfactant-alkali solution to perform desorption test. Effluent is collected and titrated as same as the adsorption test until the concentration of surfactant in effluent is equal to zero.

3.2.4. Calculate adsorption value, desorption value and degree of desorption from the mass balance equations.

3.2.5. Study effects of formation salinity by repeating task 3.2.1 to 3.2.4 with formation brine of 10,000 ppm, 20,000 ppm, and 35,000 ppm.

3.2.6. Study effects of injection rate by repeating task 3.2.1 to 3.2.4 at the injection rate 0.2, and 0.8 cm^3/min.

3.2.7. Study effects of temperature by repeating task 3.2.1 to 3.2.4 at the controlled temperature of 70°C.

3.2.8. Operate the optimum condition with the operating parameters obtained from 3.25, 3.26, and 3.27 that can achieve the highest surfactant active monomers in aqueous phase.

The flow chart of methodology in static and dynamic tests are illustrated in figure 4.9 and 4.10, respectively.

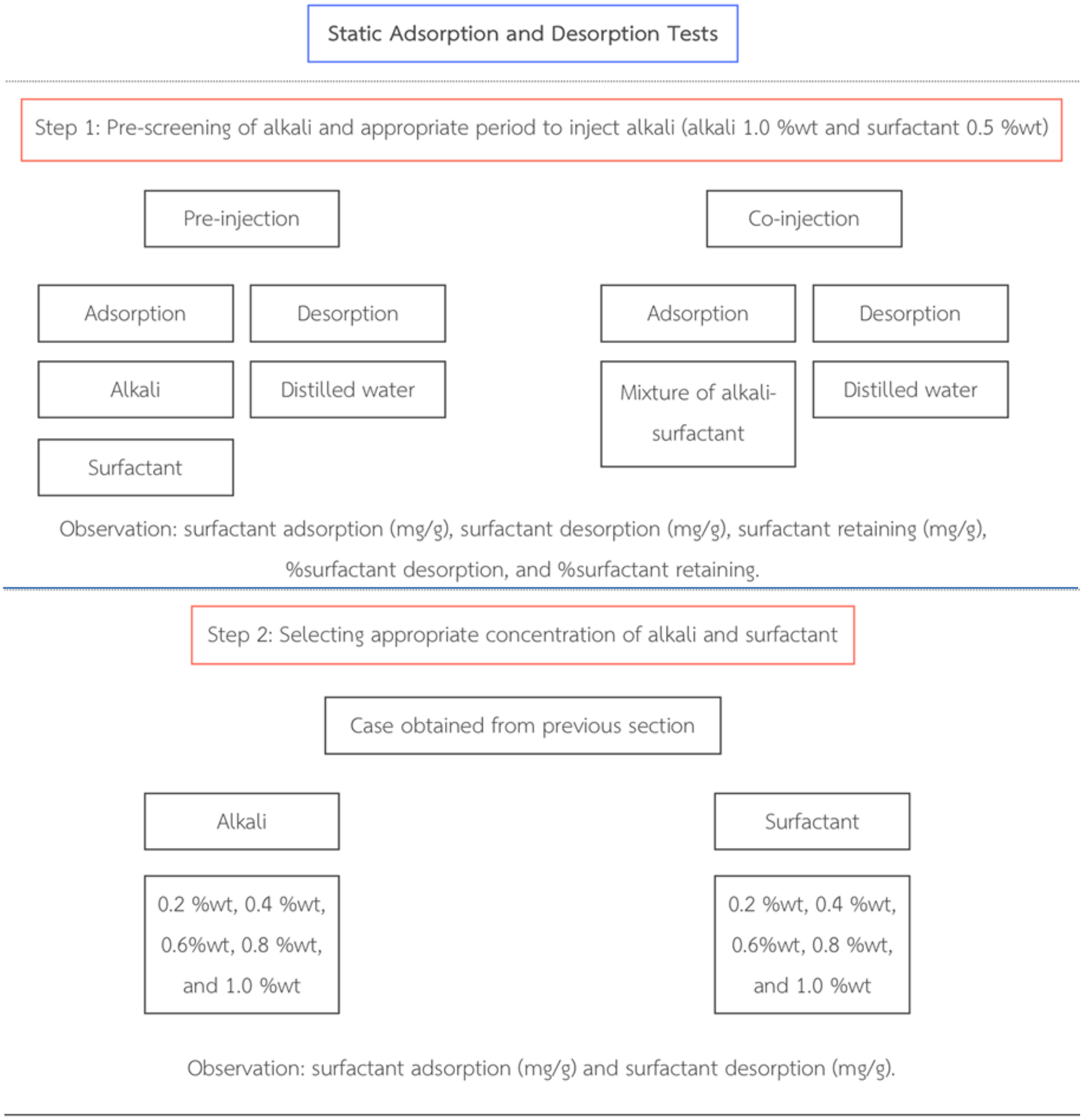

Figure 4.9 Summary of steps in static adsorption and desorption tests

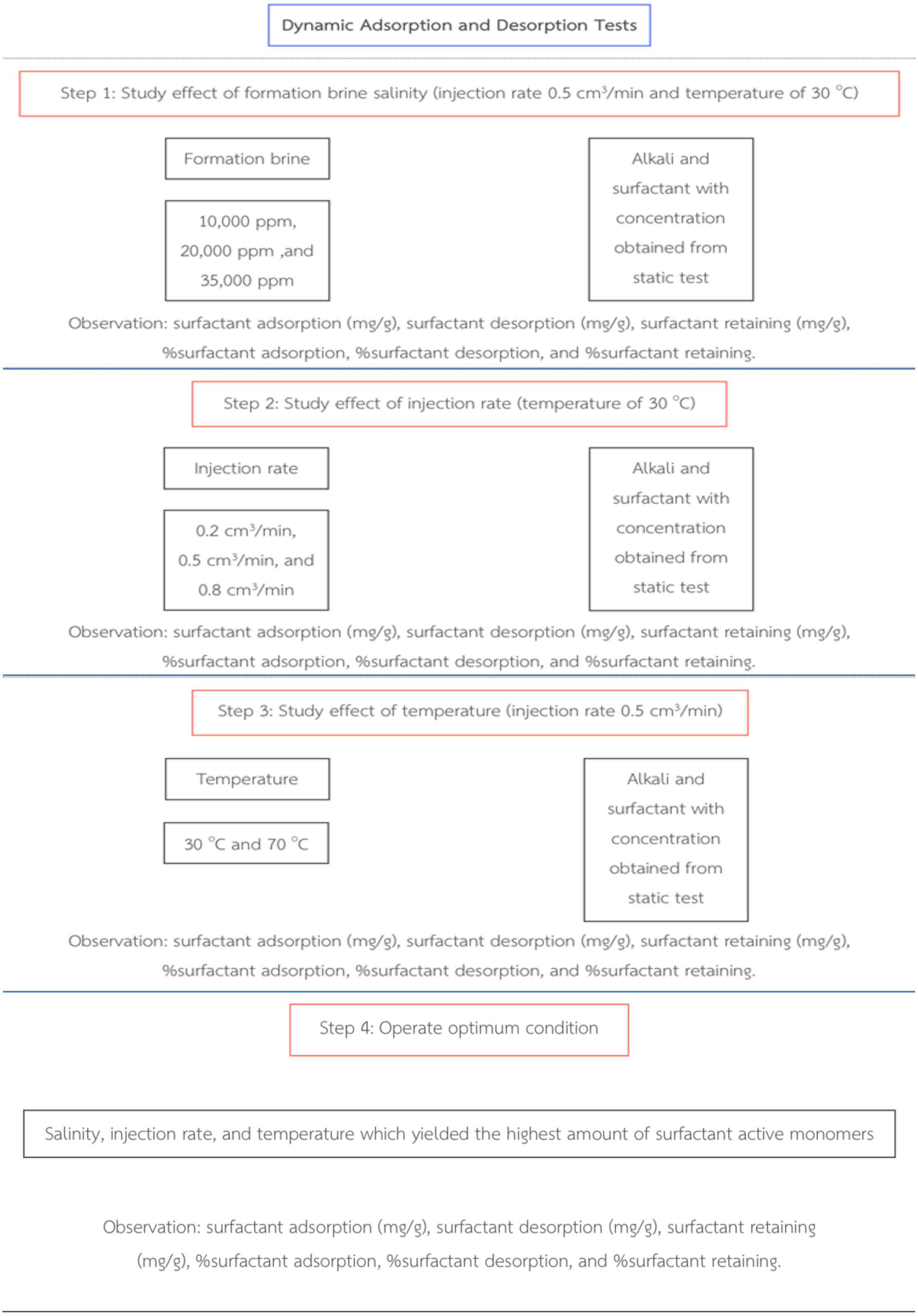

Figure 4.10 Summary of steps in dynamic adsorption and desorption tests

CHAPTER 5

RESULTS AND DISCUSSION

In this study, a main goal is to reduce adsorption value and in turn, to increase amount of active surfactant monomers remained in the aqueous phase during surfactant flooding by an aid of alkaline substances. The experiment is designed and performed as previously mentioned in Chapter 4. Results and discussion in this chapter follow the designed experiment. Summary of results are as followed:

5.1 Petrophysical Properties of Rock Samples
5.2 Static Adsorption and Desorption Tests
5.3 Dynamic Adsorption and Desorption Tests
5.4 Optimum Case with the Least Surfactant Adsorption

5.1 Petrophysical Properties of Rock Samples

Outcrop Silurian dolomite is chosen for the entire study to represent characteristics of carbonate reservoir. The form sample can be separated into grain-size and cylindrical core samples dedicated for the study of adsorption and desorption of surfactant in static and dynamic modes, respectively. Petrophysical properties of core and grain samples are summarized in table 5.1 and 5.2 respectively.

Table 5.1 Properties of core sample

Parameters	Values	Units
Permeability	43.60	millidarcy
Pore Volume	10.20	cm^3
Porosity	0.15	fraction

Table 5.2 Properties of grain-size samples

Parameters	Values	Units
Grain Size	75-125	Microns
Grain Density	2.80	g/cm^3

5.2 Static Adsorption and Desorption Tests

5.2.1 Results of Pre-Screening Type of Alkali

From the pre-screening section, results from static test in terms of adsorption, desorption, and retaining surfactant onto rock surface in unit of milligrams per one gram of rock are summarized in table 5.3 and figure 5.1.

Table 5.3 Results of pre-screening of type of alkali and period of injection

Cases	Alkali concentration (%wt)	Adsorption (mg/g)	Desorption (mg/g)	Retaining (mg/g)
Solely Surfactant	0	9.58	1.81	7.76
Pre-inject with NaOH	1	7.90	1.18	6.72
Co-inject with NaOH	1	6.44	2.09	4.35
Pre-inject with $NaHCO_3$	1	7.90	2.30	5.60
Co-inject with $NaHCO_3$	1	5.39	1.60	3.79
Pre-inject with Na_2CO_3	1	7.76	2.51	5.26
Co-inject with Na_2CO_3	1	4.00	1.67	2.33

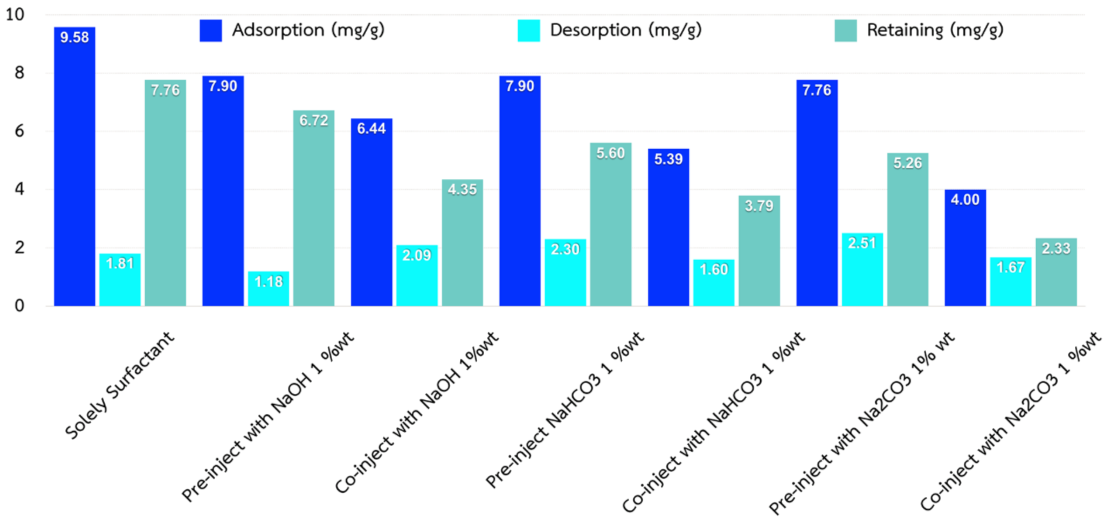

Figure 5.1 Summary of prescreening type of alkali and period of injection

From results in this section, it can be observed that surfactant adsorption and desorption in case of solely surfactant or without alkaline substance is relatively higher than other cases with alkaline substance. This can be explained that surfactant molecules are easily absorbed onto rock surface due to the opposite charges of carbonate surface which is positively charged in neutral pH value and ionized surfactant which is negatively charged. According to period of adding alkali, adsorption values in all cases of pre-injection are higher than that of co-injection as well as desorption data. As carbonate surface is positively charged, injected alkali is quickly depleted as alkali exhibits negative charge when ionized in aqueous phase. As pH value is above 9 which is point of zero charge of carbonate, surface is switched to negative charge. Once surfactant is proceeded, pH value is reduced again since surfactant has no ability to raise pH value as same as alkaline substance. This results in switching of surface charge of carbonate surface back to positive again. Anionic surfactant is hence easily adsorbed.

Comparing to the co-injection process, anionic surfactant and alkali possess similar charge properties. They are then competitive in adsorption onto carbonate surface and as a consequence, amount of adsorbed surfactant is less than the case of pre-injection of alkali.

Desorption data for every type of alkali is slightly lower in co-injection process. This is due to less amount of adsorbed surfactant molecules. However, retaining surfactant molecules is obviously less in case of co-injection that confirms the benefit of co-injection of surfactant together with alkali.

Comparing between different types of alkali in co-injection process, sodium hydroxide which is the strongest base, causes the highest surfactant adsorption. As ionization of hydroxide ion is completed, active hydroxide ions also push surfactant to be closer to rock surface while it is competing with surfactant in adsorption. Sodium hydrogen carbonate which is the weakest base also results in high surfactant adsorption. As pH value provided by this weak base may not exceed the point of zero charge of carbonate surface, anionic surfactant can still be adsorbed onto rock surface.

In case sodium carbonate which is moderately strong base, the least adsorption value is observed. Moreover, the highest desorption can be also achieved. Adequate ionization property of sodium carbonate preferentially competes surfactant adsorption, pushing surfactant to adsorb onto rock surface as in case of hydroxide ion but less amount. Nevertheless, at the same time, pH value of sodium carbonate is high enough to switch charge of rock surface. In order to sum up the results in this section, the values of surfactant, desorption and retaining in percentage of adsorption are provided as in table 5.4.

Table 5.4 Percentage of surfactant desorption and retaining in the proportion of adsorption values

Cases	Alkali Concentration (%wt)	Desorption (%)	Retaining (%)
Solely Surfactant	0	18.89	81.11
Pre-inject with NaOH	1	14.94	85.06
Co-inject with NaOH	1	32.45	67.55
Pre-inject with $NaHCO_3$	1	29.11	70.89
Co-inject with $NaHCO_3$	1	29.68	70.32
Pre-inject with Na_2CO_3	1	32.35	67.65
Co-inject with Na_2CO_3	1	41.75	58.25

According to the results in table 5.4, summation of desorption and retaining surfactant is 100 % which is total amount of adsorbed surfactant. Moreover, from the table it can be seen that co-injection of sodium carbonate illustrates the least retaining surfactant in percentage. From table 5.3 and 5.4 co-injection of surfactant with sodium carbonate is then selected for following step to verify the optimum concentrations for both alkali and surfactant.

5.2.2 Optimum Concentrations of Alkali and Surfactant

In this section, mixtures of alkali-surfactant with various concentrations of 0.2, 0.4, 0.6, 0.8, and 1.0 %wt for both alkali and surfactant are prepared in order to identify the optimum concentrations. Adsorption data for all combinations are demonstrated in table 5.5, whereas figure 5.2, and figure 5.3 graphically illustrate results of surfactant adsorption as a function of surfactant concentration and alkali concentration, respectively.

Table 5.5 Summary of surfactant adsorption from various concentrations of both alkali and surfactant

Category		Surfactant Concentration (%wt)				
		0.20	**0.40**	**0.60**	**0.80**	**1.00**
Alkali Concentration (%wt)	**0.20**	2.34	7.01	7.35	8.64	10.16
	0.40	2.00	6.41	6.31	6.20	7.08
	0.60	1.99	4.11	3.80	2.72	3.34
	0.80	3.13	4.38	4.01	3.50	3.76
	1.00	3.45	4.53	4.12	4.18	4.37

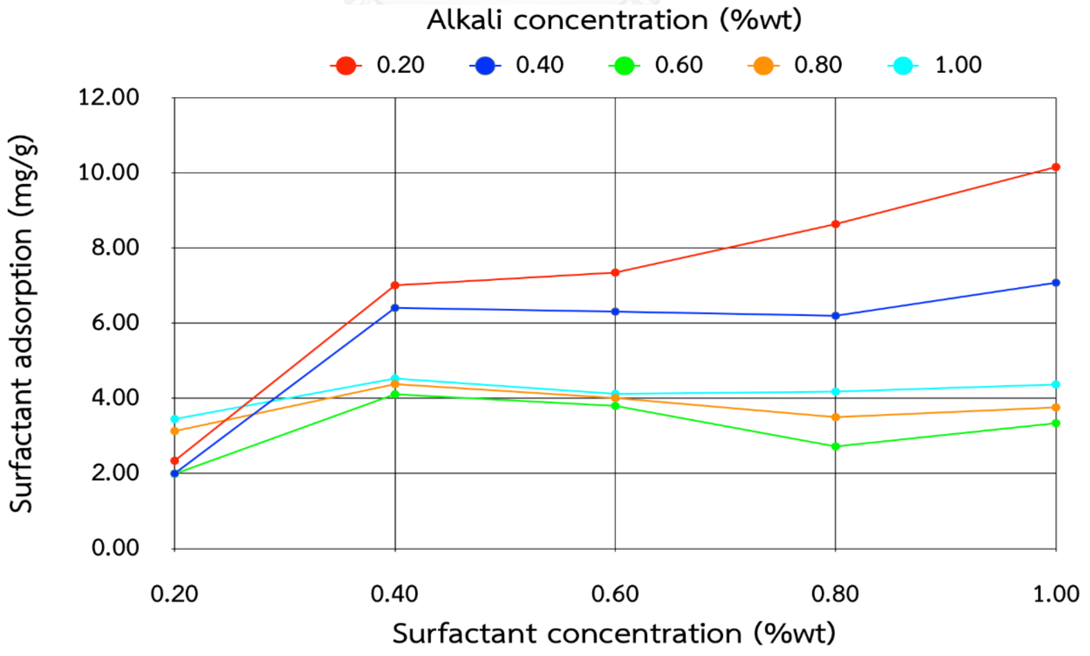

Figure 5.2 Surfactant adsorption (mg/g) as a function of surfactant concentration (%wt)

From figure 5.2, increasing surfactant concentration in low surfactant concentration zone (0.2-0.4 %wt) results in increment of surfactant adsorption for every alkali concentration as can be explained by isotherm diagram [12]. As monomers freely move and rock surface, which is active adsorption site, contains less adsorbed molecules of surfactant, increasing surfactant concentration increases chances of monomers to be adhered onto rock surface. Beyond surfactant concentration of 0.4%, adsorption starts to differentiate. With alkali concentration of 0.2%, this concentration shows only increasing trend from the start due to inadequate sacrificial alkali agent. In another word, the effects from charge of surfactant is stronger than charge provided by alkaline substance.

Higher alkali concentration than 0.4 %wt starts showing decreasing of adsorption value. Interestingly, increasing surfactant concentration results in reduction of surfactant adsorption in cases of alkali concentration from 0.4 to 1.0 %wt. In case of alkali concentration of 0.6 %wt, decrease of surfactant concentration is the most obvious. It could be explained that, both surfactant and alkali are attracted by carbonate surface at the same level. From this figure, it can be observed that adsorption of each component is dependent on concentration of themselves as well as concentration of another presenting component. In another word, higher surfactant concentration may force molecule alkali at 0.6 %wt to be adsorbed as sacrificial agent and hence, surfactant adsorption is substantially reduced.

From figure 5.3, adsorption data is illustrated as a function of alkali concentration. Even the adsorption is very small in case of low surfactant concentration representing by red line, this concentration may not be favorable in terms of operating condition as low surfactant concentration will corresponds to high interfacial tension data. Moreover, surfactant depletion may cause a rapid change of interfacial value and as a consequence, displacement recovery can be difficultly expected. Besides surfactant concentration of 0.2 %wt, this figure shows an optimum alkali concentration which is at 0.6 %wt. However, the optimum alkali concentration may not be the same in every system. This can be dependent on type of surfactant, type of alkali, salinity of water and also type of rock surface.

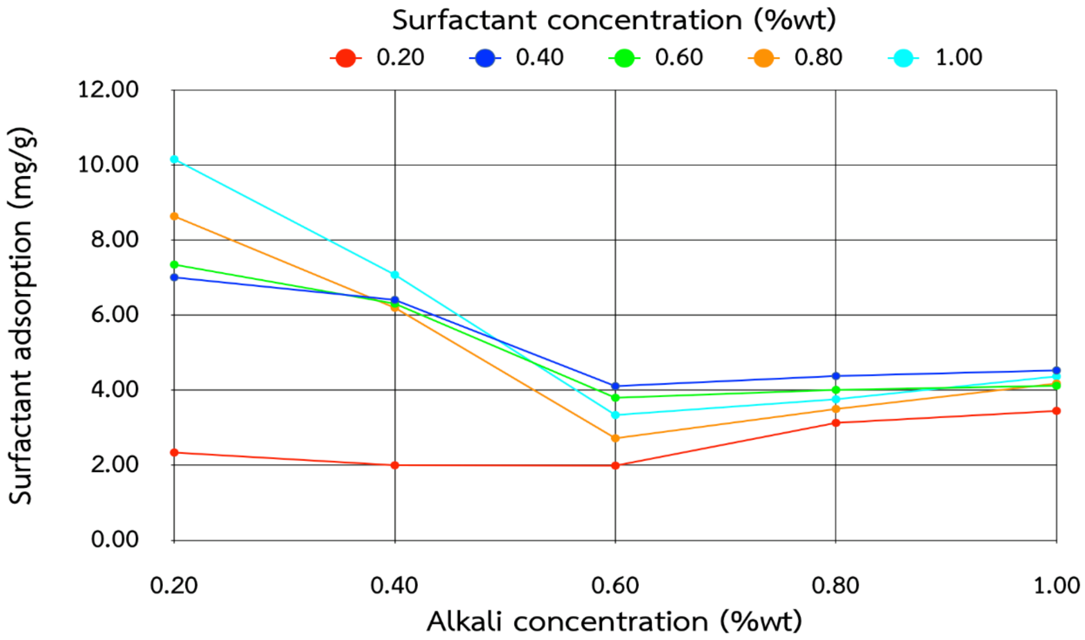

Figure 5.3 Surfactant adsorption (mg/g) as a function of alkali concentration (%wt)

After adsorption data is obtained, desorption test is performed by using distilled water to desorb previously adsorbed onto rock surface and summary of values of desorption in mg/g is shown in table 5.6. Again, in order to illustrate tendency of desorption data, figures 5.4 and 5.5 are plotted as a function of surfactant concentration and alkali concentration, respectively.

Table 5.6 Summary of surfactant desorption from various concentrations of both alkali and surfactant

Category		Surfactant Concentration (%wt)				
		0.20	**0.40**	**0.60**	**0.80**	**1.00**
Alkali Concentration (%wt)	**0.20**	0.21	0.62	0.78	0.96	1.12
	0.40	0.35	0.80	0.97	1.20	1.50
	0.60	0.84	1.40	1.89	2.14	2.33
	0.80	1.25	1.80	2.23	2.44	2.61
	1.00	1.58	2.00	2.50	2.67	2.84

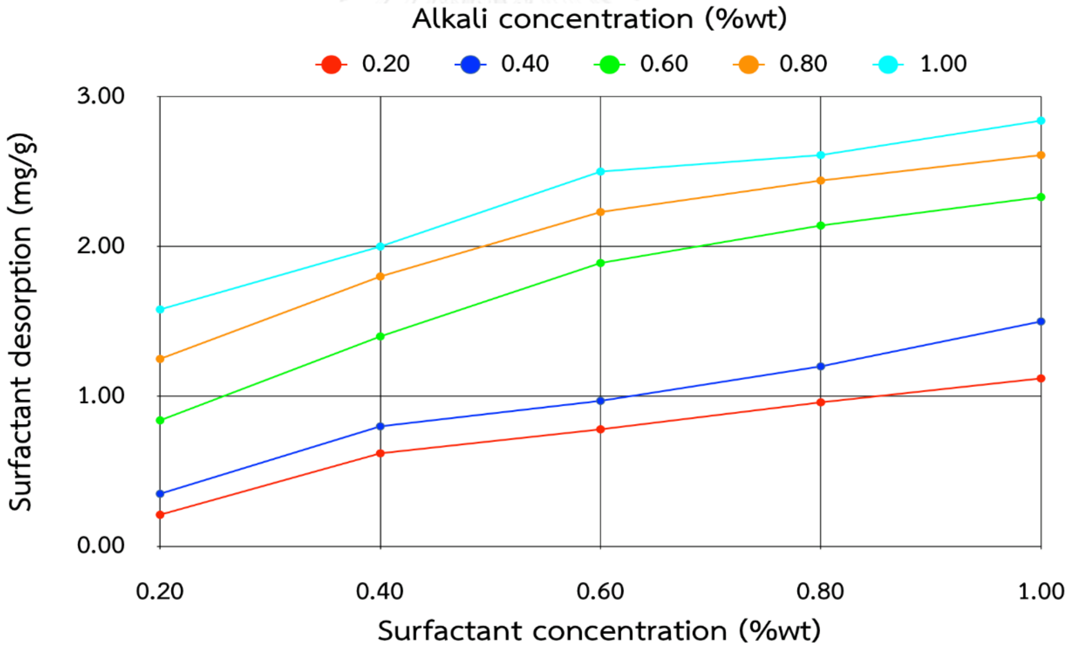

Figure 5.4 Surfactant desorption (mg/g) as a function surfactant concentration (%wt)

From figure 5.4 it shows that desorption is increased with an increment of surfactant concentration as well as alkali concentration. Even though adsorption data shows an optimal value at specific alkali and surfactant concentration, desorption tends to have direct relationship with both concentrations.

At 0.2-0.4 %wt of alkali concentration, desorption is hardly occurred since negative charge from alkali is too small to switch carbonate surface to negatively-charged condition. At the optimal concentrations (0.8% wt surfactant and 0.6% wt alkali) where the smallest number of surfactant is absorbed onto rock surface, desorption is still dependent on concentrations of both alkali and surfactant. This can be additionally explained that, at smaller number of adsorbed surfactant, more molecules of alkali are adsorbed as sacrificial agent and hence, adsorbed monomers can be desorbed at high degree by this reason. For, higher adsorption values, monomers may be adsorbed onto rock surface in different patterns such as double layers adsorption and hence, higher alkali concentration may result in loosely pack of these layers and therefore, absorbed monomers can desorb in high degree as well.

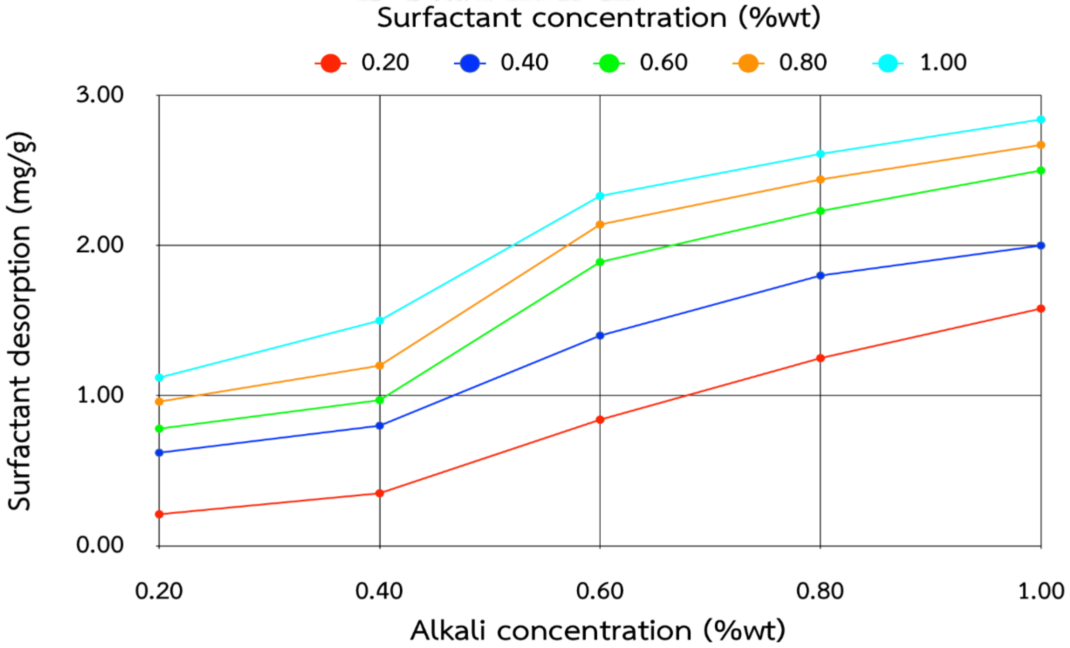

Figure 5.5 Surfactant desorption (mg/g) as a function of alkali concentration (%wt)

Figure 5.5 also confirms similar explanation of figure 5.4 that desorption of surfactant does not depend on adsorbed amount but it is dependent mainly on both surfactant concentration and alkali concentration. More than just previous explanations, figure 5.5 shows that desorption value increases strikingly from alkali concentration of 0.40 to 0.60 %wt which could explain that this range of alkali concentration, alkali starts to compete with surfactant to be adsorbed onto rock surface and hence, desorption is increased due to switching of charge property. At higher alkali concentration beyond 0.6 %wt, desorption still increases but less than previous range. The presence of less steep slopes may be due to concentration of negative charge onto rock surface and hence, desorption starts to gradually change.

From static adsorption experiment, surfactant concentration of 0.8% and alkali concentration of 0.6% are selected for dynamic adsorption and desorption tests by coreflood apparatus. These concentrations result in the highest active monomers remain in aqueous solution as alkali competes at higher degree to be adsorbed onto rock surface instead of surfactant molecules which is a favorable condition for sacrificial agent. Nevertheless, it is also observed that desorption is independent from adsorbed amount but it depends mainly on both concentrations of surfactant and alkali.

5.3 Dynamic Adsorption and Desorption Tests

Dynamic test is performed to observe effects of salinity of simulate formation brine, injection rate, and temperature. The test is conducted using only one core sample to observe effects of all the mentioned parameters with attempt to exclude effects from heterogeneity of rock samples. In this part, sodium carbonate and SDBS with the concentration of 0.6 %wt and 0.8 %wt, respectively are prepared as a mixture and filled in accumulator B to perform co-injection of alkali-surfactant.

5.3.1 Effects of Salinity of Simulate Formation Brine

As already mentioned, formation brine with salinity of 10,000, 20,000, and 35,000 ppm are prepared and in order to avoid precipitation of surfactant by divalent ions, all formation brines are prepared without divalent ions. The injection rate of 0.5 cm^3/min and temperature of 30°C are applied throughout experiment in this section. Result composing of amount of adsorbed surfactant, amount of desorbed surfactant, amount of retaining surface onto rock surface, percent adsorption, percent desorption and percent retaining are summarized in table 5.7 and figure 5.8.

Table 5.7 Summary of surfactant adsorption, surfactant desorption, and surfactant retaining in cases with various formation brine salinities

Observation parameters	**Salinities**		
	10,000 ppm	**20,000 ppm**	**35,000 ppm**
Surfactant adsorption (mg/g)	0.88	1.15	1.50
Surfactant desorption (mg/g)	0.62	0.54	0.49
Surfactant retaining (mg/g)	0.26	0.62	1.01
Adsorption (%)	43.39	44.12	47.01
Desorption (%)	70.64	46.59	32.88
Retaining (%)	29.36	53.41	67.12

In order to confirm the adsorption and desorption due to changing of surface charge property in dynamic adsorption and desorption tests, pH value is measured by pH paper every 2 cm^3 of each collected effluent to compare P.Z.C. of carbonate rock (about 9). The measurement of pH is performed in the initial case with salinity of 10,000 ppm, injection rate of 0.5 cm^3/min, and temperature of 30°C. The results are illustrated in table 5.8 and figure 5.6. From the table, it can be seen that pH value starts from 7 which is the value of formation brine with salinity of 10,000 ppm with less amount of alkali and surfactant concentrations. Once injected chemical is about to arrive, pH value starts to raise and it is eventually higher than value of 9 until the collected effluent reaches 46 cm^3 with the surfactant concentration is equal to 0.8 %wt as injected surfactant concentration. After that, formation brine is injected to perform desorption test and due to mixing of alkali solution and formation brine, pH value starts to decline again.

Table 5.8 Summary of surfactant remaining (%wt) and pH value in every 2 cm^3 of effluent

Collected effluent (cm^3)	Surfactant remaining (%wt)	pH value
2	0.00	7
4	0.01	7
6	0.03	7
8	0.03	7
10	0.12	7
12	0.17	7
14	0.20	7
16	0.31	7
18	0.36	7
20	0.45	8
22	0.52	8
24	0.60	8
26	0.65	8
28	0.68	8
30	0.72	9
32	0.74	9
34	0.75	9
36	0.77	9
38	0.78	9
40	0.79	11
42	0.80	11
44	0.80	11
46	0.80	11
48	0.78	10
50	0.72	9
52	0.70	9
54	0.66	8
56	0.60	8
58	0.56	8
60	0.45	8
62	0.33	8
64	0.22	8
66	0.10	8
68	0.03	8
70	0.00	8

Figure 5.6 Measurement of pH by pH paper

From the results, it can be observed that surfactant adsorption is higher when salinity of formation brine is increased. This can be explained that surfactant molecules which ionize in aqueous phase are encountered with more amount of ionized species in water, forcing surfactant molecule to get closer to rock from repulsion force from anionic ions (chloride ion, sulfate ion and hydrogen carbonate ion). The higher the salinity therefore, brings more anionic ions that cause repulsion force and consecutively, higher surfactant adsorption value. Illustration of adsorption mechanism caused by repulsion force between same charge properties is shown in figure 5.7. However, there are alkali ions also adsorbed on the rock surface at the same time as a sacrificial agent.

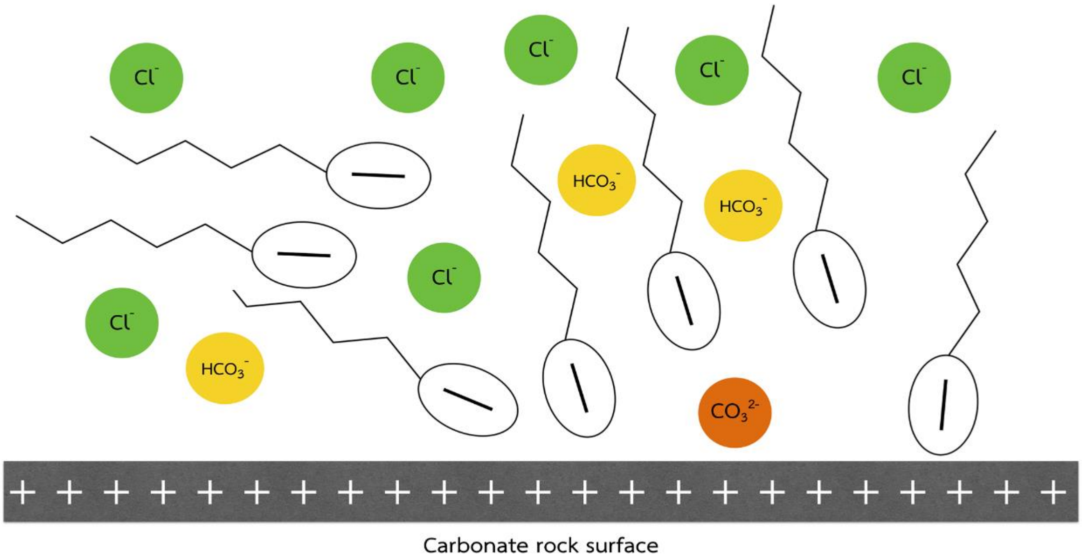

Figure 5.7 Adsorption of surfactant active monomers caused by repulsion force of negative ions in simulate formation brine

Once adsorption occurs, adsorption strength is developed and it is higher in case of high salinity formation brine as can be observed from the desorption percent which are 70.64, 46.59, and 32.88 for the formation brine concentrations of 10,000, 20,000, and 35,000 ppm, respectively. Moreover, higher brine salinity results in higher amount of occupying anionic ions, tending to obstruct the desorption mechanism of anionic surfactant. According to this, the percentage of surfactant retaining on the rock surface is higher in the case of higher salinity as 29.36, 53.41, and 67.12 for brine concentration of 10,000, 20,000, and 35,000 ppm, respectively. In addition, in order to find the optimum condition to operate surfactant flooding in the presence of alkali substances, the simulate formation brine at the concentration of 10,000 ppm is then selected to study effects injection rate in the next section and also in optimum condition in section 5.4.

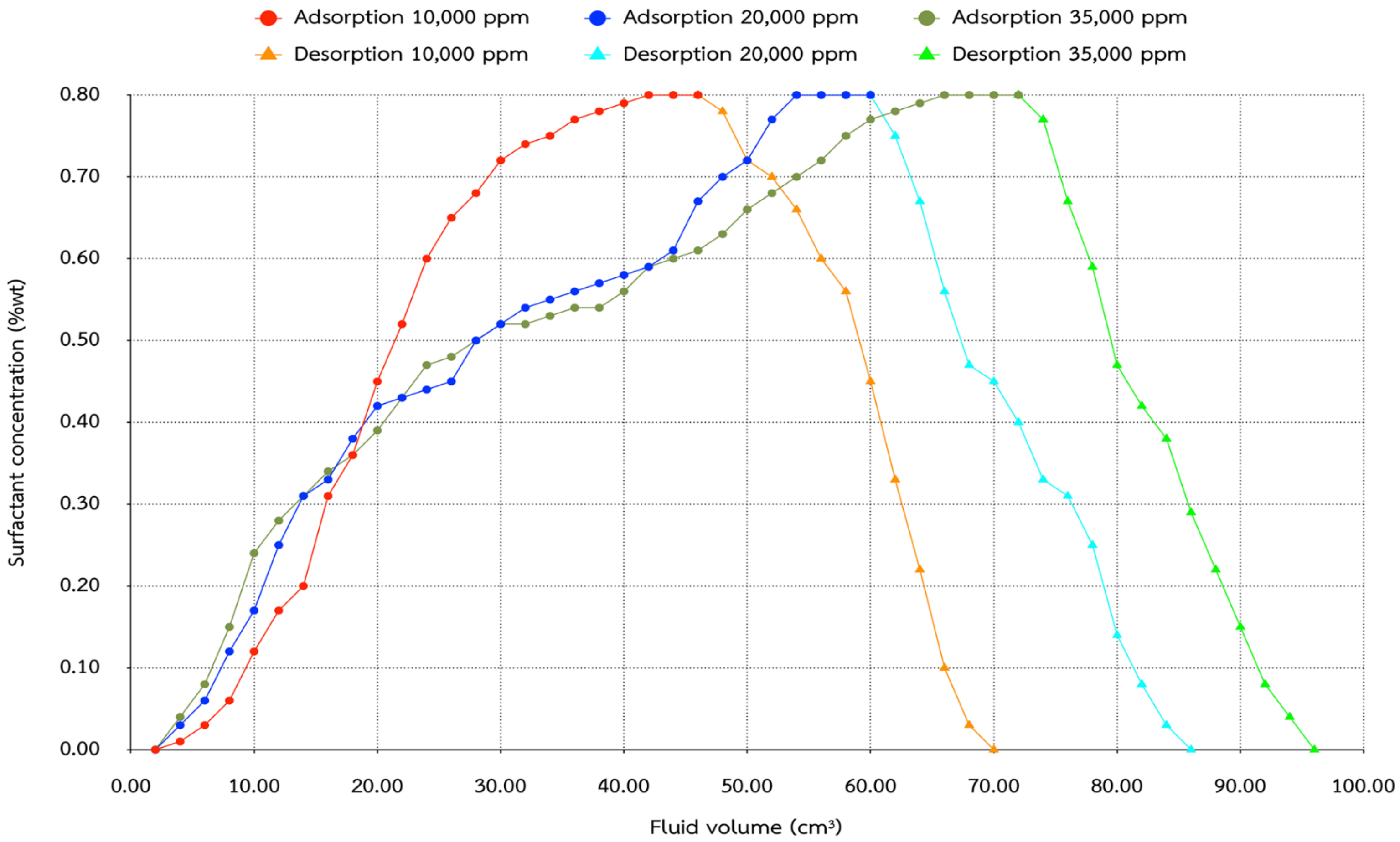

Figure 5.8 Surfactant concentration during adsorption-desorption test in dynamic mode for different formation brine concentrations as a function of fluid injected volume

5.3.2 Effects of Injection Rate

In this section, salinity of simulate formation brine of 10,000 ppm, temperature of 30°C are fixed. The injection rate of 0.2, 0.5, and 0.8 cm^3/min are performed in order to observe the effects of injection rate as retention time of surfactant onto rock surface is one of suspicious parameters for surfactant. Results obtained from coreflood experiment are demonstrated in table 5.9 and figure 5.10.

Table 5.9 Summary of surfactant adsorption, surfactant desorption, and surfactant retaining in cases with various fluid injection rates

Observation parameters	**Injection rates**		
	0.2 cm^3/min	**0.5 cm^3/min**	**0.8 cm^3/min**
Surfactant adsorption (mg/g)	1.18	0.88	0.58
Surfactant desorption (mg/g)	0.70	0.62	0.47
Surfactant retaining (mg/g)	0.48	0.26	0.11
Adsorption (%)	50.57	43.39	39.67
Desorption (%)	59.73	70.64	81.09
Retaining (%)	40.27	29.36	18.91

From the results, it can be seen that surfactant adsorption is higher with the lower injection rate. This can be explained that at low injection rate, retention time allowing contact between surfactant molecules and rock surface is longer than in high injection rate and therefore, there is enough time for surfactant molecules to react with rock surface and to generate chemisorption between opposite charges. The adsorption values are 1.18, 0.88, and 0.58 mg/g for the injection rate of 0.2, 0.5, and 0.8 cm^3/min, respectively. Illustration of interaction of surfactant molecules onto rock surface in different injection rates is illustrated in figure 5.9.

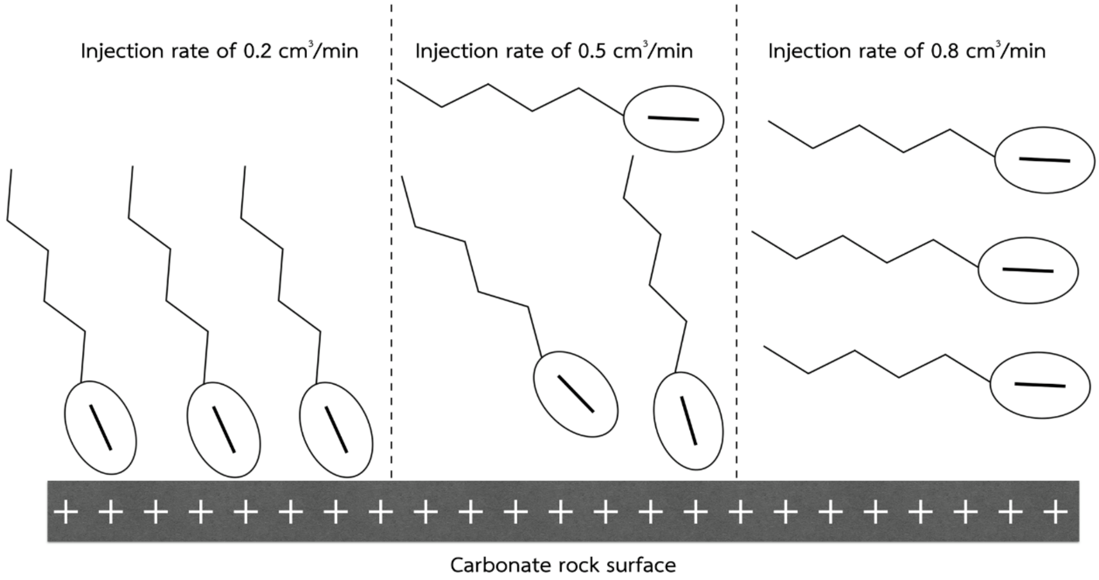

Figure 5.9 Surfactant adsorption in different injection rates

Moreover, at small injection rate, desorption is also difficult to emerge because of higher strength of bond between surfactant and rock surface is formed and this yields smaller desorption value. According to surfactant retaining, the faster surfactant molecules move pass through porous media of core, resulting in less amount of retaining molecule onto rock surface as the time to contact to rock surface is not adequate to generate high strength bond between them. Thus, the percentage of retaining molecules are 40.27, 29.36, and 18.91 for injection rate of 0.2, 0.5, and 0.8 cm^3/min, respectively. For this reason, the injection rate 0.8 cm^3/min is then selected for operating in optimum condition in section 5.4.

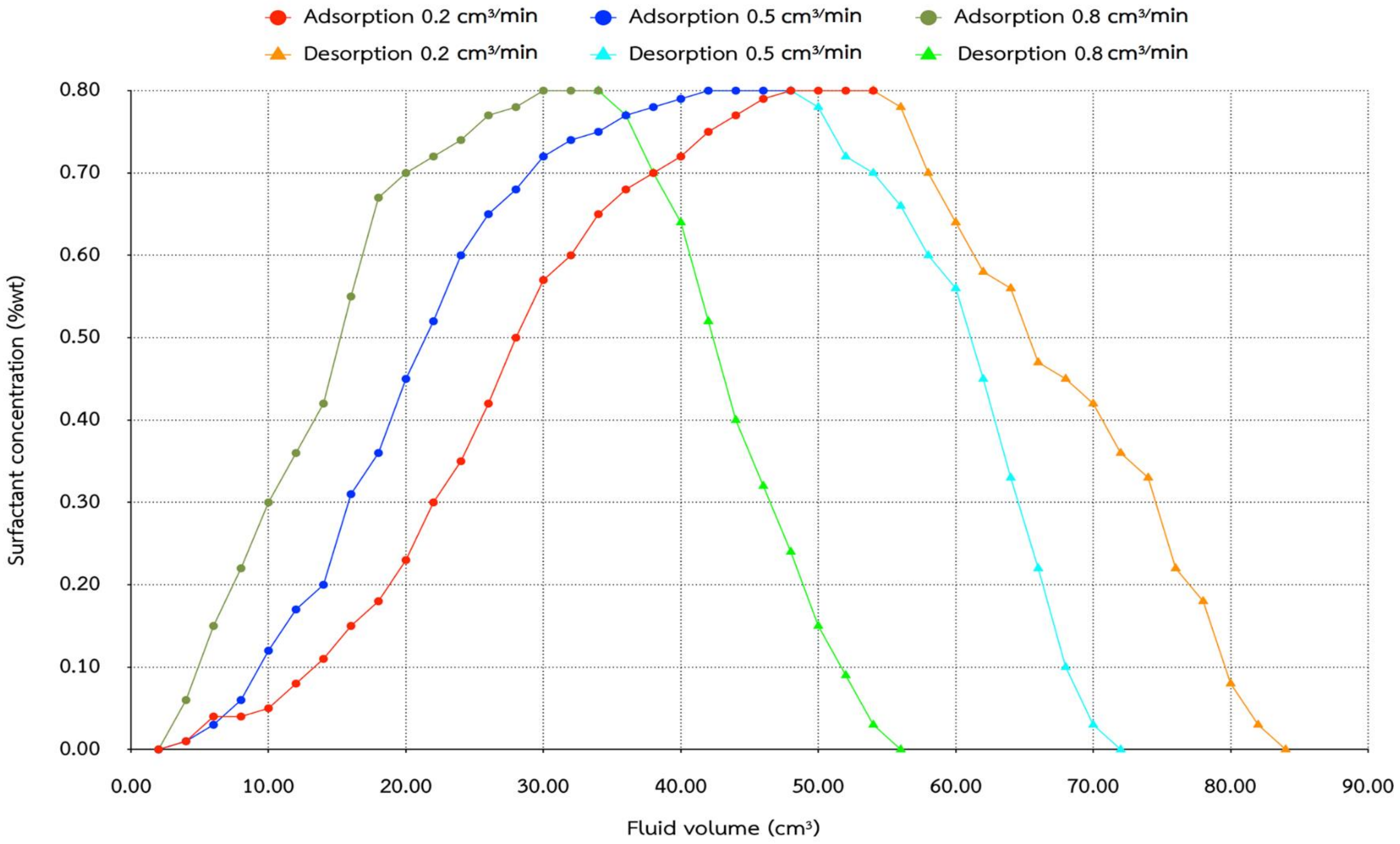

Figure 5.10 Surfactant concentration during adsorption-desorption test in dynamic mode for different injection rates as a function of fluid injected volume

5.3.3 Effects of Temperature

For this section, the injection rate of 0.5 cm^3/min and formation salinity of 10,000 ppm are utilized. Two reservoir temperatures of 30°C and 70°C are selected in order to observe the effects of temperature in adsorption-desorption. Results are summarized in table 5.10 and figure 5.12.

Table 5.10 Summary of surfactant adsorption, surfactant desorption, and surfactant retaining in cases with various temperatures

Observation parameters	Temperatures	
	30°C	70°C
Surfactant adsorption (mg/g)	0.88	0.63
Surfactant desorption (mg/g)	0.62	0.54
Surfactant retaining (mg/g)	0.26	0.09
Adsorption (%)	43.39	36.69
Desorption (%)	70.64	85.31
Retaining (%)	29.36	14.69

From the results, it can be seen that in case of higher temperature, adsorption is low compared to low testing temperature. At high reservoir temperature that is still below the temperature where surfactant starts to degrade, solubility of surfactant molecules in aqueous phase is also higher and hence, surfactant molecules preferably stay in bulk fluid instead of staying closer to rock surface. As a result, adsorption is 0.88 and 0.63 mg/g for temperatures of 30°C and 70°C, respectively. However, the difference of the mentioned values is not that much as the adsorption is still taken place at high temperature system. Interestingly, for the desorption test, the adsorbed surfactant can desorb in higher percentage at high temperature as, corresponding to 85.31 mg/g compared to value at low temperature which is 70.64 mg/g. The reason to describe this behavior is that at high temperature, surfactant molecules are more active with higher kinetic energy and they tend to move faster in random direction. Therefore, high energy molecule cannot stay paused onto rock surface and preferably stay in with more freedom which is in aqueous phase. Figure 5.11 illustrates activity of surfactant molecules at different temperatures.

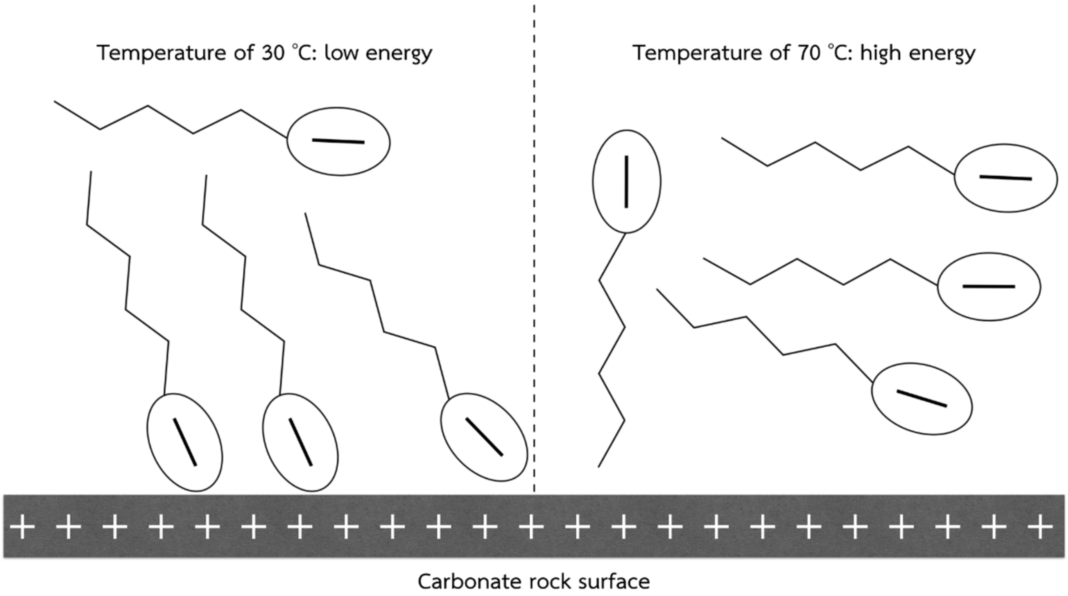

Figure 5.11 Illustration of surfactant molecules at different temperatures

Higher energy of surfactant molecules results in less contact onto rock surface or even they are into contact with rock surface, the bond between rock and surfactant molecules is not strong and so easy to break. Moreover, this also yields less in retaining surfactant in case of high temperature. For this reason, the temperature of 70°C is selected to operate in optimum condition in section 5.4.

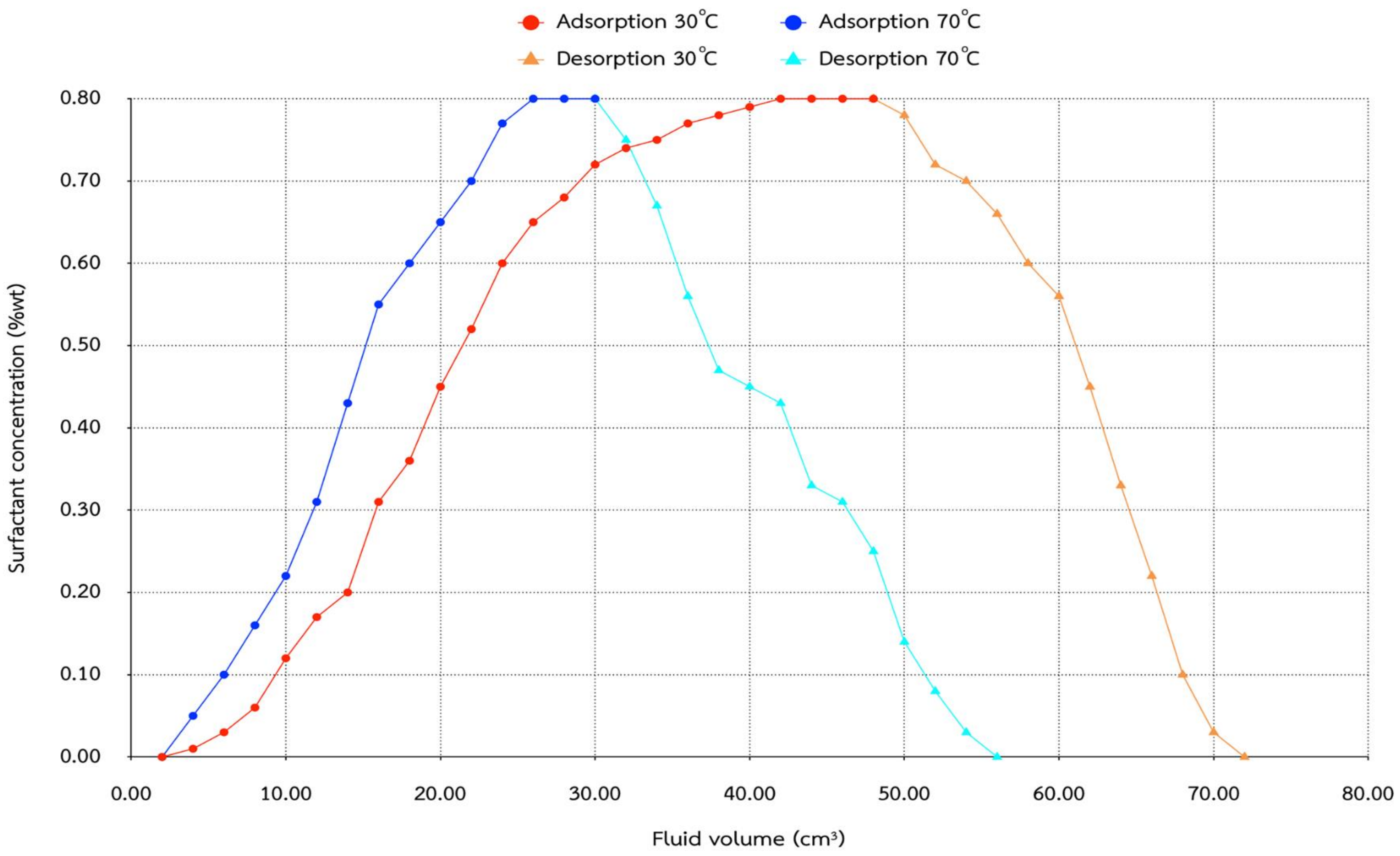

Figure 5.12 Surfactant concentrations during adsorption-desorption test in dynamic mode for different temperatures as a function of fluid injected volume

5.4 Optimum Case

After the study of effects of simulate formation brine salinity, injection rate, and temperature on surfactant adsorption, surfactant desorption, and surfactant retaining, each best value is selected and combined to confirm the optimum conditions for alkali-surfactant flooding to avoid high surfactant adsorption. Values of each parameters obtained from previous section to represent optimum case are summarized in table 5.11 and results are illustrated in table 5.12 and figure 5.13.

Table 5.11 Summary of optimum values of studied parameters obtained from previous section

Parameters	Values	Units
Simulate formation brine salinity	10,000	ppm
Injection rate	0.8	cm^3/min
Temperature	70	^oC

Table 5.12 Summary of surfactant adsorption, surfactant desorption, and surfactant retaining obtained from optimum case

Observation Parameters	Values
Surfactant adsorption (mg/g)	0.43
Surfactant desorption (mg/g)	0.39
Surfactant retaining (mg/g)	0.04
Adsorption (%)	40.11
Desorption (%)	91.22
Retaining (%)	8.78

From the results, it can be indicated that to operate surfactant flooding in the presence of alkali, the other operational parameters such as brine salinity (representing pre-flushed water or make up water), injection rate, and temperature also play important roles to reduce surfactant loss during the operation. Operating alkali-surfactant flooding with all mentioned parameters yielding the least surfactant loss in each case together can further improve adsorption value and also increase amount of active surfactant monomers in the system.

In summary, not only concentrations of alkali or surfactant should be considered, avoiding high adsorption can also be concerned from operating parameters. Salinity of pre-flushed water or make up water should be kept as small as possible. As anionic ions in water can provoke surfactant ions to adhere onto rock surface, these ions should be removed or diluted as much as possible. Reservoir temperature might be parameter that is not included in operational parameters. However, choosing to perform alkali-surfactant flooding in reservoir with high temperature can offset high loss of surfactant due to surfactant adsorption onto rock surface. Last, high injection rate should be performed when alkali-surfactant flooding is performed. Reduction of retention time is additional way to reduce surfactant adsorption.

Nevertheless, this fulfilment of data of surfactant adsorption/desorption must be balanced with interfacial tension data obtained from IFT measurement. An optimum condition for alkali-surfactant flooding may change due to the optimum point in terms of IFT condition.

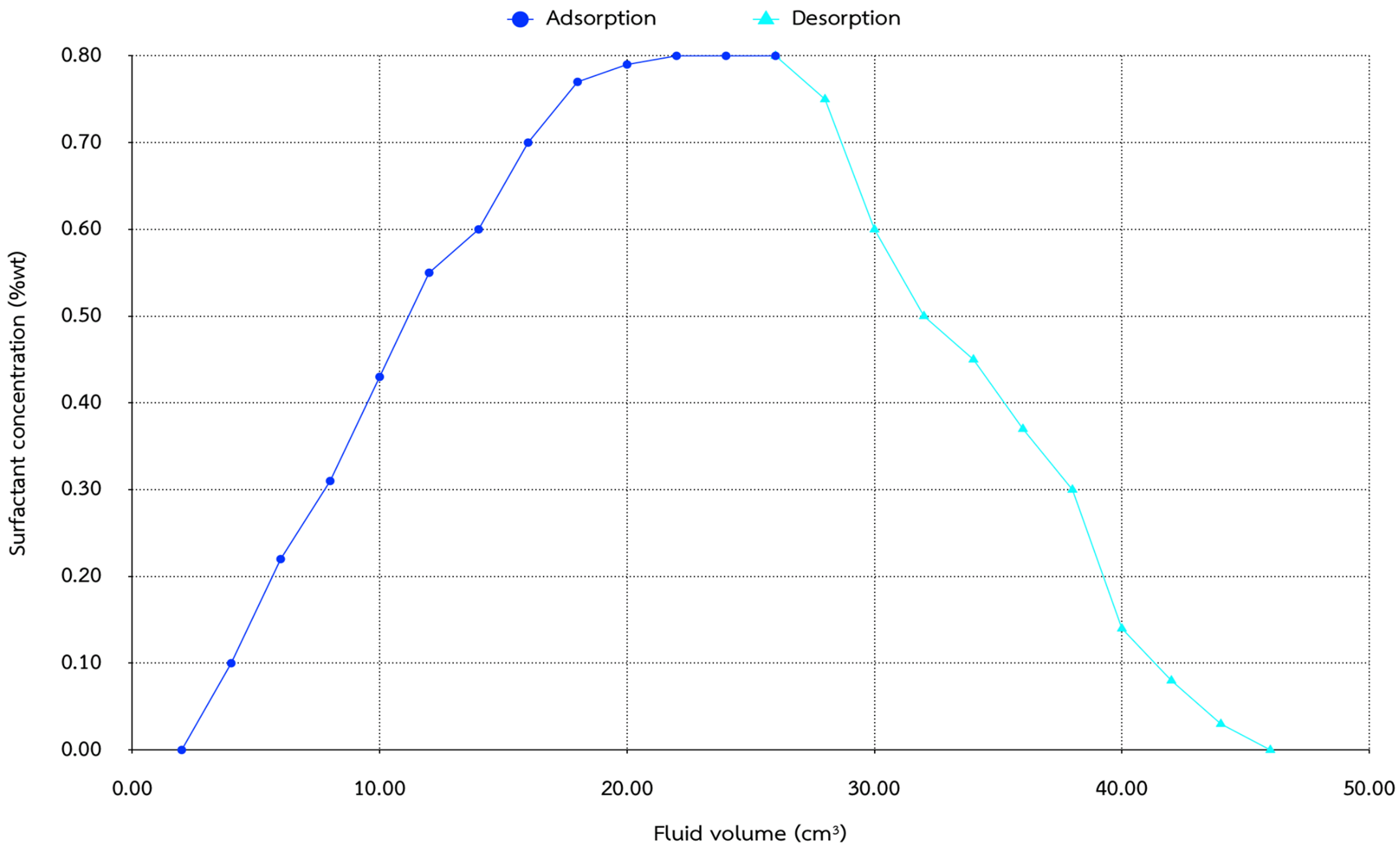

Figure 5.13 Surfactant concentrations during adsorption-desorption test in dynamic mode for case combining optimum value of each studied parameter as a function of fluid injected

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

Surfactant loss by adsorption onto rock surface is one of the major concerns in surfactant flooding especially in carbonate reservoirs where surface charge is under unfavorable condition to utilize simple anionic surfactants. Therefore, this study is performed to identify the optimum conditions of using the combination of alkali and surfactant to reduce surfactant adsorption onto the rock surface. Conclusions and recommendations from results given in the previous chapter are summarized in this chapter.

6.1 Conclusions

From results and discussion in Chapter 5, summaries of this study can be concluded as follows:

1. From static adsorption and desorption tests, co-injection of alkali, which is sodium carbonate (Na_2CO_3), yields the lowest surfactant adsorption and at the same time the highest surfactant active monomers in aqueous phase. The reason is that sodium carbonate which is moderately strong base can provide adequate amount of negative charge to compete surfactant molecules in adsorbing onto carbonate surface. At the same time, it is not too strong to push surfactant molecules to be closer to rock surface. Moreover, its pH, which is around 11, is greater than point of zero charge of carbonate rock surface (around 9) and hence, it can switch surface charge form positive to negative, resulting in less amount of adsorbed surfactant.

2. Concentrations of both surfactant and alkali also affect surfactant adsorption as well as desorption. At higher surfactant concentration, both adsorption and desorption levels are increased. For alkali concentration, optimum concentration exists. Higher alkali concentration corresponds to lowering surfactant adsorption until alkali concentration reaches 0.6 %wt. After this optimum concentration, surfactant adsorption starts to increase again due to charge competition. This study in this found

that, a mixture of alkali-surfactant at 0.6%wt. and 0.8 %wt, respectively, provides the least surfactant adsorption value of 4.00 mg/g together with desorption value of 1.67 mg/g, and as a result this yields the least retaining surfactant value of 3.33 mg/g. These conditions provide the highest amount of active surfactant monomers compared to the other cases.

3. In the study of dynamic adsorption and desorption, co-injection of alkali and surfactant at optimum concentrations is performed to study effects of brine salinity, injection rate, and temperature. Salinity plays an important role in surfactant adsorption and desorption. High salinity of makeup brine or formation brine is a condition causing high loss of surfactant through adsorption onto rock. Moreover, surfactant desorption is also inhibited. Water salinity of 10,000 ppm which is the smallest value shows the best satisfactory in terms of number of active surfactant monomer.

4. Small injection rate results in high adsorption values due to longer retention time between ionized surfactant and rock surface. Higher desorption value is obtained when high injection rate is applied as bonding of opposite charges between rock surface and surfactant molecules cannot be firmly formed and hence it is easy to break. Therefore, the highest injection rate in this study which is 0.8 cm^3/min is suggested due to less surfactant adsorption and more surfactant desorption.

5. In the study of formation temperature, higher temperature results in low level of adsorption since surfactant molecules are more active from kinetic energy and, therefore, surfactant molecules are more likely to move freely in aqueous phase instead of attaching onto rock surface. In this study, higher temperature which is 70°C.

6. Combinations of best conditions in this study shows that at very good conditions favoring the least adsorption and best desorption of surfactant, surfactant adsorption is further reduced to 0.43 mg/g with surfactant desorption is 0.39 mg/g, and eventually results in surfactant retaining is 0.04 mg/g, which can further increase the amount of surfactant active monomers in aqueous phase.

6.2 Recommendations

Several recommendations for both study parameters as well as technical aspects are provided in this section to improve level of study in the upcoming future.

1. In this study, only three types of alkali and one type of surfactant are utilized. Different types of both substance would increase understanding behavior of both chemicals during alkali-surfactant flooding.

2. Dolomite is used to represent carbonate reservoir in this study. However, dolomite which is composed of calcium magnesium carbonate is one of two carbonate rocks. A study on limestone should be conducted to confirm results for both types of carbonate rocks.

3. A study of adsorption/desorption mechanisms should be performed together with measurement of interfacial tension reduction to identify an exact optimum concentration that answers in terms of both minimizing lose and maximizing oil recovery.

4. As formation brine can be widely various, composition of water is another parameter to study. For anionic surfactant, anionic in water such as chloride ion, sulfate ion and hydrogen carbonate ion are presenting ions and their effects should be studied individually.

5. Fluid collecting from effluent is still performed manually. An automated fluid collecting system would reduce time consuming process of researcher.

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APPENDIX A
LABORATORY EXPERIMENTS

The determination of surfactant concentration in solution is performed by two-phase color titration which requires various laboratory equipment and chemical reagents.

1. Laboratory Equipment:

- 50 ml burette
- 100 and 1,000 ml beakers
- 100, 500, and 1,000 ml volumetric flasks
- 100 ml graduated cylinder
- 25 ml test tube
- Glass stirrer
- Magnetic stirrer
- 5 and 10 ml pipettes
- Mortar and pestle
- 45 microns filter paper
- Centrifugal machine
- Oven
- Coreflood apparatus

2. Reagents:

- Standard anionic surfactant: sodium dodecyl benzene sulfonate
- Titrant: hyamine 1622, standard 0.004 M solution
- Chloroform solution
- Methylene blue powder and solution
- Sulfuric acid solution
- Sodium hydroxide powder and solution
- Sodium chloride powder

- Sodium sulfate powder
- Sodium carbonate powder and solution
- Sodium hydrogen carbonate powder and solution
- Phenolphthalein indicator solution

3. Two-phase Color Titration Procedures:

- Transfer surfactant or alkali-surfactant solution after stirring process to 100 ml volumetric flask and dilute with distilled water.
- Transfer 10 ml of solution using 10 ml pipette to 100 ml graduated cylinder
- Add 2 or 3 drops of sodium hydroxide solution to ensure pH of solution is above 10
- Add 25 ml methylene blue solution
- Add 15 ml chloroform solution
- Titrate against hyamine solution by adding drop by drop
- Stir the solution vigorously by glass stirrer during titration
- End point is reached when two phases reach separated color intensity

APPENDIX B
SIMULATE FORMATION BRINE PREPARATION

The variation of salinities of 10,000, 20,000, and 35,000 ppm are composed of different types of cation and anion. In this research, the total amount of each ion is obtained from the average of three references of formation brine in carbonate reservoirs which are provided in table B.1.

Table B.1 Composition of ions of each formation brine from three references in ppm

Compositions	**Zahid et al. [14] (ppm)**	**Mohanty and Chandrasekhar [15] (ppm)**	**Romanuka et al. [16] (ppm)**
Na^+	59,491	49,933	64,900
Ca^{2+}	19,040	15,992	508
Mg^{2+}	2,439	1,282	16,592
SO_4^{2-}	350	234	3,310
HCO_3^-	354	0	61
Cl^-	132,060	111,810	136,423

As already mentioned in Chapter 4, simulate formation brine is prepared without divalent ions including Ca^{2+} and Mg^{2+} ions to prevent the precipitation. Therefore, ppm of previously mentioned ions are compensated by adding Na^+ as shown in table B.2.

Table B.2 Composition of ions of each formation brine without divalent ions in ppm

Compositions	**Zahid et al. [14] (ppm)**	**Mohanty and Chandrasekhar [15] (ppm)**	**Romanuka et al. [16] (ppm)**
Na^+	80,970	67,207	82,000
SO_4^{2-}	350	234	192
HCO_3^-	354	0	61
Cl^-	132,060	111,810	136,423

In order to qualify the amount of chemicals used to prepare simulate formation brine, unit of ppm is then converted to millimole per liter as summarized in table B.3.

Table B.3 Composition of ions of each formation brine without divalent ions in mmol/L

Compositions	**Zahid et al. [14] (mmol/L)**	**Mohanty and Chandrasekhar [15] (mmol/L)**	**Romanuka et al. [16] (mmol/L)**
Na^+	3,520.43	2,922.04	3,565.22
SO_4^{2-}	3.65	2.44	2
HCO_3^-	5.80	0	1
Cl^-	3,720.00	3,149.58	3,842.90
Total	7249.88	6,074.06	7,411.12

Then the converted data in %mol are summarized in table B.4.

Table B.4 Composition of ions of each formation brine without divalent ions in %mol

Compositions	**Zadit et al. [14] (%mol)**	**Mohanty and Chandrasekhar [15] (%mol)**	**Romanuka et al. [16] (%mol)**
Na^+	48.56	48.11	48.11
SO_4^{2-}	0.05	0.04	0.03
HCO_3^-	0.08	0	0.01
Cl^-	51.31	51.85	51.85
Total	100	100	100

The summary of average of %mol and mol of each ion are revealed as shown in table B.5.

Table B.5 The average %mol and mol of each ion

Compositions	**Average (%mol)**	**Average (mol)**
Na^+	48.26	0.4826
SO_4^{2-}	0.04	0.0004
HCO_3^-	0.03	0.0003
Cl^-	51.67	0.5167
Total	100	1.0000

The total gram and ppm of required chemicals are provided in table B.6.

Table B.6 The total gram and ppm of required chemicals

Chemicals	**gram**	**mg or ppm**
NaCl	28.1678	28,167.80
Na_2SO_4	0.0568	56.80
$NaHCO_3$	0.0252	25.20
Total	28.2498	28,249.80

In order to prepare simulate formation brine, the amount of chemicals used are summarized for each salinity in table B.7.

Table B.7 The chemicals used to prepare simulate formation brine at different salinities of 10,000, 20,000, and 35,000 ppm

Chemicals	**10,000 ppm**	**20,000 ppm**	**35,000 ppm**
NaCl (g)	9.97	19.94	34.90
Na_2SO_4 (g)	0.02	0.04	0.07
$NaHCO_3$ (g)	0.01	0.02	0.03

VITA

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