PHYSICAL PROPERTY MEASUREMENT OF SURFACTANT COUPLED WITH NANOPARTICLES FOR ENHANCED OIL RECOVERY

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การวัดค่าคุณสมบัติทางกายภาพของสารลดแรงตึงที่ใช้ร่วมกับอนุภาคนาโนเพื่อการผลิตน้ำมันเพิ่ม

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Field of Study	Georesources and Petroleum Engineering
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พู พวินท์ นันดาร์ : การวัดค่าคุณสมบัติทางกายภาพของสารลดแรงตึงที่ใช้ร่วมกับอนุภาคนาโนเพื่อการผลิตน้ำมันเพิ่ม. (PHYSICAL PROPERTY MEASUREMENT OF SURFACTANT COUPLED WITH NANOPARTICLES FOR ENHANCED OIL RECOVERY) อ.ที่ปรึกษาหลัก : รศ. ดร.เกรียงไกร มณีอินทร์

น้ำมันที่หลงเหลืออยู่ในแหล่งกักเก็บหลังจากการผลิตเบื้องต้นและการอัดฉีดน้ำสามารถผลิตได้โดยการเพิ่มการเคลื่อนที่ของน้ำมันหรือโดยการปรับเปลี่ยนพฤติกรรมการเปียกของหินกักเก็บและการลดแรงตึงระหว่างผิวหน้าของน้ำและน้ำมันการอัดฉีดสารลดแรงตึงผิวเป็นหนึ่งในวิธีการผลิตน้ำมันเพิ่มโดยใช้สารเคมีที่ความเข้มข้นที่เหมาะสมการอัดฉีดสารลดแรงตึงผิวสามารถทำให้เกิดแรงตึงผิวที่ต่ำซึ่งเอื้อประโยชน์ต่อการผลิตน้ำมันที่เพิ่มขึ้นในทางตรงกันข้ามการสูญเสียสารลดแรงตึงผิวที่ส่วนต่อของผิวระหว่างของแข็งกับของเหลวเนื่องจากการดูดซับจะลดปริมาณของสารลดแรงตึงผิวที่จำเป็นสำหรับการผลิตน้ำมันในระหว่างการอัดฉีดดังนั้นอนุภาคนาโนของซิลิกาจึงถูกนำมาใช้เพื่อปรับปรุงกระบวนการผลิตน้ำมันเพิ่มโดยใช้สารลดแรงตึงผิวในการลดการดูดซับของสารลดแรงตึงผิวให้น้อยที่สุดซึ่งส่งผลให้เกิดการเปลี่ยนแปลงความสามารถในการเปียกน้ำในการศึกษานี้จะสังเกตพฤติกรรมของแรงตึงผิวระหว่างน้ำมันกับส่วนต่อประสานต่างๆที่สภาวะของแหล่งกักเก็บจากผลลัพธ์ค่าแรงตึงผิวได้รับผลกระทบอย่างมากจากความเข้มข้นของสารลดแรงตึงผิวการมีอยู่ของอนุภาคนาโนในสารละลายลดแรงตึงผิวอุณหภูมิและความเค็มในตอนท้ายแรงตึงระหว่างผิวหน้าต่ำที่ต้องการจะเกิดขึ้นเมื่อใช้อนุภาคนาโน750ส่วนในล้านส่วนโดยน้ำหนักกับความเข้มข้นของสารลดแรงตึงผิว 2,000 ส่วนในล้านส่วนโดยน้ำหนัก ในสารละลายน้ำเกลือความเค็มต่ำ 750 ส่วนในล้านส่วนโดยน้ำหนัก

นอกจากนี้คุณสมบัติทางกายภาพเช่นความหนาแน่นของสารเคมีแต่ละชนิดรวมกันและความหนืดของตัวอย่างน้ำมันที่ได้มาจากแหล่งน้ำมันทางภาคเหนือของประเทศไทยจะถูกวัดโดยมีและไม่มีสารละลายลดแรงตึงผิวและอนุภาคนาโนซิลิกาช่วยแก้ปัญหาของสารลดแรงตึงผิวที่ความเข้มข้นต่างกันจากการทดลองสารลดแรงตึงผิวประจุลบโซเดียมโดเดซิลซัลเฟต(เอสดีเอส)และโซเดียมโดเดซิลเบนซีนซัลโฟเนต(เอสดีบีเอส)ถูกนำมาใช้ตามการดูดซับที่ต่ำกว่าในหินทรายเมื่อเทียบกับสารลดแรงตึงผิวประจุบวกจากผลการศึกษาได้ศึกษาพฤติกรรมการดูดซับแบบสถิตของสารลดแรงตึงผิวที่ส่วนติดต่อกับหินกักเก็บจากแหล่งน้ำมันภาคเหนือของประเทศไทยและนาโนซิลิกาสามารถลดการดูดซับของสารลดแรงตึงผิวได้จริงโดยการดูดซับที่พื้นผิวหินเองและความสามารถในการเปียกน้ำก็เปลี่ยนไปเช่นกันอย่างต่อเนื่องอย่างไรก็ตามการดูดซับอนุภาคนาโนจะมีผลเมื่อใช้ความเข้มข้นของสารลดแรงตึงผิวที่เกินความเข้มข้นของไมเซลล์วิกฤตในการเปรียบเทียบสารลดแรงตึงผิวที่มีประจุลบสองตัวเอสดีบีเอสแสดงการดูดซับบนตัวอย่างหินที่สูงกว่าการดูดซับของเอสดีเอส

กล่าวโดยสรุปจากการศึกษาการวัดคุณสมบัติทางกายภาพการเติมนาโนซิลิกาลงในสารละลายลดแรงตึงผิวช่วยเพิ่มพารามิเตอร์ที่สำคัญของการเพิ่มการผลิตน้ำมันแรงตึงผิวสามารถลดลงได้นอกจากนี้การดูดซับสารลดแรงตึงผิวยังสามารถลดลงได้หากใช้ความเข้มข้นที่สูงกว่าความเข้มข้นของไมเซลล์วิกฤตนอกจากนี้นาโนซิลิกายังสามารถช่วยลดมุมสัมผัสได้อย่างมีประสิทธิภาพและสนับสนุนการผลิตน้ำมันสำหรับการอัดฉีดโดยใช้สารลดแรงตึงผิว

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The residual oil remained in the reservoir after the primary recovery and water flooding can either be produced by increasing the mobility of the oil or by altering the reservoir rock wetting behavior and diminishing the oil water interfacial tension. The surfactant flooding is one of the chemical enhanced oil recovery methods. At the optimal concentration, the surfactant flooding can provide the low interfacial tension favoring to the enhanced oil recovery. In contrast, the loss of the surfactant at the solid-liquid interface due to an adsorption lessens the amount of the surfactant required for oil displacement during the flooding. Therefore, the silica nanoparticles are used to enhance the surfactant EOR process in minimizing the surfactant adsorption which also results in the wettability alteration. In this study, the behavior of the interfacial tension between oil and different interfaces at the reservoir conditions are observed. From the results, IFT is greatly affected by the surfactant concentration, the presence of the nanoparticles in the surfactant solution, temperature and salinity. At the end, the desired low interfacial tension is achieved when 750 ppm by weight of nanoparticles are used with 2000 ppm concentration of the surfactant in the low salinity of 750 ppm brine solution.

In addition, the physical properties such as densities of each combination of chemicals and viscosities of oil samples acquired from northern Thailand oilfield are measured with and without the surfactant solutions and the silica nanoparticles assisted the surfactant solutions at the different concentration. From the experiments, the anionic surfactants, sodium dodecyl sulfate (SDS)and sodium dodecylbenzene sulfonate (SDBS) are used according to the lower adsorption in the sandstones compared to the cationic surfactants. From the results, the static adsorption behavior of the surfactant at the interface with the reservoir rock from the northern Thailand oilfield is studied and the nano silica can indeed reduce the adsorption of the surfactant by being adsorbed at the rock surface itself and the wettability is also changed consecutively. However, the sacrificial adsorption of the nanoparticles become effective when the surfactant concentration beyond the critical micelle concentration is used. In comparison of two anionic surfactant, SDBS shows the higher adsorption on the rock sample rather than that of SDS.

In conclusion, from the study of the physical property measurement, adding the nano silica to the surfactant solutions enhances the important parameters of EOR. The IFT can be reduced. Also, the surfactant adsorption can be lowered if concentration above CMC is used. Also, the nano silica can provide the effective contact angle reduction and support the oil recovery for the surfactant flooding.

Field of Study:	Georesources and Petroleum Engineering	Student's Signature .....
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Phoo Pwint Nandar

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EOR	Enhanced Oil Recovery
IFT	Interfacial Tension
SDS	Sodium Dodecyl Sulfate
SDBS	Sodium Dodecylbenzene Sulfonate
NP	Nanoparticles
ppm	Parts Per Million
wt	Weight

CHAPTER 1
INTRODUCTION

1.1 Introduction

Oil production can be distinguished into three phases: primary recovery, secondary recovery and tertiary or enhanced oil recovery (EOR). Initially, crude oil and hydrocarbon are produced with the primary recovery method or natural flow throughout the early production in which oil displacement efficiency relies principally on the reservoir pressure. Later, it decreases to a point when the hydrocarbon can no longer be produced commercially with the assistance of natural drive mechanisms alone. Therefore, the secondary recovery method is introduced, and oil recovery factor rises once again by means of the secondary recovery methods, water flooding, gas injection and the aid of artificial lifts. Nevertheless, the oil recovered by conventional methods, primary and secondary ones, ranges from 20% to 40% depending on oil and the reservoir properties(Nikolova & Gutierrez, 2020). Also, a significant amount of residual oil is still left within the reservoir as a result of capillary pressure, the small mobility ratio, high viscous oil and reservoir heterogeneity or disadvantageous reservoir or fluid characteristics. this amount can take almost up to two-third of original oil in place (OOIP) (Gbadamosi et al., 2019). Leading to the aim of oil recovery beyond traditional recovery, the tertiary recovery methods or enhanced oil recovery methods are implemented to improve the oil production from the reservoir.

The tertiary or enhanced oil recovery (EOR) can be expressed as a process in which the natural reservoir energy is externally supplemented with the injection of foreign fluids and energy, not normally present in reservoir, to improve the sweep efficiency in the reservoir with the help of the injectants in order to produce the remaining oil which can either be residual oil or bypassed oil. The injected fluids and energy are aimed to increase the pressure difference between the reservoir and the production wells, to increase the mobility of oil by reduction of oil viscosity or decrease of the interfacial tension between the displacing fluids and oil, whereas the wettability of the reservoir rock is altered at the same time.

1.2 Types of EOR Methods

The main objectives of the EOR methods are to improve sweep efficiency by reducing the mobility ratio between the injected fluid and the reservoir fluid, to improve the displacement efficiency by reducing the interfacial tension forces and to act both functions simultaneously (Latil, 1980). Types of EOR methods are classified depending on the function served during the process and the nature of the reservoir rocks and the fluid properties. Depending on the types of fluids and energy injected into the reservoir, the principle EOR methods are thermal process, chemical process or immiscible process, miscible displacement process and biotechnology process (Green & Willhite, 1998) and the sub-divisions of each method are presented in Figure 1.1.

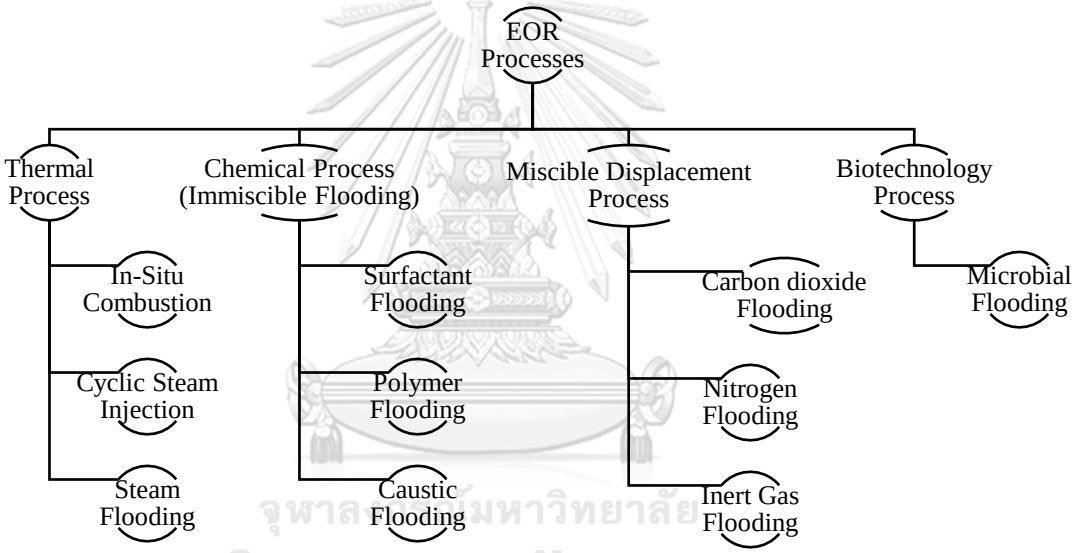


Figure 1. 1 Flow Chart of Enhanced Oil Recovery

The primary selection of EOR method to be used is based on the reservoir characteristics and the hydrocarbon in place properties. Based on the oil gravity range, the compactable methods are determined for the optimal recovery. For example, for heavy oil, the thermal method is the most suitable selection while the miscibility can be achieved in the light oil reservoirs, and the chemical processes are advantageous for the middle-ranged API oil reservoirs.

The thermal methods, steam flooding, cyclic steam injection and in-situ combustion, are the process of which involves injecting the steam generated at the

surface or in the well continuously, or in cycles. Nowadays, the thermal EOR method becomes the most efficient, widely used, and cost-effective method to enhance the oil production in case of the shallow wells having high viscous oil because the recoveries are typically between 50-60% (Carcoana, 1992) and sometimes even 75% of the original oil in place as it can either support the pressure as the gas drive when in steam form, or reduce the oil viscosity or increase the sweep efficiency when in hot water state. The downside of this method is that the applicable depth, types of formation from below and above, acceptable reservoir thickness is limited.

After a period of using water flooding, the residual oil cannot be displaced anymore by water injection alone due to the reservoir fluid rock interaction and the wetting behavior. In such conditions, the recovery can be enhanced by the aid of the chemical injections which particularly improve the sweep efficiency and displacement efficiency. This method is called immiscible flooding in which either one or more of chemicals, alkali, surfactant, and polymer, are injected into the reservoir for EOR purpose.

Unlike the above-mentioned immiscible flooding, this method uses the fluid that is miscible with the crude oil at the reservoir conditions which particularly aim to improve mainly the displacement efficiency and to augment the oil production. The principal mechanism of the miscible flooding is the oil viscosity reduction upon the injected fluid mixed with oil in all proportions without any interface between them and hence achieving the desired viscosity and improved oil recovery. Carbon dioxide, LPG, lean gas, enriched gas, and low molecular weight alcohols are the fluids extensively used in enhanced oil recovery process for their miscibility.

The microbial method involves the injection the selective microorganism to the reservoir and the oil recovery is improved from the biochemical products produced from the metabolism of the consuming crude oil as a food source. Microbes, which are generally classified as aerobe and anaerobe, produce chemical compounds as the products of their metabolism, some of which can release oil from the rock surface, some can reduce the viscosity of heavy oils and make the recovering process easier, and some can be effective for high mobility ratio as per the laboratory experiments apart from fouling of produced water and souring of oil with H_2S produced during microbial action. Nevertheless, the types of metabolites and quantities depend on the specific

microbial colony, nutrients, and favorable environmental condition. In practice, it is not likely to replace the conventional methods and the rest with the microbial EOR due to the high operation cost and not fully developed study practices.

1.3 Chemical Enhanced Oil Recovery Method

For all EOR methods, the chemical EOR process yields the positive oil recovery performance at both field and laboratory scales. It increases the oil production through the direct enhancement in the efficiency of injected water into the reservoir to displace oil.

Depending on the types of chemical EOR process, the injected chemicals along with water slug can change the fluid-fluid and fluid-rock interaction in the reservoir, which can be done by lowering the interfacial tension or the viscosity or improving the mobility; thereby maximizing the production.

Regarding the demand of EOR treatment depending on the reservoir characteristics, the three main injectants are used in chemical flooding, mainly known as surfactant flooding, polymer flooding and caustic or alkaline flooding. Polymer is suitable for improving the sweep efficiency of the injected fluid by elevating viscosity of the injection fluid along with mobility ratio between displacing fluid (injectant) and displaced fluid (hydrocarbon). Whereas the surfactant has the main advantage in the wettability alteration of the formation rock and interfacial tension reduction. On the other hand, the alkaline injectants chemically react with natural fatty acids from the reservoir compound and form the in-situ surfactants. These three methods are well-known as the conventional chemical EOR methods. It can be seen in the different applications or in the mixed use of two chemicals that can either be caustic-surfactant mix or surfactant-polymer or caustic polymer flooding. The advanced implementation of alkaline-surfactant-polymer flooding (ASP) is widely performed in the recent years for the better improved efficiency. In addition to old chemical flooding processes and upgraded mixture flooding processes, the recent advance in the nanotechnology assisted in the conventional chemical EOR process is proved to have a better result and to reduce the unfavorable reservoir limitations for former three chemicals (Suleimanov et al., 2011). The success of the chemical flooding EOR depends on the different factors

such as the cost of chemicals, the availability of chemicals, the environmental impacts, oil price and formulations, etc.

1.4 Nanotechnology in Oil and Gas Industry

In order to escalate the oil recovery to its maximum factor, the capital expenditure is drawing it back. Many recent researches Aurand et al. (2014), de Castro Dantas et al. (2017)) indicated that adding the nanoparticles into the chemicals can result in the better performance of the chemical flooding. This leads to apply the nanoparticles due to their potential to solve different formation problems such as the unfavorable reservoir and rock characteristics for the surfactant, polymer, and alkaline processes.

One of the foremost mechanisms from the nanoparticles is the wettability. The wettability, or the tendency of a fluid to spread or adhere to a solid surface in the presence of other immiscible fluids, plays an important role in an enhanced oil recovery process as it affects the relative permeability curves, oil displacement efficiency, capillary pressure, and the productivity of the reservoir (Sheng, 2010). The application of nanoparticles is proved from the experiments in the laboratory that they have the strong effect on the alteration from the oil-wet system (unfavorable condition for EOR) to the water-wet system by reducing the contact angle by means of its disjoining pressure(Ali et al., 2018). An interfacial tension reduction between oil and water in the oil reservoir is also one of the parameters that can be achieved from availing the nanotechnology in the chemical EOR process. The other focuses of nanoparticles are to reduce the oil viscosity and to use them as a sacrificial component in the surfactant flooding to reduce the adsorption of the surfactant in the reservoir and increase the success of the process.

1.5 Objectives of this study

In enhanced oil recovery, the improvement of oil displacement efficiency is readily feasible with chemical EOR such as surfactant flooding along with the use of nanoparticles. Hence, the mechanism of these method needs to be thoroughly studied. Therefore, the main objectives of conducting this research study are

1. To analyze the physical properties changes such as density, viscosity, interfacial tension and contact angle of the surfactant solution when coupled with the nanoparticles
2. To evaluate the effect of the parameters such as types of surfactants, temperature, concentration on the nano-surfactant solution with crude oil
3. To investigate the effect of nanoparticles on the adsorption of surfactant when in contact with the reservoir rock sample from Fang Oil field.

The scope of this study is to investigate the effects of nano-surfactant solution on the crude oil from northern oilfield as well as the effect of nano silica on an adsorption of the surfactant on the rock particles.

The contribution of this research is to understand more on the performance of the surfactant in combination with the silica nanoparticles and to apply with the oil sample and rock sample from northern oilfield. It will provide the valid laboratory results as the fundamental data and a concept for the successful surfactant flooding by executing with the optimum concentration of the silica nanoparticles and surfactants.

There are totally five chapters in this research. Chapter 1 introduces the enhanced oil recovery types, basic knowledge of chemical EOR processes and the application of nanotechnology in it. The detail theory of surfactant flooding and nano surfactant flooding as well as their mechanisms in EOR and the literature reviews related to these mechanisms are extensively discussed in Chapter 2. Chapter 3 presents the detail procedure and requirement of each experiment including the methodology. The results and discussion related to these experiments are followed in Chapter 4. And finally, Chapter 5 concludes all of the results and provides the important recommendation regarding this research work.

CHAPTER 2

Theory and Literature Review

2.1 Surfactant Flooding

The surface-active agents or surfactants has been using as one of the chemical methods performed to achieve the objectives of enhanced oil recovery. The injection of the surfactant fluid into the reservoir can help improving the trapped oil recovery with three main actions. The first action is that the surfactant reduces the interfacial tension with an increase in the capillary pressure at the oil-water contact and help mobilizing the trapped oil droplets through its path and coalescing into the oil slug at the producing well after the surfactant solution is injected. The second action is the wettability alteration of the rock-fluid or fluid-fluid interface to improve pore scale displacement efficiency and the last one is the combination of the above two actions in moving oil out of the reservoir. Approximately 10% to 20% of extra oil production can be feasible with the help of the surfactant flooding (Romero-Zerón, 2012).

After water flooding, the remaining oil is entrapped through the reservoir pore space as the immobilized oil globules due to the capillary force and the viscous force. To recover this oil, the capillary number which is the ratio of the viscous forces to the capillary force is needed to be increased. Whereas the numerical equation of the capillary number can be expressed as (Donaldson et al., 1989)

$$N_{ca} = \mu v / \sigma \varphi, \qquad \text{Eq 2.1}$$

where μ and v are the viscosity and the velocity of the displacing fluid and σ and φ are the interfacial tension and pore volume, respectively.

The capillary number can be increased either by increasing the displacing fluid viscosity and the velocity or by decreasing the interfacial tension between oil and water and it can be said that the interfacial tension reduction can easily and effectively contribute to the desired increase in the capillary number compared with the other three parameters under practical condition (Fayers, 1981). Therefore, one of the main functions of the surfactant flooding is to get the ultralow IFT to increase the capillary numbers.

Another reason that could cause oil entrapment is the wettability of the reservoir rock which controls the flow of the fluid within the wetting behavior such as water

wetting rock allowing the hydrocarbon to flow and oil wetting rock cause the oil entrapment by making it stick to the rock, thus reducing the oil recovery.

The surfactants are composed of two portions, which are lipophilic, an oil soluble long chain hydrocarbon portion and lipophobic, a water-soluble portion or ionic highly polar portion. Based on the portion that dominates the surfactant compounds, the surfactants can be classified as anionic (e.g., sodium dodecyl sulfate or SDS), cationic (eg. dodecyltrimethylammonium bromide), nonionic (e.g. dodecylhexaoxyethylene glycol monoether) or amphotheric (e.g. 3-dimethyldodecylamine propane sulfonate) (Donaldson et al., 1989). Out of all these types, the most widely used surfactant is anionic surfactant due to its lower adsorption on the reservoir rocks compared to other types and economical accessibility. But the nonionic surfactant is also used in EOR process mostly as the cosurfactant due to its high tolerance to salinity. The rest is rarely used in EOR because cationic has higher adsorption on reservoir rocks and the structure of amphoteric type is not compactable for EOR purpose. In this research, the anionic surfactants are mainly used for the purpose of laboratory observations.

2.2 Application of Nanoparticles in Surfactant EOR Process

As stated in the limitations for the surfactants, the high reservoir temperature is the unfavorable condition for surfactant flooding when it reaches to the point beyond the cloud point temperature and Krafft point temperature at which the surfactant, especially anionic surfactants, will become cloudy and insufficient for pore space displacement action due to the dropping out of the aqueous solution. In addition, the loss of costly surfactant due to the adsorption, the unbalanced interfacial tension impairment between oil or water phase and micro-emulsion phase, the result of high salinity are the problems degrading the performance of the surfactant flooding (Ali et al., 2018). In order to overcome the obstacles for the conventional surfactant flooding, the use of the nanoparticles in the surfactant solution is studied and it is proved that the more promising sweep efficiency can be achieved from the nanoparticles assisted surfactant flooding due to lowering the IFT, rather than the surfactant flooding alone. The nanoparticles also have the great effect on the reduction of the adsorption of the surfactant onto the reservoir rock surface (Le et al., 2011). Also, it is observed that as

nano-silica particles reduce the adsorption not only in the sandstone reservoir but also in the carbonate and shale rocks. The surfactant flooding is not only limited to the sandstone reservoir with the aid of nanoparticles.

2.3 Mechanisms of Nano-surfactant Flooding

The surfactant is one of the chemical flooding methods that have a promising result when doing it for enhancing oil production. The mechanism that happened when doing the surfactant flooding is the surfactant tries to reduce IFT between water and oil phases for improving the oil production. The problem that faces this chemical flooding is the adsorption that causes by the surfactant to the rocks. An adsorption can be reduced by adding nano silica particles. There are various parameters involved in the surfactant adsorption, such as the rock surface charge, mixture interface, surfactant structure, and thermodynamic conditions. A recent study shows that the nanoparticles have a special mechanism when applying in the heat transfer, wettability alteration, drug deliverability, gel formation, formation consolidation, and corrosive control area. (Ahmadi & Shadizadeh, 2017)

2.3.1 Effect of Surfactant on Wettability Alteration

During the surfactant flooding, the surfactant alters the wettability in form of the desorption. The surfactant desorbs the oil attached at the rock surface which is primarily oil wet after which consequent water imbibition occurs to the contact of oil desorbed surfactant slug and rock, making the oil detaching freely from the rock surface. Thus, the desorption of oil during surfactant flooding help altering the wettability. Figure 2.1 portrays before and during the process of the desorption due to the surfactant slug and in Figure 2.2, the complete wettability alteration process could be seen.

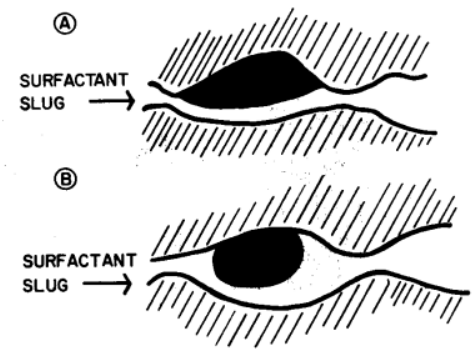


Figure 2. 1 Rock wettability and contact angle alteration stage from a to b during surfactant flooding (Fayers, 1981)

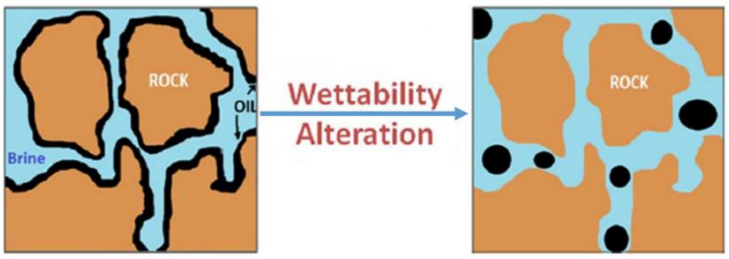


Figure 2. 2 Wettability alteration of rock from oil wet to water wet (ShamsiJazeyi et al., 2014)

2.3.2 Effect of Nanoparticles on Wettability Alteration

In case of wettability alteration, firstly, the nanoparticles form a thin layer on the rock surface at the oil and rock interface. Later, the additional disjoining pressure is exerted during flooding and as this pressure increases, the film spreads larger until the rock is completely covered with nano-thin layer, alters the oil wet rock to water wet rock and finally releases the oil which is initially attached at the rock surface. The disjoining pressure can be understood as the adhesion force of fluids towards the solid surface to separate the fluid which is actually the pressure difference between the thin layer of fluid (oil in this case) and the bulk of fluid (injection flood). It can also be intensified with the increase in the nanoparticle concentration during flooding. The idea of this is well illustrated in Figure 2.3.

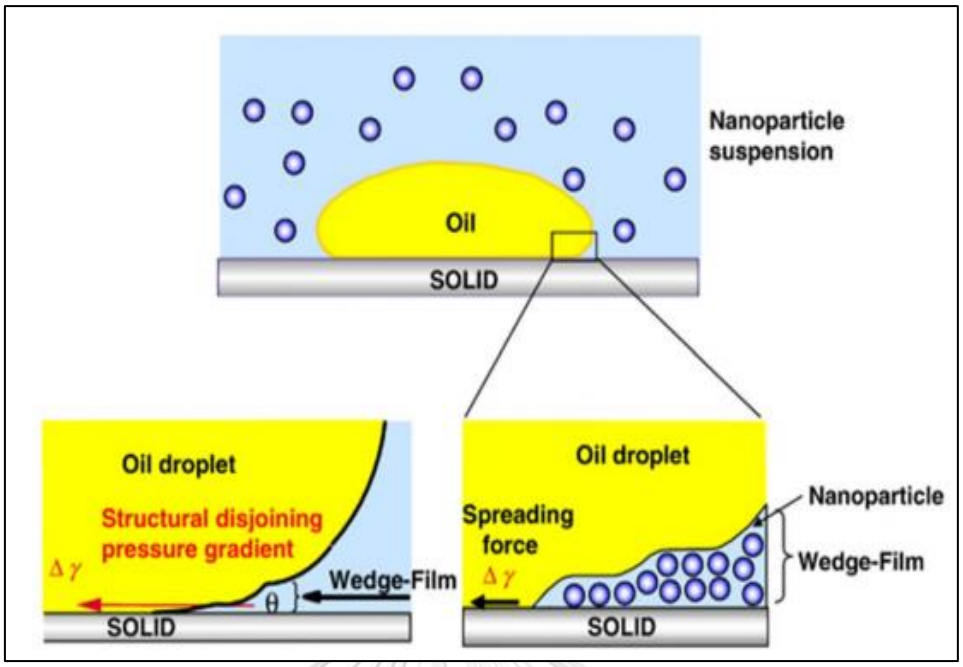


Figure 2. 3 Ordering of nanoparticles resulting in structural disjoining of oil from the solid rock surface (Kondiparty et al., 2011)

2.3.3 Effect of Surfactant on Interfacial Tension

When the surfactant is injected into the reservoir containing two immiscible fluids, hydrocarbon and water, the surfactant molecules are adsorbed as in Figure 2.4 at the interface and displace some of the hydrocarbon and water molecules as the hydrophilic part is directed into the water phase and the hydrophobic part is directed into the hydrocarbon phase which reflects the decrease in the IFT. But the IFT between the surfactant solution and the hydrocarbon phase also depends on the salinity, temperature, the surfactant concentration, surfactant type and purity, and the nature of the hydrocarbon phase. The interfacial tension decreases with increasing surfactant concentration and at a critical concentration the interfacial tension approaches its minimum value. (Cayias et al., 1977) Beyond this critical concentration, the interfacial tension increases with an increase in the surfactant concentration, and it is described in Figure 2.5.

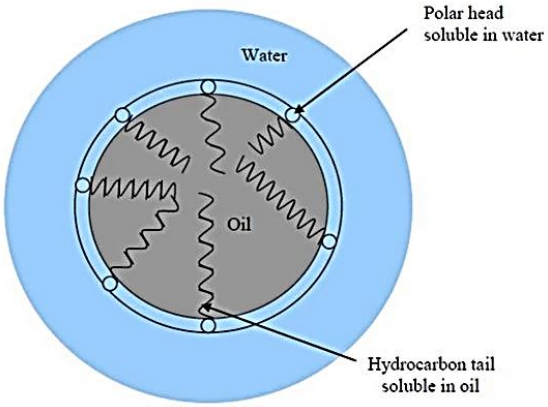


Figure 2. 4 Adsorption of surfactant on oil water interface (Olajire, 2014)

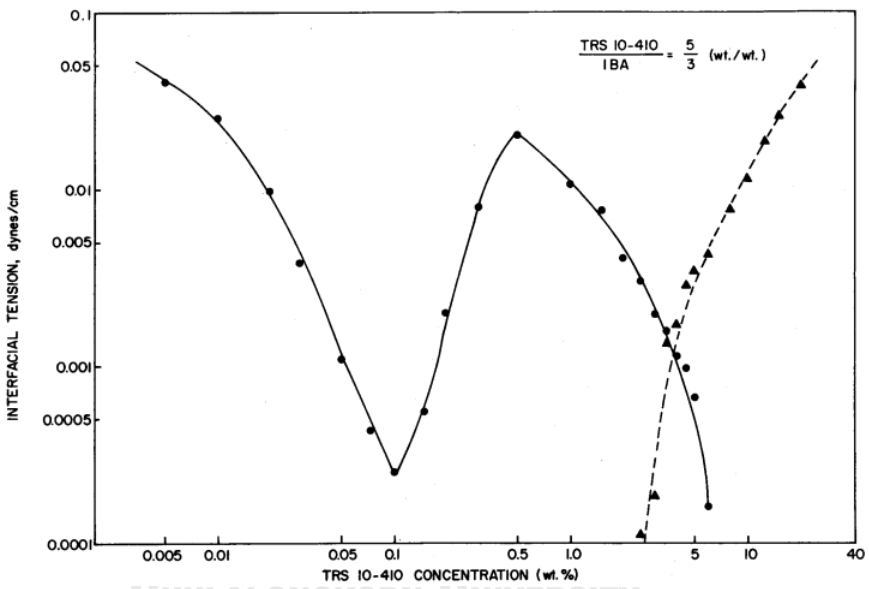


Figure 2. 5 Effects of surfactant concentration on IFT (Fayers, 1981)

2.3.4 Effect of Nanoparticles on Interfacial Tension

An interfacial tension reduction which directly influences the capillary pressure and the flow behavior of fluid in the reservoir is an important factor in EOR process. Conventionally, the IFT is reduced with the use of the expensive surfactants alone or with the addition of caustic chemicals which react with organic acid in crude oil and form an in-situ surfactant to reduce IFT. But as mentioned in previous section, the use of alkali imbalances the pros and cons. So, the nanoparticles become the important IFT reducing agents such as silicon dioxide ($SiO_{2)}$, aluminum oxide (Al_2O_3) and titanium dioxide (TiO_2). The numerous successive experiments prove that the high nanoparticles

adsorption at the oil water interface causes the great IFT reduction, in more specifically, the alumina nanoparticles are the most efficient in limestone reservoir whereas the silica nanoparticles reduce IFT more effectively together in use with the surfactant.

2.3.5 Nanoparticles and Emulsion Stabilization

For EOR purpose, an injection of nanoparticles strongly stabilizes the emulsion, which is generated when the solid particles in contact with the oil surface. The absorption of nanoparticles at the surface prevents the emulsion not to flocculate and coalesce and make it stable and plug the pathways of viscous fingers in water flood. Therefore, under the reservoir conditions, the nanoparticles enhance the emulsion stability to increase the vertical and areal sweep efficiency of the reservoir and encourage the oil recovery of chemical EOR process.

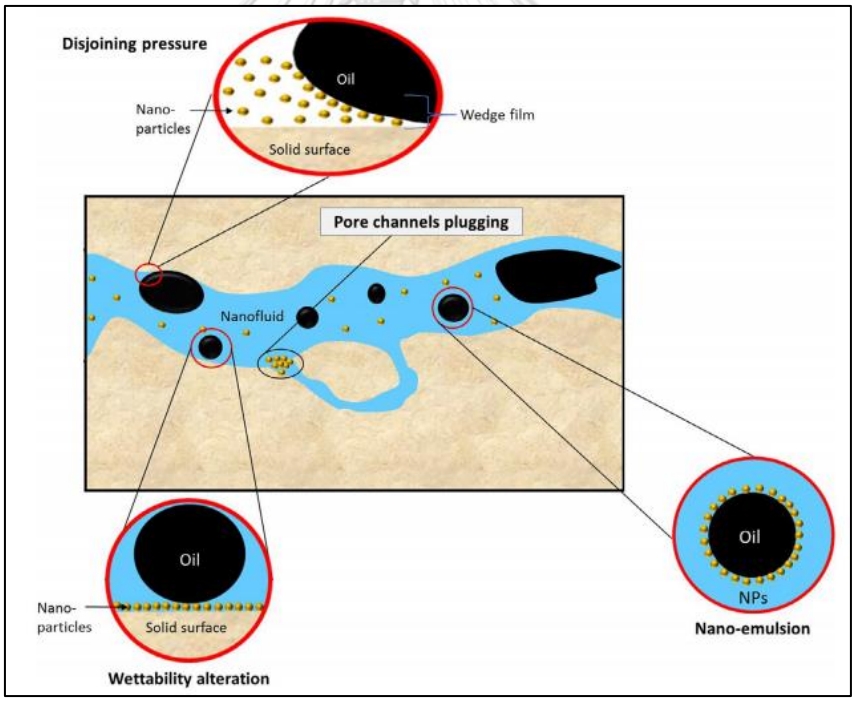


Figure 2. 6 Mechanisms of nanoparticles during chemical flooding (Ali et al., 2018)

In contradiction of the surface condition, the nanoparticles affect the emulsion stability in other way around. During the surface production process, the hydrophilic nanoparticle utilization can also decrease the emulsion stability and make the oil-water separation easier within surface production facility. This adverse phenomenon happens

due to the fact that the nanoparticles reduce the oil viscosity significantly below the wax appearance temperature at surface condition and hence the reduced viscosity help reduce the emulsion stability and the nanoparticles becomes the alternative emulsion treatment in addition to its use of EOR projects.

2.4 Surfactant Adsorption

The nature of surfactant to adsorb at the interface is to lower the free energy of that phase boundary. The objective of interfacial tension reduction is achieved when the interface or boundary between two immiscible phases is covered by surfactant molecules. If the interface that injected surfactants adsorbed on is between hydrocarbon and water, the objective could be achieved. There are five different interfaces exist in the phase behavior system: solid-solid, solid-vapor, solid-liquid, liquid-liquid and liquid-vapor. Out of all the interfaces, surfactant could also adsorb on the solid-liquid interface which is between reservoir rock and aqueous phase apart from oil-water interface. Depending on which interface that injected surfactant molecules go to adsorb could determine the success or failure of the surfactant flooding process. The greater the adsorption of surfactant on the rock surface, the greater the loss of surfactant and the lesser the surfactant molecules in the aqueous solution to reduce the interfacial tension between oil and water. Thus, the consideration of surfactant adsorption is important parameter in the surfactant EOR process.

The surfactant adsorption on the rock surface can be caused by number of different mechanisms, either in physically or chemically. The chemical mechanisms can be broken down into three types as illustrated in Figure 2.7, (1) Ion exchange which involves replacement of counter-ions adsorbed onto the rock surface from the solution with similarly charged surfactant ions, (2) Ion Pairing in which the adsorption of surfactant ions from solution occurred onto oppositely charged rock surface occupied by counter-ions and (3) Hydrogen bonding in which adsorption is caused by the formation of hydrogen bond between solution and rock surface.(Rosen, 1975)

Moreover, the adsorption taken place in the reservoir is also influenced by some certain factors such as temperature, pH, salinity or concentration of inorganic electrolytes, the molecular structure and type of the surfactant being used and rock minerals and clay content, surfactant concentration and so on. (Holmberg et al., 2014)

The salinity enhances the adsorption of surfactant whilst nonionic surfactant has more tolerant to high salinity in terms of amount of adsorption. Regarding to the surfactant types and rock minerals, anionic and nonionic surfactants show less adsorption interaction with sandstone when cationic surfactants opposingly interact. However, for limestone, cationic surfactant reversely shows lower adsorption compared to the rest.

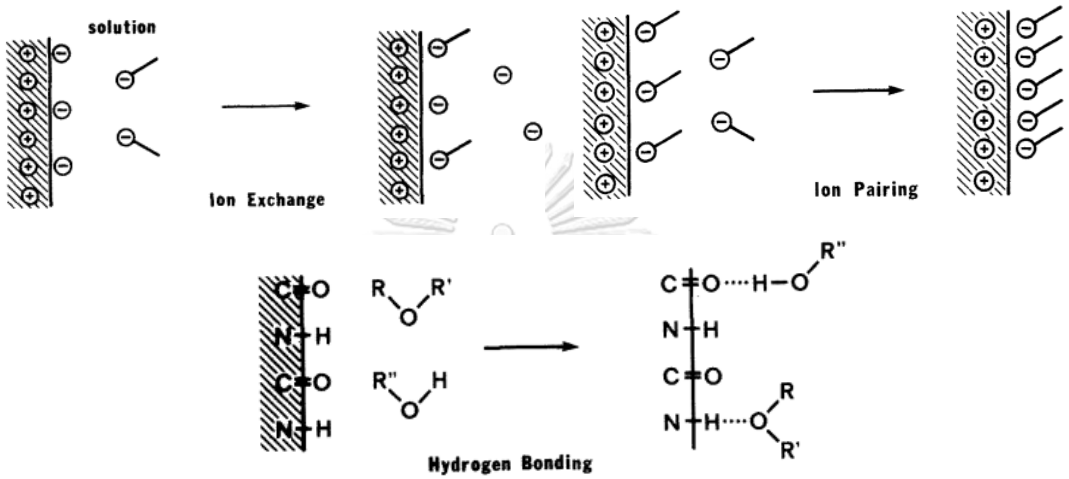


Figure 2. 7 Mechanisms of adsorption (Rosen, 1975)

Most of the hydrocarbon reservoir are composed of sandstones and thus, majority of the surfactant flooding processes consider the anionic and nonionic surfactants to use. Only the main difference is that nonionic surfactant cannot efficiently reduce IFT but it adsorbs less in high salinity environment. Therefore, anionic, and nonionic surfactants are used in coordination to get the benefit of anionic surfactants in IFT reduction and to get high saline resistance with the help of nonionic surfactants. Later, nanoparticles eventually are used with anionic surfactants which can be assumed to aid in the reduction of surfactant adsorption as well as the alteration of wettability during flooding.

2.5 Literature Review

Kamal et al. (2017) experimented the changes of rheology, interfacial tension, oil recovery and wettability alteration of the nanoparticles assisted the surfactant EOR. The different types of nano-fluids with SiO_2, Al_2O_3, Fe_2O_3, ZrO_2 are prepared in different surfactant concentrations using propanol, ethanol, brine, water as dispersion

media at different temperatures. The results are pointed out that the nanoparticles can be used to increase the recovery from the oil reservoir when the right amount of concentration and suitable nanoparticle type as well as the optimal concentration of surfactant are applied. It is also mentioned that the SiO_2 nanoparticles provide the satisfying results and availability out of the tested nanoparticles.

Prior to the application of nanoparticles in enhanced oil recovery process, the stability of nanoparticles is important. It could be very challenging to achieve the change of properties if nanoparticles are not stabilized in the bulk solution. For this case, Sofla et al. (2018) studied how well hydrophilic silica nanoparticles can stabilize in seawater for EOR implications and which mixing method can provide the better stability. This their research, silica nanoparticles with purity greater than 99.99% was used in the different concentrations of inorganic salts in deionized water and seawater for the evaluation of stability. The results pointed out that nanoparticles can be easily dispersed in low salinity water and unstable in high salinity water and adding HCL to the solution can help silica nanoparticles stabilize in high salinity water. Moreover, the preparation procedure and equipment to mix the solution also influence on particles stability. The solution prepared with magnetic stirrer can aggregate rapidly compared to the solution prepared with ultra-sonic stirrer.

Mahmoudi et al. (2019) focused on the temperature effect on the performance of nano-surfactant flooding. Apart from that the instability of nano-fluids at high concentrations is also reviewed when the critical micelle concentration is exceeded and when NaCl decreases the stability of nano-fluids. Moreover, the researchers pointed out that the concentration of nano-surfactant from 0 to 1000 ppm (wt.) does not have many effects on viscosity but what effects on viscosity is mainly temperature. The most surprising finding out is that the silica nanoparticles alone can worsen the IFT while silica nano-surfactant blend can decrease IFT better than when surfactant alone is used.

The nano-surfactant flooding research area becomes the widely experimented research area in the recent years. Hendraningrat et al. (2013) studied the possible parameters that have the influence on nano EOR. He focused on the sizes of nanoparticles and their effects using core flooding method and measured the contact angle and the results showed that the size of nanoparticles influences on the incremental oil recovery. The increasing particle size will have adverse effect in decreasing oil

recovery and the smaller the particle size, the higher the oil recovery can be achieved whereas the contact angle of aqueous phase decreases with decreased particle sizes.

Golabi et al. (2012) experimented on the wettability alteration of limestone rock from oil wet to water wet using various surfactants including sodium dodecyl benzene sulfonate (SDBS). The contact angle reduction from 162 degree (strongly water) to 66 degree is obtained at 1.5 wt% of SDBS and 2 wt% Na_2CO_3.

Hammood et al. (2019) performed the tests to select the best concentration of the nanoparticles and SDS for EOR fluids and concluded that the surfactant CMC value was about 0.158 percent by weight and regarding the nanoparticle's concentration, oil recovery would be maximum if the stable solution is injected. So, 0.5 wt% nanoparticles were the critical unstable concentrations. The contact angle measurement also dictated that SDS, and silica nanoparticles injection can alter the wettability from oil wet to water wet by decreasing contact angle from 161.34 degree to 112.6 degree.

Alhuraishawy et al. (2019) continued the work of Hammood et al. (2019) and investigated the effects of the nanoparticles and surfactant on improving oil recovery in carbonate reservoirs. The results showed that using 0.03 wt% SiO_2 with 0.158 wt% SDS can improve oil recovery by 15.1% and minimize residual oil saturation to 25.6%. The ultimate recovery of nano-silica and SDS combination is about 68.4% OOIP and the recovery changes from 62.7% OOIP when using nano-silica only. This experiment also showed that 0.03 wt% is the optimum concentration of nanoparticles injection for carbonate cores.

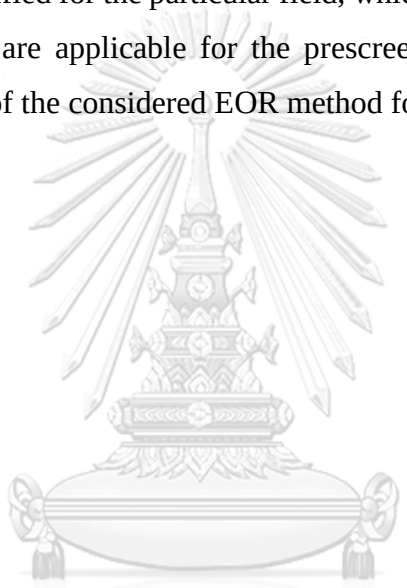
Moreover, to validate the enhancement of surfactant flooding performance with the use of nano particles, Zargartalebi et al. (2015) thoroughly researched on this area. They aimed to study whether surfactant properties, in terms of interfacial tension reduction and adsorption on rock surface, change in the presence of nano silica particles. The chemical types used in the work were hydrophilic fumed silica, AEROSIL 300, hydrophobic nano silica, AEROSIL R816, anionic surfactant named sodium dodecyl sulfate (SDS) which has CMC value of 2203 mg/l. They concluded that first, nanoparticles generally reduce the surfactant adsorption on rock surface. In terms of IFT measurements, both nanoparticles cause the lower IFT at low surfactant concentrations but adversely increase the IFT when in use with high surfactant concentrations.

Somasundaran and Hanna (1985) did a study of desorption after a reduction of surfactant concentration when the surfactant is exposed to the rock surface. The materials that were used in their study is Kaolinite, 85% pure Sodium dodecyl benzenesulfonate (SDBS), to find out the adsorption, they did it with a mixture of Na-kaolinite with water then the addition of surfactant after 2 hours of wetted, after that the sample being centrifuged to separate minerals layer with the solution. The solution will be titrated by using a two-phase titration technique, and the adsorption of the surfactant being calculated. Desorption (dilution) study also being determined in this study, which finds out the amount of adsorbed surfactant precipitate back to the solution upon dilution. And they found out that Na-kaolinite when interacting with SDDBS will achieve maximum adsorption behavior. It is caused by the surface precipitation of multivalent ions. In their work, the higher concentration of surfactant is useful for controlling adsorption and desorption.

In order to investigate the way the reduce surfactant adsorption, Wu et al. (2017) performed the test on reduction of surfactant adsorption by using the nano silica particles (SNP). In their research, both static and dynamic adsorption behaviors are studied with and without silica nanoparticles. In the test, the SDS that they used has a purity of >86%, nano silica that is being used is having particle size with a diameter of 15 nm and a core that mainly contains Quartz which is the main composition of SiO_2. The oil sample being used to enhance the oil recovery test is crude oil from the field in Xinjiang, China. The results showed that silica nanoparticles can effectively reduce the surfactant adsorption. This mitigation of surfactant adsorption also proved to increase the oil recovery during the core flooding process of the nano surfactant solutions compared to surfactant only solutions.

According to the research and literature, there are the solid proofs to present that the surfactants and nanoparticles can be used for enhancement of the oil recovery as the displacement efficiency is improved. However, more work should be done to measure the properties of the surfactant coupled with the nanoparticles. Moreover, the types of surfactants and nanoparticle such as SDS, SDBS and SiO_2, can be the potential chemicals to be studied further in detail of the rheological properties as well as the changes of IFT and contact angle with various conditions to fulfill these required properties

Most of the recent jobs measured the effect of various nanoparticles on the reduction of IFT or contact angles. Some extensively researched on the improved oil recovery from nano-surfactant or surfactant adsorption control with the help of nanoparticles. Therefore, the experiments conducted in this research are not innovative or new. However, the primary difference between this work and the previous numerous research on this topic is that this work is the combination of all of those studies such as IFT, contact angle, viscosity, density and surfactant with the selective types of two surfactants with silica nanoparticles in one work. Moreover, all of the research focus and conditions are modified for the particular field, which is northern Thailand oilfield, and hence, the results are applicable for the prescreening process if the surfactant flooding becomes one of the considered EOR method for this particular field.



CHAPTER 3
Experiment

This chapter will present the experimental detail on the measurement of the interfacial tension, contact angle, density, viscosity and adsorption of the surfactant and nanoparticles as well as the chemicals, equipment used and experimental procedures.

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3.1 Interfacial Tension and Contact Angle Measurement

Reducing the interfacial tension or changing the wettability of the reservoir rock from oil-wet to water-wet can significantly improve the oil recovery. Therefore, measurement of the IFT and contact angle changes are important in the study to improve the oil displacement efficiency.

3.1.1 Material and Equipment

For the study of the interfacial tension and contact angle measurements with the effect of the nano-surfactant solution, IFT 700 equipment, as presented in Figure 3.1, is used in this research to determine IFT at various ranges of pressures and temperature. The interfacial tension of both immiscible fluids uses the pendant/rising drop methods and the contact angle of a liquid droplet on a solid surface applies the sessile drop method. By means of a capillary needle, a droplet (drop fluid) is formed in a chamber containing the other fluid (bulk fluid), subjected to the desired pressure and temperature conditions. A state-of-the-art image capture and processing system computes the relevant geometric parameters to derive the interfacial tension. Upon reaching equilibrium, the contact angle can directly be measured with the Vinci interpretation software.

Figure 3. 1 IFT 700-HPHT interfacial tension meter

Two anionic surfactants are used in the process. Sodium dodecyl sulfate (SDS) which has the molecular weight of 88.38 g/mol and sodium dodecylbenzene sulfonate (SDBS) which has the molecular weight of 348.48 g/mol are used. Both surfactants are purchased from Sigma-Aldrich and have the purity more than 99%. For the nanoparticles, hydrophilic or water-soluble fumed silica nanoparticles named AEROSIL 200 is used. It is obtained from Evonik Industries and has the purity of 99.8%. In this research, oil sample from the northern oilfield in Thailand will be used. The composition of crude oil from C_1 to C_{35}^+ distributed by area and height of the analysis method is presented in Table 3.1.

The simulated brine solution is used in this research to obtain the reservoir condition of the Northern Thailand oilfield. The brine solution is prepared by mixing sodium chloride (NaCl) and sodium bicarbonate (Na_2CO_3) in the distilled water with the composition close to the actual salt composition of the produced water from the Northern Thailand oilfield. Both NaCl and Na_2CO_3 are purchased from Ajax, with the purity of 99.9% and 99.7% respectively.

Table 3. 1 Composition of oil

Component	% Area	% Height
n-C1	0	0
n-C2	0	0
C3s	0	0
i-C4	0	0
n-C4	0.67	2.55
i-C5	0	0
C5s	1.72	5.18
C6s	3.32	6.67
C7s	5.42	6.34
C8s	8.06	6.74
C9s	6.08	5.13
C10s	5.9	4.68
C11s	5.19	4.27
C12s	4.68	4.6
C13s	5.06	5.44
C14s	4.76	4.87
C15s	5.33	5.27
C16s	3.96	4.3
C17s	3.89	4.04
Pristanes	0.94	0.84
C18s	3.2	3.56
Phytanes	0.27	0.23
C19s	3.24	3.35
C20s	3.15	3.25
C21s	2.94	3.03
C22s	2.83	2.9
C23s	2.78	2.75
C24s	2.42	2.25
C25s	2.35	1.92
C26s	2.09	1.4
C27s	1.86	1.07
C28s	1.91	0.9
C29s	1.57	0.8
C30s	1.27	0.59
C31s	1.06	0.43
C32s	0.65	0.25
C33s	0.52	0.17
C34s	0.32	0.09
C35s +	0.6	0.14
Total	100	100

3.1.2. Procedure and Operating Condition

To start the IFT and contact angle measurements, the crude oil sample is heated prior to the injection inside the chamber of the IFT 700 machine to avoid the small connecting metal tubes getting blocked with the wax. The surfactant solution is then injected into the chamber followed by the drop-by-drop releasing of crude oil droplet in the rising up position into the solution. The HPHT machine can support the measurements to be done at desired temperature and pressure close to the reservoir

condition. The integrated software provided by the Vinci company will provide the real time results of the IFT and contact angle. The operating conditions for the IFT and contact angle measurements are shown in Table 3.2. Depending on the results, the best condition from this study of the IFT and contact angle tests will be picked for the next steps of the measurements, such as density, viscosity and adsorption of the surfactant.

Table 3. 2 Operating conditions for IFT and contact angle measurement

Parameter	Value
Temperature (˚C)	70, 80, 90
Salinity (ppm (wt.))	0, 500, 750, 1000
Surfactant concentration (ppm (wt.))	0, 1000, 2000, 3000, 4000
Nanoparticles concentration (ppm (wt.))	0, 250, 500, 750, 1000

3.2 Density Measurement

Prior to the actual field application of nano-surfactant flooding, it is required to study how much nanoparticles can affect on the properties not only for the improved oil recovery mechanisms such as IFT and contact angle, the density changes of the surfactant solutions due to nanoparticles also need to be kept track of to access the viscoelastic nature of the injected fluid.

3.2.1 Material and Equipment

For the measurement of density, the density meter from Anton Paar Company is used with the model of DMA 4200M. The machine can measure in the range of 0 to 3 g/cm^3 with the 10^{-5} decimal precision and it is used for the measuring surfactant solution and the nano-surfactant solution density in this research. Temperature can be measured up to 100˚C and pressure can be increased to the maximum of 10 bars. The same two anionic surfactants and the nanoparticles are used to measure the density of the surfactant solutions and the density of surfactant mixed with the silica nanoparticles.

Figure 3. 2 The DMA 4200 M density meter (Paar, 2016)

3.2.2 Procedure and Operating Condition

The surfactant solutions and the nano-surfactant solutions at the concentrations shown in Table 3.3 are prepared with distilled water. The solution samples are slowly fed into the density meter to avoid the air bubble trapping in the glass tube which could interfere the measurement of the density. The purpose of this measurement is to understand how much the nanoparticles can affect on the surfactant solutions prior to mixing with the formation brine or the formation oil.

Table 3. 3 Operating conditions for density measurement

Parameter	Value
Temperature (˚C)	60, 70, 80
Surfactant concentration (ppm (wt.))	1000, 2000, 3000, 4000
Nanoparticles concentration (ppm (wt.))	750

3.3 Viscosity Measurement

For EOR, not only the displacement efficiency is important, but also the sweep efficiency is also equally important. The sweep efficiency can be improved by injecting the high viscous solution like in polymer flooding method or by reducing the viscosity of the fluid to be replaced such as the crude oil in the reservoir. Therefore, the viscosity of the crude oil before and after mixing with chemical are measured to study if the latter effect can be achieved to improve the sweep efficiency.

3.3.1 Material and Equipment

Regarding the study of the viscosity changes due to the silica nanoparticles and the surfactant, two types of viscometers are used in this research. The first one to be used for the measurement of oil and oil nano-surfactant blended solution is Brookfield viscometer LV DV2T model. The second viscometer used in this research is the U-tube glass viscometer for the viscosity measurement of less viscous fluid such as the single surfactant solution and the surfactant-nanoparticles solution. Along with the two viscometers, the water bath is also needed to be used in order to maintain the desired temperature. Therefore, Julabo F26 model water bath filled with glycol and SI Analytics CT 72 model water bath filled with deionized water are used for Brookfield viscometer and U-tube glass viscometer, respectively.

Figure 3. 3 U-tube capillary viscometer and water bath from SI Analytics

Figure 3. 4 Brookfield viscometer and Julabo water bath

3.3.2 Procedure and Operating Condition

The operating conditions for both U-tube viscometer and Brookfield viscometer are listed in Table 3.4. The concentrations of brine and the nanoparticles are selected based on the results from the IFT and contact angle measurements which provide the best condition of this study for enhanced oil recovery.

Table 3. 4 Operating conditions for viscosity measurement

Parameter	Value
U-tube Viscometer	
Temperature (˚C)	60, 70, 80
Surfactant concentration (ppm (wt.))	1000, 2000, 3000, 4000
Nanoparticles concentration (ppm (wt.))	750
Brookfield Viscometer	
Temperature (˚C)	60, 70, 80
Shear rate (s^{-1})	6, 12, 18
Salinity (ppm (wt.))	750
Surfactant concentration (ppm (wt.))	1000, 2000, 3000, 4000
Nanoparticles concentration (ppm (wt.))	750

3.4 Adsorption Measurement

Apart from providing the slight change in contact angle and the wettability alteration, surfactant adsorption is the favorable in EOR process. As discussed before, surfactant adsorption successively comes with reduction of surfactant content in the injected fluid phase which could lead to the inadequate amount of surfactant to reduce IFT. Finally, the whole surfactant flooding process can be ineffective when the excessive adsorption occurs. Therefore, the behavior of surfactant adsorption is in need of study extensively along with the remedies to reduce it.

3.4.1 Material and Equipment

The same surfactants and nanoparticles are used again in the study of adsorption behavior between rock, surfactants, and nanoparticles. For the determination of the surfactant concentration after the adsorption, two-step titration method with methylene blue is used and it needs to use a titrant of the hyamine 1622, standard 0.004 M solution with the surfactant solution. Standard anionic surfactants, sodium dodecyl benzene sulfonate, sodium dodecyl sulfate and chloroform as a reagent additive as well as methylene blue powder, and solution (as a color indicator), sulfuric acid, phenolphthalein indicator solution are used for this experiment with anhydrous sodium sulfate, sodium hydroxide solution. The titration process needs the use of various equipment, such as a burette, beakers, volumetric flasks, pipettes, and graduated cylinders.

The formation rock sample used in the process is taken from the northern Thailand oilfield to conduct the study of the adsorption with the surfactant and nanoparticles. The rock mineralogy of the sample is assessed by using X-Ray Fluorescence (XRF) which detects the elements contained in the sample. The assessment of the rock composition is important in the experimenting the nature of the adsorption and are listed in Table 3.5.

Table 3. 5 Mineral composition of the rock sample

Compound	Concentration	
Mg	0.876	%
Al	7.644	%
Si	69.526	%
P	0.468	%
S	970.3	ppm (wt.)
K	3.005	%
Ca	4.138	%
Ti	0.592	%
V	130.7	ppm
Cr	181.5	ppm (wt.)
Mn	0.309	%
Fe	12.888	%
Ni	189.1	ppm (wt.)
Cu	210.3	ppm (wt.)
Zn	237.8	ppm (wt.)
Ga	21.3	ppm (wt.)

As	84.7	ppm (wt.)
Rb	298	ppm (wt.)
Sr	102	ppm (wt.)
Y	72.5	ppm (wt.)
Zr	270.3	ppm (wt.)
Nb	17.4	ppm (wt.)
Sn	401.8	ppm (wt.)
Sb	75.1	ppm (wt.)
Te	167.9	ppm (wt.)
Ba	548.4	ppm (wt.)
Eu	0.129	%
Yb	33.4	ppm (wt.)
Re	3.9	ppm (wt.)
Pb	96.6	ppm (wt.)
Th	147.5	ppm (wt.)

3.4.2 Procedure and Operating Condition

In order to explain the procedure of the adsorption measurement, the process can be explained with two stages. The first stage is the overall preparation for the static adsorption measurement and the second stage is the explanation in detail of the titration method used to determine the surfactant concentration. The operating conditions are tabulated in Table 3.6.

Table 3. 6 Operating conditions for adsorption measurement

Parameter	Value
Salinity (ppm (wt.))	750
Surfactant concentration (ppm (wt.))	1000, 2000, 3000, 4000
Nanoparticles concentration (ppm (wt.))	0, 750

3.4.2.1 Procedure for Static Adsorption Measurement

The amount of surfactant adsorption can be determined either by static or dynamic tests. In this research, the static method is applied in determining the amount of adsorption and desorption. The static adsorption test is being tested with the mixing of sandstone samples, with an anionic surfactant, and the mixture is stirred for 6 hours to let adsorption occur at a specific temperature. Next, the mixed solution is filtered with filter paper and leave it overnight to separate the rock particles with the surfactant adsorbed on it and the solution that contains remaining surfactant. The filtrated water is used for the titration in the next procedure to find out the contamination of solid particles by using the formula in Equation 3.1.

$$Ad = V / m\,(Co - Ce) \qquad \text{Eq 3.1}$$

where Ad is adsorption concentration,

V is the surfactant solution volume (ml),

m is the mass of rock (g),

Co is the surfactant initial concentration,

Ce is the surfactant concentration after adsorption.

For the desorption test, the ground rock sample left from adsorption process is collected again and put in an oven with a temperature of 75°C to prevent water content that diluting in the surfactant solution. After the rock sample is dry, it will be mixed and titrated again with distilled water to do desorption tests at a specific temperature. After that, the desorption test will be the same as the adsorption test which left the sample being stirred for 6 hours and the sample being filtrated, so the filtrated water will be titrated.

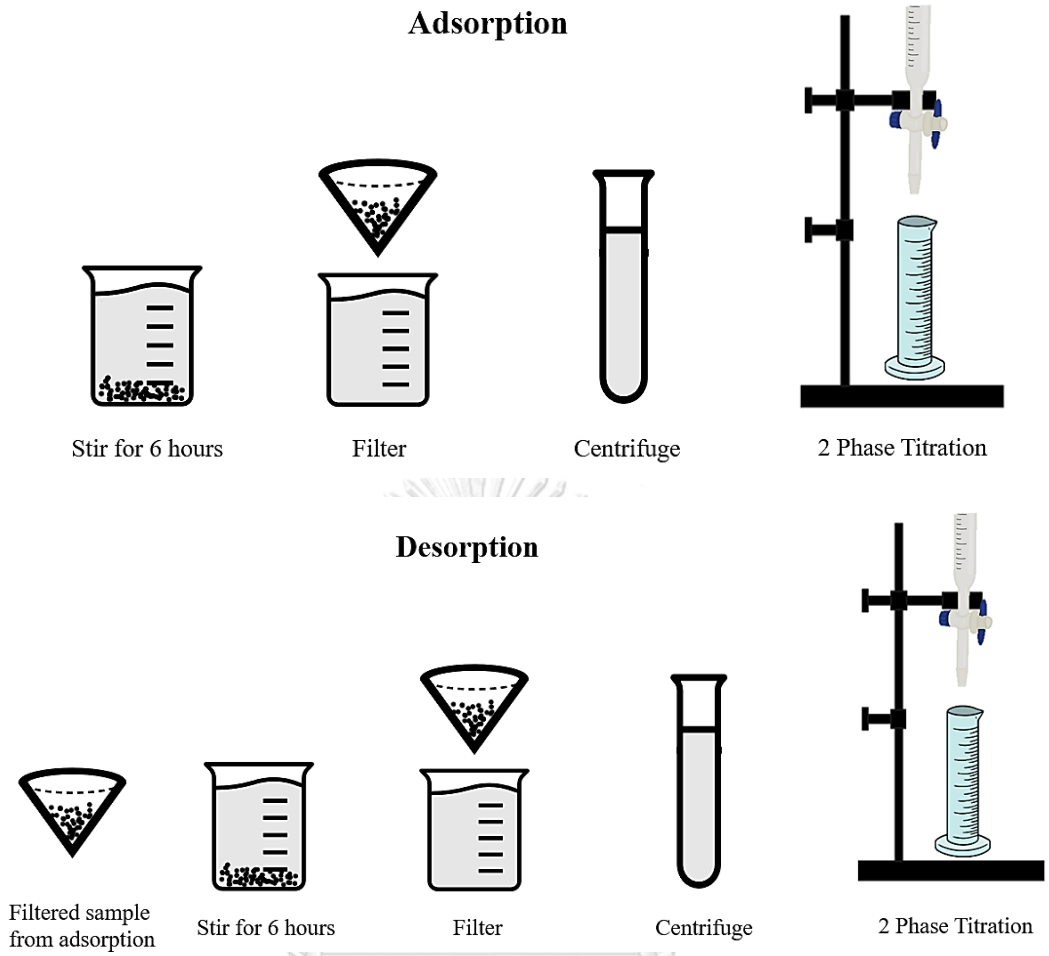
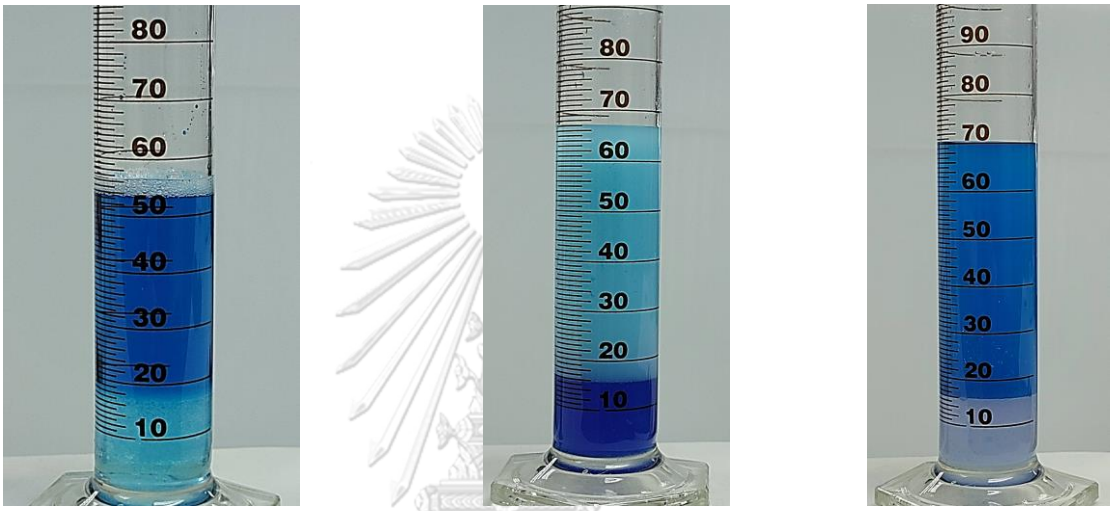


Figure 3. 5 Schematic diagram of static adsorption and desorption procedure

3.4.2.2 Titration Process

To determine the surfactant concentration, the surfactant solution needs to do a titration called a two-phase titration technique by using various chemical solutions. The preparation of the Methylene Blue solution is done by dissolving 30 mg of methylene blue and 50 g of anhydrous sodium sulfate in 500 ml of distilled water. After that mixture is transferred to a 1000 ml volumetric flask, carefully add 6.5 ml of sulfuric acid and dilute it with 1000 ml of distilled water. The preparation of the surfactant solution is done by weighing the surfactant solution sample into a small beaker with the amount of the desired concentration that it needed. Lastly, dilute the surfactant sample to 150 ml with distilled water. For the titration process, firstly, 10 ml of the diluted surfactant sample is put in the graduated cylinder and add 2-3 drops of the phenolphthalein solution. Then add a drop of NaOH solution and drop it in a slow rate

until the pink color is achieved. After that, 25 ml of the diluted sulfuric acid is cautiously added in the cylinder followed by 15 ml of chloroform. Finally, the hyamine solution is added drop by drop until the mixture solution reaches from the starting point to mid-point and all the way to the end point as presented in Figure 3.6. When the end point is achieved, the titration process is completed, and the required remaining concentration of the surfactant can be determined from the amount of hyamine used in the process.



(a) Start point (b) Mid-point (c) End point

Figure 3. 6 Color changes during methylene blue two-phase titration in determining remaining surfactant concentration

3.5 Methodology

This research consists of four main experiments including interfacial tension and contact angle measurement of the crude oil in presence of nano-surfactant solutions, density and viscosity measurements of the chemical combinations, density measurement of the crude oil with chemical solutions and observation of the surfactant adsorption on the rock sample to fulfil the research objectives. The procedures are listed in the Figure 3.7, Methodology Flow Chart.

1. Review related theory and literature.
2. Collect the required chemicals and prepare the solutions to test the physical properties.
3. Collect the oil sample from Northern Thailand Oil Field.
4. Perform IFT and contact angle measurement with the collected nanoparticles, surfactants and oil sample. And determine the best operating condition and concentration that can provide the best results.
5. Measure the density and viscosity changes of the surfactant solutions by the addition of nanoparticles before the chemicals are used in the measurement of crude oil.
6. Measure the density of crude oil before and after mixing with nano-surfactant solutions.
7. Collect the rock samples from the Northern Thailand Oil Field and perform the static adsorption test.
8. Analyze and discuss the results

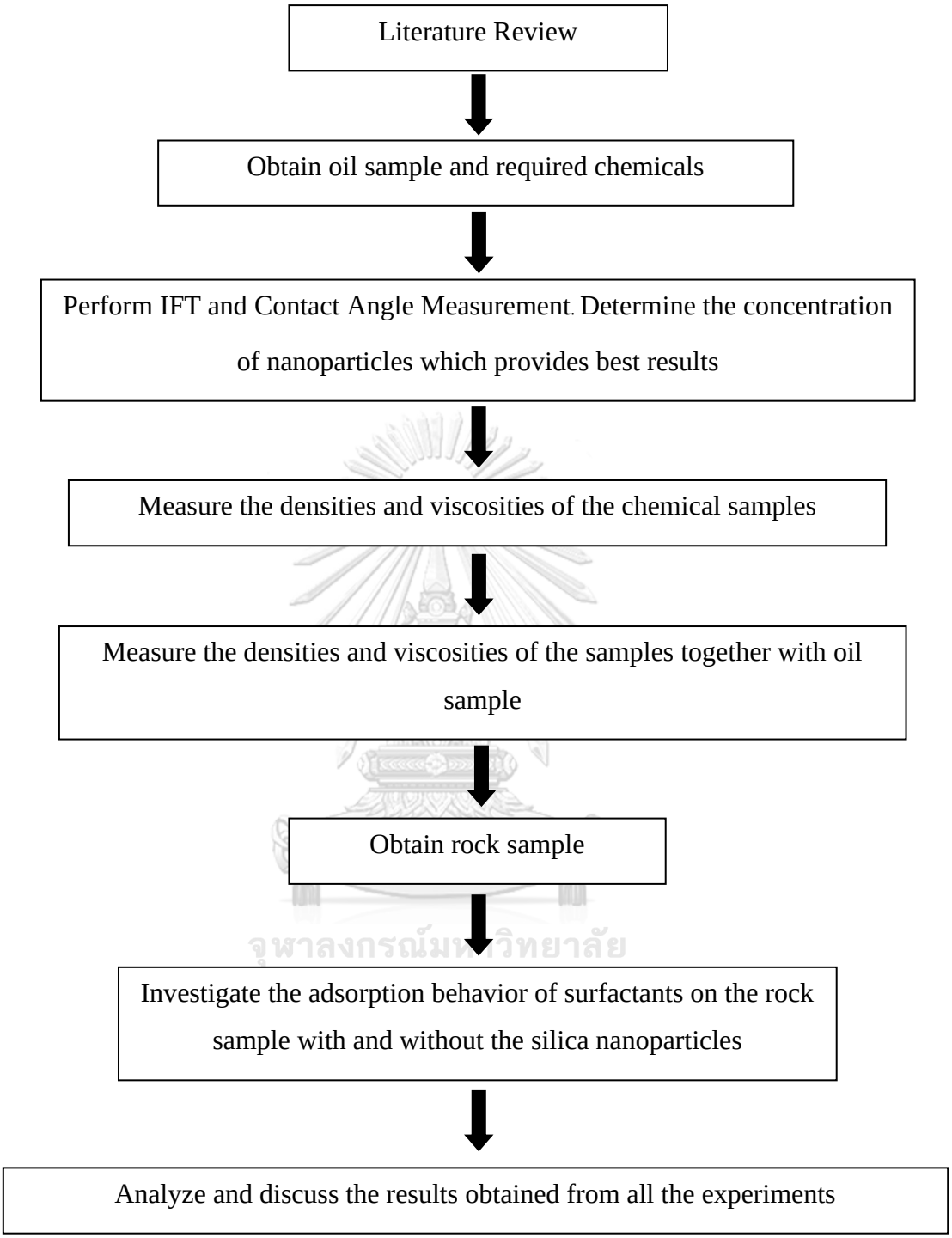


Figure 3. 7 Methodology in flowchart

CHPATER 4
Results And Discussion

This chapter will present the results of the experiment from various measurement of interfacial tension, contact angle, density, viscosity and chemical adsorption on the rock surface. Also, the discussion will be provided.

4.1 Interfacial Tension Measurement

4.1.1 Effect of Surfactant Types and Concentrations on the Interfacial Tension

In this study, two types of anionic surfactants are used which are sodium dodecyl sulfate (SDS) and sodium dodecylbenzene sulfonate (SDBS). The results of two different surfactants in brine with and without nanoparticles are presented in Table 4.1- 4.2 and Figure 4.1.

According to the results, SDBS provides the smaller IFT value compared to SDS for every conditions. At 70˚C, IFT of 750 ppm (wt.) brine solution is initially 18.1 nN/m. As the typical salinity of brine is at 750 ppm (wt.) for this study, the comparisons are made with this 750 ppm (wt.) brine solution. When SDS is introduced in the brine solutions, IFT values drops to 4 nN/m or higher. On the other hand, when SDBS is added in the same brine solutions, the IFT drops drastically from 18.1 nN/m to less than 3 nN/m. For comparison, at the brine concentration 750 ppm (wt.) and surfactant concentration 1000 ppm (wt.) at 70˚C, SDBS and SDS can reduce the interfacial tension at the same oil sample by 87% and 69% respectively.

Table 4. 1 Result of IFT of SDS solutions with brine and silica nanoparticles at different concentrations

Nanoparticles concentration, ppm (wt.)	Salinity, ppm (wt.)	SDS concentration, ppm (wt.)	IFT (nN/m)		
			70˚C	80˚C	90˚C
0	750	0	18.1	19.9	20.3
		1000	5.6	5.7	5.9
		2000	4.1	4.2	4.5
		3000	4.2	4.2	4.3
		4000	4.4	4.5	4.6
750	750	0	15.9	16.4	17.2
		1000	3.5	3.4	3.6
		2000	3.3	3.4	3.4
		3000	3.3	3.5	3.6
		4000	3.7	4.0	4.3

Table 4. 2 Result of IFT of the SDBS solutions with brine and silica nanoparticles at different concentrations

Nanoparticles concentration, ppm (wt.)	Salinity, ppm (wt.)	SDBS concentration, ppm (wt.)	IFT (nN/m)		
			70˚C	80˚C	90˚C
0	750	0	18.1	19.9	20.3
		1000	2.3	2.4	2.6
		2000	2.1	2.2	2.4
		3000	2.1	2.2	2.3
		4000	2.4	2.4	2.6
750	750	0	15.9	16.4	17.2
		1000	1.8	2.0	2.1
		2000	1.7	2.0	2.1
		3000	1.7	1.9	2.0
		4000	1.8	1.9	2.1

Both SDS and SDBS are anionic surfactants and have the molecular weights not very different. However, SDBS has better effect in IFT reduction than SDS at same conditions as presented in Figure 4.1. The molecular structure of these two anionic surfactants exhibits the difference in the results. The presence of the benzene ring in the SDBS molecular structure provides the better results. In fact, the benzene ring helps the hydrophobic portion of the surfactant more soluble in crude oil and thus more IFT is being reduced. (Chuaicham, 2016)

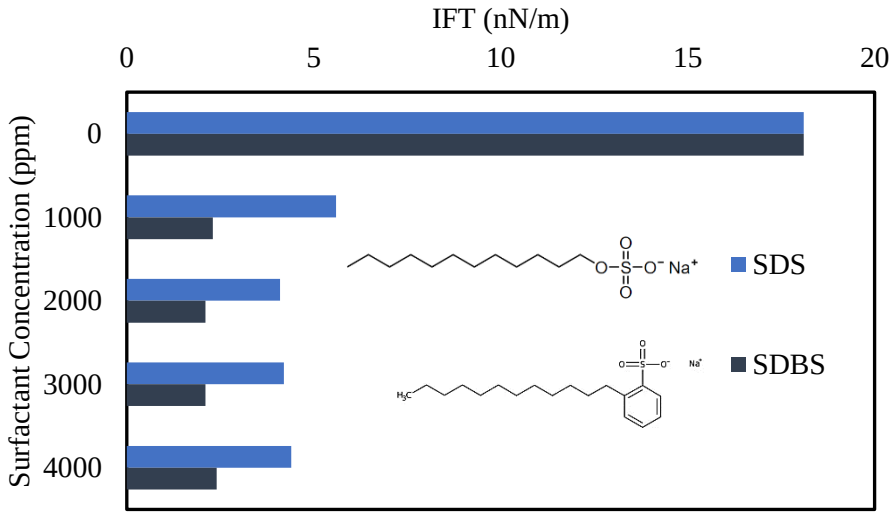


Figure 4. 1 Comparison of IFT results of SDS and SDBS in 750 ppm brine solution at 70˚C

Also, the effect of the surfactant concentrations on IFT is observed by varying from 0 ppm (wt.) to 4000 ppm (wt.) for all surfactants. The purpose of this observation is to select the optimum surfactant concentration for further experiments. From Figure 4.1, it is seen that the IFT is reduced when the surfactant concentration is increased from 0 ppm (wt.) to 1000 ppm (wt.) in the case of both SDS and SDBS. When the concentration is increased to 2000 ppm (wt.), IFT continues to drop. It can be explained that the more surfactant is added in the solution, the more surfactant monomers can be attached at the oil and aqueous phase, resulting in surface tension reduction (Karnanda et al., 2013) Surfactant effect on IFT is different depending on the concentration. Below the certain concentration, IFT decreases with increasing surfactant content but after the concentration exceeds that specific concentration, IFT drop will stable or even increases

slightly. That concentration is called critical micelle concentration and it determines the effect of surfactant concentration on IFT. Similarly, in this research, the IFT seems to be relatively stable at 3000 ppm (wt.) and 4000 ppm (wt.). The reason is when the surfactant concentration exceeds the critical micelle concentrations, the sufficient number of monomers are already staying at the interface and reduced the IFT. While the exceeding monomers attached to each other in the form of micelles in the surfactant solution phase and are not involved in the IFT reduction at the interface. Therefore, the concentration at 2000 ppm (wt.) of the surfactant is chosen to perform the further experiments. Also, using the higher concentration than 2000 ppm (wt.) will not provide any further effective IFT reduction.

4.1.2 Effect of Nanoparticles on the Interfacial Tension Measurement

The hydrophilic silica nanoparticles named AEROSIL 200 is selected to use in this study depending on its ability to support the enhanced oil recovery mechanisms of the surfactant flooding. The concentrations of 0 ppm (wt.), 250 ppm (wt.), 500 ppm (wt.), 750 ppm (wt.) and 1000 ppm (wt.) are selected to study the effect of the concentration of the nanoparticles and the results are presented in Table 4.3 - 4.4 and Figure 4.2-4.5.

Firstly, the IFT results of the nanoparticles at all concentrations with 750 ppm (wt.) brine are observed to choose the optimum concentration of the nanoparticles and are graphically described in Figure 4.2. According to the results, the successive decline of IFT happens throughout the concentration from 0 ppm (wt.) to 750 ppm (wt.) and it increases again at 1000 ppm (wt.). The nanoparticles exhibit the lowest IFT, that can be achieved by using only nanoparticles at 500 ppm (wt.) concentration. As reducing the IFT is not the primary mechanisms of the nanoparticles, the other mechanisms such as reducing the surfactant adsorption by being adsorbed on the rock, need to be taken into account in consideration of the selection of concentration. From the results, 500 ppm (wt.) stands out as the best condition but after considering the potential of the nanoparticles being adsorption instead of the surfactant, the higher concentration with similar result becomes the better option. Hence, 750 ppm (wt.) concentration is selected for the further experiments.

Table 4. 3 Result of IFT of the silica nanoparticles with brine and SDS at different concentrations

Salinity, ppm (wt.)	SDS concentration, ppm (wt.)	SiO_2 Concentration, ppm (wt.)	IFT (nN/m)		
			70˚C	80˚C	90˚C
750	0	0	18.1	19.9	20.3
		250	17.7	18.8	19.6
		500	15.3	15.6	16.7
		750	15.9	16.4	17.2
		1000	20.8	20.7	20.8
750	2000	0	4.1	4.2	4.5
		250	3.2	3.5	3.6
		500	3.3	3.4	3.8
		750	3.3	3.4	3.4
		1000	3.6	3.9	4.0

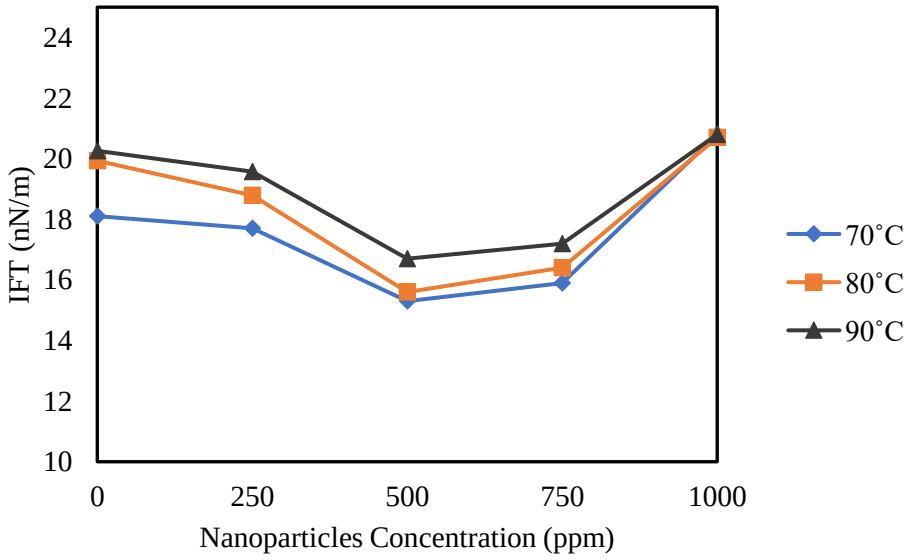


Figure 4. 2 Effect of nanoparticles concentration on IFT in 750 ppm brine solution

Table 4. 4 Result of IFT of the silica nanoparticles with brine and SDBS at different concentrations

Salinity, ppm (wt.)	SDBS concentration, ppm (wt.)	SiO_2 Concentration, ppm (wt.)	IFT (nN/m)		
			70˚C	80˚C	90˚C
750	0	0	18.1	19.9	20.3
		250	17.7	18.8	19.6
		500	15.3	15.6	16.7
		750	15.9	16.4	17.2
		1000	20.8	20.7	20.8
750	2000	0	2.1	2.2	2.4
		250	2.3	2.3	2.5
		500	2.2	2.3	2.4
		750	1.7	2.0	2.1
		1000	1.7	2.1	2.2

Subsequently, the effects of the concentration of the nanoparticles to the surfactant brine solution are focused and compared in Figure 4.3 - 4.5. The results in Figure 4.3 are presented the fixed values of brine concentration at 750 ppm (wt.) and the surfactant concentration at 2000 ppm (wt.) to study the changes along with the change in concentration of the nanoparticles. It is observed that the nanoparticles are not much effective in reducing IFT when they are used alone in the brine solution. They even increased the IFT at specific concentration.

However, when the results of with and without the nanoparticles are compared, they become very effective when combined with the surfactant. In Figure 4.4 and 4.5, the nanoparticles concentration and brine concentration are fixed at 750 ppm (wt.) with the altering of the surfactant concentrations and study the effect of NP on SDS and SDBS, respectively. According to the results, it is found out that the significant reduction in IFT is directly related to the presence of the nanoparticles when other parameters such as surfactant concentration, temperature, salinity are the same. For instance, the IFT drops to as low as 3.3 nN/m in 2000 ppm (wt.) SDS-brine coupled with 750 ppm (wt.) NP from 4.1 nN/m in the solution excluding NP. Similarly, the low

IFT of 1.7 nN/m can be achieved in 2000 ppm (wt.) SDBS-brine coupled with750 ppm (wt.) NP when only SDBS-brine solution at the same concentration shows 2.1 nN/m without the nanoparticles. From this result, it can be concluded that the nanoparticles are not effective as a IFT reducer when used alone but they can support the better IFT reduction results for the surfactant flooding even better than the surfactant can perform by itself.

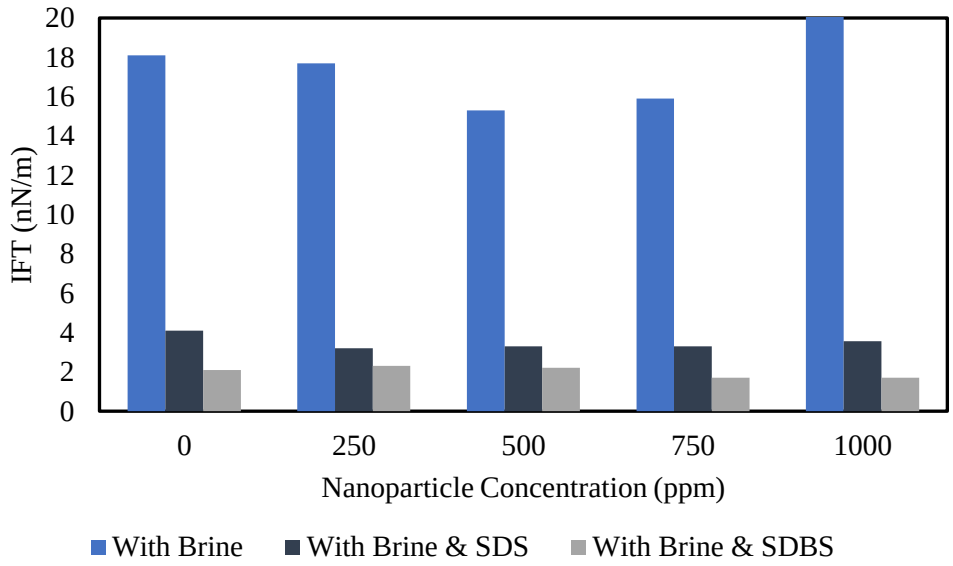


Figure 4. 3 Effect of nanoparticles on IFT in 750 ppm brine solution with SDS/SDBS at 2000 ppm

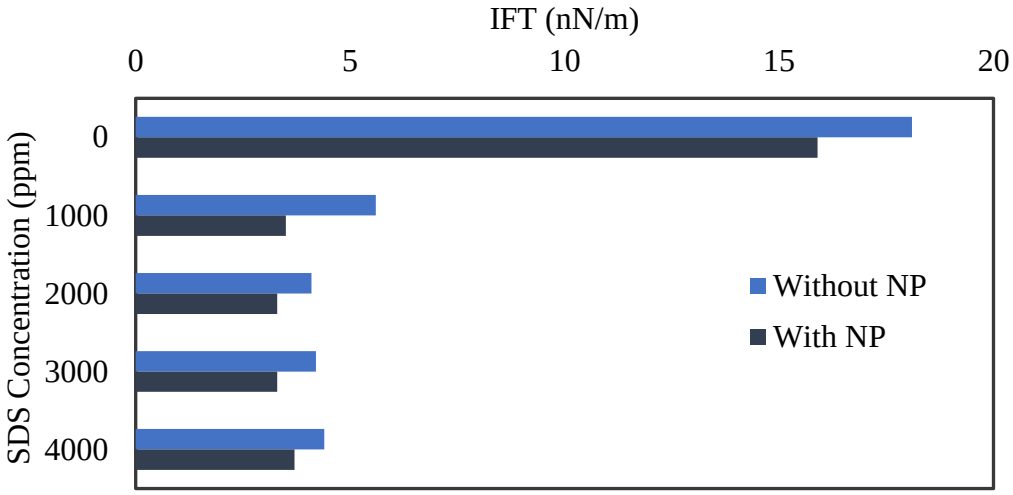


Figure 4. 4 Effect of nanoparticles with SDS in 750 ppm brine

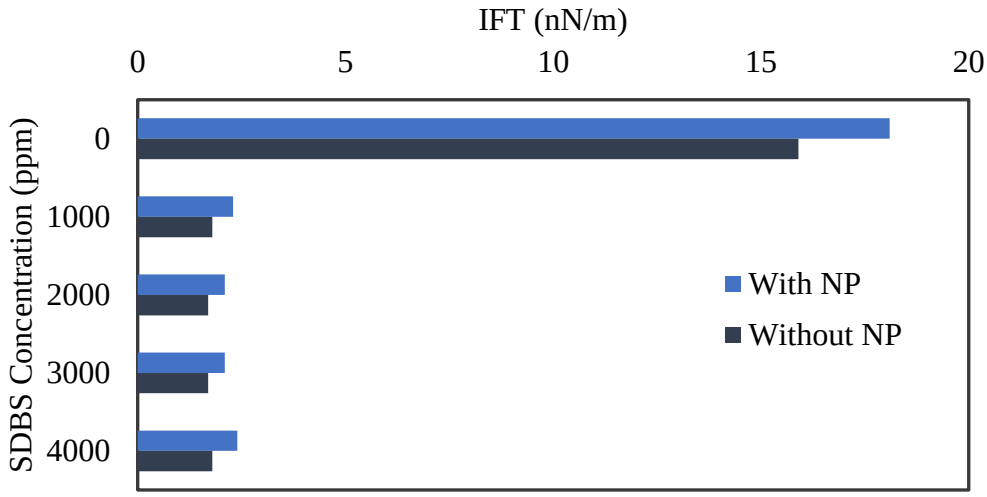


Figure 4. 5 Effect of nanoparticles with SDBS in 750 ppm brine

4.1.3 Effect of Salinity and Temperature on the Interfacial Tension Measurement

Before testing, the interfacial tension of distilled water is measured. The amount of salinity of water is measured to study the effect of salinity on IFT. The results are shown in Table 4.5 and Figure 4.6. From the results, it is presented that the interfacial tension between oil and brine system decreases slightly with an increase in salinity from 0 ppm (wt.) to 1000 ppm (wt.). This could be due to the formation of microemulsion at the oil water interface. According to Ruckenstein and Rao (1987), the salinity has complex effect on interfacial tension. At low salt concentrations, oil-in-water microemulsion coexists with an excess oil and the IFT between those two liquids decreases with an increase in salinity. On the other hand, at higher salinity, water-in-oil microemulsion coexists with an excess water and the IFT between them increases with the increased salinity. Therefore, with oil-in-water microemulsion, the salinity used in this research are relatively low concentration range and thus, IFT reduction is achieved with higher salinity. This is also one of the reasons why the low salinity water become an option in enhanced oil recovery methods. However, in this work, the salinity of the produced water from the designated oil field is relatively low and the properties of low saline water is already achieved. According to the actual formation data, the fixed salinity of 750 ppm (wt.) will be used in further experiments.

Table 4. 5 IFT of the brine solutions at different salinity and temperature

Salinity, ppm (wt.)	IFT (nN/m)		
	70˚C	80˚C	90˚C
0	22.3	22.5	22.7
500	19.1	20.1	20.5
750	18.1	19.9	20.3
1000	17.8	19.4	20.0

As presented in the Figure 4.6, the IFT increases when the temperature is higher. This is because at higher temperature, the number of hydrogen bonds in surrounding water decreases to attach with surfactant head groups. Therefore, the solubility of surfactant in water become less temperature effect and hence it results in increasing the IFT at higher temperature (Ivanova et al., 2020)

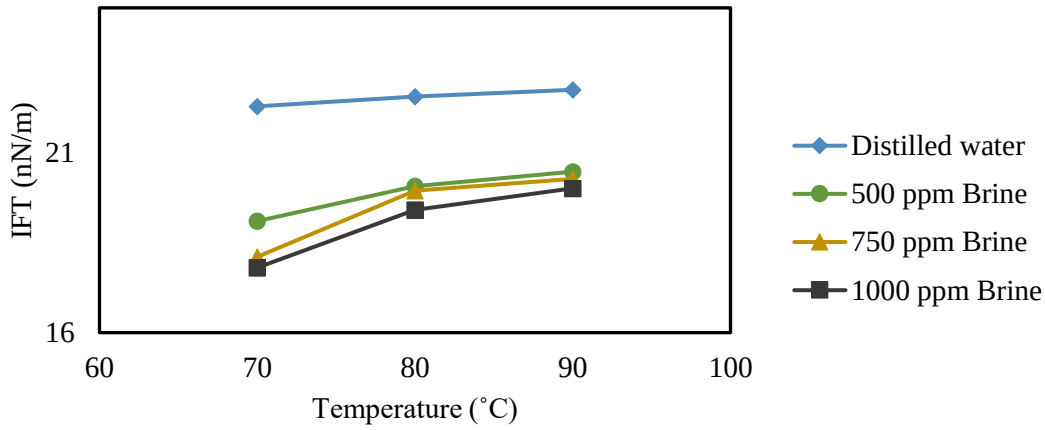


Figure 4. 6 Interfacial tension between oil and brine solutions as function of temperature

4.2 Contact Angle Measurement

In this section, the contact angle change of crude oil droplet is exclusively observed in the relation with the surfactant types and concentration, nanoparticle application, temperature and salinity in the surfactant-brine solution. As the contact angle measurement can be done with the same equipment with IFT measurement, the same operating temperature and concentrations are adopted in this section.

However, due to the lack of availability of rock sample disc from the designated oil field, the contact angle measurements are not conducted with the actual rock sample. Instead, the built-in stainless-steel disc is used throughout the experiment. Therefore, the obtained results may only represent the contact angle relation between stainless-steel, chemical solutions and the oil. It may not represent the potential wettability alteration that could happen in the reservoir rock when the surfactant and nanoparticles are used. However, the effect of the surfactant and nanoparticles on contact angle can be studied to see the tendency with other parameters like concentration, temperature and salinity.

4.2.1 Effect of Surfactant Types and Concentrations on Contact Angle

Due to the nature of the surfactant, the adsorption can occur at every interface encountered. If the surfactant adsorbs at the oil and water interfaces, the interfacial tension reduction is achieved. If the adsorption interface is rock or solid surface with oil, the contact angle reduction or wettability alteration can be achieved. To study this effect, the series of the contact angle measurement between the solid surface and oil in the surfactant-brine solutions and surfactant-brine-nanoparticles solutions are performed. The results are tabulated in Table 4.6 - 4.7 and Figure 4.7.

According to the results, both SDS and SDBS can effectively reduce the contact angle of oil on the solid surface. One thing in common is that at 70˚C, contact angle of oil droplet in 750 ppm (wt.) brine solution is initially 69.7˚, when SDS and SDBS are introduced in the brine solutions, the angle is getting smaller to as small as 31˚ steadily. Therefore, as the comparison, both of the two anionic used can be similarly reduced the contact angle of the oil droplet on the surface.

Table 4. 6 Result of contact angle of the SDS solutions with brine and silica nanoparticles at different concentrations

Nanoparticles concentration, ppm (wt.)	Salinity, ppm (wt.)	SDS concentration, ppm (wt.)	Contact Angle (˚)		
			70˚C	80˚C	90˚C
0	750	0	69.7	66.8	65.4
		1000	33.9	32.8	30.6
		2000	33.1	30.8	30.0
		3000	32.7	30.3	29.6
		4000	31.0	30.1	29.0
750	750	0	24.1	22.6	21.3
		1000	30.7	29.1	28.4
		2000	30.7	30.4	30.0
		3000	30.6	30.1	28.9
		4000	30.8	30.0	29.1

Table 4. 7 Result of contact angle of the SDBS solutions with brine and silica nanoparticles at different concentrations

Nanoparticles concentration, ppm (wt.)	Salinity, ppm (wt.)	SDBS concentration, ppm (wt.)	Contact Angle (˚)		
			70˚C	80˚C	90˚C
0	750	0	69.7	66.8	65.4
		1000	34.5	34.1	33.8
		2000	32.6	32.2	31.9
		3000	31.9	31.1	30.8
		4000	31.0	30.7	30.4
750	750	0	24.1	22.6	21.3
		1000	32.5	31.9	31.1
		2000	31.6	31.2	31.9
		3000	31.2	30.8	30.6
		4000	30.1	30.0	30.2

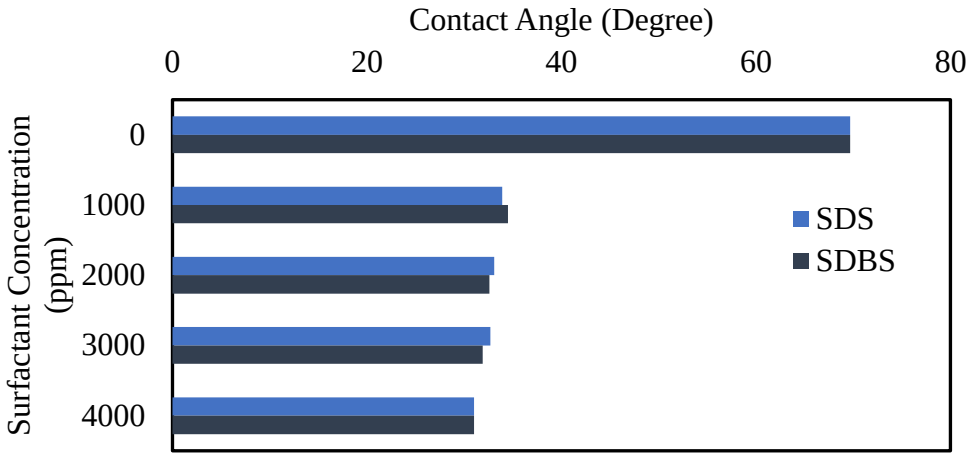


Figure 4. 7 Comparison of contact angle results of SDS and SDBS in 750 ppm brine solution at 70˚C

In addition, the effect of the surfactant concentration on the contact angle is observed by varying the surfactant concentration from 0 ppm (wt.) to 4000 ppm (wt.) for all cases. From the Figure 4.7, it can be seen that the contact angle is smaller when the surfactant concentration is increased from 0 ppm (wt.) to 1000 ppm (wt.) in the case of both SDS and SDBS. When the concentration is continuously added to 2000 ppm (wt.), 3000 ppm (wt.) and 4000 ppm (wt.), the contact angle continues to drop. This behavior of the contact angle change with the surfactant solution is because of the surfactant adsorption on the surface as well. The wettability alteration by the surfactant is mainly depending on the electrostatic attraction between the surfactant molecules and the rock surface, surfactant aggregation on rock, in other words, the contact angle change occurs as the result of the surfactant adsorption on the rock surface. (Ahmadi & Shadizadeh, 2015; Somasundaran & Zhang, 2006)

4.2.2 Effect of Nanoparticles on the Contact Angle

Although the wettability alteration happens in the surfactant solution, the surfactant adsorption which causes contact angle change is undesirable in EOR process. Therefore, the nanoparticles are used to achieve more water-wet rock effectively and harmlessly for the surfactant concentration in the aqueous phase. In this section, the contact angles between oil and solid surface are measured in the combinations of the

brine-surfactant and nanoparticles medium. The results are separately reported in Table 4.8 - 4.9 and Figure 4.8-4.10.

Table 4. 8 Result of contact angle of the silica nanoparticles with brine and SDS at different concentrations

Salinity, ppm (wt.)	SDS concentration, ppm (wt.)	SiO_2 Concentration, ppm (wt.)	Contact Angle (˚)		
			70˚C	80˚C	90˚C
750	0	0	68.5	66.8	65.4
		250	28.1	25.5	23.7
		500	26.9	24.8	23.5
		750	24.1	22.6	21.3
		1000	23.6	21.9	21.1
750	2000	0	33.1	30.8	30.0
		250	28.9	28.4	28.1
		500	30.0	29.7	29.0
		750	30.7	30.4	30.0
		1000	30.1	30.3	29.1

The effect of nanoparticles with brine solution is observed prior to the use of the surfactant. The results of the contact angle measurement for oil droplet by increasing the concentration of the nanoparticles in the brine solution are shown in Figure 4.8. As presented, the rapid drop in the contact angle between oil, surface in brine solution occurs once the nanoparticles are introduced to the solution. Initially, the contact angle is 68.5˚ in the 750 ppm (wt.) brine solution at 70˚C and it abruptly changed to 22˚ when 250 ppm (wt.) of the nanoparticles are added. It is 68.5% of the original contact angle and the nanoparticles simply change the wettability towards more water wet. As the concentration is increased, the contact angle moderately declines until it stabilizes around 20˚.

Table 4. 9 Result of contact angle of the silica nanoparticles with brine and SDBS at different concentrations

Salinity, ppm (wt.)	SDBS concentration, ppm (wt.)	SiO_2 Concentration, ppm (wt.)	Contact Angle (˚)		
			70˚C	80˚C	90˚C
750	0	0	68.5	66.8	65.4
		250	28.1	25.5	23.7
		500	26.9	24.8	23.5
		750	24.1	22.6	21.3
		1000	23.6	21.9	21.1
750	2000	0	32.6	32.2	31.9
		250	31.0	27.0	28.0
		500	31.0	32.0	31.0
		750	31.6	31.2	31.9
		1000	32.2	31.7	30.4

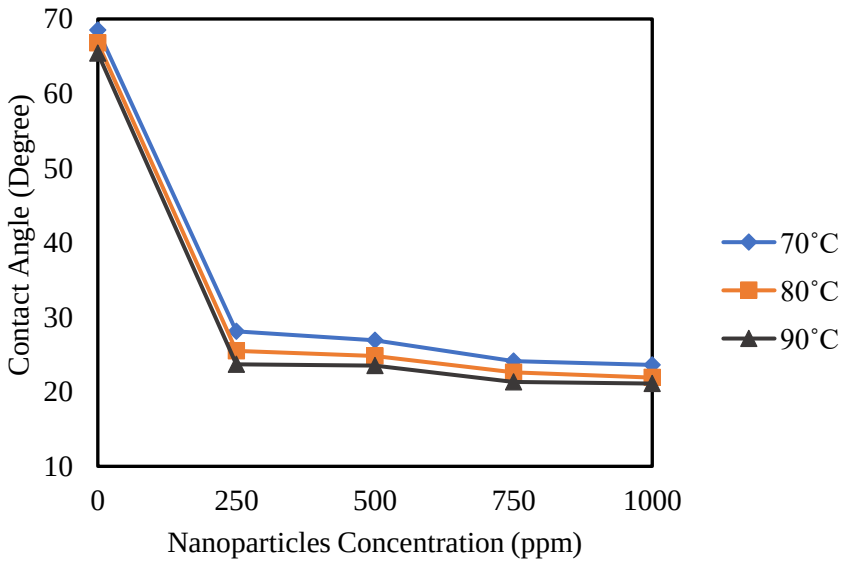


Figure 4. 8 Effect of nanoparticles concentration on contact angle in 750 ppm brine solution

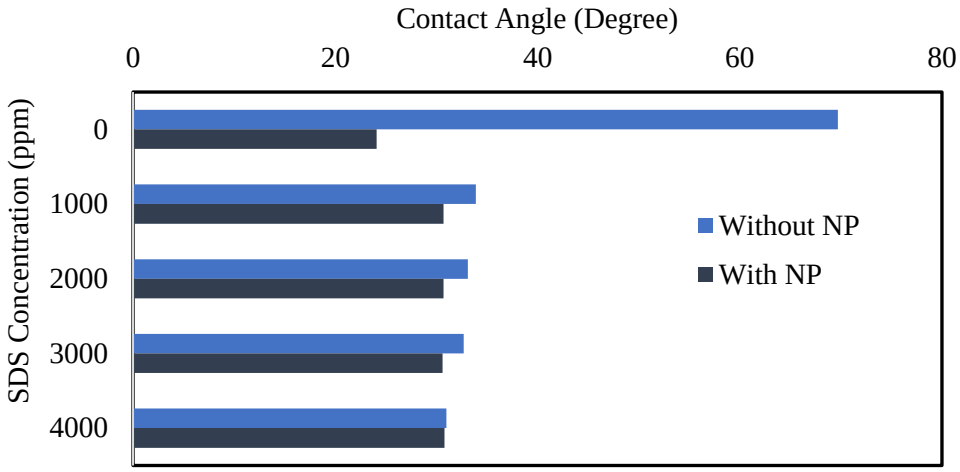


Figure 4. 9 Effect of nanoparticles with SDS in 750 ppm brine

Later, the effect of the nano-surfactant solutions on the contact angle is studied. From the comparison in Figure 4.9 and Figure 4.10, it is apparent that the reduction in the contact angle is higher when the nanoparticles are added in the nano-surfactant solutions than the surfactant solutions. However, the lowest contact angle is achieved if the surfactant is not used in the system. The results portrayed that the only nanoparticle solution is better than the nano-surfactant solution. This could also be the consequence of the lack of the rock pellet use to measure the contact angle which is why the effects due to the ion-exchange or nanoparticles replacing the surfactant adsorbed on the rock surface are not dominant because the formation of ion-pair between rock and nanoparticles could strip off the oil and alter the wettability significantly (Tavakkoli et al., 2022). Nevertheless, even on the stainless-steel surface, the nanoparticles help reducing the contact angle of the surfactant solution.

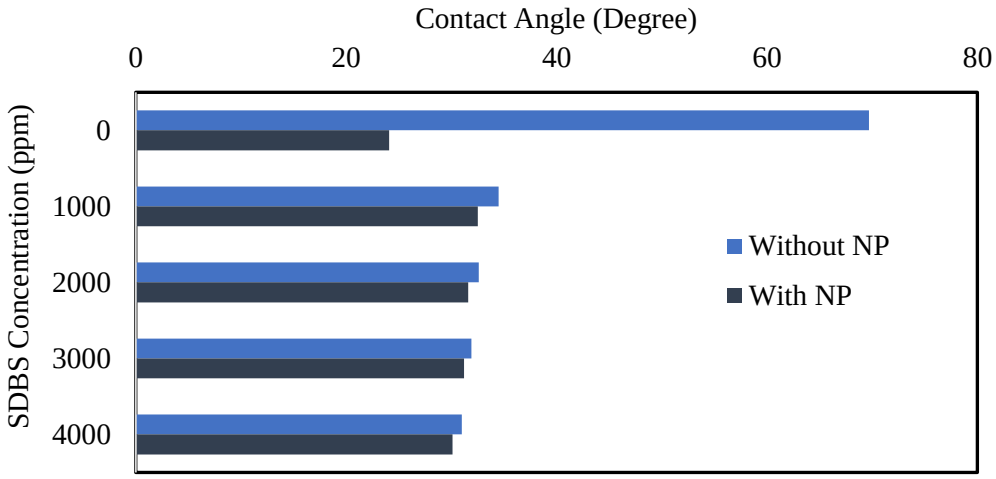


Figure 4. 10 Effect of nanoparticles with SDS in 750 ppm brine

4.2.3 Effect of Salinity and Temperature on the Contact Angle

Prior to the study of the wettability alteration due to the contact angle change with the help of the nanoparticles and surfactant, the impacts of the salinity on contact angle are measured to keep as the reference base value for the whole experiment. The results are shown in Table 4.10 and the graphical comparisons of the effect of the salinity and temperature on contact angles are illustrated in Figure 4.11.

Table 4. 10 Results of contact angle of the Brine solutions at different concentration

Salinity, ppm (wt.)	Contact Angle (˚)		
	70˚C	80˚C	90˚C
0	90.0	88.1	85.3
500	69.7	68.9	68.0
750	68.5	66.8	65.4
1000	67.9	66.4	65.0

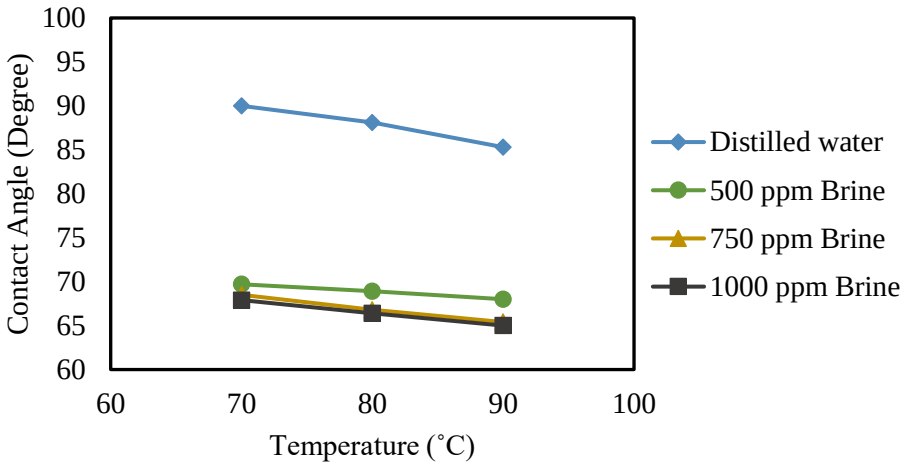


Figure 4. 11 Contact angle between oil and brine solutions as function of temperature

The contact angle between the solid surface and oil droplets in the medium of distilled water is initially at 90˚. Therefore, the studied surface is assumed to be intermediate oil wet. As the salinity is increased, it can be seen in the Figure 4.11 that the contact angle drops below 75˚. From these results, it is apparent that the salinity plays partially in the wettability alteration of the studied solid surface. On the other hand, the linear decline of the contact angle also occurs as the temperature of the system gets higher. The temperature helps the surface to slightly change from intermediate wetting surface to partial water-wet surface.

4.3 Density and Viscosity Measurement

In this section, the properties of the surfactant solution such as the density and viscosity are measured and observed. The focus of this section is to witness the effect of the nanoparticles on the surfactant before using in the flooding process. Hence, the impact of salinity, the interaction with crude oil and reservoir rock are excluded in this section. Moreover, the wide range of the operating temperature is selected in this section. However, the conditions selected for the previous experiments such as the IFT, contact angle measurement and upcoming experiments such as crude oil-chemical viscosity measurement and adsorption behavior study may be different from this study.

4.3.1 Effect of Nanoparticles on Surfactant Solution Viscosity

The dynamic viscosities of the chemicals are measured with the Ubbelohde capillary viscometers. The concentration of the surfactant selected in this experiment are the same as the previous study which are 1000 ppm (wt.) to 4000 ppm (wt.) with the increment of 1000 ppm (wt.) each. Also, the nanoparticles concentration is 750 ppm (wt.). The viscosities are measured starting from 30˚C to 80˚C at every 10 ˚C. The results are shown in the Table 4.11-4.12 and Figure 4.12-4.13.

Table 4. 11 Viscosity measurement results of SDS solutions with and without nanoparticles

SiO_2 Concentration, ppm (wt.)	SDS Concentration, ppm (wt.)	Viscosity (cp)					
		30˚C	40˚C	50˚C	60˚C	70˚C	80˚C
0	0	0.82	0.66	0.57	0.49	0.44	0.41
	1000	0.96	0.79	0.69	0.60	0.55	0.53
	2000	0.95	0.80	0.71	0.62	0.55	0.52
	3000	0.96	0.83	0.74	0.65	0.57	0.53
	4000	0.98	0.80	0.69	0.62	0.55	0.54
750	0	0.82	0.66	0.57	0.49	0.44	0.41
	1000	0.95	0.81	0.70	0.64	0.56	0.52
	2000	0.96	0.82	0.72	0.62	0.57	0.50
	3000	0.97	0.84	0.72	0.64	0.59	0.52
	4000	0.97	0.84	0.72	0.64	0.60	0.57

Table 4. 12 Viscosity measurement results of SDBS solutions with and without nanoparticles

SiO_2 Concentration, ppm (wt.)	SDBS Concentration, ppm (wt.)	Viscosity (cp)					
		30˚C	40˚C	50˚C	60˚C	70˚C	80˚C
0	0	0.82	0.66	0.57	0.49	0.44	0.41
	1000	0.91	0.79	0.67	0.61	0.55	0.52
	2000	0.96	0.78	0.68	0.61	0.55	0.51
	3000	0.98	0.80	0.71	0.62	0.55	0.52
	4000	0.98	0.81	0.71	0.62	0.57	0.53
750	0	0.82	0.66	0.57	0.49	0.44	0.41
	1000	0.97	0.82	0.70	0.64	0.56	0.51
	2000	0.97	0.84	0.71	0.63	0.58	0.53
	3000	0.98	0.82	0.72	0.64	0.57	0.53
	4000	1.00	0.82	0.73	0.64	0.58	0.52

From the results, the viscosity results are compared. The nanoparticles do not have much impact on the viscosities of the surfactant solutions. The results with and without the nanoparticles are plotted against each other under the same conditions in Figure 4.12 and 4.13 for SDS and SDBS, respectively. The lines are the results of the surfactant in the solution without the nanoparticles and the scattered marks are the results of the surfactant solution with the nanoparticles. It can be clearly seen that adding the nanoparticles will only make a small change to the surfactant solutions which means they have less effect on the viscosity for both solutions of the surfactant flooding.

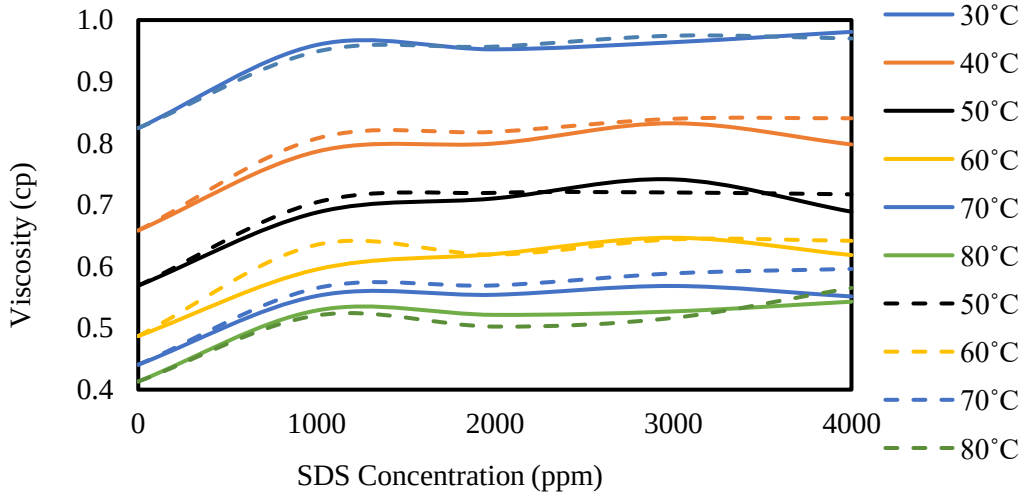


Figure 4. 12 Viscosity measurement results of SDS

(Straight lines are the viscosity results of SDS solutions and dashed lines are the viscosity results of SDS solutions with nanoparticles)

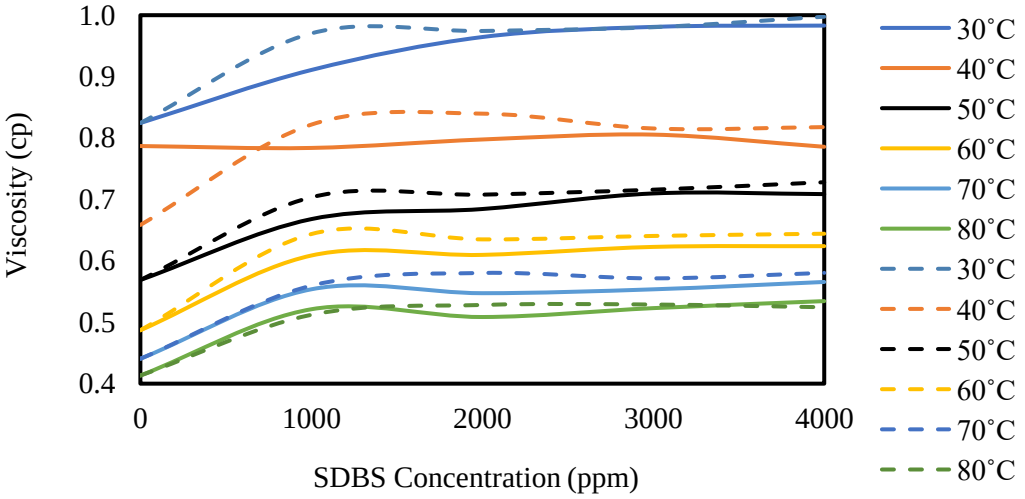


Figure 4. 13 Viscosity measurement results of SDBS

(Straight lines are the viscosity results of SDBS solutions and dashed lines are the viscosity results of SDBS solutions with nanoparticles)

4.3.2 Effect of Nanoparticles on Surfactant Solution Density

The effect of the nanoparticles on the density of the surfactant solutions is studied and discussed in this section. The measurements are done at the same operating conditions with the viscosity measurement by using the Anton Parr density meter

Model DMA-4500 which has the accuracy of ±0.0002 g/cm^3. The results of the measurements are shown in Table 4.13-4.14 and Figure 4.14-4.15.

Similarly, the nanoparticles have less effect on the density of the surfactant solutions. The results of the nano-surfactant solutions, represented by the scattered points, fall in line represented for the surfactant solutions for the results of SDS and SDBS solutions as presented in Figure 4.14 and Figure 4.15, respectively.

From both viscosity and density measurements, the nanoparticles do not have significant impact on the density and viscosity of the surfactant solutions in the case that only these chemicals are mixed.

However, it is observed from both density and viscosity measurements, temperature has the strong impact on both viscosity and density for all cases. The higher the temperature, the lower the viscosity and density of the solutions. This temperature effect should be carefully considered in the actual field application of the surfactant solutions as the reservoir temperature would be higher than the standard conditions.

Table 4. 13 Density measurement results of SDS solutions with and without nanoparticles

SiO_2 Concentration, ppm (wt.)	SDS Concentration, ppm (wt.)	Density (g/cm^3)					
		30˚C	40˚C	50˚C	60˚C	70˚C	80˚C
0	0	0.9957	0.9922	0.9877	0.9803	0.9745	0.9702
	1000	0.9960	0.9925	0.9883	0.9835	0.9780	0.9690
	2000	0.9961	0.9923	0.9880	0.9834	0.9767	0.9691
	3000	0.9963	0.9928	0.9886	0.9837	0.9768	0.9698
	4000	0.9964	0.9926	0.9887	0.9838	0.9775	0.9724
750	0	0.9957	0.9922	0.9877	0.9803	0.9745	0.9702
	1000	0.9962	0.9922	0.9884	0.9835	0.9762	0.9721
	2000	0.9963	0.9929	0.9879	0.9829	0.9773	0.9723
	3000	0.9966	0.9931	0.9883	0.9840	0.9775	0.9725
	4000	0.9967	0.9933	0.9886	0.9842	0.9776	0.9727

Table 4. 14 Density measurement results of SDBS solutions with and without nanoparticles

SiO_2 Concentration, ppm (wt.)	SDBS Concentration, ppm (wt.)	Density (g/cm^3)					
		30˚C	40˚C	50˚C	60˚C	70˚C	80˚C
0	0	0.9957	0.9922	0.9877	0.9803	0.9745	0.9702
	1000	0.9961	0.9926	0.9884	0.9836	0.9774	0.9720
	2000	0.9964	0.9929	0.9888	0.9839	0.9785	0.9725
	3000	0.9967	0.9932	0.9890	0.9842	0.9787	0.9727
	4000	0.9970	0.9935	0.9893	0.9844	0.9790	0.9730
750	0	0.9957	0.9922	0.9877	0.9803	0.9745	0.9702
	1000	0.9963	0.9927	0.9879	0.9827	0.9782	0.9722
	2000	0.9967	0.9933	0.9891	0.9842	0.9788	0.9728
	3000	0.9970	0.9936	0.9894	0.9845	0.9791	0.9731
	4000	0.9973	0.9938	0.9896	0.9848	0.9793	0.9733

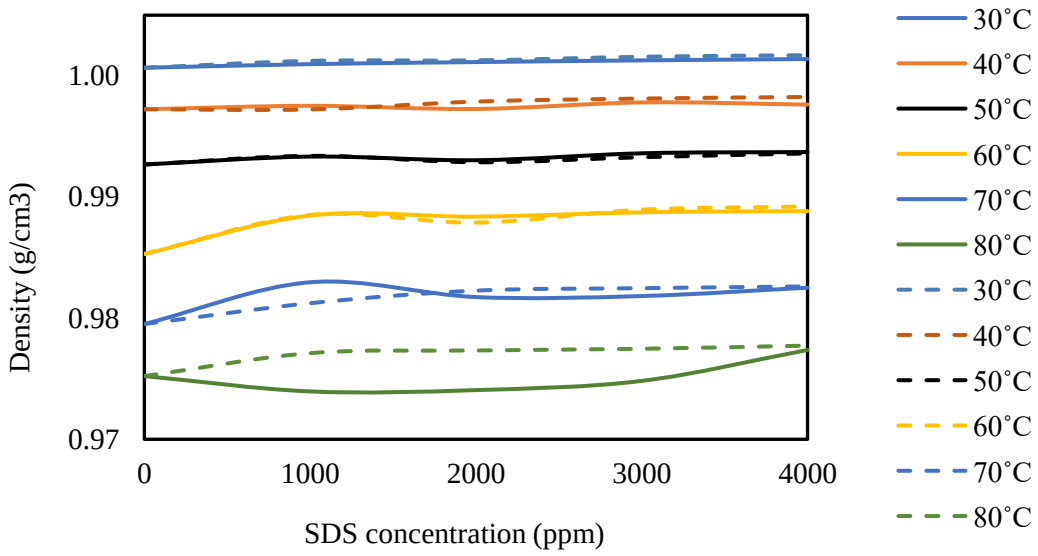


Figure 4. 14 Density measurement results of SDS solutions

(Straight lines are the density results of SDS solutions and dashed lines are the density results of SDS solutions with nanoparticles)

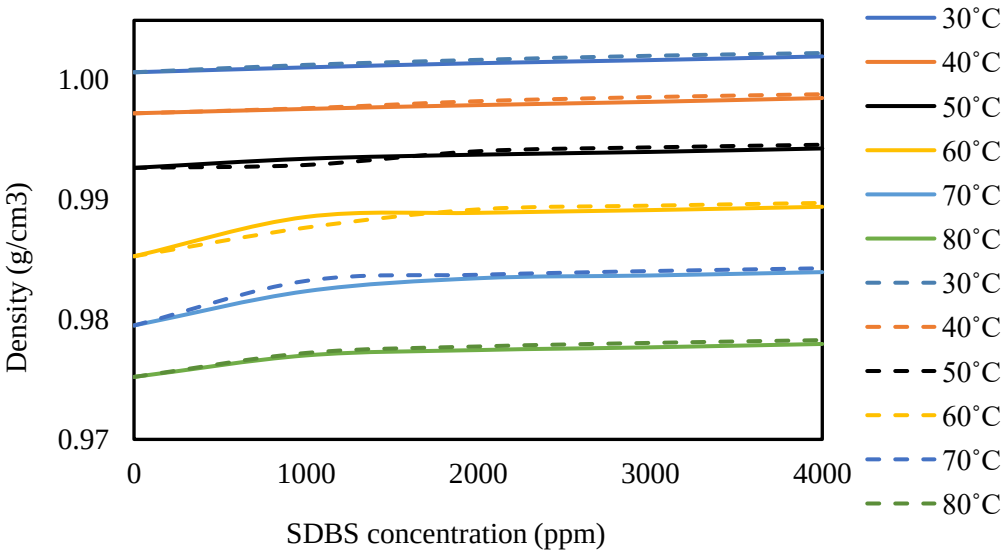


Figure 4. 15 Density measurement results of SDBS solutions

(Straight lines are the density results of SDBS solutions and dashed lines are the density results of SDBS solutions with nanoparticles)

4.4 Viscosity Measurement of Oil Sample Mixed with Chemicals

4.4.1 Effect of Temperature on Oil Viscosity

The viscosity of the oil sample acquired from the northern Thailand oilfield is measured using the Brookfield Viscometer. The parameters are temperature from 60˚C to 80˚C and shear rate from 6 s^{-1} to 18 s^{-1}. The results are shown in Table 4.15 and Figure 4.16.

From the results, it is observed that the oil viscosity is greatly sensitive to the temperature. The viscosity of the oil decreases as the temperature gets higher from 60˚C to 80˚C in Figure 4.16. The sharp decline in viscosity indicates that high temperature helps the oil molecules acquire high energy from the heat to make the oil less viscous and make the oil easier to flow or move. Also, the shear rate makes the slight changes in oil viscosity. In Figure 4.16, the oil viscosity slightly decreases at the higher shear rate which is the consequence of the water droplet in the oil breaking up to the smaller size as shear rate is higher (Richardson, 1950). This relation between shear rate and viscosity also points out that the sample is non-Newtonian fluid Juntarasakul (2015). However, the effect of shear rate on viscosity is insignificant.

Table 4. 15 Viscosity measurements of the oil sample

	Temperature (˚C)	Shear Rate (1/s)	Viscosity (cp)
Oil	60	6	16.55
		12	16.32
		18	16.10
	70	6	11.92
		12	11.58
		18	11.16
	80	6	9.90
		12	9.64
		18	9.21

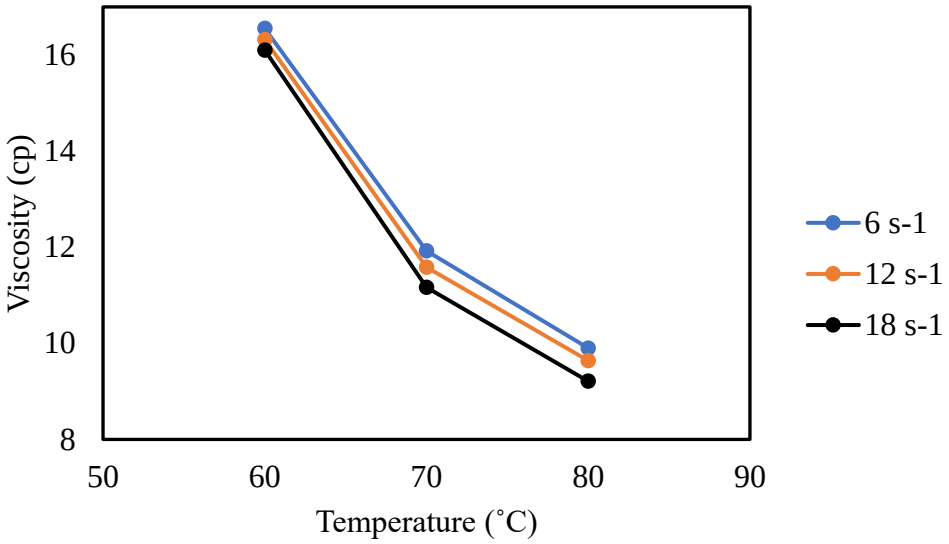


Figure 4. 16 Effect of temperature on oil viscosity

4.4.2 Effect of surfactant on oil viscosity

In order to enhance the oil recovery, improving the displacement efficiency by reducing IFT and altering wettability is not enough. The sweep efficiency also needs to be improved which can either be achieved by increasing the injected fluid viscosity or decreasing the viscosity of the fluid to be replaced, which is crude oil from reservoir. Therefore, the measurement of oil viscosity after being mixed with the surfactant solution is conducted in this section to study how much viscosity can be reduced by adding surfactant. As salinity assumed stable at 750 ppm (wt.) of brine is based in every surfactant solution. A 40% (by volume) of the total measured fluid is the chemical solution and the rest 60% is crude oil. The measured temperatures are at 60˚C, 70˚C and 80˚C. The results are shown in the Table 4.16-4.17 and Figure 4.17-4.18.

By adding surfactants, crude oil becomes less viscous as the surfactant acts as the emulsifier and stabilizes the oil in the surfactant-water emulsion in dispersed phase from the continuous phase to prevent the further coalescence of the oil droplets. Thus, not only low IFT is achieved but also the viscosity is reduced. Figure 4.17 and Figure 4.18 show that the oil viscosity mixed with the surfactant solution is lower than the initial viscosity. In terms of the qualitative comparison between 2 surfactants, SDS is apparently better in improving sweep efficiency of crude oil from northern Thailand oilfield than SDBS as all the results are pointing to the lower apparent viscosities when compared to the results of SDBS at the same conditions.

Table 4. 16 Results of the oil viscosity mixed with SDS and brine solution

Solution	Surfactant Concentration, ppm (wt.)	Temperature (˚C)	Shear Rate (1/s)	Viscosity (cp)
Oil + SDS + Brine	1000	60	6	14.97
			12	10.32
			18	9.21
		70	6	14.20
			12	9.59
			18	8.31
		80	6	13.82
			12	9.21
			18	8.44
Oil + SDS + Brine	2000	60	6	9.59
			12	9.02
			18	8.70
		70	6	9.11
			12	8.00
			18	7.55
		80	6	8.83
			12	7.68
			18	7.42
Oil + SDS + Brine	3000	60	6	10.75
			12	9.02
			18	8.57
		70	6	9.59
			12	7.91
			18	7.03
		80	6	7.68
			12	7.29
			18	6.91
Oil + SDS + Brine	4000	60	6	10.60
			12	9.21
			18	8.63
		70	6	8.44
			12	7.91
			18	7.50
		80	6	7.99
			12	7.19
			18	6.71

Table 4. 17 Results of the oil viscosity mixed with SDBS and brine solution

Solution	Surfactant Concentration, ppm (wt.)	Temperature (˚C)	Shear Rate (1/s)	Viscosity (cp)
Oil + SDBS + Brine	1000	60	6	10.90
			12	10.30
			18	9.98
		70	6	9.85
			12	9.79
			18	9.21
		80	6	8.79
			12	8.75
			18	8.93
Oil + SDBS + Brine	2000	60	6	11.20
			12	10.70
			18	10.36
		70	6	10.75
			12	9.25
			18	9.07
		80	6	8.44
			12	8.40
			18	8.30
Oil + SDBS + Brine	3000	60	6	10.49
			12	10.19
			18	10.20
		70	6	9.48
			12	9.32
			18	9.30
		80	6	9.22
			12	9.10
			18	9.04
Oil + SDBS + Brine	4000	60	6	9.98
			12	10.01
			18	9.77
		70	6	9.52
			12	9.29
			18	9.11
		80	6	8.90
			12	8.83
			18	8.59

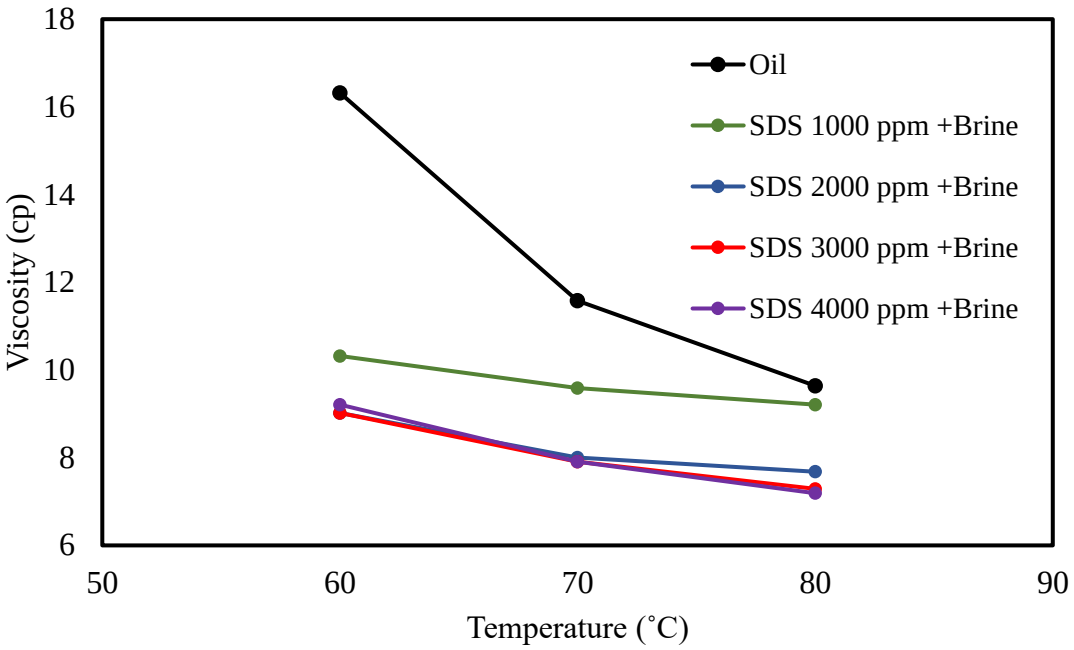


Figure 4. 17 Effect of SDS concentration on oil viscosity

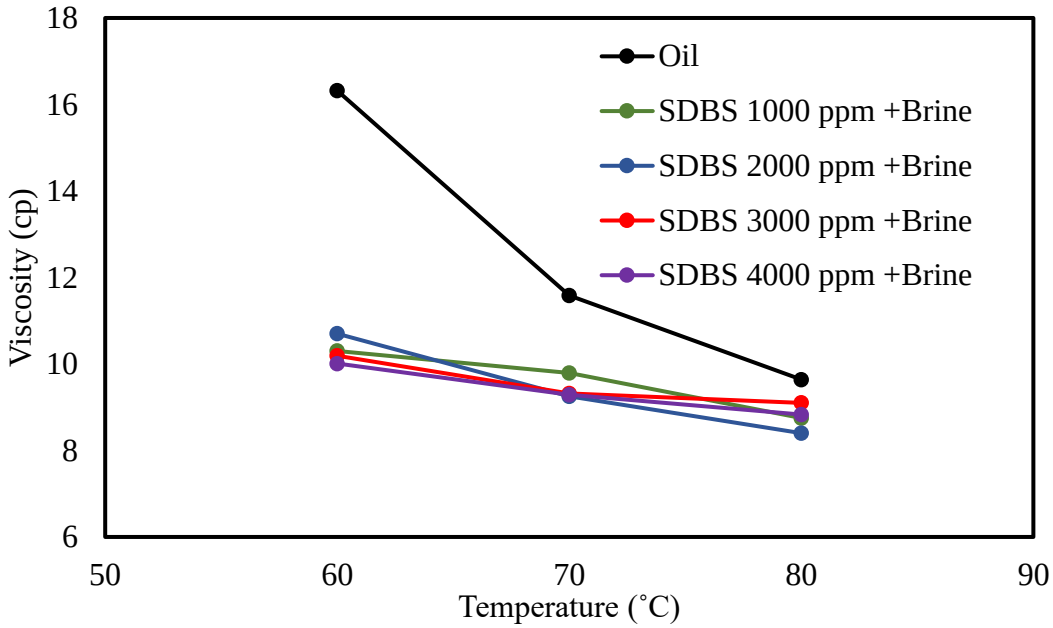


Figure 4. 18 Effect of SDBS concentration on oil viscosity

4.4.3 Effect of surfactant coupled with nanoparticles on oil viscosity

The effect of the nanoparticles on the oil viscosity is observed in this section. The concentration of brine and nanoparticles are fixed at 750 ppm (wt.) according to the results from the previous study. Only the surfactant concentration is varied during this experiment. The chemical solution content in all sample is 40%. and the results of the measurements are separately put in Table 4.18 for SDS and Table 4.19 for SDBS. The viscosity changes between the presence of the nanoparticles in the system and the absence of the nanoparticles are then compared in the Figure 4.19 and Figure 4.20.

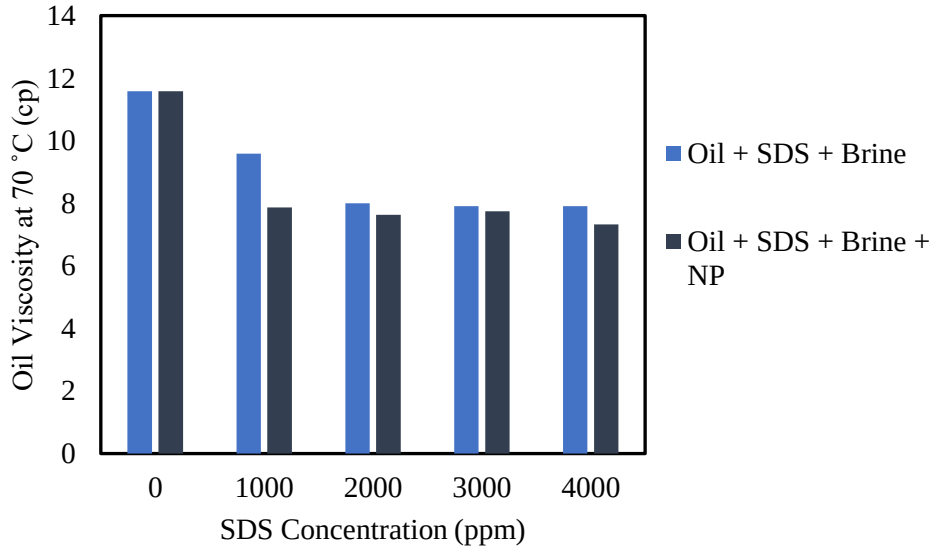


Figure 4. 19 Effect of nanoparticles on oil viscosity mixed with SDS-brine solutions

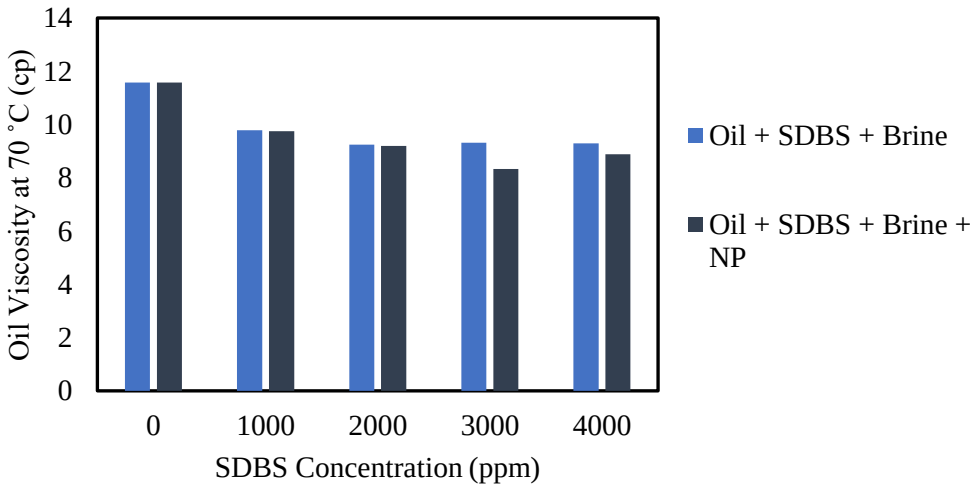


Figure 4. 20 Effect of nanoparticles on oil viscosity mixed with SDS-brine solutions

Table 4. 18 Results of the oil viscosity mixed with SDS mixed with nanoparticles and brine solution

Solution	Surfactant Concentration, ppm (wt.)	Temperature (˚C)	Shear Rate (1/s)	Viscosity (cp)
Oil + SDS + Brine + Nano	1000	60	6	8.96
			12	8.84
			18	8.68
		70	6	7.21
			12	7.87
			18	7.17
		80	6	7.68
			12	7.29
			18	7.01
Oil + SDS + Brine + Nano	2000	60	6	8.83
			12	8.80
			18	8.83
		70	6	7.59
			12	7.63
			18	7.31
		80	6	7.44
			12	7.21
			18	7.13
Oil + SDS + Brine + Nano	3000	60	6	8.83
			12	8.68
			18	8.05
		70	6	7.68
			12	7.74
			18	7.88
		80	6	7.44
			12	7.18
			18	6.90
Oil + SDS + Brine + Nano	4000	60	6	9.34
			12	9.08
			18	8.95
		70	6	7.85
			12	7.32
			18	7.21
		80	6	7.43
			12	7.32
			18	7.76

Table 4. 19 Results of the oil viscosity mixed with SDBS mixed with nanoparticles and brine solution

Solution	Surfactant Concentration, ppm (wt.)	Temperature (˚C)	Shear Rate (1/s)	Viscosity (cp)
Oil + SDBS + Brine + Nano	1000	60	6	10.36
			12	10.59
			18	10.06
		70	6	9.98
			12	9.75
			18	9.74
		80	6	9.10
			12	8.69
			18	8.60
Oil + SDBS + Brine + Nano	2000	60	6	9.52
			12	9.71
			18	9.88
		70	6	9.10
			12	9.20
			18	8.90
		80	6	8.98
			12	8.72
			18	8.63
Oil + SDBS + Brine + Nano	3000	60	6	8.07
			12	8.45
			18	8.71
		70	6	8.26
			12	8.33
			18	8.45
		80	6	7.84
			12	7.88
			18	7.90
Oil + SDBS + Brine + Nano	4000	60	6	9.10
			12	9.60
			18	9.10
		70	6	8.76
			12	8.88
			18	8.95
		80	6	8.22
			12	8.61
			18	7.73

From the results, the nanoparticles provide little effect on oil viscosity reduction in the surfactant flooding. This is because of the Ostwald Ripening Process (Patel et al., 2018) in which the smaller particles tend to coalesce and form larger and more stable structures. As a consequence, the agglomeration of these structures reduces the viscosity of bulk oil.

4.5 Surfactant Adsorption Experiment

4.5.1 Effect of types of surfactants and concentration on adsorption behavior

In this section, the chemical adsorption behaviors of two different surfactants used are studied before introducing the nanoparticles. The surfactant concentrations are varied from 1000 ppm (wt.) to 4000 ppm (wt.) throughout the experiment. As salinity set at 750 ppm (wt.) of brine concentration is applied for every surfactant solution. The sandstone acquired from the northern Thailand oilfield is crushed and used as the adsorbent. The results of the static adsorption and desorption of the surfactant in the brine solutions are demonstrated in Table 4.20 and Figure 4.21.

Table 4. 20 Results of Adsorption-Desorption of surfactants on rock surface

Surfactant type	Salinity, ppm (wt.)	Surfactant concentration, ppm (wt.)	Adsorption (mg/g)	Desorption (mg/g)
SDS	750	1000	3.00	1.07
		2000	4.15	1.20
		3000	8.54	2.18
		4000	10.61	2.27
SDBS	750	1000	3.24	0.73
		2000	6.02	1.00
		3000	19.44	0.90
		4000	26.44	1.66

As the adsorption of the surfactants are carefully analyzed, the amount of the surfactant adsorbed increases as the surfactant concentration is increased as shown in Figure 4.21. This behavior is unfavorable for the surfactant flooding as it would lead to

the degradation in the performance of the surfactant in the aqueous phase. According to the theory of Ngo et al. (2019), the continuous augmentation of the adsorption value over the surfactant concentrations occurs due to electrostatic attraction between surfactant and rock surface charge, aggregation of surfactant monomer on the rock surface and bi-layer surfactant formation successively. This is also illustrated in Figure 4.22

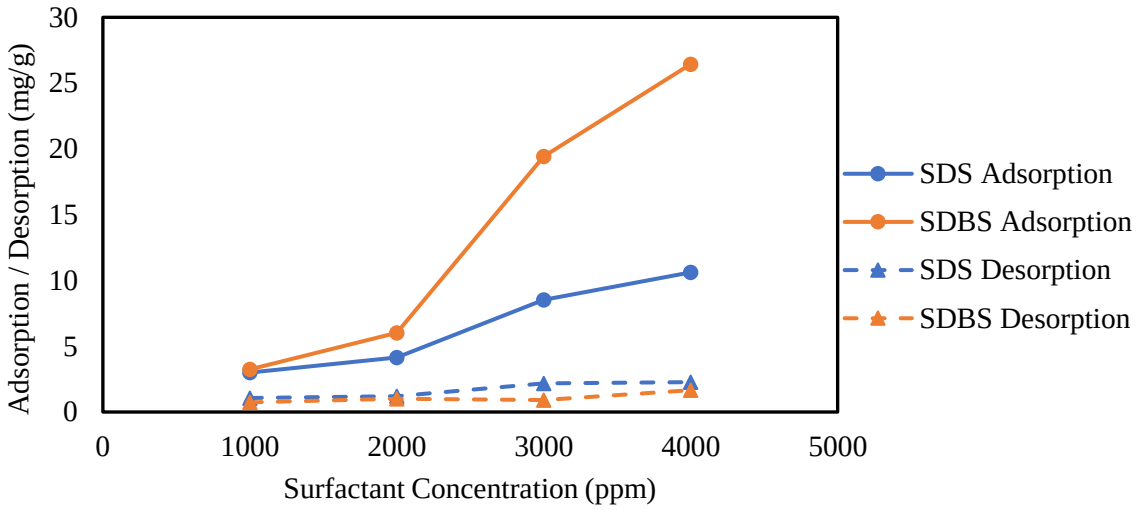


Figure 4. 21 Comparison of Adsorption-Desorption results of SDS and SDBS

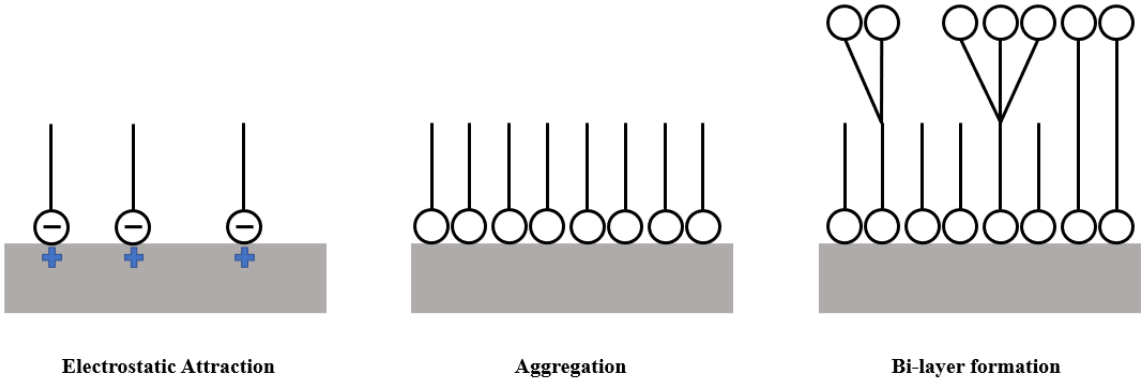


Figure 4. 22 Surfactant Adsorption Behavior due to different concentration

Regarding the effect of surfactant used in the experiment, SDBS adsorbs more on the rock surface than SDS and desorbs back to the aqueous phase less than SDS. At 4000 ppm (wt.) concentration which can be said as worst case for both of surfactants,

SDS adsorbs 10.61 mg/g of rock sample and desorbs back 2.27 mg/g whilst SDBS adsorbs 26.44 mg of surfactant per 1g of rock and desorbs only 1.66 mg/g back to the aqueous phase. In other word, SDS retains 78% of adsorbed surfactant molecules on the rock while SDBS retain 93.7%. In comparison, the adsorption of SDBS is higher than SDS and the desorption value is also lower than SDS. The majority of the surfactant molecules of SDBS tends to be adsorbed on the rock and will not easily desorb back to the surfactant flood either.

4.5.2 Effect of Nanoparticles on Adsorption Behavior

The surfactant adsorption has always been the drawback of the surfactant flooding in the majority of the application. In this section, the effect of nanoparticles on the surfactant adsorption is studied. In the experiment, the nanoparticles concentration and salinity are fixed at 750 ppm (wt.). The same adsorption-desorption process is repeated using the same rock sample from the northern oilfield and the same surfactant concentrations are used to observe the difference of the effect of the nanoparticles. The results are listed in Table 4.21 and shown in Figure 4.23-4.24.

Table 4. 21 Results of Adsorption-Desorption of surfactants coupled with nanoparticles on rock surface

Surfactant type	Salinity, ppm (wt.)	NP Concentration, ppm (wt.)	Surfactant concentration, ppm	Adsorption (mg/g)	Desorption (mg/g)
SDS	750	750	1000	2.54	1.41
			2000	3.00	1.66
			3000	5.84	2.40
			4000	6.38	2.76
SDBS	750	750	1000	2.96	1.01
			2000	3.93	1.18
			3000	17.35	1.88
			4000	19.19	2.15

The results of the effect of the nanoparticles on an adsorption and desorption behavior of SDS and SDBS are separately illustrated in Figure 4.23 and Figure 4.24**.** From the results, it is proved that adding nanoparticles is effective in reducing the surfactant adsorption. Nanoparticles works as the sacrificial adsorbent and hence less surfactant is adsorbed on the rock surface. Regarding the surfactant types used together with the nanoparticles, it is apparent that SDS works well with the nanoparticles and the reduction in the amount of adsorption is larger than that of SDBS. With SDBS, the reduced amount is small except for the best case at 4000 ppm. At 4000 ppm (wt.), the adsorption of SDS is reduced by 39.9% and that of SDBS is reduced by 27.4% with the help of the nanoparticles. At 2000 ppm, the amount of adsorption is reduced from 4.15 mg/g of rock to 3 mg/g of rock in SDS solutions while the amount of adsorption decreases from 6.02 mg/g of rock to 3.93 mg/g of rock in SDBS solutions. The theory of the nanoparticles replaces the surfactants to adsorb can also be confirmed by higher desorption results. In all of the experiments with SDS and SDBS, the solutions with nanoparticles always give the higher desorption values. Therefore, it can be concluded that the nanoparticles not only reduce the amount of surfactant adsorption, but also help more surfactant desorbed back to the aqueous phase during the flooding process making less surfactant remained on the rock surface.

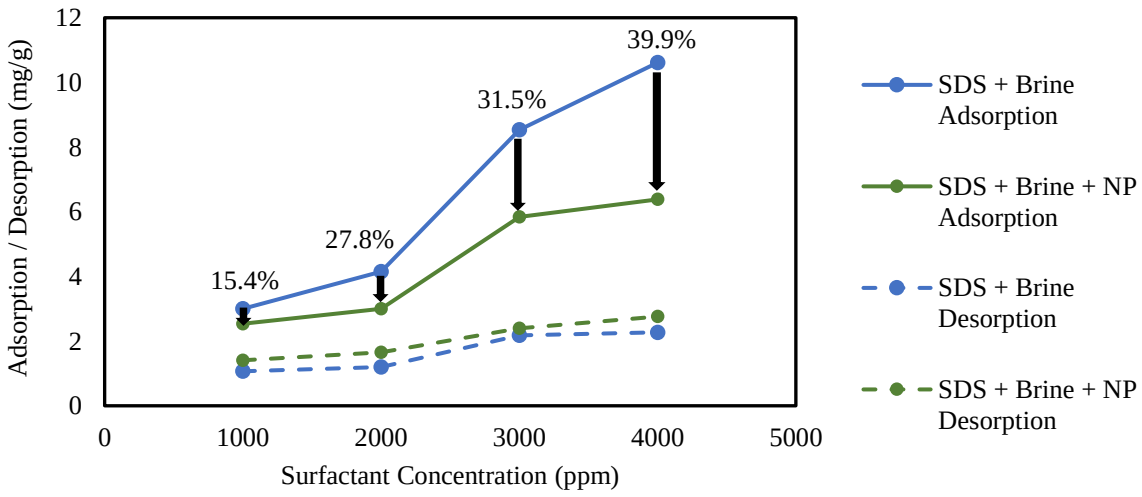


Figure 4. 23 Effect of nanoparticles on SDS adsorption-desorption behavior

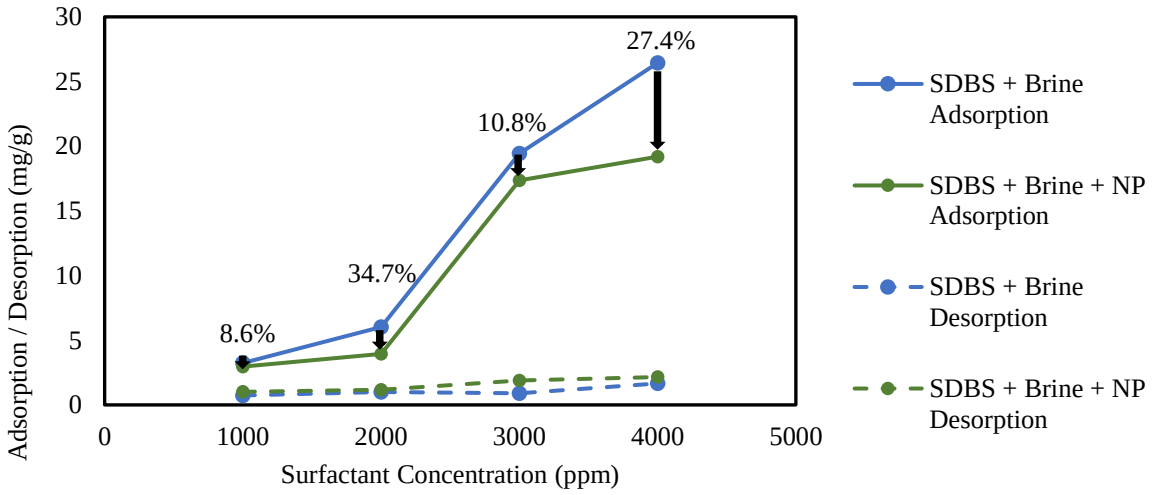


Figure 4. 24 Effect of nanoparticles on SDBS adsorption-desorption behavior

CHAPTER 5
Conclusions and Recommendation

This chapter summarizes all results presented in the Chapter 4. Also, the recommendation on the surfactant coupled with the nanoparticles are provided for further study.

5.1 Conclusions

1. Numerous comparisons confirm that SDBS yields the lower interfacial tensions out of the two surfactants used which are SDS and SDBS in this research. Regarding the surfactant concentration selection, the concentration of 2000 ppm (wt.) of both SDS and SDBS appears to be the suitable and effective concentration to perform the IFT reduction.
2. Based on the theory and the experimental results, the nanoparticles cannot effectively reduce the IFT when they are used solely. But the nanoparticles can help the surfactant achieve the low IFT when they are used together. The optimum concentration is 750 ppm (wt.) for the nanoparticles
3. An increase in the salinity within the low concentration can slightly reduce the IFT of oil-in-water emulsion interface.
4. Regarding the contact angle measurement, there are 3 main investigations gained from this research. Firstly, it is found out that an increase in temperature can reduce the contact angle to intermediate-wet to more water-wet. Secondly, both SDS and SDBS reduce the contact angle effectively and the increase in the surfactant concentration offers slight change in contact angle. Lastly, the nanoparticles reduce the contact angle significantly either it is used alone or used with the surfactants.
5. According to the overall experiments, the nanoparticles do not have significant effect on the viscosity and density of the surfactant solutions.
6. When the surfactant solutions are mixed with crude oil, it indeed reduces the oil viscosity which can be advantageous in sweep efficiency. However, being the fumed particles with small concentration, the nano silica solutions contribute less effect in terms of oil viscosity reduction.

7. From the observation of the surfactant adsorption measurement, the surfactant adsorption increases as the concentration increases which falls in line with the theory. Therefore, the nanoparticles are used to replace the adsorption surfactant. The effect of the nanoparticles is more apparent in SDS solutions. Moreover, the amount of surfactant desorption can be augmented with the help of nanoparticles.
8. Another issue from the adsorption measurement is that when the adsorptions of two surfactants are compared, SDBS is adsorbed at the higher amount while SDS is adsorbed with less amount for all concentrations.
9. After combining the proper conditions from all experiments, in terms of IFT reduction, SDBS can provide the lower IFT. On the other hand, having lower amount of adsorption than that of SDBS makes SDS a better candidate for the surfactant flooding.

5.2 Recommendations

Some recommendation is presented for the future study as follows:

1. The contact angle measurement would be more accurate if the core samples from the designated field could be used instead of the stainless-steel plate to consider the rock-fluid interaction in the wettability alteration process.
2. After doing the static adsorption using the rock sample from the northern Thailand oilfield, the dynamic adsorption can be performed using the core samples from the same field to observe the adsorption happened at the reservoir conditions.
3. The core flooding using the nano-surfactant solutions should be performed to observe the effectiveness of the nanoparticles in the oil recovery process.

REFERENCES

[1] Nikolova, C., & Gutierrez, T. (2020). Use of Microorganisms in the Recovery of Oil From Recalcitrant Oil Reservoirs: Current State of Knowledge, Technological Advances and Future Perspectives [Review]. *Frontiers in Microbiology*, *10*(2996). https://doi.org/10.3389/fmicb.2019.02996

[2] Gbadamosi, A. O., Junin, R., Manan, M. A., Agi, A., & Yusuff, A. S. (2019). An overview of chemical enhanced oil recovery: recent advances and prospects. *International Nano Letters*, *9*(3), 171-202.

[3] Latil, M. (1980). *Enhanced oil recovery*. Éditions Technip.

[4] Green, D. W., & Willhite, G. P. (1998). *Enhanced oil recovery* (Vol. 6). Henry L. Doherty Memorial Fund of AIME, Society of Petroleum Engineers ….

[5] Carcoana, A. (1992). Applied enhanced oil recovery.

[6] Suleimanov, B. A., Ismailov, F., & Veliyev, E. (2011). Nanofluid for enhanced oil recovery. *Journal of Petroleum science and Engineering*, *78*(2), 431-437.

[7] Aurand, K. R., Dahle, G. S., & Torsæter, O. (2014). Comparison of oil recovery for six nanofluids in Berea sandstone cores. the International Symposium of the Society of Core Analysts held in Avignon, France,

[8] de Castro Dantas, T. N., de Souza, T. T. C., Neto, A. A. D., de Alencar Moura, M. C. P., & de Barros Neto, E. L. (2017). Experimental study of nanofluids applied in EOR processes. *Journal of Surfactants and Detergents*, *20*(5), 1095-1104.

[9] Sheng, J. J. (2010). *Modern chemical enhanced oil recovery: theory and practice*. Gulf Professional Publishing.

[10] Ali, J. A., Kolo, K., Manshad, A. K., & Mohammadi, A. H. (2018). Recent advances in application of nanotechnology in chemical enhanced oil recovery: Effects of nanoparticles on wettability alteration, interfacial tension reduction, and flooding. *Egyptian journal of petroleum*, *27*(4), 1371-1383.

[11] Romero-Zerón, L. (2012). *Introduction to enhanced oil recovery (EOR) processes and bioremediation of oil-contaminated sites*. BoD–Books on Demand.

[12] Donaldson, E. C., Chilingarian, G. V., & Yen, T. F. (1989). *Enhanced oil recovery, II: Processes and operations*. Elsevier.

[13] Fayers, F. J. (1981). Enhanced oil recovery.

[14] Le, N. Y. T., Pham, D. K., Le, K. H., & Nguyen, P. T. (2011). Design and screening of synergistic blends of SiO2 nanoparticles and surfactants for enhanced oil recovery in high-temperature reservoirs. *Advances in Natural Sciences: Nanoscience and Nanotechnology*, *2*(3), 035013.

[15] Ahmadi, M. A., & Shadizadeh, S. R. (2017). Nano-surfactant flooding in carbonate reservoirs: A mechanistic study. *The European Physical Journal Plus*, *132*(6), 1-13.

[16] ShamsiJazeyi, H., Miller, C. A., Wong, M. S., Tour, J. M., & Verduzco, R. (2014). Polymer-coated nanoparticles for enhanced oil recovery. *Journal of Applied Polymer Science*, *131*(15).

[17] Kondiparty, K., Nikolov, A., Wu, S., & Wasan, D. (2011). Wetting and spreading of nanofluids on solid surfaces driven by the structural disjoining pressure: statics analysis and experiments. *Langmuir*, *27*(7), 3324-3335.

[18] Cayias, J., Schechter, R. S., & Wade, W. (1977). The utilization of petroleum sulfonates for producing low interfacial tensions between hydrocarbons and water. *Journal of Colloid and Interface Science*, *59*(1), 31-38.

[19] Olajire, A. A. (2014). Review of ASP EOR (alkaline surfactant polymer enhanced oil recovery) technology in the petroleum industry: Prospects and challenges. *Energy*, *77*, 963-982.

[20] Rosen, M. (1975). Relationship of structure to properties in surfactants. III. Adsorption at the solid-liquid interface from aqueous solution. *Journal of the American Oil Chemists Society*, *52*(11), 431-435.

[21] Holmberg, K., Lindman, B., & Kronberg, B. (2014). *Surface chemistry of surfactants and polymers*. John Wiley & Sons.

[22] Kamal, M. S., Hussein, I. A., & Sultan, A. S. (2017). Review on surfactant flooding: phase behavior, retention, IFT, and field applications. *Energy & fuels*, *31*(8), 7701-7720.

[23] Sofla, S. J. D., James, L. A., & Zhang, Y. (2018). Insight into the stability of hydrophilic silica nanoparticles in seawater for Enhanced oil recovery implications. *Fuel*, *216*, 559-571.

[24] Mahmoudi, S., Jafari, A., & Javadian, S. (2019). Temperature effect on performance of nanoparticle/surfactant flooding in enhanced heavy oil recovery. *Petroleum Science*, *16*(6), 1387-1402.

[25] Hendraningrat, L., Li, S., & Torsæter, O. (2013). Effect of some parameters influencing enhanced oil recovery process using silica nanoparticles: an experimental investigation. SPE Reservoir Characterization and Simulation Conference and Exhibition,

[26] Golabi, E., Azad, F. S., Ayatollahi, S. S., Hosseini, S. N., & Akhlaghi, N. (2012). Experimental study of wettability alteration of limestone rock from oil-wet to water-wet using various surfactants. SPE Heavy Oil Conference Canada,

[27] Hammood, H. A., Alhuraishawy, A. K., Hamied, R. S., & AL-Bazzaz, W. H. (2019). Enhanced Oil Recovery for Carbonate Oil Reservoir by using Nano-Surfactant: Part I. SPE Gas & Oil Technology Showcase and Conference,

[28] Alhuraishawy, A. K., Hamied, R. S., Hammood, H. A., & AL-Bazzaz, W. H. (2019). Enhanced Oil Recovery for Carbonate Oil Reservoir by Using Nano-Surfactant: Part II. SPE Gas & Oil Technology Showcase and Conference,

[29] Zargartalebi, M., Kharrat, R., & Barati, N. (2015). Enhancement of surfactant flooding performance by the use of silica nanoparticles. *Fuel*, *143*, 21-27.

[30] Somasundaran, P., & Hanna, H. S. (1985). Adsorption/desorption of sulfonates by reservoir rock minerals in solutions of varying sulfonate concentrations. *Society of Petroleum Engineers Journal*, *25*(03), 343-350.

[31] Wu, Y., Chen, W., Dai, C., Huang, Y., Li, H., Zhao, M., He, L., & Jiao, B. (2017). Reducing surfactant adsorption on rock by silica nanoparticles for enhanced oil recovery. *Journal of Petroleum science and Engineering*, *153*, 283-287.

[32] Paar, A. (2016). *DMA 4200 M from Anton Paar: The all-rounder density meter for petroleum samples.* . https://www.anton-paar.com/corp-en/products/details/density-meter-dmatm-4200-m/

[33] Chuaicham, C. (2016). *Interfacial tension reduction of light oil with sulfonate-structured surfactants for enhanced oil recovery application* Chulalongkorn University].

[34] Karnanda, W., Benzagouta, M., AlQuraishi, A., & Amro, M. (2013). Effect of temperature, pressure, salinity, and surfactant concentration on IFT for surfactant flooding optimization. *Arabian Journal of Geosciences*, *6*(9), 3535-3544.

[35] Ruckenstein, E., & Rao, I. (1987). Interfacial tension of oil—brine systems in the presence of surfactant and cosurfactant. *Journal of Colloid and Interface Science*, *117*(1), 104-119.

[36] Ivanova, A. A., Phan, C., Barifcani, A., Iglauer, S., & Cheremisin, A. N. (2020). Effect of nanoparticles on viscosity and interfacial tension of aqueous surfactant solutions at high salinity and high temperature. *Journal of Surfactants and Detergents*, *23*(2), 327-338.

[37] Ahmadi, M. A., & Shadizadeh, S. R. (2015). Experimental investigation of a natural surfactant adsorption on shale-sandstone reservoir rocks: Static and dynamic conditions. *Fuel*, *159*, 15-26.

[38] Somasundaran, P., & Zhang, L. (2006). Adsorption of surfactants on minerals for wettability control in improved oil recovery processes. *Journal of Petroleum science and Engineering*, *52*(1-4), 198-212.

[39] Tavakkoli, O., Kamyab, H., Shariati, M., Mohamed, A. M., & Junin, R. (2022). Effect of nanoparticles on the performance of polymer/surfactant flooding for enhanced oil recovery: A review. *Fuel*, *312*, 122867.

[40] Richardson, E. (1950). The formation and flow of emulsion. *Journal of colloid science*, *5*(4), 404-413.

[41] Juntarasakul, O. (2015). *Viscosity measurement and correlation for oil and its emulsion from Fang oilfield* Chulalongkorn University].

[42] Patel, H., Shah, S., Ahmed, R., & Ucan, S. (2018). Effects of nanoparticles and temperature on heavy oil viscosity. *Journal of Petroleum science and Engineering*, *167*, 819-828.

[43] Ngo, I., Srisuriyachai, F., Sasaki, K., Sugai, Y., & Nguele, R. (2019). Effects of reversibility on enhanced oil recovery using sodium dodecylbenzene sulfonate (SDBS). *Journal of the Japan Petroleum Institute*, *62*(4), 188-198.

[44] Saengnil, S. (2015). *Interfacial tension measurement on light oil from fang oilfield with alkaline solution* Chulalongkorn University].

APPENDIX A

Simulated Brine Preparation

The brine used in this study is obtained by mixing sodium chloride and sodium bicarbonate in the distilled water to make the property close to that of Fang oilfield. The salinity is prepared at 500, 750, and 1000 ppm. Simulated brine is prepared based on main components in the produced water which are sodium (26.7%), chloride (2.2%), carbonate (5.6%), and bicarbonate (62.5%). The composition of the produced water is described in the table below.

Table A. 1 Composition of the produced water (Saengnil, 2015)

Chemical ions	Concentration (ppm)
Sodium, Na	256
Calcicum, Ca	6.58
Magnesium, Mg	2.13
Barium, Ba	0.74
Chloride, Cl	21
Sulfate, SO_4	18.7
Carbonate, CO_3	54.0
Bicarbonate, HCO_3	598
Hydroxide, OH	0

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