NOVEL MICROEMULSION FORMATION BY THE HYDROPHILIC-LIPOPHILIC DEVIATION CONCEPT USING CARBOXYLATE EXTENDED SURFACTANTS FOR EOR APPLICATION

Suchawadee Kumkhuntod

A Thesis Submitted in Partial Fulfilment of the Requirements
for the Degree of Master of Science
The Petroleum and Petrochemical College, Chulalongkorn University
in Academic Partnership with
The University of Michigan, The University of Oklahoma,
Case Western Reserve University, and Institut Français du Pétrole
2018

Thesis Title: Novel Microemulsion Formation by the Hydrophilic-Lipophilic Deviation Concept Using Carboxylate Extended Surfactants for EOR Application

By: Suchawadee Kumkhuntod

Program: Petrochemical Technology

Thesis Advisors: Dr. Ampira Charoensaeng
Prof. Bor-Jier Shiau
Asst. Prof. Uthaiporn Suriyapraphadilok

Accepted by The Petroleum and Petrochemical College, Chulalongkorn University, in partial fulfilment of the requirements for the Degree of Master of Science.

.... College Dean
(Prof. Suwabun Chirachanchai)

Thesis Committee:

....	....
(Dr. Ampira Charoensaeng)	(Prof. Bor-Jier Shiau)
....	....
(Asst. Prof. Uthaiporn Suriyapraphadilok)	(Prof. Boonyarach Kitiyanan)

....
(Dr. Sirinthip Kittisrisawai)

ABSTRACT

6071012063: Petrochemical Technology Program
Suchawadee Kumkhuntod: Novel Microemulsion Formation by the Hydrophilic-Lipophilic Deviation Concept Using Carboxylate Extended Surfactants for EOR Application
Thesis Advisors: Dr. Ampira Charoensaeng, Prof. Bor-Jier Shiau, and Asst. Prof. Uthaiporn Suriyapraphadilok 81 pp.

Keywords: Microemulsion / Carboxylate based extended surfactant / Binary surfactant system / Enhanced oil recovery / Hydrophilic- Lipophilic Deviation method / IFT measurement /

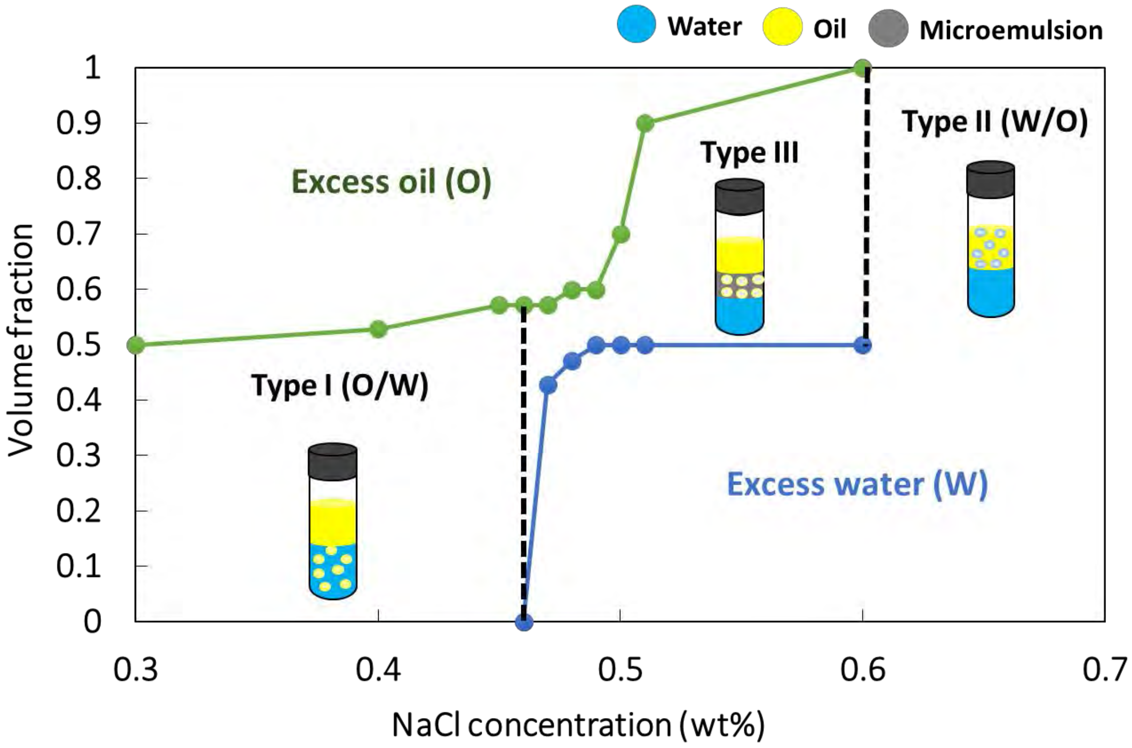
The Winsor type III (middle phase) microemulsion formation is widely used for enhanced oil recovery (EOR) application. A novel carboxylate surfactant has been an attractive surfactant for the oil recovery due to high chemical stability in harsh reservoir conditions (i.e., high brine concentration and high temperature). This study aims to formulate the middle phase microemulsion in order to obtain the minimum IFT and high solubilization capacity with binary anionic surfactant system using sodium dioctyl sulfosuccinate (AOT) and carboxylate extended surfactants with varying the polyethylene oxide number (EO = 2, 4 and 6) at three mixing molar ratios of 5:5, 7:3 and 9:1 in heptane, octane, decane, dodecane and hexadecane. The results showed that the decrease in the carboxylate extended surfactant fraction in the mixture significantly decreased the optimal salinity (S*). The S* increased with the increasing number of EO groups. The Hydrophilic-Lipophilic Deviation (HLD) equation was used to estimate the optimal condition, where the determined K and Cc values of the carboxylate extended surfactant were conducted and compared. In addition, the batch adsorption of the carboxylate extended surfactant onto quartz sand surface showed less adsorption capacity compared with other surfactants. The increasing of EO groups decreased the surfactant adsorption. Therefore, the carboxylate based extended surfactants could be an appropriate system for preventing the surfactant losses by the adsorption and economic viability of surfactant flooding in EOR application.

บทคัดย่อ

สุชาวดี คุมขุนทด : การผลิตไมโครอิมัลชันด้วยสารลดแรงตึงผิวชนิดคาร์บอกซิเลทที่มีส่วนขยายโดยใช้แนวคิดเฮชแอลดีสำหรับการผลิตน้ำมันขั้นตติยภูมิ (Novel Microemulsion Formation by the Hydrophilic-Lipophilic Deviation Concept Using Carboxylate Extended Surfactants for EOR Application) อ. ที่ปรึกษา : ดร. อัมพิรา เจริญแสง, ศ.ดร.บอร์ เจียร์ เชาว์ และ ผศ. ดร. อุทัยพร สุริยาประภาดิลก 81 หน้า

การสร้างไมโครอิมัลชันวินเซอร์ชนิดที่ 3 หรือวัฏภาคไมโครอิมัลชันแบบกึ่งกลางได้รับความนิยมนำมาใช้ในกระบวนการผลิตน้ำมันขันตติยภูมิ (enhanced oil recovery, EOR) สารลดแรงตึงผิวคาร์บอกซิเลทได้มีการนำมาประยุกต์ใช้ในการผลิตน้ำมันเพราะมีเสถียรภาพทางเคมีสูงในสภาวะความเข้มข้นเกลือและอุณหภูมิสูง งานวิจัยนี้มีวัตถุประสงค์เพื่อสร้างวัฏภาคไมโครอิมัลชันแบบกึ่งกลางเพื่อให้ได้ค่าแรงตึงผิวระหว่างน้ำและน้ำมันต่ำ (Minimum interfacial tension, IFT) และค่าการละลายสูงด้วยระบบสารลดแรงตึงผิวชนิดประจุลบผสมกันสองชนิดระหว่างโซเดียมไดออกทิวซัลโฟซักซิเนต (Sodium dioctyl sulfosuccinate, AOT) กับ สารลดแรงตึงผิวคาร์บอกซิเลทที่มีส่วนขยายด้วยจำนวนกลุ่มโพลีเอธิลีนออกไซด์ต่างกัน (EO = 2, 4, 6) ในอัตราส่วน 5: 5 7:3 และ 9:1 (อัตราส่วนโดยโมลาร์) ในเฮปเทน ออกเทน เดคเคน โดเดคเคน และ เฮกซะเดคเคน ผลการศึกษาพบว่าเมื่อลดอัตราส่วนของสารลดแรงตึงผิวคาร์บอกซิเลทที่มีส่วนขยายในระบบสารลดแรงตึงผิวแบบผสม ค่าเกลือที่เหมาะสม (Optimal salinity, S*) จะลดลงอย่างมีนัยสำคัญ จำนวนกลุ่มของโพลีเอธิลีนออกไซด์เพิ่มขึ้นส่งผลให้ค่าเกลือที่เหมาะสมเพิ่มขึ้น แนวคิดค่าเบี่ยงเบนในการชอบน้ำและน้ำมัน (Hydrophilic-Lipophilic Deviation, HLD) ได้นำมาประยุกต์ใช้คำนวณหาและเปรียบเทียบสภาวะที่เหมาะสม ค่าตัวแปร K และ Cc ของสารลดแรงตึงผิวคาร์บอกซิเลทที่มีส่วนขยาย นอกจากนี้สารลดแรงตึงผิวคาร์บอกซิเลทที่มีส่วนขยายมีความสามารถในการดูดซับบนพื้นผิวทรายควอตซ์ (Quartz sand) น้อยกว่าเมื่อเปรียบเทียบกับสารลดแรงตึงผิวชนิดอื่น การเพิ่มจำนวนกลุ่มโพลีเอธิลีนออกไซด์ช่วยลดความสามารถการดูดซับของสารลดแรงตึงผิวได้ ดังนั้นสารลดแรงตึงผิวคาร์บอกซิเลทที่มีส่วนขยายจึงเป็นระบบที่เหมาะสมสำหรับการป้องกันการสูญหายของสารลดแรงตึงผิวอันเนื่องมาจากการดูดซับและการพิจารณาศักยภาพทางเศรษฐกิจในการผลิตน้ำมันขั้นตติยภูมิ

GRAPHICAL ABSTRACT



Phase volume fraction of AOT:$C_{13}(EO)_2COO^-$ mixed surfactant with octane at 0.015 M total surfactant concentration under room temperature (25±2 °C)

ACKNOWLEDGEMENT

The author is Suchawadee Kumkhuntod grateful for the full scholarship and full funding of the thesis work provided by the Petroleum and Petrochemical College. I would like to express my sincerest gratitude to the advisors, Dr. Ampira Charoensaeng, Prof. Bor-Jier Shiau and Asst. Prof. Uthaiporn Suriyapraphadilok for their guidance, encouragement and the support provided throughout this research. In addition, I would like to thank my committee, Prof. Boonyarach Kitiyanan and Dr. Sirinthip Kittisrisawai for their guidance and support on this project. I also would like to thank the officers and my friends at the Petroleum and Petrochemical College for help and warmth toward me throughout. Finally, I would like to express my appreciation to my family for providing their love, encouragement and support.

TABLE OF CONTENTS

CHAPTER **PAGE**

CHAPTER **PAGE**

CHAPTER **PAGE**

LIST OF TABLES

TABLE **PAGE**

LIST OF FIGURES

FIGURE **PAGE**

FIGURE **PAGE**

FIGURE **PAGE**

CHAPTER I

INTRODUCTION

Crude oil is one of the most important energy sources which contributes to a variety of products such as diesel, gasoline and valuable intermediate and downstream petrochemical products. The demand for crude oil is continuously increasing because of industrial and population growth. It is typically recovered by drilling; the primary and secondary recovery stage can recover oil by 10-40 percent of original oil in place (OOIP) while the tertiary recovery stage or enhanced oil recovery (EOR) can recover oil by 30-60 percent of OOIP. The EOR is classified into three methods, thermal recovery, gas injection and chemical injection. Among them, the most common method of chemical injection is surfactant flooding by which can recovery oil through increasing mobility ratio and solubilization.

Microemulsions are a transparent thermodynamically stable dispersion that consists of oil (non-polar), water (polar) and surfactants. They can reduce the interfacial tension (IFT) between oil and water, which leads to an improvement of the oil recovery. Among, the microemulsion's type, a middle phase microemulsion has been applied in EOR process because it shows maximum oil solubilization and minimum interfacial tension. Notwithstanding, the formation of the microemulsion is not only consuming time to experiment but also the cost for chemical usages. Hydrophilic-lipophilic deviation (HLD) method has been developed to counteract these problems. HLD is an empirical correlation of thermodynamically derived equation to explain the microemulsion behavior. The main advantages of HLD concept are including important parameters that represent the oil polarity, hydrophobicity, temperature and co-surfactant.

Most of the reservoirs are in harsh conditions; high brine concentration and high temperature. Anionic surfactants, therefore, are typically preferred in sandstone reservoir because they had a low tendency to adsorb on the surface. However, monovalent and divalent cations (e.g., Ca^{2+}, Mg^{2+}) dissolved in the reservoir especially under brine concentration leading to surfactant precipitation. Even more, most of the surfactants also degraded at high temperature. Both problems can be solved using carboxylate surfactants. Carboxylate surfactants showed stability at high brine concentration and high temperature. Recently, the new class of surfactants, called extended surfactants has been used in various applications. Due to the fact that they exhibit high solubilization and ultralow interfacial tension. The extended surfactants have an intermediate group between the hydrophilic head and hydrophobic tail such as polyethylene oxide (EO) and polypropylene oxide (PO) group.

In this study, carboxylate based extended surfactants with different polyethylene oxide numbers (EO = 2, 4, 6) are selected to formulate middle phase microemulsion. The microemulsion phase scan and interfacial tension measurement are conducted to determine the optimum condition. The surfactant characteristics in terms of Cc and K values are calculated in order to develop the HLD equation for determining the optimum condition of the carboxylate extended surfactants. In addition, the surfactant adsorption of the carboxylate extended surfactant onto quartz sand surface is investigated to observe their potential use for the oil recovery application.

CHAPTER II
THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Enhanced Oil Recovery (EOR)

Crude oil production is typically classified into three stages comprising of primary, secondary, and tertiary recovery stage, known as Enhanced Oil Recovery (EOR). In the primary stage, oil production arises from natural reservoir force and can recover crude oil only 10 percent of original oil in place (OOIP). For the second stage, water and gas injections are used to displace oil which can recover crude oil about 25-40 percent OOIP. Although all the oils are removed by water flooding, some of the oil have left in the reservoir because of high interfacial tension (IFT) between two phases. These problems can be solved by the tertiary stage or enhanced oil recovery (EOR). EOR process is proposed to recover crude oil about 30-60 percent of OOIP (Satter *et al.*, 2008). There are three main categories of EOR technology as following;

1. Thermal recovery method, the injection of heat such as steam for reducing the viscosity of crude oil and enhancing mobility. For increasing the mobility of the oil, it will affect an increase in oil production rate.

2. Gas injection method, the injection of gases such as natural gas, nitrogen (N_2), carbon dioxide (CO_2) or other gases to expand in the reservoir and to push gases through reservoir for decreasing viscosity of crude oil.

3. Chemical injection method, the injection of chemicals such as polymers, alkalines, and surfactants into the reservoir to increase the efficiency of water flooding. Chemicals are used to reduce the surface tension of crude oil and enhanced oil production rate.

Surfactant flooding is the most common method in chemical injection. In EOR process, surfactants can be injected either single or mixed surfactants which depend on reservoirs. Anionic surfactants are applied in sandstone reservoirs because they show low adsorption on the solid surface. In contrast, cationic surfactants are typically used in the carbonate reservoir conditions.

Most of the reservoirs are in harsh conditions; high brine concentration and high temperature. Monovalent and divalent cations are dissolved in the reservoir especially under brine concentration, which can affect to the precipitation of surfactant solubility products. Moreover, the temperature in the reservoirs would be above 65°C which affects to the chemical stability of surfactants. Therefore, the formulation of appropriate surfactant systems in brine and/or high-temperature condition has been rising in attention.

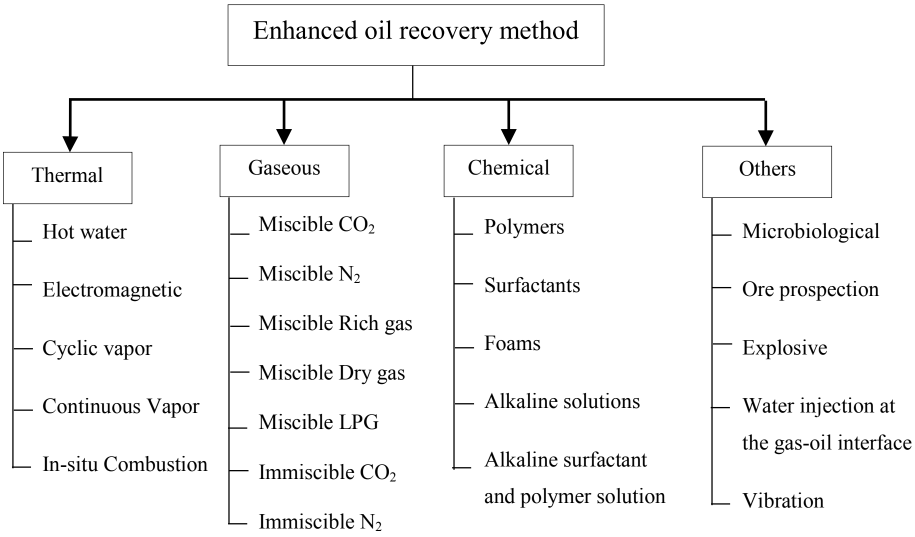


Figure 2.1 Categories of enhanced oil recovery method (Gurgel *et al.*, 2008).

2.2 Surfactants

2.2.1 Definition Structure and Types

Surfactants (surface active agent) are commonly used in a cleaning process. They can reduce the surface tension and interfacial due to adsorbing at the surfaces (water-air) and interfaces (water-oil), respectively.

The molecular structure of surfactants is an amphiphile molecule of which is composed of two main parts; a hydrophilic part and a hydrophobic part as shown in Figure 2.2. For the hydrophilic part or polar (water-loving), it locates at the head group. For the hydrophobic part or non-polar (oil-loving), it locates at the tail group (Olajire, 2014).

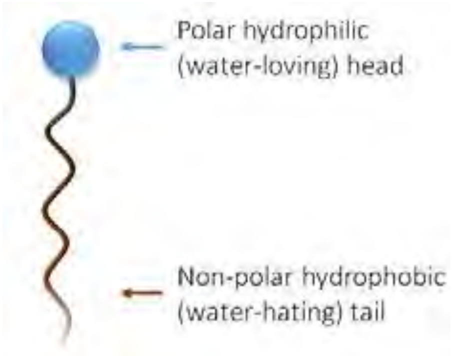


Figure 2.2 Surfactant structure (Bristol, 2017).

The formulation of microemulsion systems must be considered above the critical micelle concentration (CMC) which is defined as a minimum surfactant concentration to form micelle or micellization (Olajire, 2014). Surfactants can be classified into four types which depend on the nature of the head group as following;

2.2.1.1 Anionic Surfactants

Anionic surfactants have a negative charge as surfactant head group. These surfactants tend to adsorb onto a positive charge surface (e.g., sandstone surface). There are many polar head groups of the anionic surfactant such as carboxylate (COO^-), sulfate (SO_4^-) and sulfonate (SO^-_3) (Negin *et al.*, 2017).

2.2.1.2 Cationic Surfactants

Cationic surfactants have a hydrophilic part as a positive charge. Most of the cationic surfactants have good stability in a wide range of pH. They are more expensive than others because of the high-pressure hydrogenation reaction to be carried out during their synthesis. Typically, cationic surfactants are used as fabric softeners, antistatic agents, biocides, etc.

2.2.1.3 Nonionic Surfactants

Nonionic surfactants have no significant electric charge in the hydrophilic part. There are many head groups of nonionic surfactants such as alcohol, phenol, ether, ester, amine amide, ethoxylate, polypropylene glycol, polyether, etc. Nonionic surfactants are mostly used as a detergent and wetting agent because they have suitable dispersant and soluble ability in both water and organic solvents. Moreover, these surfactants are stable in the presence of salt but sensitive with temperature.

2.2.1.4 Zwitterionic Surfactants

Zwitterionic surfactants have both negative and positive charge in the head part. These surfactants are very sensitive to pH, can be ionic at high pH or cationic at low pH or nonionic in solution depending on the acidity.

In EOR process, surfactant flooding is carried out in the sandstone reservoirs. Anionic surfactants have been used in EOR technology since they have low adsorption in sandstone reservoirs. Moreover, they are inexpensive when compared to others.

2.2.2 Surfactant Properties

2.2.2.1 Solubilization

The solubilization is defined as an increase in equilibrium between oil and water (Salager *et al.*, 2005). The surfactants are commonly used to enhance the solubilization in the microemulsion. To characterize the microemulsion behavior, the solubilization parameter (SP) is the amount of solubilized phase per amount of surfactants. Typically, the solubilization can be determined by two methods. The first method can be determined using SP. Another way is a titration method. The clear surfactant solution was titrated until it turned to be a turbid solution. At this point, the solubilization of the microemulsion was observed (Bera *et al.*, 2014).

An increase in the interaction between surfactant and oil can be achieved by lipophilic linkers or extended surfactant molecules (Uchiyama *et al.*, 2000). In addition, the maximum solubilization of the microemulsion is found in the middle phase microemulsion or Winsor type III microemulsion (Sheng, 2015).

2.2.2.2 Interfacial Tension (IFT)

Interfacial tension is an attractive force between two liquids at the interface. The unit of IFT value is defined as free energy per unit surface area (i.e., dynes/cm or mN/m.). The IFT experiments are measured using a spinning drop tensiometer. The IFT value depends on pressure, temperature and composition of the phases. Surfactants adsorbed at the interface between two different fluids can reduce the interfacial tension and lead to an increase in the amount of oil recovery (Udeagbara, 2009).

2.2.2.3 Critical Micelle Concentration (CMC)

The critical micelle concentration (CMC) is the minimum surfactant concentration which formed a micelle. The CMC is determined using plotting between surface tension and surfactant concentration. At dilute surfactant concentration, surfactant molecules are individually dispersed in the solution that can reduce the surface tension. An increasing the surfactant concentration causes the surfactant molecules tend to adsorb at the surface until they are full. The surface tension can't be reduced further above this point (Yue *et al.*, 2017). The CMC is an important characteristic of the surfactant system because it is used as the minimum concentration of surfactants for microemulsion formulation. (Rosen *et al.,* 2000).

2.3 Surfactant Mechanism in EOR

There are two main functions of surfactants in oil recovery (Sheng, 2015);

2.3.1 Interfacial Tension Reduction

The oil sweep efficiency is improved by an injection of surfactants that can reduce residual saturation, increases permeability and decreases interfacial tension (Lv *et al.*, 2011).

2.3.2 Wettability Alteration

Wettability alteration is the process of changing the reservoir property from oil-wet to water-wet (Mohammed *et al.*, 2015). The thermal and chemical process have been used for wettability alteration.

2.4 Surfactant Applications in EOR

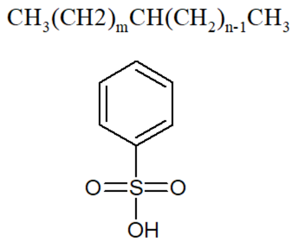
The surfactants have been used in different reservoirs that depending on the reservoir conditions and specific properties of surfactants.

2.4.1 Anionic Surfactants

In EOR process, most of the reservoirs are sandstone reservoirs. Anionic surfactants are applied in sandstone reservoirs since they have low adsorption on the solid surfaces. Moreover, they are inexpensive when compared to others (Sheng, 2015).

2.4.1.1 Alkyl Aryl Sulfonate

The structure of alkyl aryl sulfonate is shown as Figure 2.3. It showed high chemical stability with various types of crude oil at high temperature. However, it was ineffective in high salinity under the reservoir conditions. This problem can be solved using a co-surfactant (e.g., polyethoxylated alcohol, alkylpolyethoxylated sulfate (Shupe *et al.*, 1978).



$CH_3(CH2)_mCH(CH_2)_{n-1}CH_3$

Figure 2.3 Alkyl aryl sulfonate structure (Negin *et al.*, 2017).

2.4.1.2 Sodium Dodecyl Sulfate (SDS)

The structure of SDS is shown in Figure 2.4. According to the high temperature in the reservoirs, the chemical stability of surfactants can be enhanced using a combination with SDS (Shupe *et al.*, 1978). In addition, the mixed system between SDS below its CMC and nanoparticles exhibited the low IFT reduction in EOR process (Esmaeilzadeh *et al.*, 2014).

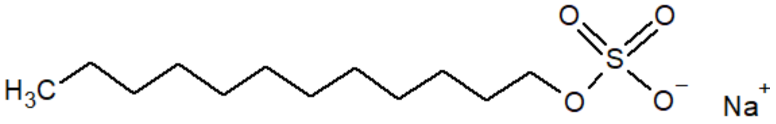


Figure 2.4 Sodium dodecyl surface structure (Negin *et al.*, 2017).

2.4.1.3 Alkyl Ethoxy Sulfate (AES)

AES structure is shown in Figure 2.5. Adkins and coworkers (2010) studied the effects of AES structure on chemical stability under high temperature and high salinity for long periods. They found that AES is stable at high temperatures up to 85 °C and high salinity. This reason provided the AES to become an attractive surfactant for EOR technology.

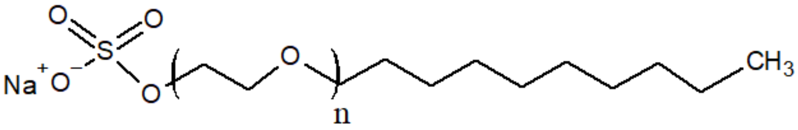
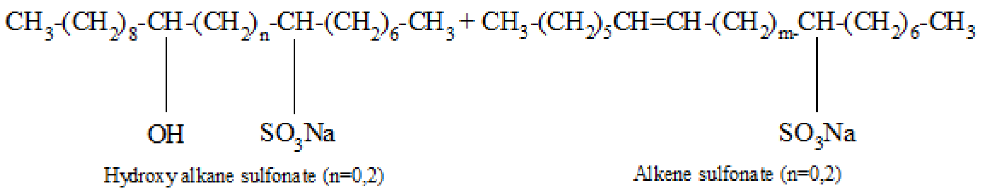


Figure 2.5 Alkyl ethoxy sulfate structure (Negin *et al.*, 2017).

2.4.1.4 Internal Olefin Sulfonate (IOS)

The IOS surfactants have a hydrocarbon chain length from C_{15-18} to C_{24-28} with twin tails that are shown as Figure 2.6. They have been used in chemical flooding under high temperature condition because they showed their chemical stability at the high-temperature up to 150 °C (Barnes *et al.*, 2008). However, these surfactants are limited to high salinity (Negin *et al.*, 2017).



$CH_3\text{-}(CH_2)_8\text{-}CH(OH)\text{-}(CH_2)_n\text{-}CH(SO_3Na)\text{-}(CH_2)_6\text{-}CH_3 + CH_3\text{-}(CH_2)_5CH{=}CH\text{-}(CH_2)_m\text{-}CH(SO_3Na)\text{-}(CH_2)_6\text{-}CH_3$

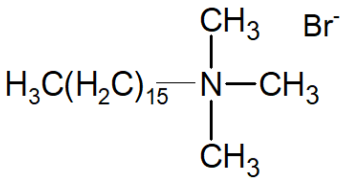
Figure 2.6 Internal olefin sulfonate structure (Negin *et al.*, 2017).

2.4.2 Cationic Surfactants

The cationic surfactants have a positive charge in the head part of surfactants. They are preferred in carbonate reservoirs because they have low adsorption on the positive surface. For example, cationic surfactants are applied in EOR application as following;

2.4.2.1 Cetyl Trimethyl Ammonium Bromide (CTAB)

The structure of CTAB is shown in Figure 2.7. This surfactant prefers in a carbonate reservoir because it has low adsorption on positive surfaces. Moreover, CTAB also showed a good partner with nano-silica particles in EOR technology. The increasing the temperature caused to an increase IFT (Vatanparast *et al.*, 2011).



$H_3C(H_2C)_{15}\text{-}N(CH_3)_3\ Br^-$

Figure 2.7 Cetyl trimethyl ammonium bromide (CTAB) structure (Negin *et al.*, 2017).

2.4.2.2 Dodecyl Trimethyl Ammonium Bromide (DTAB)

The structure of DTAB is shown in Figure 2.8. DTAB has shown excellent performance with high chemical stability at high temperature and high brine in the carbonate reservoirs. Moreover, the mixing between cationic and nonionic surfactants showed an increase in the chemical stability and performed oil recovery about 70-80 % of OOIP (Sharma *et al.*, 2013).

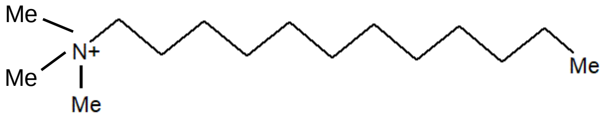


Figure 2.8 Dodecyl trimethyl ammonium bromide (DTAB) structure (Negin *et al.*, 2017).

2.4.3 Nonionic Surfactants

2.4.3.1 Alkyl Polyglycoside (APG)

The structure of APG is composed of alcohol and glycoside as shown in Figure 2.9. The microemulsion formulation of APG with a co-surfactant was investigated under harsh condition (Santa *et al.*, 2011). They found that APG with a co-surfactant showed a stable microemulsion at high temperature (80°C) and high salinity (18,000 ppm). In addition, APG also exhibited the low IFT for crude oil and water systems even in the harsh condition.

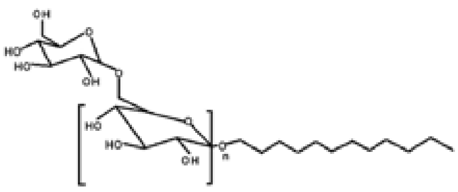


Figure 2.9 Alkyl polyglycoside (APG) structure (Negin *et al.*, 2017).

2.4.3.2 Polyethoxylated Alkyl phenols

The structure of polyethoxylated alkyl phenols is shown in Figure 2.10. Shupe and coworkers (1978) studied the use of nonionic surfactants for chemical flooding. They found that these surfactants displayed an effective surfactant for EOR process under high temperature and high salinity.

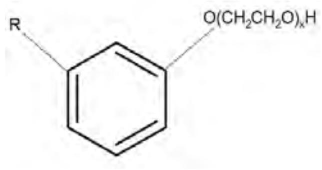


Figure 2.10 Polyethoxylated alkyl phenols structure (Negin *et al.*, 2017).

2.4.4 Zwitterionic Surfactants

Zhang *et al.* (2015) studied the use of zwitterionic surfactant derived from a castor oil, for EOR application. They found that it provided the excellent performance in lowering surface properties with a low surfactant concentration. Also, it exhibited strong chemical stability at high brine concentration and high temperature.

The advantages and dominant characteristics of each surfactant in EOR are concluded as shown in Table 2.1.

Table 2.1 The advantages and dominant characteristics of surfactants in EOR technology (Negin *et al.*, 2017)

Type of surfactants	Advantages	Dominant mechanism
Cationic	- Stability in brine condition - Cationic surfactants are preferred in carbonate reservoirs.	- IFT reduction - Wettability alteration
Anionic	- Anionic surfactants are preferred in sandstone reservoirs.	- Reducing IFT - Inexpensive cost
Nonionic	- Effective surfactant flooding in formations containing high salinity water or hard water	- IFT reduction - High solubilization

Table 2.1 The advantages and dominant characteristics of surfactants in EOR technology (Negin et al., 2017) (Continued)

Type of surfactants	**Advantages**	**Dominant mechanism**
Zwitterionic	- The new generation of surfactants has strong electrolyte tolerance, temperature resistance and thermal stability. - Better wetting and foaming performance.	- IFT reduction - Wettability alteration

2.5 Extended Surfactant

The extended surfactants are a novel surfactant class that has an intermediate group between the hydrophilic head and hydrophobic tail. The intermediate polarity groups are, such as polypropylene oxide (PO) and polyethylene oxide (EO) chains, inserting between the head and tail of the surfactant. The introduction of PO groups in the hydrophobic tail helps to extend the tail's interaction further into the oil phase. In contrast, the addition of EO groups can enhance surfactant's interaction in the water phase. The presence of the intermediate groups is expected to improve the interfacial performance of the surfactants by generating an ultralow IFT ($<10^{-2}$ mN/m) (He *et al.*, 2014). Moreover, the extended surfactants can reduce an optimal salinity for microemulsion formulation (Witthayapanyanon *et al.*, 2006).

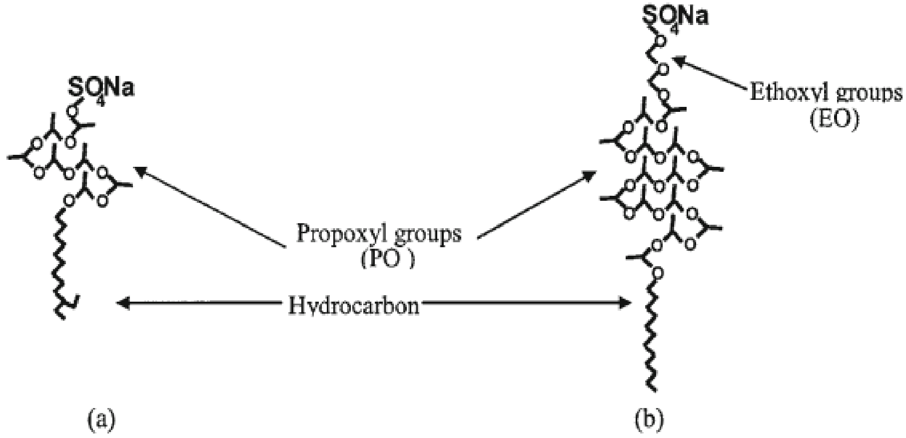


Figure 2.11 Structure of extended surfactants: (a) alkyl-PO sulfate C_{14-15}-$(PO)_8$-SO_4Na, (b) alkyl-PO-EO sulfate C_{12}-$(PO)_{14}$-$(EO)_2$-SO_4Na (Witthayapanyanon *et al.*, 2006).

Perez *et al.* (1995) studied the effect of the number of propylene oxide group (PO) on CMC value and cloud point temperature. The extended surfactants, so-called Alkyl polypropylene oxide ether sulfate, were used with the different number of polypropylene oxide (PO = 6, 4 and 10). The phase behavior and phase volume fraction were observed for determining the solubilization parameters. The results showed that increasing the number of PO group causes to decrease in both CMC value and cloud point temperature due to the decrease in hydrophilicity.

Witthayapanyanon *et al.* (2006) investigated the effect of the surfactant structure with the different number of polypropylene oxide (PO) and polyethylene oxide (EO) on the parameters affecting microemulsion formation with triglyceride oils. Sodium alkyl polypropylene oxide sulfate (R-$(PO)_x$-SO_4Na) and sodium alkyl polypropylene oxide-polyethylene oxide sulfate (R-$(PO)_y$-$(EO)_z$-SO_4Na) were used in this research. They found that the extended surfactants had lower CMC and critical microemulsion concentration (CμC) when compared to other systems. The results also showed that the increase in the number of PO and EO in the extended surfactant affected to the decrease of CMC, CμC, IFT, and optimal salinity.

Phan *et al.* (2011) studied the effect of surfactant structure on microemulsion formation and IFT with triglyceride oils. Sodium alkyl polypropylene oxide sulfate surfactants were used in this work. The phase behavior was studied by varying NaCl concentrations. The results showed that an increasing the numbers of PO group cause a decrease in the optimum salinity and minimum IFT. The surfactants with PO≥4 and PO≥8 reached to ultralow IFT with tricaprylin and canola oil, respectively. Moreover, the 8-PO extended surfactants were observed for microemulsions Winsor type I to III to II with both tricaprylin and canola oil.

He *et al.* (2014) synthesized alkylaryl sulfate extended surfactant with phenyl and polypropylene oxide (PPO) groups. The comparison performance of extended surfactant on the CMC, efficiency of surface tension and electrolyte resistance with phenyl-free counterpart was investigated. Increasing the number of polypropylene oxides decreased the CMC values due to more lipophilic property. Moreover, the addition of the electrolyte decreased the CMC values for all surfactant systems because of the reduction of repulsive force between surfactant head groups. The electrolyte resistance can be enhanced by adding the phenyl groups. The intermediate molecule (PPO and phenyl group) reduced the surface tension and enhanced the surfactant adsorption at the interface between air and water phase.

Liu *et al.* (2016) studied the effects of propylene oxide (PO) group, electrolyte concentration, and surfactant concentration on the surface tension, interfacial tension (IFT) and emulsification using sodium dodecyl polypropylene oxide sulfate and sodium dodecyl polypropylene oxide-polyethylene oxide sulfate ($C_{12}P_8E_2S$) as a surfactant. They found that increasing the numbers of the PO group decreased the CMC, optimal salinity and IFT. This is because the PO groups increased the hydrophobicity of the surfactant system that causes an increase in the surface area occupied and a decrease in the surface charge density of the micelle. Moreover, the presence of $CaCl_2$ resulted in the compression of electrical double layer at the head group and thus decrease in the electrostatic repulsive force. This surfactant orientation at the interface affects to the decreasing in the IFT value to the ultralow interfacial tension at the optimum salinity.

2.6 Carboxylate Surfactants

In this research study, the carboxylate based extended surfactants are used to formulate the middle phase microemulsions with achieving the low IFT value and high oil solubilization. The chemical structure of the carboxylate extended surfactants used is composed of the hydrophobic alkyl chain, hydrophilic polyoxyethylene part and carboxylic termination as shown in Figure 2.12. The carboxylic termination can be enhanced by sodium or potassium salts which make them be anionic surfactants (Rapp, 2017). These surfactants not only shows excellent performance and stability at high temperature and salinity but also high oil recovery in both carbonate and sandstone reservoirs (Jurgenson *et al.*, 2015).

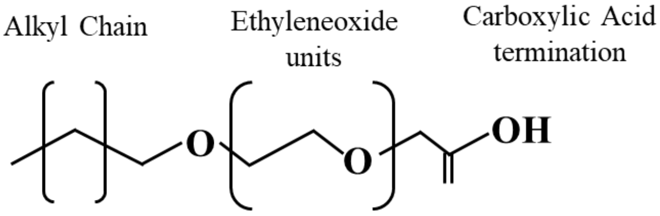


Figure 2.12 Carboxylate-base extended surfactant structure (Chiappisi, 2017).

The significant affecting parameters for the use of the carboxylate based extended surfactants for EOR application have been investigated in several published studies elsewhere are including a pH-sensitive, temperature responsive, number of EO group and alkyl chain length, the details are as following;

Hussain *et al.* (1997) investigated the effect of pH and number of the ethylene oxide groups (EO) on the microemulsion phase behavior. The alkyl ether carboxylic acid surfactants ($C_{15}H_{31}$-O-$(CH_2CH_2O)_n$-COOH) with n= 2.5, 4 and 7 were titrated using NaOH. They found that the increasing pH of the solution can cause an increase in the hydrophilic part and the micelle size. Moreover, the increasing of EO groups resulted in an increase in the hydrophilicity of surfactants, thus an increase in the IFT.

Attaphong *et al.* (2012) investigated the phase behavior of the Winsor Type II microemulsion using carboxylate-based extended surfactant for an alternative renewable biofuel. Four anionic carboxylate-based extended surfactants were used. These surfactants have different structures (branched and liner structure) and different ethylene oxide (EO) groups. The results showed that the decreasing EO groups lead to a reduction of 3 to 4% surfactant concentration to attain single phase microemulsion. Moreover, carboxylate based extended surfactants could conduct reverse micelle without adding salt.

Jurgenson *et al.* (2015) characterized the interfacial properties and phase behavior of the novel alkyl ether carboxylate surfactant under the harsh reservoir conditions. All samples were kept at 80°C and 120°C for the investigation of thermal stability by HPLC. The results showed that no loss of the material in any sample, i.e. no loss in the concentration of surfactants for the controlled period. In addition, the qualities of the material are the same as the original sample. Therefore, the carboxylate surfactant is an attractive option for EOR, as it showed high chemical stability under harsh conditions (high temperature and high salinity).

Chiappisi (2017) studied the physical and chemical properties of polyoxyethylene alkyl carboxylic acid (AEC). The $C_{12}E_{10}CH_2COOH$, $C_{18}E_9CH_2COOH$ and $C_{12}E_{4.5}CH_2COOH$ were investigated in terms of alkyl chain lengths and number of EO groups as a function of pH, ionic strength and temperature. The properties of AEC showed the characteristics of both ionic and nonionic surfactants. In terms of the ionic counterpart, they exhibited the pH-dependent and they can be enhanced using a strong base solution. They also showed a clear solution in alkaline solution because of an increased charge of the head group. Moreover, the addition of electrolyte to the ionic surfactant solution resulted in a reduce the electrostatic force especially repulsion force between surfactant head groups. AEC also exhibited as nonionic surfactant property by varying the temperature. Its cloud point temperature also depended on the variation of pH vice versa it is not sensitive to temperature in the alkaline solution.

2.7 Microemulsions

Microemulsions are used in various industrial applications such as cleaning and detergent application, enhancing oil recovery, liquid-liquid extraction, pharmaceutical and cosmetic formulation (Burguera *et al.*, 2012). The design of the formulation in these applications depends on specific properties and microemulsion phase behavior.

Microemulsions are a thermodynamically stable dispersion of transparent liquid mixture that can be formed by colloidal droplets with diameters ranging of 10 – 100 nm. They consist of non-polar (oil) phase, polar (water) phase and stabilized by a surfactant(s). Microemulsions can form with additive substances such as a co-surfactant, fatty acid, lipophilic and hydrophilic linkers for enhancing specific properties of the applications (Quintero *et al.*, 2013). Typically, the micelle structure can be classified into two types (Malik *et al.*, 2012). First, oil in water (O/W), oil-swollen in the water phase, can be defined as normal micelles. Second, water in oil (W/O), water-swollen in the oil phase, can be defined as reverse micelles as shown in Figure 2.13.

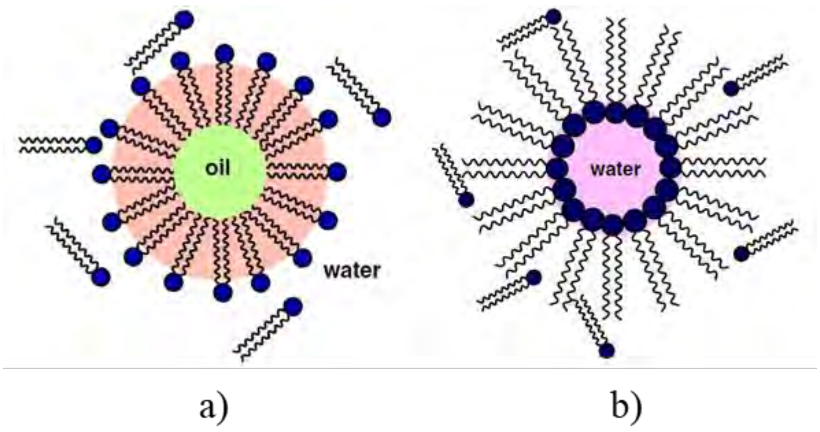


Figure 2.13 Structure of micelle a) O/W microemulsion and b) W/O microemulsion (Malik *et al.*, 2012).

According to Winsor type system, microemulsions are classified into four main types.

Type I: oil in water (O/W) microemulsion, oil-swollen in water phase where surfactants present as monomers at small concentration.

Type II: water in oil (W/O) microemulsion, water-swollen in oil phase that can form reverse micelles.

Type III: middle phase microemulsion in equilibrium with excess water and oil phase. This type exhibits the lowest interfacial tension and the highest solubility in the microemulsion system.

Type IV: single-phase microemulsion, is formed by the addition of a sufficient quantity of surfactant that completely miscible in the oil and water phase.

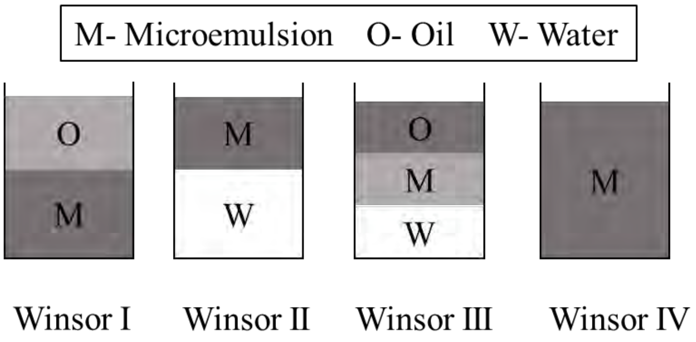


Figure 2.14 Schematic showing Winsor’s classification (Santanna *et al.*, 2012).

Winsor (1947) proposed the ratio of interactions (R) between the surfactant-oil and surfactant-water to describe the microemulsion phase behavior.

$$R=\frac{A_{CO}}{A_{CW}} \tag{2.1}$$

Where A_{CO} represents the interaction between surfactant and oil phase, A_{CW} is the interaction between surfactant and water phase. The results obtained from phase behavior studies are used to build the phase diagram. When the surfactant molecules at the interface have a stronger interaction with the water phase than the oil phase, R is less than one (R<1). In contrast, R is greater than one (R>1) when the interface tends to increase the interaction with oil. The middle phase obtained at equal interaction between oil and water, R is equal to one (R=1).

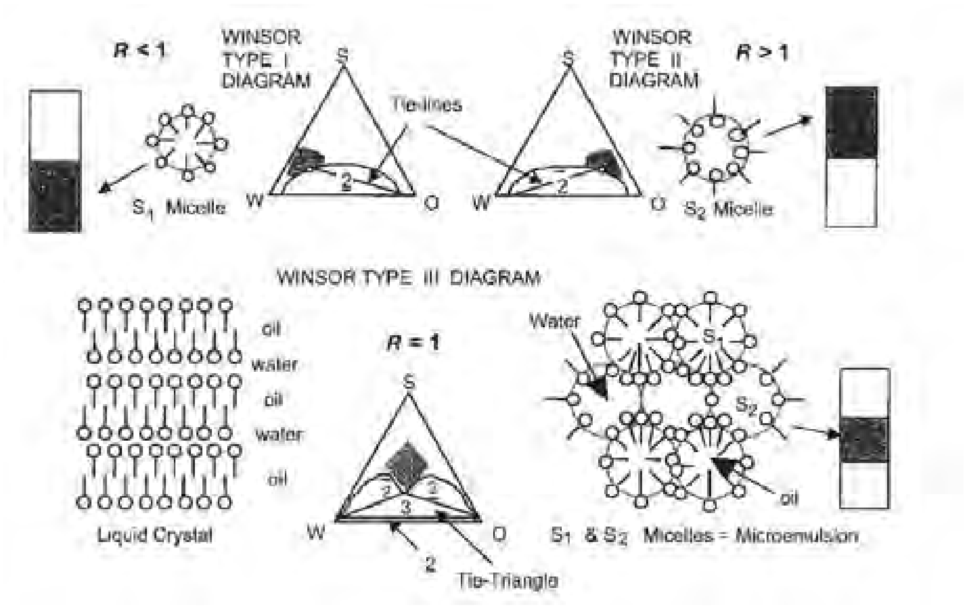


Figure 2.15 The three types of phase behavior for surfactant (S)–oil (O)–water (W) systems according to Winsor type system. Shading indicates the surfactant-rich phase (Salager *et al.*, 2005).

The phase behavior of microemulsions can be determined through varying the tuning parameters. An electrolyte is a tuning parameter for ionic surfactant systems. Increasing the electrolyte concentration causes to decrease in the electrostatic repulsion between the hydrophilic head group and changes the microemulsion from type I (W/O microemulsion) to type III (middle phase microemulsion) to II (O/W microemulsion). For nonionic surfactant systems, a temperature is a tuning parameter in the microemulsion formulations (Gudina *et al.*, 2013).

The gamma or well-known as the fish diagram shows the microemulsion phase study with an equivalent ratio of water to oil (Salager *et al.*, 2005). The fish diagram is plotted between a formulation parameter (i.e., electrolyte concentration, temperature) and surfactant concentration. In the diagram, the single-phase region (1Ø) defined as a fishtail that represents Winsor type IV microemulsion formulation. Winsor type I, II and III are formed below a critical point or optimum point as shown in Figure 2.16. In the three-phase region (3Ø) or known as a middle phase, is an important region to determine the highest solubilization of microemulsion formulation.

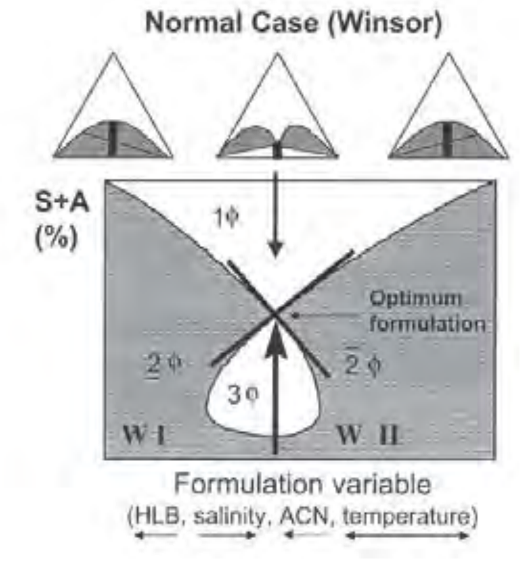


Figure 2.16 Phase behavior of a surfactant/alcohol/water/oil system at a constant water to oil ratio (Salager *et al.*, 2005).

2.8 Factor Affecting Microemulsion

2.8.1 Temperature

The temperature is an important parameter for microemulsion formulations. For anionic surfactants, their solubility depends on a Krafft temperature, which is defined as a minimum temperature that formed the first micelle. They become ineffective or precipitate below their Krafft point (Negin *et al.*, 2017). For nonionic surfactant, temperature also strongly affects to phase behavior of nonionic surfactants. The increasing interaction between the hydrophilic part (ethylene oxide) of the nonionic surfactants can be enhanced by increasing temperature (Quintero *et al.*, 2013).

2.8.2 Salinity

The salinity is an important parameter that affects the changing of microemulsions, especially for ionic surfactants. The salt is added to the solution for reducing the repulsion between the ionic head groups, thus changing in the phase transition from Winsor type I to III to II, respectively. Furthermore, the optimal salinity is defined as the salt concentration at which can form the middle phase microemulsions (Quintero *et al.*, 2013). In EOR technology, the optimal salinity is a significant parameter for operating oil production since it is not only performed maximum solubilization but also obtained minimum IFT (Salager *et al.*, 2005).

2.8.3 Co-Surfactants

The co-surfactant (e.g., short chain alcohol) can increase the interaction of the surfactant between the oil and water phase. The addition of co-surfactant can cause several effects including; an increase in equilibrium time to form microemulsions; increase in solubilization capacity; and decrease in IFT value (Negin *et al.*, 2017). In contrast, phase separation of the microemulsion can form at high co-surfactant concentration due to an increase in the attractive inter-droplet interaction (Quintero *et al.*, 2013).

2.8.4 Linker Molecules

The advantage of the linkers is unnecessary to use as an alcohol or co-surfactant in the microemulsion system (Negin *et al.*, 2017). The linkers are used to enhance the interfacial property and solubilization. The linkers introduced between the surfactant molecules, lead to increase solubilization and decrease IFT value (Hirasaki *et al.*, 2008). The addition of ethylene oxide (EO) and propylene oxide (PO) groups is applied to the surfactant molecule as an internal-hydrophilic and -lipophilic linkers, respectively or so-called extended surfactants.

2.9 Hydrophilic-Lipophilic Deviation (HLD) Concept

Salager *et al.* (1979) proposed the hydrophilic-lipophilic deviation (HLD) concept. HLD equation is thermodynamically derived correlation to explain the type of a microemulsion system. It is a dimensionless form of the thermodynamically derived surfactant affinity difference (SAD) equation. HLD concept is used for predicting microemulsion formulation which concludes important parameters affecting the microemulsion formation including salinity, oil polarity or hydrophobicity, temperature, co-surfactant and surfactant structure. Winsor type I, III and II exhibit the HLD values as negative, zero and positive values, respectively. There are two general forms of HLD equation; ionic surfactants and nonionic surfactants as shown in Eq. 2.2 and Eq. 2.3, respectively (Quintero *et al.*, 2013).

HLD equation for ionic surfactants;

$$\mathrm{HLD} = \ln(S^*) - K^*\mathrm{ACN} - f(A) - \alpha\Delta T + C_c \qquad (2.2)$$

HLD equation for nonionic surfactants;

$$\mathrm{HLD} = b(S^*) - K^*\mathrm{ACN} - \varphi(A) - c\Delta T + C_{cn} \qquad (2.3)$$

where S^* is the optimum salinity of microemulsion system (wt%), K is an empirical constant based on the surfactant head group, ACN or EACN is an alkane carbon number of the oil, f(A) and $\varphi(A)$ are functions of alcohol/co-surfactant type and concentration, α is a surfactant characteristic parameter, ΔT is the temperature difference from the reference temperature (298 K), C_c and C_{cn} are the characteristic curvatures.

The optimum condition, which is also known as an optimum salinity or S*, exhibits the middle phase microemulsion at which HLD = 0 because there is no difference between hydrophilic and lipophilic interaction energy (Kohli *et al.*, 2013).

If anionic surfactants are selected for microemulsion formulation without alcohol system (f(A)=0) at room temperature (25°C). Thus, the refined HLD equation for this system can be simplified as shown below;

For single anionic surfactants:

$$\ln S^* = K(ACN) - Cc \tag{2.4}$$

For mixed anionic surfactants:

$$\ln S^*_{mix} = K_{mix}(ACN) - Cc_{mix} \tag{2.5}$$

According to linear mixing rule (Salager *et al.*, 2013), the parameters in Eq.5 can be estimated as a following;

$$\ln S^*_{mix} = \sum x_i \ln S_i^* \tag{2.6}$$

$$K_{mix} = \sum x_i K_i \tag{2.7}$$

$$Cc_{mix} = \sum x_i Cc_i \tag{2.8}$$

Where, i is the individual components and x_i is the mole fraction of surfactant in the mixed system. The binary anionic surfactant system, the general HLD equation can be modified with $x_2 = 1 - x_1$ as shown below:

$$\ln S^*_{mix} = [(Cc_1 - Cc_2) + (K_2 - K_1)(ACN)x_2] + \ln S^*_1 \tag{2.9}$$

2.10 Surfactant Adsorption

The surfactant adsorption is a crucial parameter that leads a major to concern in many applications such as cleaning and oil recovery (Paria *et al.*, 2004). Due to the fact that the surfactant losses can directly affect the economic consideration of the application.

The surfactant adsorption is a process of transferring of surfactant molecules from the bulk solution phase to the interface (i.e., solid surface) (Lv *et al.*, 2011). The hydrophilicity or hydrophobicity of the solid surface is an important parameter for indicating the affinity of material to the water. The solid surface can exhibit the surface charges of the positive, negative or neutral surface from the surface equilibrium of potential determining ions (Paria *et al.*, 2004). The net charge on the solid surface depends on pH, ionic strength and solution condition (Robertson *et al.*, 1997). For example, the changing of pH solution affects to charges of a solid substrate. Of which, it exhibits a positively charged site at low pH due to adsorption of protons (H^+) from the solution onto the surface and shows a negatively charged site at high pH values due to hydroxyl group adsorbed (OH^-) onto the surface (Rosen *et al.*, 2012).

Typically, the mechanisms of surfactant adsorption included ion exchange, ion pairing, adsorption by polarization of π electrons, adsorption by dispersion forces and hydrophobic bonding (Rosen *et al.*, 2012).

2.10.1 Ion Exchange

The replacement of counterions adsorbed on to the solid surface from the bulk solution by the same charge of the surfactant head group.

2.10.2 Ion Pairing

Adsorption of surfactant molecule from the bulk solution onto the oppositely charged site.

2.10.3 Adsorption by Polarization of π Electrons

Surfactant adsorption occurs by an attractive force between electron-rich aromatic nuclei of the adsorbate and positive charges on the substrate.

2.10.4 Adsorption by Dispersion Forces

Surfactant adsorption occurs by London-van der Waals force between adsorbent and adsorbate molecules that increase with increasing the molecular weight of adsorbate.

2.10.5 Hydrophobic Bonding

Surfactant adsorption occurs by a combination of attraction between the hydrophobic groups and surfactant molecules present in the bulk solution.

In general, the surfactant adsorption isotherm of an ionic surfactant onto an oppositely charged surface can be shown with four main regions.

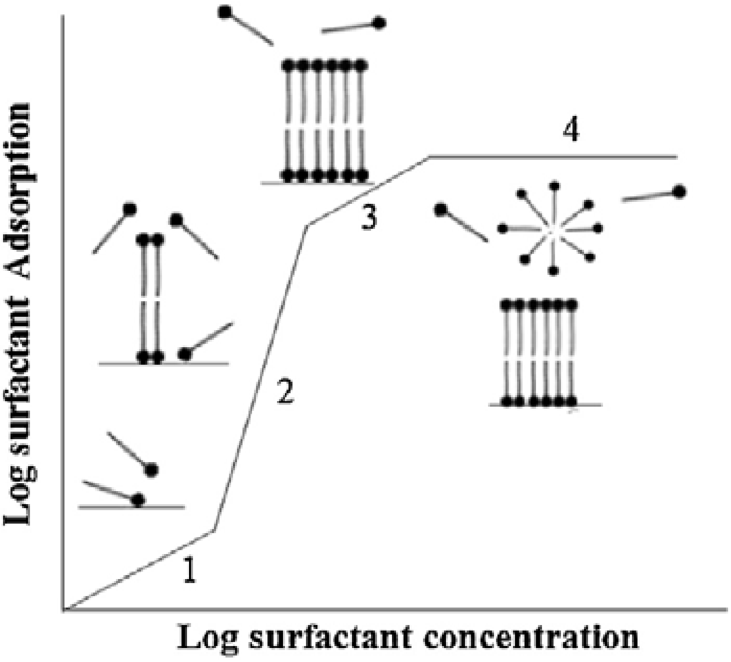


Figure 2.17 Surfactant adsorption isotherm (Budhathoki *et al.*, 2016).

According to Figure 2.17, the surfactant adsorption isotherm can be explained as follows;

Region 1, the physical adsorption of an ionic surfactant at low concentration of surfactant molecules occurs by the electrostatic force between the surfactant head groups and hydrophilic substrate.

Region 2, surfactant aggregates which hemi-micelles (monolayer) or admicelles (bilayer) with an increase surfactant concentration.

Region 3, surfactant aggregate called bilayer provides a slower surfactant adsorption rate.

Region 4, the surfactant concentration reaches to the CMC, the surfactant adsorption is constant because the monomer concentration does not change with the more micelle are added to the solution.

To minimize surfactant adsorption in EOR technology, the use of the surfactant with the same charge as the reservoir rock can prevent the surfactant adsorption. The anionic and cationic surfactant were used for the negatively charged surface of sandstone reservoir and positively charged surface of carbonate reservoirs, respectively.

CHAPTER III
EXPERIMENTAL

3.1 Objective

The objective of this research was to formulate the middle phase microemulsion (Winsor type III) through HLD concept using the carboxylate based extended mixed surfactant system for EOR application. The sub-objectives of this research are;

1. To study the effect of pH on carboxylate based extended surfactant.
2. To study the effect of carboxylate based extended surfactant structures with the different number of polyethylene oxide group (EO = 2, 4, 6) and their mixing ratio on the microemulsion phase behaviors for various alkane oils with different ACN.
3. To study the effect of ACN on the middle phase microemulsion formation (Winsor type III).
4. To determine K and Cc values of the carboxylate based extended surfactants based on the HLD concept.
5. To study the effect of carboxylate based extended surfactant structures with different numbers of the EO groups (EO = 2, 4, 6) on the surfactant adsorption onto quartz sand.

3.2 Scopes of Research

The scope of this research will cover the following:

1. Carboxylate based extended and AOT surfactants were used to formulate the middle phase microemulsion.
2. The temperature of the systems was controlled at room temperature (25± 2°C).
3. HLD concept for mixed anionic-anionic surfactant at Winsor type III microemulsion formation was applied.

3.3 Materials and Equipment

3.3.1 Equipment:

- Spinning drop tensiometer (Dataphysics, Model SVT20)
- Tensiometer (Kruss Easydyne, Model K100)
- pH meter (Mettler Toledo, Model FP20)
- Flat bottom vials 15 ml
- Total organic carbon (Shimadzu, TOCV-csh)

3.3.2 Chemicals:

3.3.2.1 Anionic Surfactants

- Fatty alcohol ethoxylated carboxymethylated (SOLOTERRA 941)
- Fatty alcohol ethoxylated carboxymethylated (SOLOTERRA 172)
- Fatty alcohol ethoxylated carboxymethylated (SOLOTERRA 938)
- Sodium dioctyl sulfosuccinate (AOT)

Table 3.1 Surfactant properties

Trade name	Name	No. of EO groups	M.W.	HLB	%active
SOLOTERRA 941	$C_{13}(EO)_2COO^-$	2	332	21.7[*a]	90
SOLOTERRA 172	$C_{13}(EO)_4COO^-$	4	456	22.2[*a]	90
SOLOTERRA 938	$C_{13}(EO)_6COO^-$	6	508	23.1[*a]	90
Sodium dioctyl sulfosuccinate	AOT	-	445	10.5[*b]	97

* a reported by Sasol North America company.
* b reported by Prakash (2010).

3.3.2.2 Oils (purity 99%)

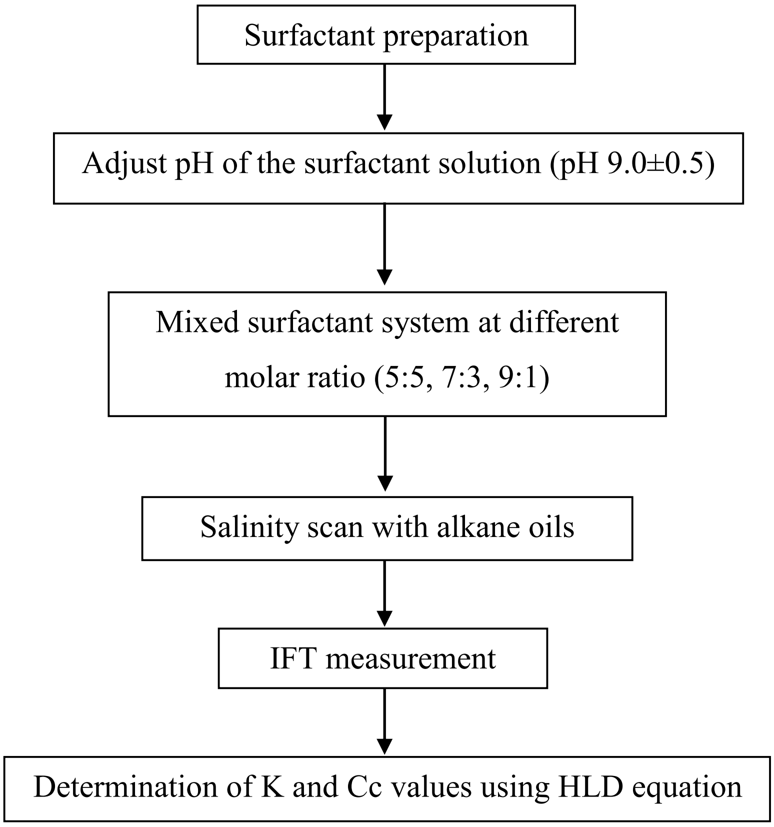
- n-heptane
- n-octane
- n-decane
- n-dodecane

- n-hexadecane

3.3.3 Other (purity 99%)

- Potassium hydroxide
- Sodium Chloride

3.4 Experimental Procedures



CMC measurement

- The effect of pH solution
- The effect of surfactant structure with the different number of EO groups (EO = 2, 4, 6)
- The effect of mixed surfactants

Surfactant adsorption

- The effect of surfactant structure with the different number of EO groups (EO = 2, 4, 6)

3.4.1 Surfactant Preparation

The carboxylate based extended surfactants obtained from the manufacture are acid forms. Although the carboxylate based extended surfactant showed a low solubility in acid forms, a clear solution was obtained at high alkaline solutions (Chiappisi, 2017). All pH of the surfactant solution was measured using pH meter (Mettler Toledo, Model FP20). The pH of the stock surfactant solutions was adjusted using a strong base solution of potassium hydroxide (Kohli *et al.*) to obtain the controlled pH at 9.0±0.5.

3.4.2 CMC Measurement

The CMC was determined using the plot between surface tension versus surfactant concentration. The surface tension was measured using a tensiometer (Kruss, Easydyne) at room temperature (25±2°C). At dilute surfactant concentration, surfactant molecules are individually dispersed in the aqueous solution. As the concentration of surfactant increases, the surfactant molecules tend to adsorb at the air surface until the surface saturated. Above this point, the surface tension becomes constant. The CMC values determine at the intersections of the plot. In this study, the correlation factors (R^2) of each plot were above 0.95 suggesting that plotting is consistent with the experimental data.

3.4.3 Middle Phase Microemulsion Formation

To study the phase behavior of the microemulsion system, all experiments were conducted by varying NaCl concentrations (salinity scan). The surfactant solution was mixed with an alkane oil with the water-to-oil ratio to one in a glass vial. The mixture was shaken and left to equilibrate at room temperature (25±2°C). The microemulsion phase was kept and observed for a month in order to ensure the middle phase microemulsion.

3.4.4 IFT Measurement

The equilibrium interfacial tension (IFT) of the excess water and excess oil was measured using a spinning drop tensiometer (Dataphysics, Model SVT20). The excess water phase of microemulsion was added into a spinning drop tube and the excess oil phase was added into the same tube as the second phase. The IFT value was measured after 30 minutes at a constant rotational velocity (5,000 rpm) and constant temperature (25±2°C).

3.4.5 Surfactant Adsorption

The surfactant solution was prepared with various concentration and also adjusted the pH solution using KOH to the controlled value at the solution pH of 9. This pH value was used to ensure the anionic carboxylate extended surfactant and a negatively charged surface of quartz sand. The adsorption study was performed by adding 30 ml of the surfactant solution to 3 g of quartz sand (80 mesh). The composition of quartz sand is shown in Table 3.2. The samples were shaken at 200 rpm for 24 hours and left them to equilibrium for 48 hours at room temperature (25±2°C). The supernatants were filtrated by a glass fiber of 55 mm diameter and analyzed by a total organic compound method (Shimadzu, TOCV-csh). The amount of adsorbed surfactant can be calculated using Eq.3.1

$$\text{Amount of adsorbed surfactant} = \frac{(C_1\text{-}C_2) \times V}{m} \tag{3.1}$$

where C_1 and C_2 are the surfactant concentration at before and after adsorption test, respectively. V is a volume of surfactant solution and m is mass of solid or adsorbent.

Table 3.2 Composition of quartz sand

Composition	Amount (wt.%)[*c]
SiO_2	99.15
Al_2O_3	0.436
Fe_2O_3	0.037
TiO_2	0.021
CaO	0.040
MgO	0.011
K_2O	0.004
Na_2O	0.002
LOI	0.290

* c reported by herosign marketing company.

CHAPTER IV
RESULTS AND DISCUSSION

In this study, the microemulsions were formed using binary surfactant system of carboxylate surfactants with the aim to enhance the efficiency of oil recovery. Sodium dioctyl sulfosuccinate (AOT) and carboxylate based extended surfactants with three different EO groups ($C_{13}(EO)_nCOO^-$, n = 2, 4, 6) were used as a primary and secondary surfactant, respectively. The binary anionic surfactant systems were investigated by varying the ratio of mixed surfactants with 0.015 M of total surfactant concentration at the room temperature (25±2°C) The observation at the middle phase microemulsion was conducted by varying NaCl concentrations known as a salinity scan where the optimal salinity (S*) is obtained. Moreover, the interfacial tension (IFT) measurement was used to study the effect of mixed surfactant ratios and surfactant structure on their interfacial tension property. Five alkane oils (heptane, octane, decane, dodecane and hexadecane) were selected to study the effect of its alkyl chain length (ACN) on the optimal salinity. The K and Cc value of carboxylate based extended surfactants can be determined using HLD concept. Also, the surfactant adsorption onto the quartz sand was investigated to observe the potential use in EOR application.

4.1 The Microemulsion Phase Behavior Study

The microemulsion phase behavior was conducted in 15 ml flat-bottom glass vials. The aqueous and oil phases were mixed at the water-to-oil ratio to one in the glass vial. The mixture was shaken and left to equilibrate at room temperature (25±2°C). The microemulsion phase was kept and observed for a month in order to ensure the Winsor type III or middle phase microemulsion. The middle phase was observed by the phase volume fraction indicating with the equal volume between the aqueous and oil phases. In this study, the microemulsion phase behavior was investigated at pH=9. An increase in pH of the surfactant solution cause the surfactant being more hydrophilicity due to an increasing degree of ionization from carboxylic (COOH) to carboxylate (COO^-) forms. The higher optimal salinity was observed with an increased pH of the surfactant solution until all surfactant molecules were completely ionized (Qutubuddin *et al.*, 1984). The pH of surfactant solution was rechecked after their equilibrium and the results were in the range of 8±1.0.

4.1.1 Effect of Mixed Surfactant Ratios

The ratios of binary anionic surfactants, AOT and carboxylate based extended surfactants, were varied with three different molar ratios (5:5, 7:3 and 9:1 AOT: $C_{13}(EO)_nCOO^-$, where n is a number of EO group) at 0.015 M of the total surfactant concentration. The salinity scan was conducted by varying NaCl concentrations ranging from 0.2 – 6 wt%. The phase transition of the microemulsions occurred from Winsor type I to III and to II for all systems. The results indicated that the middle phase microemulsions of the mixed surfactant systems were clearly observed at 9:1 AOT: $C_{13}(EO)_nCOO^-$.

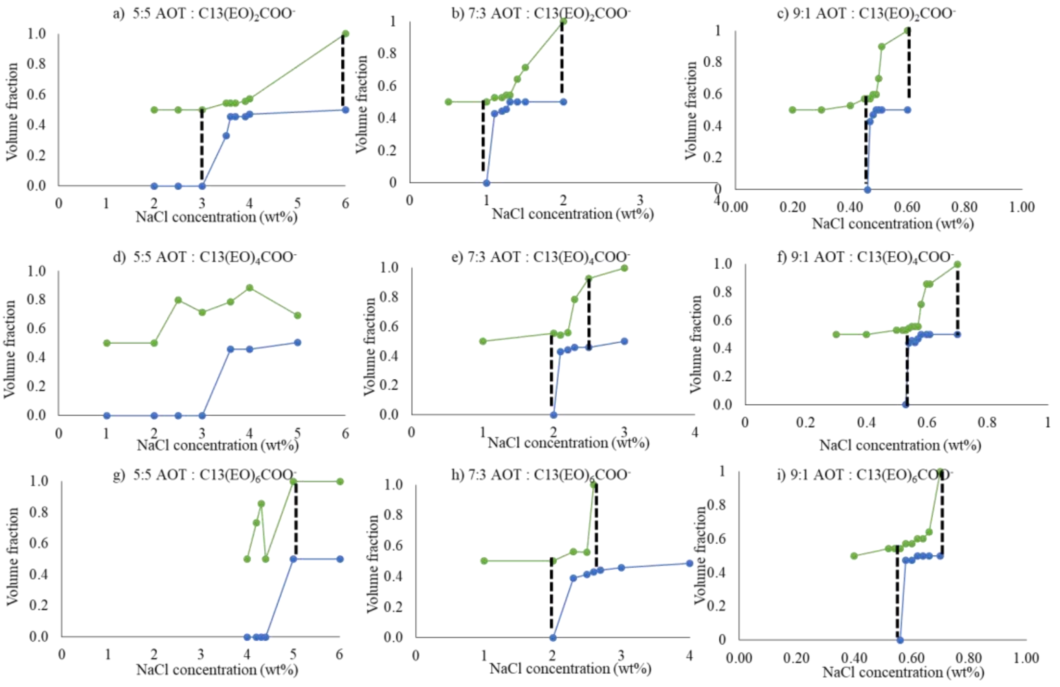


Figure 4.1 The relationship between phase volume fraction of AOT:$C_{13}(EO)_nCOO^-$ mixed surfactant system and NaCl concentrations with octane at 0.015 M total surfactant concentration under room temperature (25±2 °C).

It can be noted that the carboxylate based extended surfactant alone could not form the middle phase. Of which, the surfactant gel phase was observed at the high surfactant concentrations. The use of the mixed surfactant system, e.g., with different hydrophobicity, is an alternative method to balance these interactions of the oil and water, resulting in microemulsion formation (Nguyen *et al.*, 2018). In this study, AOT was added in the carboxylate extended surfactant as a binary mixture and was used as a reference surfactant.

Figure 4.1 showed the relationship between the phase volume fraction of the mixed surfactant systems with three different mixing molar ratios in octane as an oil phase. It can be seen that the decreasing of carboxylate based extended surfactant fraction in the mixture not only reduced the salt concentration required to obtain the middle phase but also the more transparent middle phase was observed.

4.1.2 Effect of Surfactant Structures

The binary mixture of AOT and $C_{13}(EO)_nCOO^-$ was conducted to form the middle phase with the aim to study the effect of variation of polyethylene oxide group (EO = 2, 4, 6) in the carboxylate extended surfactant on their optimal salinity (S*).

The effect of EO groups (n= 2, 4 and 6) in the carboxylate extended surfactants on their optimal salinity at 9:1 molar ratio of AOT: $C_{13}(EO)_nCOO^-$ mixed system were investigated with octane as shown in Table 4.1 and Figures 4.2 to 4.4.

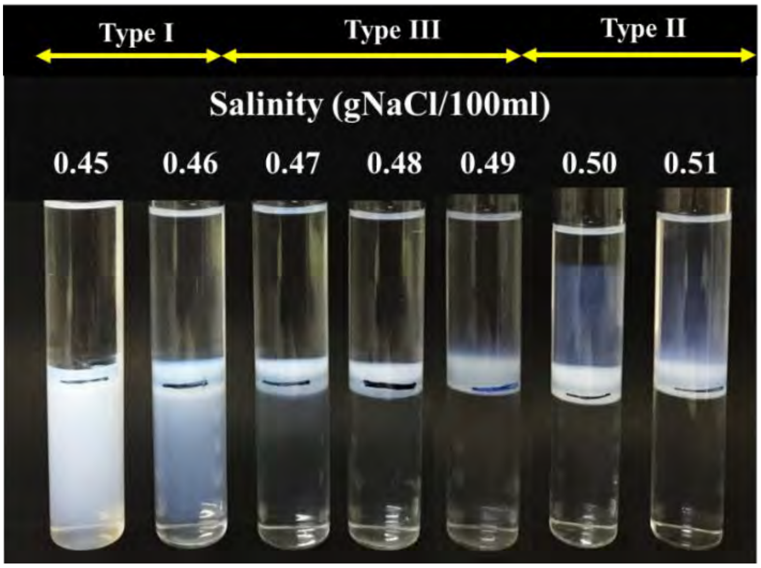


Figure 4.2 The microemulsion phase scan of AOT : $C_{13}(EO)_2COO^-$ (9:1 by molar ratio) mixed surfactant system with octane as an oil phase at 0.015 M total surfactant concentration under room temperature (25±2°C).

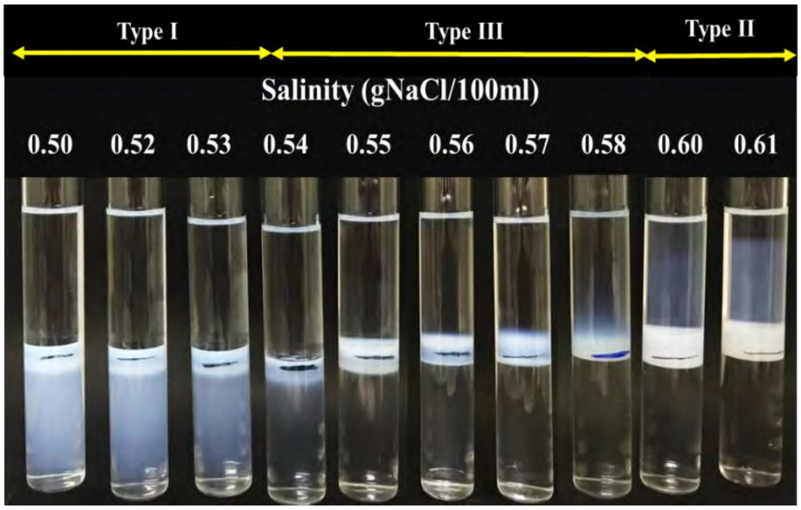


Figure 4.3 The microemulsion phase scans of AOT : $C_{13}(EO)_4COO^-$ (9:1 by molar ratio) mixed surfactant system with octane as an oil phase at 0.015 M total surfactant concentration under room temperature (25±2°C).

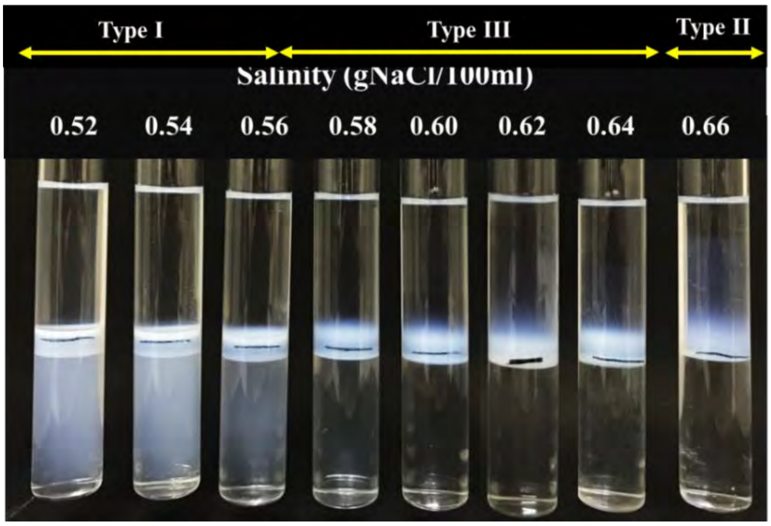


Figure 4.4 The microemulsion phase scans of AOT : $C_{13}(EO)_6COO^-$ (9:1 by molar ratio) mixed surfactant system with octane as an oil phase at 0.015 M total surfactant concentration under room temperature (25±2°C).

Table 4.1 Summarizes the optimal salinities of AOT: $C_{13}(EO)_nCOO^-$ with 9:1 molar ratio at 0.015 M total surfactant concentration with octane as an oil phase under room temperature (25±2 °C)

Surfactants	No. of EO groups	Middle phase observation	Optimal salinity (S*) (wt%)
AOT : $C_{13}(EO)_2COO^-$	2	Turbid	0.48
AOT : $C_{13}(EO)_4COO^-$	4	Turbid	0.56
AOT : $C_{13}(EO)_6COO^-$	6	Turbid	0.60

According to Table 4.1, it can be seen that the number of EO group increases, the optimal salinity increases (0.48 to 0.60 wt%). This result is consistent with the Winsor R concept (Winsor, 1947) that the ratio of net surfactant-oil interactions, A_{so}, to the net surfactant–water interaction, A_{sw}. Increasing the number of EO groups increases A_{sw}. To balance this effect, adding salt helps to reduce the net surfactant-water interaction, A_{sw} Thus, the more salt concentration is required when the numbers of EO group increases to obtain the middle phase microemulsion.

In addition, the effect of EO groups on the optimal salinity was investigated with various alkane oils. The similar trend was observed as presented for octane as shown in Figure 4.5 and Appendix B.

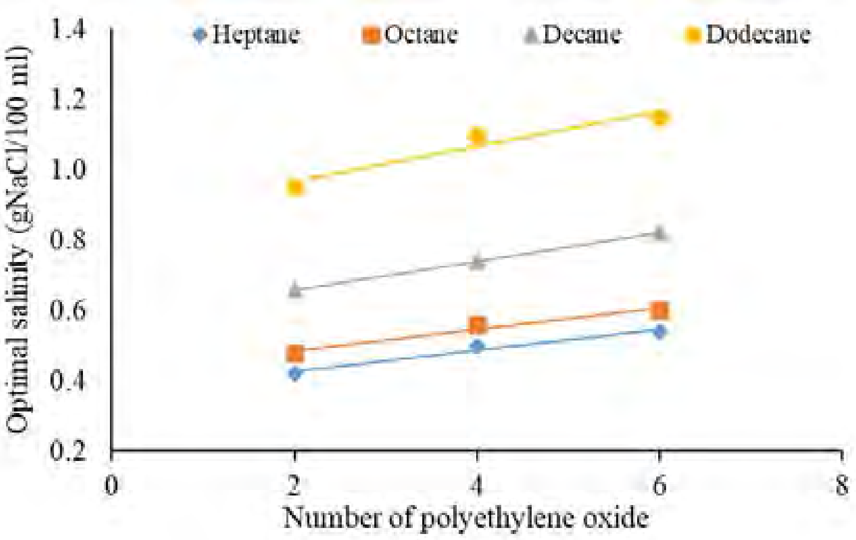


Figure 4.5 The optimal salinity of the binary surfactant system versus the number of polyethylene oxide in carboxylate surfactant.

4.1.3 Effect of Alkane Oils

The middle phase microemulsion was formulated using the binary anionic surfactant system of AOT and $C_{13}(EO)_nCOO^-$ (n=2, 4 and 6) in alkane oil with different alkane carbon number (ACN) including; heptane, octane, decane, dodecane and hexadecane. The effects of ACN on the microemulsion formation and the optimal salinity (S*) are shown in Table 4.2 and Figure 4.6. As noted, the middle phase did not form in the microemulsion systems with hexadecane. This result can be explained by Nguyen *et al.* (2018) that the alkane oils of low ACN or less hydrophobic are required to form the microemulsion with the hydrophilic surfactants while the alkane oils of high ACN or high hydrophobic are needed to form with the hydrophobic surfactants.

Table 4.2 Summarizes the optimal salinities of AOT: $C_{13}(EO)_nCOO^-$ at 9: 1 molar ratio at 0.015 M total surfactant concentration with different alkane oils (ACN) under room temperature (25±2 °C)

Surfactant system	Alkane oil	Phase behavior	Optimal salinity (S*) (wt%)
AOT : $C_{13}(EO)_2COO^-$	n-heptane	Type I, III, II	0.42
	n-octane	Type I, III, II	0.48
	n-decane	Type I, III, II	0.66
	n-dodecane	Type I, III, II	0.95
	n-hexadecane	No middle phase	-
AOT : $C_{13}(EO)_4COO^-$	n-heptane	Type I, III, II	0.50
	n-octane	Type I, III, II	0.56
	n-decane	Type I, III, II	0.74
	n-dodecane	Type I, III, II	1.10
	n-hexadecane	No middle phase	-
AOT : $C_{13}(EO)_6COO^-$	n-heptane	Type I, III, II	0.54
	n-octane	Type I, III, II	0.60
	n-decane	Type I, III, II	0.82
	n-dodecane	Type I, III, II	1.15
	n-hexadecane	No middle phase	-

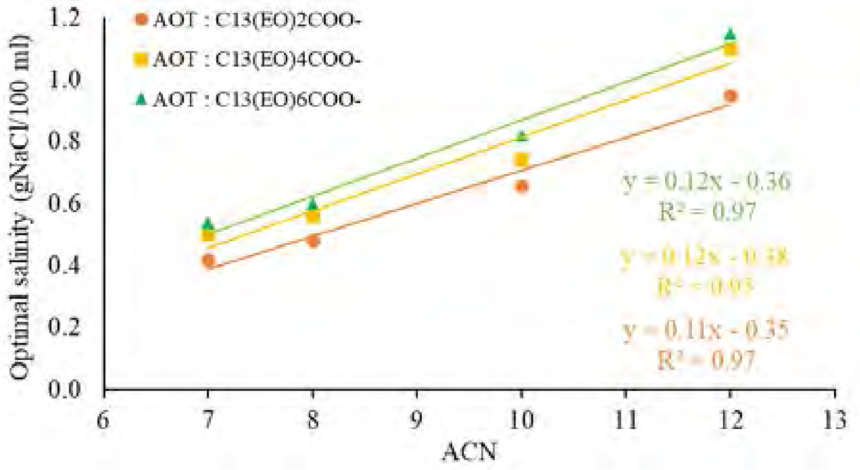


Figure 4.6 The optimal salinity of the binary surfactant system with different EO groups in carboxylate surfactant versus alkane oils with different ACN.

Table 4.2 and Figure 4.6 showed the optimal salinity obtained by the mixed surfactant systems in different alkane oils. For all mixed surfactant systems with different EO groups in the carboxylate extended surfactants, the results showed that the ACN increases with increasing the optimal salinity. This observed trend is consistent with the Winsor R concept that the increasing of ACN affects an increase in oil interaction, A_{oo} and a reduction in the net interaction of surfactant-oil, A_{so}. Thus, more salt is required to reduce the interaction of surfactant-water, A_{sw} (Salager *et al.*, 2005).

4.2 Interfacial Tension Measurement

The important characteristic of surfactant flooding for EOR technology is a reduction of the interfacial tension between the oil and water phase (Sheng, 2015). This work, the interfacial tension (IFT) measurement of the designed surfactant systems was conducted to determine the ability of interfacial tension reduction between the excess water and excess oil phase by a spinning drop tensiometer (Dataphysics, Model SVT20). The equilibrium IFT value was measured after 30 minutes at the constant rotational velocity (5,000 rpm) and constant temperature (25±2°C).

The plot between equilibrium IFT values and NaCl concentrations was conducted, where the salt concentration at which the minimum IFT observed is defined as an optimal salinity (S*) or optimal for microemulsion formulation (Salager *et al.*, 2005).

4.2.1 Effect of Mixed Surfactant Ratios

The IFT values of the binary surfactant system, AOT: $C_{13}(EO)_2COO^-$ with varying the mixing ratios (5:5, 7:3 and 9:1 by molar ratio) at 0.015 M total concentration in octane were measured. The results showed that the IFT of the mixed surfactants reached to the ultralow IFT (< 0.01 mN/m). Moreover, the changing in the fraction of carboxylate surfactant in the mixture did not affect the reduction of IFT values which opposed to the significantly reducing the optimal salinity which is shown in Figure 4.7 and Table 4.3.

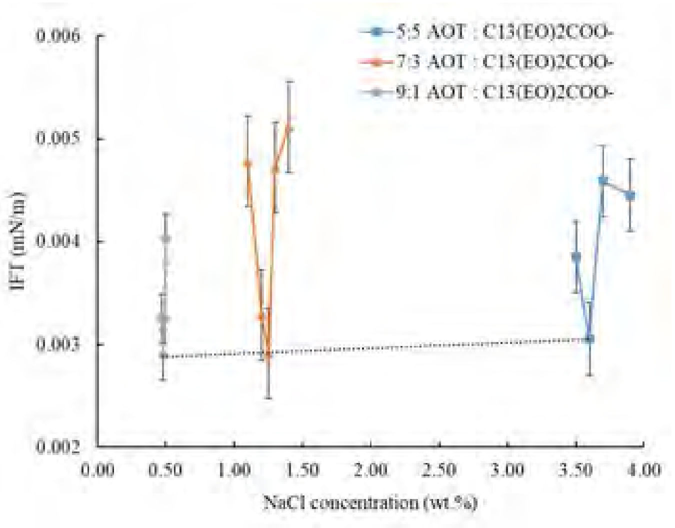


Figure 4.7 The IFT values of AOT: $C_{13}(EO)_2COO^-$ microemulsion systems with octane as an oil phase at 0.015 M total concentration by varying the molar ratio of mixed surfactants.

Table 4.3 Summarize the IFT values for the microemulsion system of AOT: $C_{13}(EO)_2COO^-$ with varying the molar ratio of the mixed surfactant system in octane at room temperature (25±2°C)

Primary surfactant	Secondary surfactant	Molar ratio	NaCl concentration (wt.%)	IFT (mN/m)
AOT	$C_{13}(EO)_2COO^-$	5:5	3.50	0.00385
			3.60	0.00305*
			3.70	0.00459
			3.90	0.00445
AOT	$C_{13}(EO)_2COO^-$	7:3	1.10	0.00478
			1.20	0.00329
			1.25	0.00292*
			1.30	0.00472
			1.40	0.00511
AOT	$C_{13}(EO)_2COO^-$	9:1	0.47	0.00325
			0.48	0.00289*
			0.49	0.00325
			0.50	0.00403

* the minimum IFT value

4.2.2 Effect of Surfactant Structure

The IFT values of the microemulsion systems using the binary surfactant systems of AOT: $C_{13}(EO)_2COO^-$ (n =2, 4, 6) at 9:1 molar ratio of 0.015 M total surfactant concentration in heptane as an oil phase were determined.

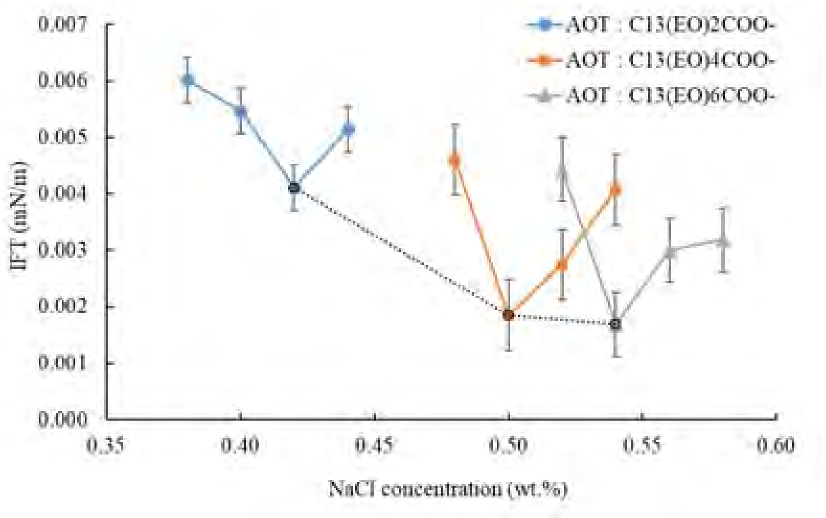


Figure 4.8 The IFT values of the microemulsion system using the binary surfactant systems of AOT and $C_{13}(EO)_nCOO^-$ (n =2, 4, 6) at 9:1 molar ratio of 0.015 M total surfactant concentration in heptane as an oil phase at room temperature (25±2°C).

Table 4.4 Summarize the IFT values of binary surfactant system of AOT and $C_{13}(EO)_2COO^-$ (n =2, 4, 6) at 9:1 molar ratio of 0.015 M total surfactant concentration in heptane as an oil phase at room temperature (25±2°C)

Surfactant	NaCl concentration (wt.%)	IFT (mN/m)
AOT : C13(EO)2COO-	0.38	0.00602
	0.40	0.00547
	0.42	0.00411*
	0.44	0.00514

* the minimum IFT value

Table 4.4 Summarize the IFT values of binary surfactant system of AOT and $C_{13}(EO)_2COO^-$ (n =2, 4, 6) at 9:1 molar ratio of 0.015 M total surfactant concentration in heptane as an oil phase at room temperature (25±2°C) (Continued).

Surfactant	NaCl concentration (wt.%)	IFT (mN/m)
AOT : C13(EO)4COO-	0.48	0.00460
	0.50	0.00186*
	0.52	0.00274
	0.54	0.00408
AOT : C13(EO)6COO-	0.52	0.00444
	0.54	0.00169*
	0.56	0.00300
	0.58	0.00318

* the minimum IFT value

As shown in Figure 4.8 and Table 4.4, it can be observed that the IFT values decrease with increasing the EO groups in the carboxylate based extended surfactant. The presence of intermediate-polarity groups, EO groups, in the surfactant molecule provides a smoother interfacial transition between the surfactant and water phase resulting in an increase in the solubilization capacity of oil phase (Phan *et al.*, 2011).

According to Chun-Huh equation, the equation described the relationship between solubilization parameter and interfacial tension of a microemulsion system, as shown in Eq.4.1 (Chun, 1979).

$$SP = \frac{C}{IFT^2} \tag{4.1}$$

Where SP is a solubilization parameter (ml of oil/g of surfactant), C is a Chun-Huh constant characteristic of surfactant and IFT is interfacial tension between excess oil and water phases (mN/m).

The solubilization parameter and IFT value are inversely proportional as shown in Eq.4.1. Therefore, the increasing of EO groups in the carboxylate surfactant decreases the IFT value of the microemulsion system.

4.2.3 Effect of Alkane Oils

The IFT values of the microemulsion system using the binary surfactant systems of AOT: $C_{13}(EO)_4COO^-$ at 9:1 molar ratio of 0.015 M total surfactant concentration, in the oil phase with varying ACN (i.e., heptane, octane, decane, and dodecane) were investigated.

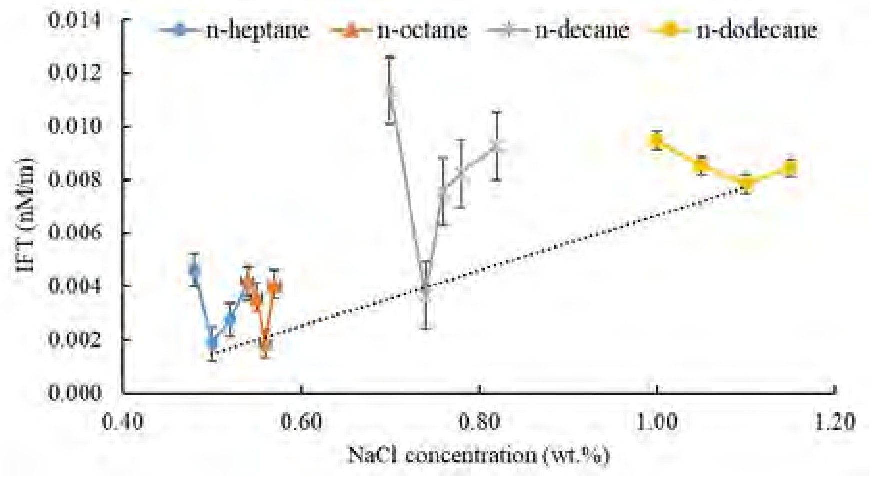


Figure 4.9 The equilibrium IFT values of AOT: $C_{13}(EO)_4COO^-$ with 9:1 molar ratio at 0.015 M total surfactant concentration by varying alkane oils.

Table 4.5 Summarize the IFT values of AOT: $C_{13}(EO)_4COO^-$ with 9:1 molar ratio at 0.015 M total surfactant concentration by varying alkane oils

Alkane oil	NaCl concentration (wt.%)	IFT (mN/m)
n-heptane	0.48	0.00460
	0.50	0.00186
	0.52	0.00274*
	0.54	0.00408
n-octane	0.54	0.00420
	0.55	0.00360
	0.56	0.00188*
	0.57	0.00407
n-decane	0.70	0.01137
	0.74	0.00368*
	0.76	0.00758
	0.78	0.00824
	0.82	0.00928
n-dodecane	1.00	0.00947
	1.05	0.00854
	1.10	0.00784*
	1.15	0.00844

* the minimum IFT value

The results showed that the minimum IFT values slightly increased in heptane and octane but significantly increased in decane and dodecane. The increasing in ACN forced the system more hydrophobicity and less oil solubilization by the surfactants (Tongcumpoua *et al.*, 2003). Thus, the higher IFT values were observed with higher ACN for the binary surfactant system.

4.3 HLD Calculation

4.3.1 Determination of K and Cc Values Using a Binary Surfactant System

Salager *et al.* (1979) proposed the hydrophilic-lipophilic deviation (HLD) concept which is the thermodynamically derived correlation to explain the microemulsion system. The HLD concept accounts the terms of formulation variables into the calculation for guiding microemulsion formulation. The K and Cc values are an important variable for determining the microemulsion system. Where, the K and Cc values of a conventional single anionic surfactant can be calculated from the HLD equation that contrasts with an extended surfactant (Witthayapanyanon *et al.*, 2006). In this study, the carboxylate based extended surfactants alone cannot form the middle phase at the designed condition. The binary surfactant system, sodium dioctyl sulfosuccinate (AOT) and carboxylate based extended surfactants ($C_{13}(EO)_2COO^-$, $C_{13}(EO)_4COO^-$ and $C_{13}(EO)_6COO^-$), was applied to formulate the middle phase microemulsion for the sake of determining the K and Cc value of the carboxylate based extended surfactants.

In order to determine K and Cc value of the carboxylate based extended surfactants in the binary surfactant system, the general HLD equation is combined with the linear mixing rule (Salager *et al.*, 2013) as shown in Eq.4.1

$$\ln S^*_{mix} = (x_1K_1+x_2K_2)(ACN) + (x_1Cc_1+x_2Cc_2) \qquad (4.1)$$

where the subscript 1 and 2 represented primary and secondary surfactants, AOT and $C_{13}(EO)_nCOO^-$, respectively. The binary surfactant system was formed at room temperature (25±2°C) with the alcohol-free system ($f(A) = 0$) at 9:1 molar ratio of 0.015 M total surfactant concentration. The K and Cc values of the surfactant can be determined from plotting between $\ln S^*_{mix}$ and can as shown below;

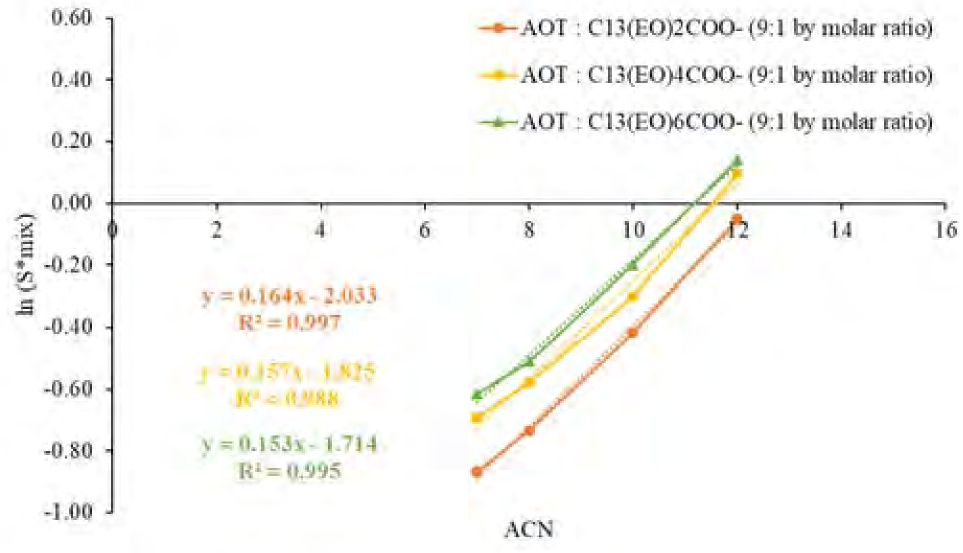


Figure 4.10 The plot between ln S^*_{mix} and ACN of the binary surfactant system of AOT: $C_{13}(EO)_nCOO^-$ with 9:1 molar ratio at 0.015 M total surfactant concentration under room temperature (25±2 °C).

The linear mixing rule was applied to the experiments and the result is shown in Figure 4.10. The correlation factor (R^2) of each plot was more than 0.98 suggesting that the plot is in good agreement with the experimental data. According to Eq.4.1, the slope and y-intercept are the definition of $x_1K_1+x_2K_2$ and $x_1Cc_1+x_2Cc_2$, respectively. The K_1 and Cc_1 are 0.17 and 2.42, respectively (Witthayapanyanon *et al.*, 2008). For example, the linear regression of 9:1 molar ratio of AOT: $C_{13}(EO)_2COO^-$ is shown in Eq. 4.2 and x_1 and x_2 are the known factors. Thus, the K_2 and Cc_2 values of each surfactant can be calculated from Eq.4.1 as a following;

$$\ln S^*_{mix} = 0.16\,(ACN) - 2.03 \tag{4.2}$$

$$K_2 = \frac{0.16-(0.9\times 0.17)}{0.1} = 0.11 \tag{4.3}$$

$$Cc_2 = \frac{2.03-(0.9\times 2.42)}{0.1} = \text{-}1.45 \tag{4.4}$$

Therefore, the K and Cc values of each surfactant can be calculated using the above equations and are summarized in Table 4.6.

Table 4.6 Summary of the *K* and Cc values of $C_{13}(EO)_nCOO^-$ (n=2, 4, 6)

Surfactant	slope	y-intercept	R^2	K	Cc	Cc/K
$C_{13}(EO)_2COO^-$	0.16	2.03	0.99	0.108	-1.45	-13.46
$C_{13}(EO)_4COO^-$	0.16	1.83	0.98	0.043	-3.53	-82.09
$C_{13}(EO)_6COO^-$	0.15	1.71	0.99	0.003	-4.64	-1546

In general, K value is an empirical constant based on the surfactant head group and hydrophilicity. K values of anionic surfactant are reported in the range of 0.004 - 0.17 (Budhathoki *et al.*, 2016). Nguyen *et al.* (2018) reported the K values of carboxylate extended surfactant in the range of 0.14 – 0.32. According to Table 4.6, K values of carboxylate based extended surfactant are in the range of 0.003 – 0.108.

The characteristic parameters of surfactants (Cc) can be in the range from a negative to a positive value. For a negative Cc value, the surfactant tends to form oil-swollen in an aqueous phase (O/W microemulsion). In contrast, a positive Cc value means that the surfactant tends to form water-swollen in an oil phase (W/O microemulsion) (Budhathoki *et al.*, 2016). The Cc value of conventional carboxylate surfactant is reported to be + 0.97 (Antonio, 2015). According to Table 4.6, the results showed that all carboxylate based extended surfactants had more negative Cc values than the conventional carboxylate surfactant. An increasing the number of polyethylene oxide (EO) groups affected to a decrease in the Cc values of the carboxylate based extended surfactant. This could be because the addition of EO groups bring an increase in the hydrophilicity of surfactant (Witthayapanyanon *et al.*, 2006) meaning that the more negative Cc values is obtained than the conventional carboxylate surfactant.

4.3.2 Determination of Predicted Optimal Salinity (S*)

The optimal salinity for the microemulsions of the binary surfactant system, AOT and $C_{13}(EO)_nCOO^-$, can be calculated using HLD equation for free alcohol system (f(A) = 0) at the room temperature (25±2 °C). The correlation between the experimental results and the theoretical HLD estimation was compared.

Table 4.7 Comparison the optimal salinities of AOT: $C_{13}(EO)_nCOO^-$ between experimental results and the theoretical HLD estimation with 9: 1 molar ratio at 0.015 M total surfactant concentration with different alkane oils under room temperature (25±2 °C)

Primary surfactant	Secondary surfactant	Molar ratio	Alkane oils	S^*_{mix} Experiment (wt%)	S^*_{mix} Predicted (wt%)	S^* error (%)
AOT	$C_{13}(EO)_2COO^-$	9:1	n-heptane	0.42	0.41	1.83
			n-octane	0.48	0.49	1.18
			n-decane	0.66	0.67	2.11
			n-dodecane	0.95	0.94	1.56
			n-hexadecane	No middle phase	1.80	-
AOT	$C_{13}(EO)_4COO^-$	9:1	n-heptane	0.50	0.48	3.03
			n-octane	0.56	0.57	1.33
			n-decane	0.74	0.78	5.03
			n-dodecane	1.10	1.06	3.22
			n-hexadecane	No middle phase	2.00	-
AOT	$C_{13}(EO)_6COO^-$	9:1	n-heptane	0.54	0.53	2.44
			n-octane	0.60	0.61	2.35
			n-decane	0.82	0.83	1.76
			n-dodecane	1.15	1.13	1.41
			n-hexadecane	No middle phase	2.09	-

Table 4.7 shows the comparison of optimal salinity obtained from experiments and HLD calculations with the errors of deviation less than 5% at 9:1 molar ratio of AOT and carboxylate based extended surfactant. Of which, the characteristic parameters (K and Cc values) of the carboxylate based extended surfactant can be applied to determine the optimal condition for the microemulsion system.

Moreover, the comparison of optimal salinity of experiments and HLD calculation at 5:5 and 7:3 molar ratio of AOT and carboxylate based extended surfactant in an octane oil was observed.

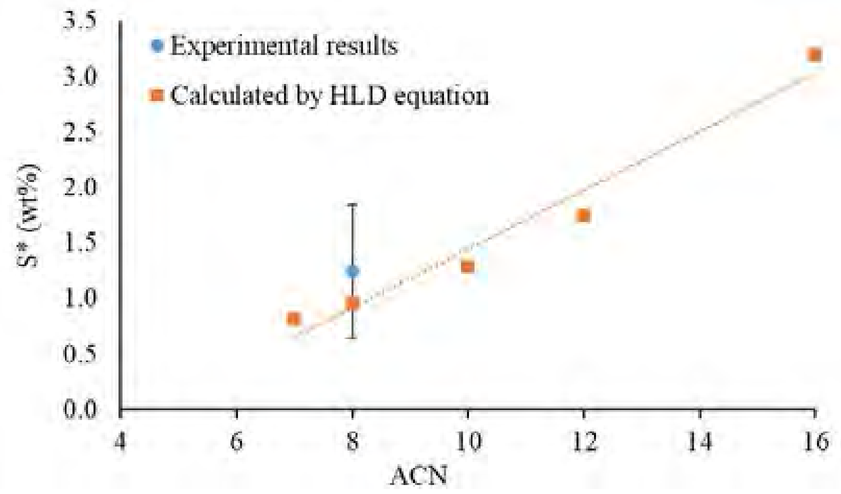


Figure 4.11 Comparison the optimal salinities of AOT: $C_{13}(EO)_2COO^-$ between experimental results and the theoretical HLD estimation with 5:5 molar ratio at 0.015 M total surfactant concentration with different alkane oils under room temperature (25±2 °C).

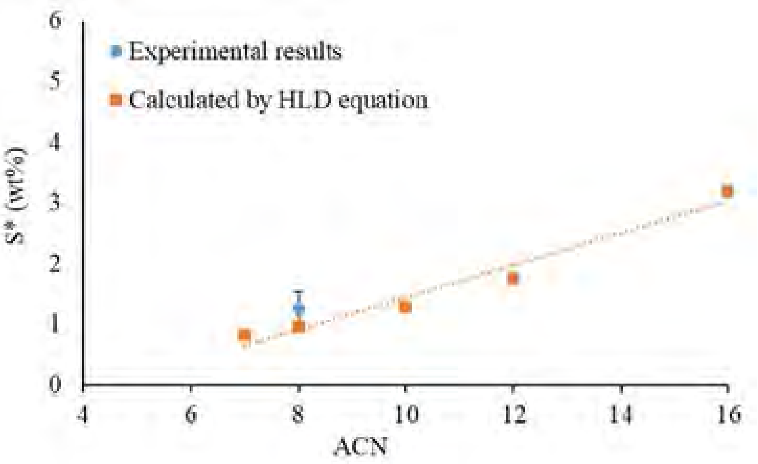


Figure 4.12 Comparison the optimal salinities of AOT: $C_{13}(EO)_2COO^-$ between experimental results and the theoretical HLD estimation with 7:3 molar ratio at 0.015 M total surfactant concentration with different alkane oils under room temperature (25±2 °C).

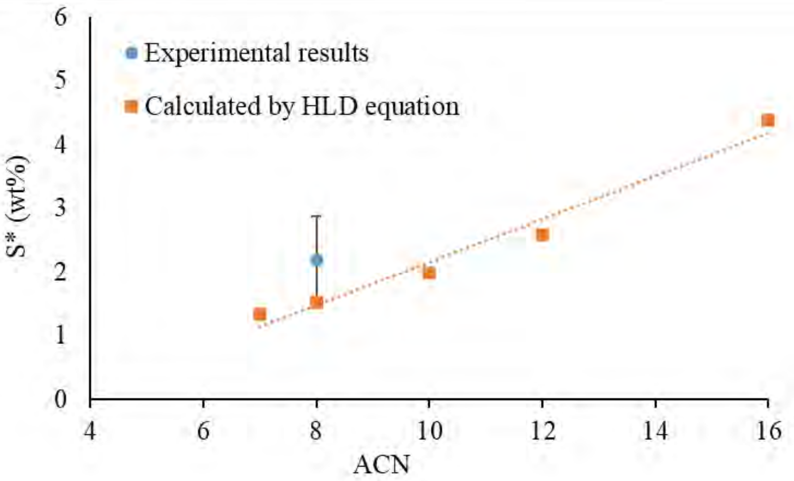


Figure 4.13 Comparison the optimal salinities of AOT: $C_{13}(EO)_4COO^-$ between experimental results and the theoretical HLD estimation with 7:3 molar ratio at 0.015 M total surfactant concentration with different alkane oils under room temperature (25±2 °C).

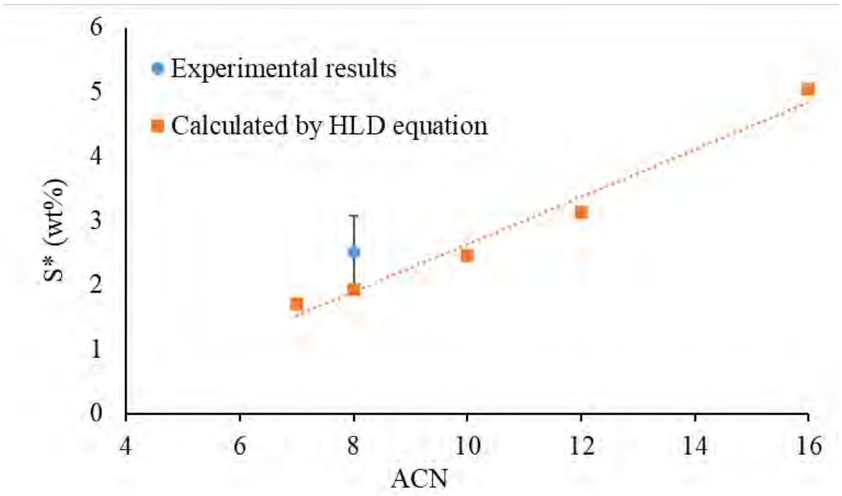


Figure 4.14 Comparison the optimal salinities of AOT: $C_{13}(EO)_6COO^-$ between experimental results and the theoretical HLD estimation with 7:3 molar ratio at 0.015 M total surfactant concentration with different alkane oils under room temperature (25±2 °C).

As note that the middle phase microemulsion could not observe at 5:5 molar ratio of binary surfactant system with $C_{13}(EO)_4COO^-$ and $C_{13}(EO)_6COO^-$. According to figure 4.11 to 4.14, the errors of deviation were 47.9, 23.6, 30.8 and 22.8, respectively. However, the reason for this deviation needs to further study.

4.3.3 Comparison of Cc Values Versus HLB Number

Davies's equation is a useful tool for indicating the hydrophilic and lipophilic balance for ionic surfactants (Davies, 1957) as shown in Eq. 4.5.

$$\text{HLB} = 7 + \sum(\text{hydrophilic groups}) + \sum(\text{lipophilic groups}) \qquad (4.5)$$

The Cc values of each surfactant were compared with the calculated HLB number as shown in Table 4.8.

Table 4.8 Comparison between the Cc values of $C_{13}(EO)_nCOO^-$ (n = 2, 4, 6) and the HLB value

Surfactants	No. of EO groups	Cc	HLB*
$C_{13}(EO)_2COO^-$	2	-1.45	21.7
$C_{13}(EO)_4COO^-$	4	-3.53	22.2
$C_{13}(EO)_6COO^-$	6	-4.64	23.1

* reported by Sasol North America company.

Table 4.8 shows the comparison between the Cc and HLB values for the carboxylate based extended surfactants. It can be observed that the more negative Cc value exhibits more HLB values. These results are consistent with the calculation from Eq. 4.5, the addition of one EO group increases HLB number with 0.33 (Davies, 1957).

4.4 Critical Micelle Concentration Measurement

In this study, the critical micelle concentrations (CMC) of single carboxylate based extended surfactant and their mixed surfactant system were observed to study the surface tension property. The surface tension of the surfactant system was measured using tensiometer (Kruss Easydyne, K100) at room temperature (25±2°C). The CMC value is determined using the plot between surface tensions and surfactant concentrations (Schramm, 2000). At the dilute surfactant concentration, the surfactant molecules accumulate at the surface of water and vapor phase that reduce the surface tension. As the concentration of surfactant increases, the surfactant molecules tend to adsorb at the surface until the surface is saturated by the surfactants. The surface tension cannot be reduced further above this concentration (Yue *et al.*, 2017).

4.4.1 Effect of pH on CMC

The presence of carboxylic acid as a head group make the surfactant sensitive to the changing of pH solution due to the degree of ionization (Chiappisi, 2017). The effect of pH on CMC of the carboxylate based extended surfactants was investigated. In this study, the surfactant solution was prepared at two different conditions of acid and base (pH = 3 and pH = 9) using KOH solution for adjusting pH of the solution.

The surface tension (γ) profiles and surfactant concentrations were plotted to describe the effects of pH on the surface tension properties at pH = 3 and pH = 9 as shown in Figures 4.15 and 4.16, respectively.

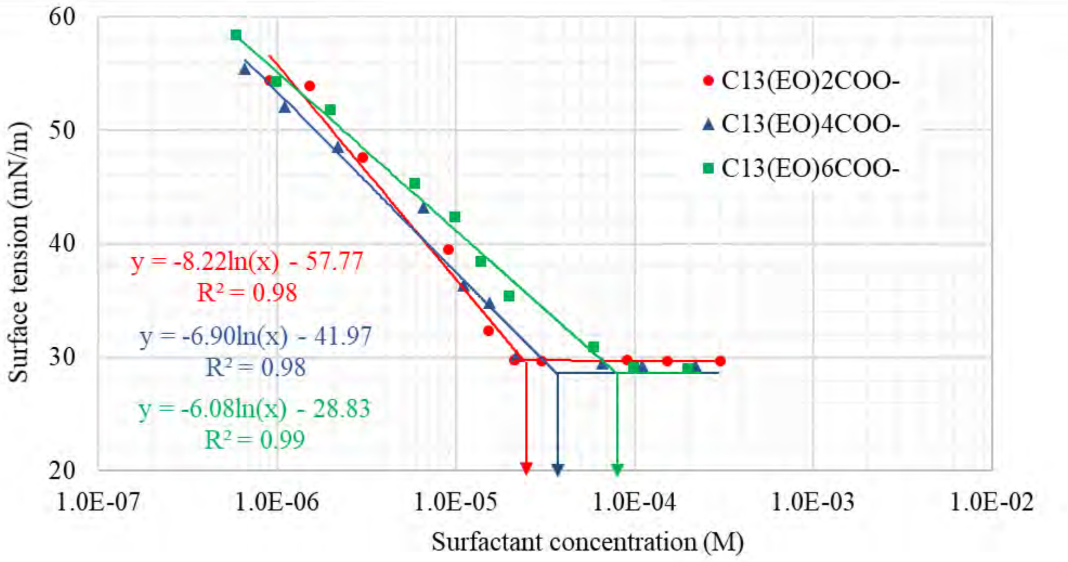


Figure 4.15 The surface tension of $C_{13}(EO)_nCOO^-$ at pH = 3 and room temperature (25±2°C).

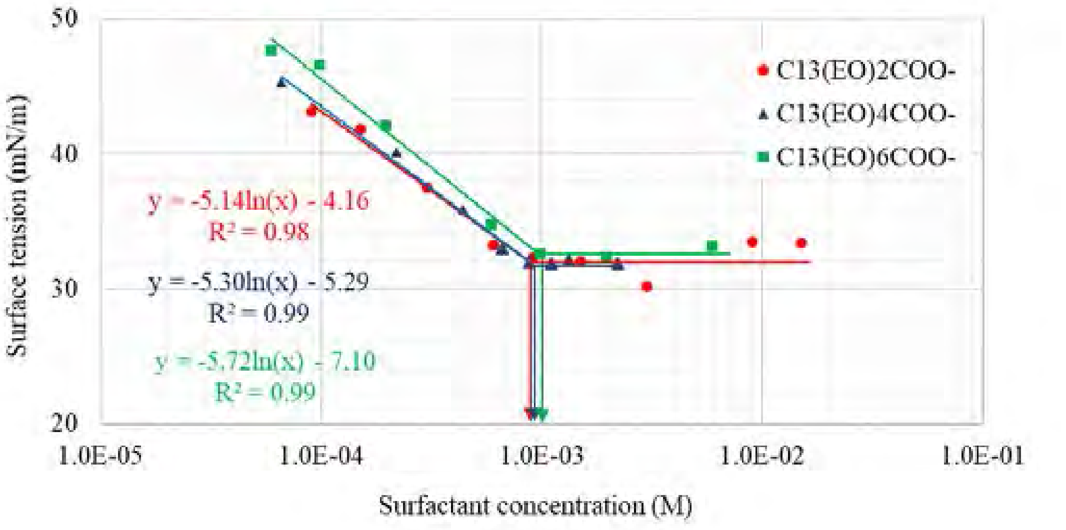


Figure 4.16 The surface tension of $C_{13}(EO)_nCOO^-$ at pH = 9 and room temperature (25±2°C).

Table 4.9 Summarize the CMC values of the carboxylate based extended surfactant at room temperature (25±2°C)

Surfactant	Number of EO groups	CMC (M)	
		pH 3	pH 9
$C_{13}(EO)_2COO^-$	2	2.23×10^{-5}	8.78×10^{-4}
$C_{13}(EO)_4COO^-$	4	2.70×10^{-5}	8.79×10^{-4}
$C_{13}(EO)_6COO^-$	6	6.63×10^{-5}	1.07×10^{-3}

As shown in Figures 4.15 and 4.16, the CMC is determined from the plot between surface tension and surfactant concentration, the transition point is defined as the CMC.

Table 4.9 shows the CMC values of carboxylate based extended surfactant with varying the pH of solution. It can be seen that the increasing pH causes the increase CMC value. This because of the increasing degree of ionization of carboxylic head group and hydrophilicity (Hussain *et al.*, 1997). The ionization of the head group causes an increase in the electrical charge repulsion. The carboxylate based extended surfactants act as a nonionic surfactant in acid solution (pH = 3) and an ionic surfactant in base solution (pH = 9). The CMC value of nonionic surfactants requires lower surfactant concentrations to form micelles because they are absent from the effect of electrical repulsion (Mandavi *et al.*, 2008).

4.4.2 Effect of Surfactant Structure

The CMC value of surfactant depends on the surfactant structure. The effect of surfactant structure on CMC value was studied using $C_{13}(EO)_nCOO^-$ (n = 2, 4, 6). In Table 4.9, the CMC of carboxylate based extended surfactants increases with an increasing number of EO groups. This is because an increasing ethylene oxide group or hydrophilic moiety increases in the repulsive forces (e.g., steric hindrance) involving in self-aggregate phenomena of the surfactant molecules that cause to an increase in CMC value (Rosen *et al.*, 2012).

In addition, the CMC of the binary surfactant system using AOT and $C_{13}(EO)_nCOO^-$ (n = 2, 4, 6) with 9:1 molar ratio at room temperature (25±2°C) was investigated. The surface tension (γ) profiles and surfactant concentrations were plotted to describe the effect of the binary surfactant system as shown in Figure 4.17 and Table 4.10.

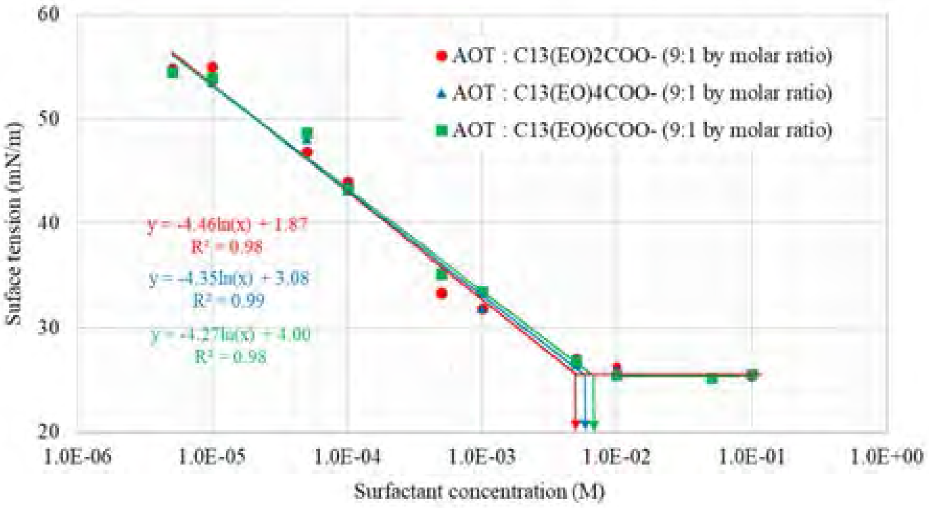


Figure 4.17 The surface tension profiles and molar concentration of AOT and $C_{13}(EO)_nCOO^-$ at pH 9 and room temperature (25±2°C).

Table 4.10 Summarize the CMC values of binary surfactant system with 9:1 molar ratio of AOT and $C_{13}(EO)_nCOO^-$ at pH 9 and room temperature (25±2°C)

Surfactants	No. of EO groups	Critical micelle concentration (M)
AOT : $C_{13}(EO)_2COO^-$	2	4.94×10^{-3}
AOT : $C_{13}(EO)_4COO^-$	4	5.62×10^{-3}
AOT : $C_{13}(EO)_6COO^-$	6	6.68×10^{-3}

Table 4.10 shows the CMC values of the mixed surfactant system with 9:1 molar ratio of AOT and $C_{13}(EO)_nCOO^-$ at room temperature (25±2°C). It can be noted that the CMC value of AOT was reported at 0.0022 M (Binks, 1993). Comparing between the surfactant system, all CMC values of the mixed surfactant system were larger than that of the single AOT and carboxylate based extended surfactant. This indicated that the mixture of binary anionic surfactants of AOT and $C_{13}(EO)_nCOO^-$ at 9:1 molar ratio exhibited antagonism or negative synergism (Rosen *et al.*, 2012).

4.5 Surfactant Adsorption

The surfactant adsorption is an important parameter for many applications such as cleaning, mineral flotation, dispersion, oil recovery and so on (Paria *et al.*, 2004). The surfactant adsorption is a process of transfer of surfactant molecules from the bulk solution phase to the interface (Lv *et al.*, 2011). For surfactant flooding, the surfactant adsorption does not only affect the surfactant efficiency but also affect the economic consideration due to the surfactant losses. Thus, the surfactant selection is an essential process for improving oil recovery.

The batch adsorption of carboxylate based extended surfactant onto the quartz sand surface was investigated in this study. The pH of the surfactant solution was adjusted by KOH to the controlled value at the solution pH of 9. This pH value was used to ensure a negatively charged surface of the quartz sand and the anionic carboxylate based extended surfactant. The surfactant concentration was analyzed using a total organic compound method (Shimadzu, TOCV-csh) at room temperature (25±2°C). The amount of adsorbed surfactant was calculated by the difference between the initial and final values of surfactant concentration as shown in Figure 4.18.

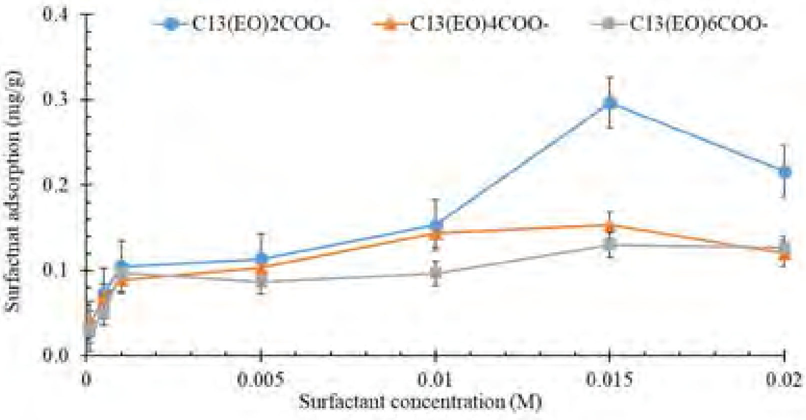
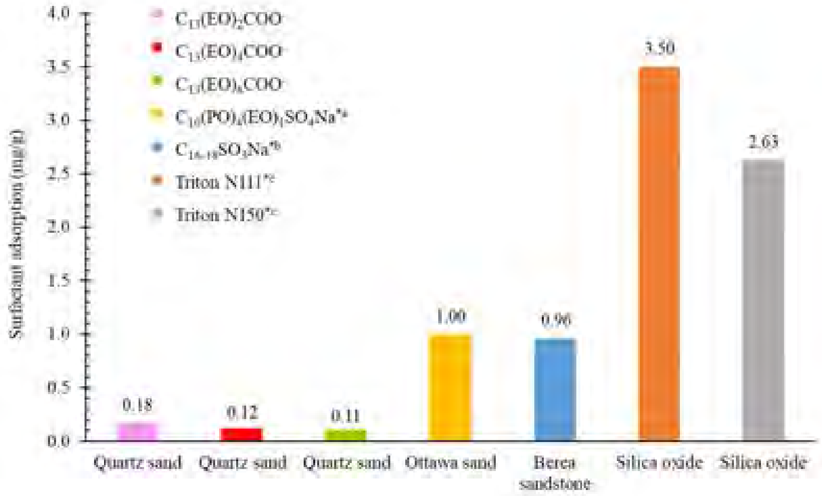


Figure 4.18 Adsorption isotherm of carboxylate based extended surfactant onto 3 g of quartz sand surface with 30 ml surfactant solution at room temperature (25±2 °C).

Figure 4.18 shows the surfactant adsorption of carboxylate based extended surfactant with the different number of EO groups (EO = 2, 4, 6) onto quartz sand surface. The results showed that the increasing surfactant concentration caused an increase surfactant adsorption because of the hydrogen bonding between oxygen atoms of ethoxylate molecule and hydroxyl groups on the solid surface at low surfactant concentration. When the surfactant concentration reaches to the CMC, an increase in surfactant concentration leads to the micellization, but the adsorbed surfactant onto the adsorbent is kept constant. However, the $C_{13}(EO)_2COO^-$ showed the maximum adsorption at 0.015 M and then slightly dropped after this point. It can be explained with the precipitation of surfactant molecules by multivalent ions exchanged from quartz sand and redissolution of the precipitate by micellar solution (Lv *et al.*, 2011).

Moreover, the effect of surfactant structure on surfactant adsorption was investigated. The result showed that increasing of EO groups in the surfactant molecule reduced the maximum surfactant adsorption capacity due to the higher area occupied per surfactant molecule (Lawrence *et al.*, 1987).



* reported by [a] Budhathoki *et al.* (2016),[b] Azam *et al.* (2013),[c] Lawrence *et al.* (1987)

Figure 4.19 The amount of adsorbed surfactant of carboxylate based extended surfactant with varying EO number at room temperature (25±2 °C).

Typically, the net surface charge of mineral oxides depends on pH, ionic strength and solution conditions (Robertson *et al.*, 1997). The point of zero charge (PZC) is defined as a pH value at which the zero charge on a solid surface. The net charge of surface exhibited as a positively and negatively charged surface at below and above PZC, respectively (Paria *et al.*, 2004). The PZCs of silica and alumina oxide were reported at 2-3 (Wang *et al.*, 2010) and 9.1 (Yopps *et al.*, 1964), respectively. In this study, the pH of the surfactant solution was adjusted to be pH = 9±0.5 to ensure a negatively charged of the quartz sand surface. Budhathoki *et al.* (2016) and Azam *et al.* (2013) investigated the surfactant adsorption onto Ottawa sand (99.77% SiO_2, 0.051% Al_2O_3 and 0.026% Fe_2O_3) and Berea sandstone at a neutral solution, respectively. The results were attributed to the electrostatic attraction of the anionic head group and positively charged surface, which resulted in the pH solution below their PZC. Moreover, Lawrence *et al.* (1987) studied the adsorption of nonionic surfactants onto silica oxide surface with a neutral solution at 45°C. They found that the surfactant adsorption occurred with the absence of electrostatic interaction and the amount of adsorbed surfactant increased with increasing temperature because of increasing their CMC value. However, the amount of carboxylate based extended surfactant adsorption is less than the other surfactants. Therefore, these surfactants could be an effective system in terms of preventing surfactant losses by the adsorption in reservoirs and improving the economic efficiency in EOR application.

CHAPTER V
CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The middle phase microemulsions were formed with the binary anionic surfactant system using sodium dioctyl sulfosuccinate (AOT) and carboxylate based extended surfactants with varying polyethylene oxide number (EO = 2, 4 and 6) as a primary and secondary surfactant, respectively at a mixing molar ratio of 5:5, 7:3 and 9:1. The microemulsion behavior exhibited the phase transition from Winsor type I to III (or middle phase) and to II for all surfactant system. As noted, the carboxylate extended surfactant alone tended to form a gel phase at the wide range of concentrations. The mixed surfactant systems showed that the decreasing fraction of the carboxylate based extended surfactant not only decreased the optimal salinity (S*) but also observed the more transparent middle phase. Interestingly, the optimal salinity of mixed surfactant system containing carboxylate extended surfactant is less than the previous study. The additional performance in terms of interfacial properties of the carboxylate extended surfactant are as following;

The increasing of EO groups in the extended surfactants increased the optimal salinity (S*) to obtain the middle phase microemulsion. These results can be described through Winsor R concept. The increasing EO groups increase the interaction forces between surfactant and water. Thus, the higher NaCl concentration was required to balance these interaction forces. Also, when the alkyl chain length of the alkane oil (ACN) increased, the addition of salt increased to form the middle phase.

The IFT values of the binary surfactant systems were in the range of 0.001-0.004 mN/m, which are an ultralow IFT (< 10^{-2} mN/m). The increasing of EO groups in the carboxylate extended surfactant significantly decreased the IFT value of the microemulsion system. This because the more EO groups can increase the interaction of the water phase, thus the proper surfactant orientation at the adsorbed interface (w/o) which is conversely proportional to the IFT values.

The HLD concept was applied to determine K and Cc values of the carboxylate based extended surfactant. The K and Cc values were in the range of 0.003 to 0.108 and -1.454 to - 4.640, respectively. More negative Cc value means that the carboxylate extended surfactant tends to form W/O microemulsions that were observed from the experiment with the more EO groups.

The batch adsorption study for the carboxylate based extended surfactant alone system onto the quartz sand surface was investigated. The increasing of EO groups in the extended surfactant molecule reduced the surfactant adsorption. This could be due to the coiling effect of the larger polyethylene oxide group. Therefore, the carboxylate based extended surfactant in the mixed surfactant system can be used as an alternative formulation for the economic viability of surfactant flooding in EOR technology.

5.2 Recommendations

Even though, the single carboxylate based extended surfactant forms a gel phase at the wide range of the concentrations, its mixture of the binary surfactant system especially for hydrophobic surfactant can be formulated to balance the interaction between surfactant-oil phase. Either the carboxylate extended surfactants with polypropylene oxide (PO) or the surfactant with long alkyl chain length could be used as an alternative option to form the microemulsion.

REFERENCES

Antonio, B.M.J. (2015). Characteristic Curvature Evaluation of Anionic Surfactants for Enhanced Oil recovery applications. Proceedings of the National Conference On Undergraduate Research (NCUR) 2015.

Attaphong, C., Do, L. and Sabatini, D.A. (2012). Vegetable oil-based microemulsions using carboxylate-based extended surfactants and their potential as an alternative renewable biofuel. Fuel 94, 606-613.

Azam, M.R., Tan, I.M., Ismail, L., Mushtaq, M., Nadeem, M. and Sagir, M. (2013). Static adsorption of anionic surfactant onto crushed Berea sandstone. Journal of Petroleum Exploration and Production Technology 3, 195-201.

Barnes, J.R., Smit, J.P., Smit, J.R., Shpakoff, P.G., H, K. and Puerto, M.C. (2008). Development of Surfactants for Chemical Flooding at Difficult Reservoir Conditions. Society of petroleum engineers.

Bera, A., Kumar, T., Ojha, K. and Mandal, A. (2014). Screening of microemulsion properties for application in enhanced oil recovery. Fuel 121, 198-207.

Binks, B.P. (1993). Emulsion type below and above the CMC in AOT microemulsion systems. Colloids and Surfaces 71, 167-172.

Bristol, U.o. (2017). "What Are Surfactants." from http://www.bristol.ac.uk/chemistry/research/eastoe/what-are-surfactants/.

Budhathoki, M., Barnee, S.H.R., Shiau, B.J. and Harwell, J.H. (2016). Improved oil recovery by reducing surfactant adsorption with polyelectrolyte in high saline brine. Colloids and Surfaces A: Physicochemical and Engineering Aspects 498, 66-73.

Budhathoki, M., Hsub, T.P., Lohateeraparpa, P., Robertsa, B.L., Shiaub, B.J. and Harwella, J.H. (2016). Design of an optimal middle phase microemulsion for ultra high saline brine using hydrophilic lipophilic deviation (HLD) method. Colloids and Surfaces A: Physicochemical and Engineering Aspects 488, 36-45.

Burguera, J.L. and Burguera, M. (2012). Analytical applications of emulsions and microemulsions. Talanta 96, 11-20.

Chiappisi, L. (2017). Polyoxyethylene alkyl ether carboxylic acids: An overview of a neglected class of surfactants with multiresponsive properties. Advances in Colloid and Interface Science 250, 79-94.

Chun, H. (1979). Interfacial tensions and solubilizing ability of a microemulsion phase that coexists with oil and brine. Journal of Colloid and Interface Science 71(2), 408-426.

Davies, J.T. (1957). A Quantitative Kinetic Theory of Emulsion type.I. Physical Chemistry of the Emulsifying Agent. Proceedings of 2nd International Congress Surface Activity.

Esmaeilzadeh, P., Hosseinpour, N., Bahramian, A., Fakhroueian, Z. and Arya, S. (2014). Effect of ZrO2 nanoparticles on the interfacial behavior of surfactant solutions at air–water and n-heptane–water interfaces. Fluid Phase Equilibria 361, 289-295.

Gudina, E.J., Rangarajan, V., Sen, R. and Rodrigues, L.R. (2013). Potential therapeutic applications of biosurfactants. Trends in Pharmacological Sciences 34(12), 667-675.

Gurgel, A., Moura, M.C.P.A., Dantas, T.N.C., Neto, B.E.L. and Neto, D.A.A. (2008). A review on chemical flooding methods applied in enhanced oil recovery. Brazilian Journal of Petroleum and Gas 2, 83-95.

He, Z.q., Zhang, M.j., Fang, Y., Jin, G.y. and Chen, J. (2014). Extended surfactants: A well-designed spacer to improve interfacial performance through a gradual polarity transition. Colloids and Surfaces A: Physicochemical and Engineering Aspects 450, 83-92.

Hirasaki, G.J., Miller, C.A. and Puerto, M. (2008). Recent Advances in Surfactant EOR. Society of petroleum engineers.

Hussain, A., Luckham, P.F. and Tadros, T.F. (1997). Phase behavior of pH dependent microemulsions at high temperature and high salinity. Institut Français du Pétrole 52, 228-231.

Jurgenson, G.A., Bittner, C., Kurkal, S. and Oetter, G. (2015). Alkyl Ether carboxylate surfactants for chemical enhanced oil recovery in harsh field conditions. Society of petroleum engineers.

Kohli, R. and Mittal, K.L. (2013). Developments in Surface Contamination and Cleaning. Oxford: Elsevier.

Lawrence, S.A., Pilc, J.A., Readma, J.R. and Sermon, P.A. (1987). Unexpectedly low extent of adsorption of non-ionic ethoxylated surfactants on alumina. Journal of the Chemical Society, 1035-1036.

Liu, X., Zhao, Y., Li, Q. and Niu, J. (2016). Surface tension, interfacial tension and emulsification of sodium dodecyl sulfate extended surfactant. Colloids and Surfaces A: Physicochemical and Engineering Aspects 494, 201-208.

Lv, W., Bazin, B., Ma, D., Liu, Q., Han, D. and Wu, K. (2011). Static and dynamic adsorption of anionic and amphoteric surfactants with and without the presence of alkali. Journal of Petroleum Science and Engineering 77(2), 209-218.

Malik, M.A., Wani, M.Y. and Hashim, M.A. (2012). Microemulsion method: A novel route to synthesize organic and inorganic nanomaterials. Arabian Journal of Chemistry 5(4), 397-417.

Mandavi, R., Santosh, K. and Rathore, N. (2008). Critical Micelle Concentration of Surfactant, Mixed Surfactant and Polymer By Different Methods at Room Temperature And Its Importance. Journal of Chemistry 24(2), 559-564.

Mohammed, M. and Babadagli, T. (2015). Wettability alteration: A comprehensive review of materials/methods and testing the selected ones on heavy-oil containing oil-wet systems. Adv Colloid Interface Sci 220, 54-77.

Negin, C., Ali, S. and Xie, Q. (2017). Most common surfactants employed in chemical enhanced oil recovery. Petroleum 3(2), 197-211.

Nguyen, T., Morgan, C., Poindexter, L. and Fernandez, J. (2018). Application of Hydrophilic-Lipophilic Deviation (HLD) Concept to Surfactant Characterization and Surfacant Selection for Enhanced Oil Recovey. Journal of Surfactants and Detergents, 1-36.

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.

Paria, S. and Khilar, K.C. (2004). A review on experimental studies of surfactant adsorption at the hydrophilic solid-water interface. Advances in Colloid and Interface Science 110(3), 75-95.

Perez, M.M., Alain, G., Lachaise, J. and Salager, J.L. (1995). Solubilization of polar oils with extended surfactants Colloids and Surfaces 100, 217-224.

Phan, T.T., Attaphong, C. and Sabatini, D.A. (2011). Effect of Extended Surfactant Structure on Interfacial Tension and Microemulsion Formation with Triglycerides. Journal of the American Oil Chemists' Society 88(8), 1223-1228.

Prakash, A.S. (2010). Selecting surfactants for the maximum inhibition of the activity of the multidrug resistance efflux pump transporter, P-glycoprotein conceptual development. Journal of Excipients and Food Chemicals 1(3), 51-59.

Quintero, L. and Carnahan, N.F. (2013). Microemulsions for Cleaning Applications. Developments in Surface Contamination and Cleaning**:** 65-106.

Qutubuddin, S., Miller, C.A. and Fort, T.J. (1984). Phase behavior of pH-dependent microemulsions. Journal of Colloid and Interface Science 101(1).

Rapp, B.E. (2017). Surface Tension. Microfluidics: Modelling, Mechanics and Mathematics**:** 421-444.

Robertson, A.P. and Leckie, J.O. (1997). Cation Binding Predictions of Surface Complexation Models Effects: of pH, Ionic Strength, Cation Loading, Surface Complex, and Model Fit. Journal of Colloid and Interface Science 188, 444-472.

Robertson, A.P. and Leckie, J.O. (1997). Cation Binding Predictions of Surface Complexation Models: Effects of pH, Ionic Strength, Cation Loading, Surface Complex, and Model Fit. Journal of Colloid and Interface Science 188, 444-472.

Rosen, M.J. and Kunjappu, J.T. (2012). Surfactants and Interfacial Phenomena. Canada: Jonh Wiley & Sons.

Salager, J.L., Antón, R.E., Sabatini, D.A., Harwell, J.H., Acosta, E.J. and Tolosa, L.I. (2005). Enhancing solubilization in microemulsions—State of the art and c urrent trends. Journal of Surfactants and Detergents 8(1), 3-21.

Salager, J.L., Forgiarini, A.M. and Bullo´n, J. (2013). How to Attain Ultralow Interfacial Tension and Three-Phase behavior with surfactant formulation for Enhanced Oil Recovery : A review. Part1 Optimum formulation for simple Surfactant-Oil-water ternary system. 16, 449-472.

Salager, J.L., Morgan, J.C., Schechter, R.S., Wade, W.H., SPE-AIME and VASQUEzt, E. (1979). Optimum Formulation of Surfactant/Water/Oil Systems for Minimum Interfacial Tension or Phase Behavior. Society of petroleum engineers 19(02), 107-115.

Santa, M., GmbH, C., Alvarez-Jürgenson, G., Birnbrich, P., GmbH, C. and Spindler, C. (2011). Sustainable Surfactants in Enhanced Oil Recovery. Society of petroleum engineers.

Santanna, V.C., Dantas, T.N.D.C. and Neto, A.A.D. (2012). The Use of Microemusion Systems in Oil Industry. Microemulsions - An Introduction to Properties and Applications**:** 161-174.

Satter, A., Ghulam, M., Iqbal and James, L., Buchwatter (2008). Practical Enhanced Reservoir Engineering. Oklahoma: PennWell.

Schramm, L.L. (2000). Surfactants Fundamentals and Applications in the Petroleum Industry. United Kingdom: Cambridge University.

Sharma, G., Hughes, B. and Mohanty, K.K. (2013). Wettability Alteration in High-Temperature and High-Salinity Carbonate Reservoirs. Society of petroleum engineers 18(04).

Sheng, J.J. (2015). Status of surfactant EOR technology. Petroleum 1(2), 97-105.

Shupe, R.D. and Maddox, J. (1978). Surfactant oil recovery process usable in high temperature, high salinity formation. United States Patent.

Tongcumpoua, C., Acostab, E.J., Quencerc, L.B., A.F. Josephc, Scamehornb, J.F., Sabatinib, D.A., Chavadeja, S. and Yanumeta, N. (2003). Microemulsion formation and detergency with oily soils: I. Phase behavior and interfacial tension. Surfactants and Detergents 6(3), 191-203.

Uchiyama, H., Acosta, E., Tran, S., Sabatini, D.A. and Harwell, J.H. (2000). Supersolubilization in Chlorinated Hydrocarbon Microemulsions: Solubilization Enhancement by Lipophilic and Hydrophilic Linkers. Industrial & Engineering Chemistry Research 39, 2704-2708.

Udeagbara, S.G. (2009). Effect of temperature and Impurities on surface tension of crude oil. Florida: Boca Raton.

Vatanparast, H., Alizadeh, A.H., Bahramian, A. and Bazdar, H. (2011). Wettability Alteration of Low-permeable Carbonate Reservoir Rocks in Presence of Mixed Ionic Surfactants. Petroleum Science and Technology 29(18), 1873-1884.

Wang, M. and Revil, A. (2010). Electrochemical charge of silica surfaces at high ionic strength in narrow channels. J Colloid Interface Sci 343(1), 381-386.

Winsor, P.A. (1947). Hydrotropy, solubilisation and related emulsification processes part I. Trans. Faraday Soc 44, 376-398.

Witthayapanyanon, A., Acostab, E.J., Harwell, J.H. and Sabatinia, D.A. (2006). Formulation of Ultralow Interfacial Tension system using Extended surfactant. Journal of Surfactants and Detergents 9, 331-339.

Witthayapanyanon, A., Harwell, J.H. and Sabatini, D.A. (2008). Hydrophilic-lipophilic deviation (HLD) method for characterizing conventional and e xtended surfactants. J Colloid Interface Sci 325(1), 259-266.

Yopps, J.A. and Fuerstenau, D.W. (1964). The zero point of charge of alpha-alumina. Journal of Colloid Science 19, 61-71.

Yue, X., Fan, X., Li, Q., Chen, X. and Wang, C. (2017). Aggregation behaviors of alkyl ether carboxylate surfactants in water. Journal of Molecular Liquids 227, 161-167.

Zhang, Q.Q., Cai, B.X., Xu, W.J., Gang, H.Z., Liu, J.F., Yang, S.Z. and Mu, B.Z. (2015). Novel zwitterionic surfactant derived from castor oil and its performance evaluation for oil recovery. Colloids and Surfaces A: Physicochemical and Engineering Aspects 483, 87-95.

APPENDIX

Appendix A Calculation of Solution Preparation

A1. Salt Solution Preparation

The microemulsion phase behavior was investigated with varying NaCl concentration to obtain the middle phase microemulsion. The example of calculation for salt solution preparation is shown below.

Assume 1000mL of 20 gNaCl/100mL solution

$$\text{Desired NaCl weight (g)} = \frac{\text{gNaCl}}{\text{100mL solution}} \times \text{Stock volume (mL)}$$

$$= \frac{\text{20gNaCl}}{\text{100mL solution}} \times \text{1000 mL solution}$$

$$= 20\text{ g}$$

Assume 2.5 mL of 2 gNaCl/100mL solution

$$\text{Stock solution volume} \times \frac{\text{gNaCl stock solution}}{\text{100mL solution}} = \frac{\text{Desired gNaCl}}{\text{100mL solution}} \times \text{Desired solution (mL)}$$

$$\text{Stock solution volume} \times \frac{\text{20 gNaCl stock solution}}{\text{100mL solution}} = \frac{\text{2 Desired gNaCl}}{\text{100mL solution}} \times 2.5\text{ mL}$$

$$\text{Stock solution volume} = 0.25\text{ mL}$$

A2. Surfactant Solution Preparation

In this study, the surfactant concentration was 0.015 M. The properties of surfactant are shown in Table A1

Table A 1 Properties of surfactant

Surfactant	Molecular weight	%active
AOT	444.5	97
$C_{13}(EO)_2COO^-$	332	90
$C_{13}(EO)_4COO^-$	456	90
$C_{13}(EO)_6COO^-$	508	90

Assume 250 mL of 0.015 M AOT solution

$$\text{Surfactant weight (g)} = \frac{0.015\text{ mol}}{\text{L}} \times \frac{\text{g Mw}_{\text{surfactant}}}{1\text{ mol}} \times \frac{1\text{ L}}{1000\text{ mL}} \times \frac{1}{\text{\%active}} \times \text{Stock Volume (mL)}$$

$$\text{Surfactant weight (g)} = \frac{0.015\text{ mol}}{\text{L}} \times \frac{444.5\text{ g Mw}_{\text{surfactant}}}{1\text{ mol}} \times \frac{1\text{ L}}{1000\text{ mL}} \times \frac{1}{0.97} \times 250\text{mL}$$

$$\text{Surfactant weight (g)} = 1.7184\text{ g}$$

Assume 250 mL of 0.015 M $C_{13}(EO)_nCOO^-$

$$\text{C13(EO)2COO - weight (g)} = \frac{0.015\text{ mol}}{\text{L}} \times \frac{332\text{ g}}{1\text{ mol}} \times \frac{1\text{ L}}{1000\text{ mL}} \times \frac{1}{0.9} \times 250\text{ mL} = 1.383\text{ g}$$

$$\text{C13(EO)4COO - weight (g)} = \frac{0.015\text{ mol}}{\text{L}} \times \frac{456\text{ g}}{1\text{ mol}} \times \frac{1\text{ L}}{1000\text{ mL}} \times \frac{1}{0.9} \times 250\text{ mL} = 1.9\text{ g}$$

$$\text{C13(EO)6COO - weight (g)} = \frac{0.015\text{ mol}}{\text{L}} \times \frac{508\text{ g}}{1\text{ mol}} \times \frac{1\text{ L}}{1000\text{ mL}} \times \frac{1}{0.9} \times 250\text{ mL} = 2.116\text{ g}$$

Appendix B Microemulsion Phase Behaviour Study

The microemulsion phase behavior was investigated as binary surfactant system using AOT and carboxylate based extended surfactant with varying polyethylene oxide number (EO = 2, 4 and 6) as a primary and secondary surfactant, respectively at 0.015 M total surfactant concentration in heptane, octane, decane, dodecane and hexadecane. Note that no middle phase microemulsion observed with hexadecane.

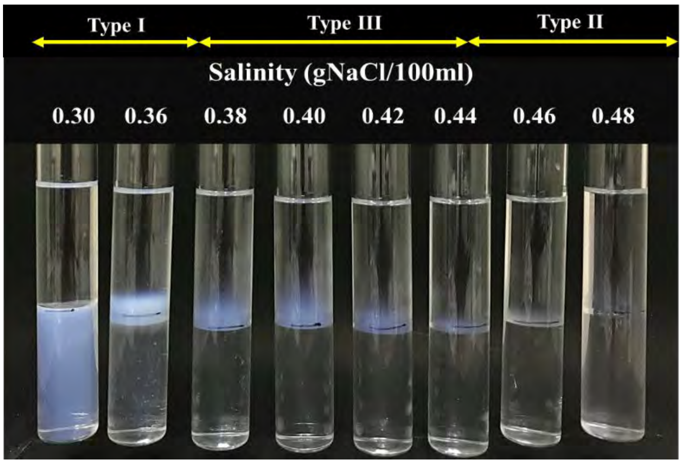


Figure B1 The microemulsion phase behavior of AOT : $C_{13}(EO)_2COO^-$ (9:1 by molar ratio) mixed surfactant system with heptane as an oil phase at 0.015 M total surfactant concentration under room temperature (25±2°C).

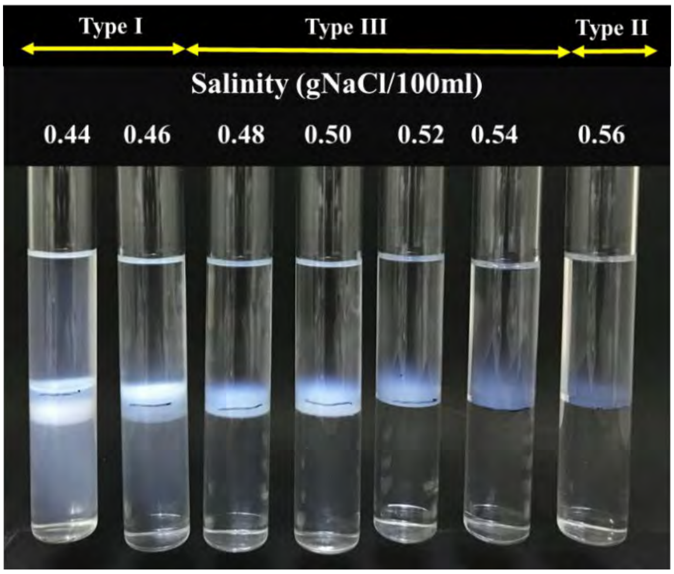


Figure B2 The microemulsion phase behavior of AOT : $C_{13}(EO)_4COO^-$ (9:1 by molar ratio) mixed surfactant system with heptane as an oil phase at 0.015 M total surfactant concentration under room temperature (25±2°C).

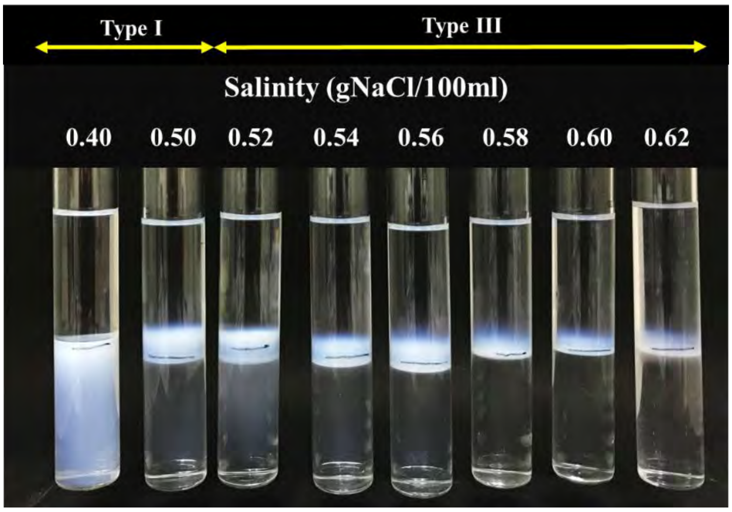


Figure B3 The microemulsion phase behavior of AOT : $C_{13}(EO)_6COO^-$ (9:1 by molar ratio) mixed surfactant system with heptane as an oil phase at 0.015 M total surfactant concentration under room temperature (25±2°C).

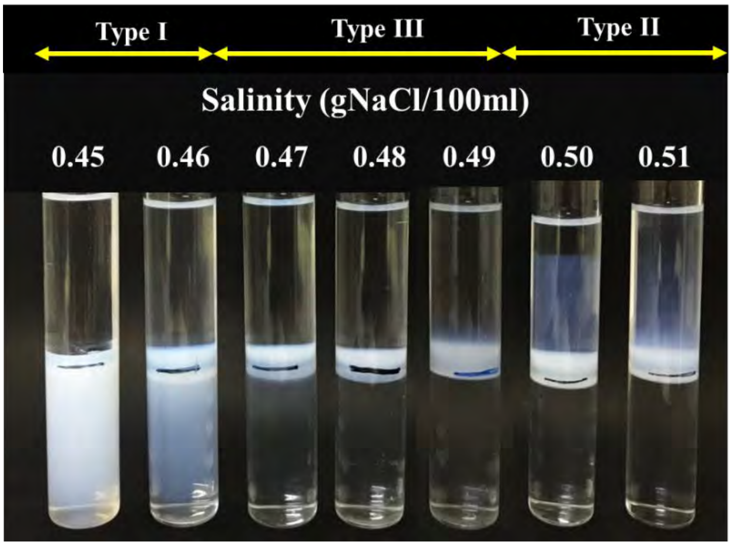


Figure B4 The microemulsion phase behavior of AOT : $C_{13}(EO)_2COO^-$ (9:1 by molar ratio) mixed surfactant system with octane as an oil phase at 0.015 M total surfactant concentration under room temperature (25±2°C).

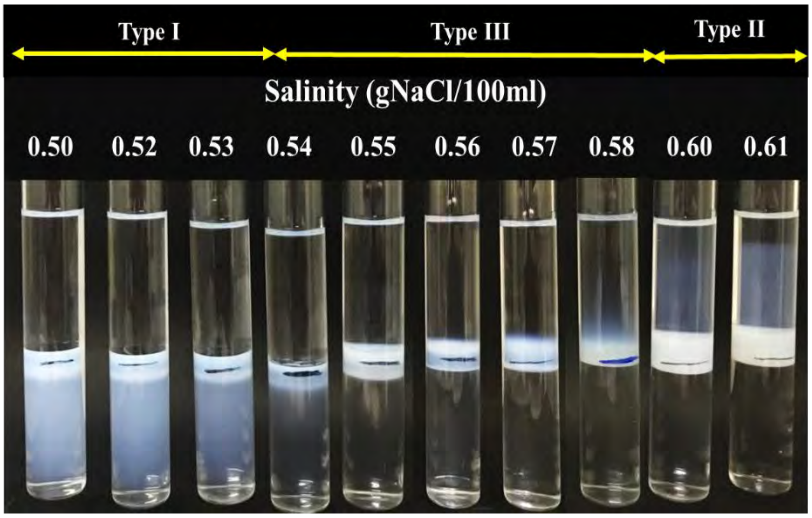


Figure B5 The microemulsion phase behavior of AOT : $C_{13}(EO)_4COO^-$ (9:1 by molar ratio) mixed surfactant system with octane as an oil phase at 0.015 M total surfactant concentration under room temperature (25±2°C).

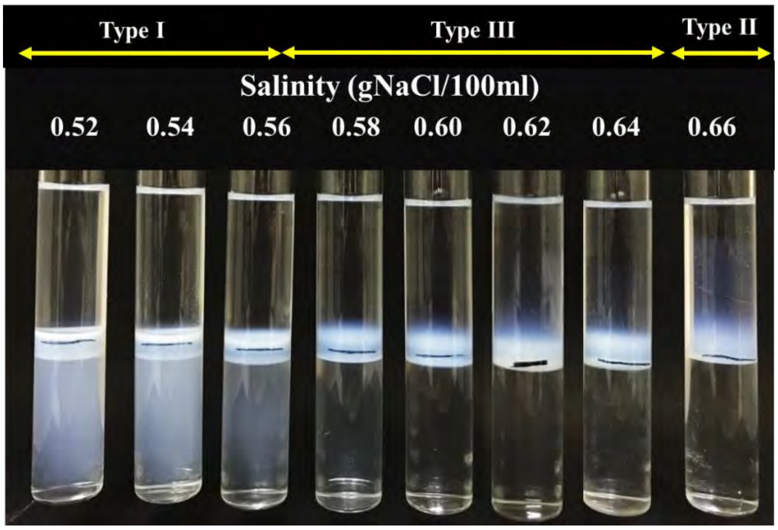


Figure B6 The microemulsion phase behavior of AOT : $C_{13}(EO)_6COO^-$ (9:1 by molar ratio) mixed surfactant system with octane as an oil phase at 0.015 M total surfactant concentration under room temperature (25±2°C).

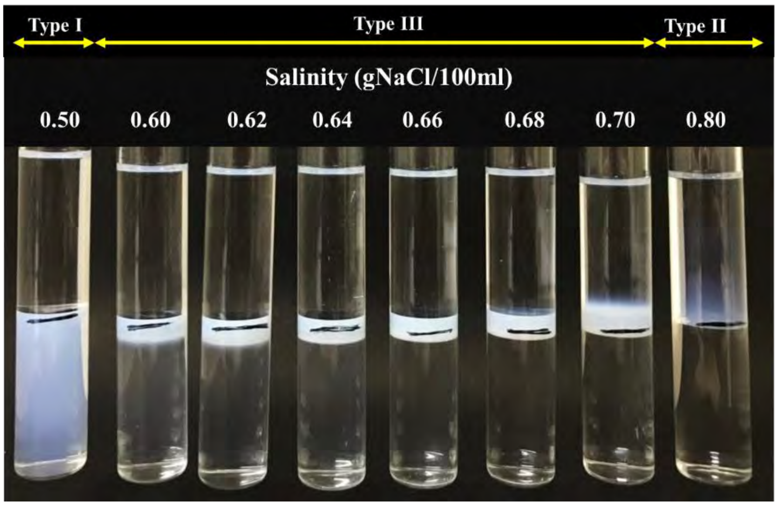


Figure B7 The microemulsion phase behavior of AOT : $C_{13}(EO)_2COO^-$ (9:1 by molar ratio) mixed surfactant system with decane as an oil phase at 0.015 M total surfactant concentration under room temperature (25±2°C).

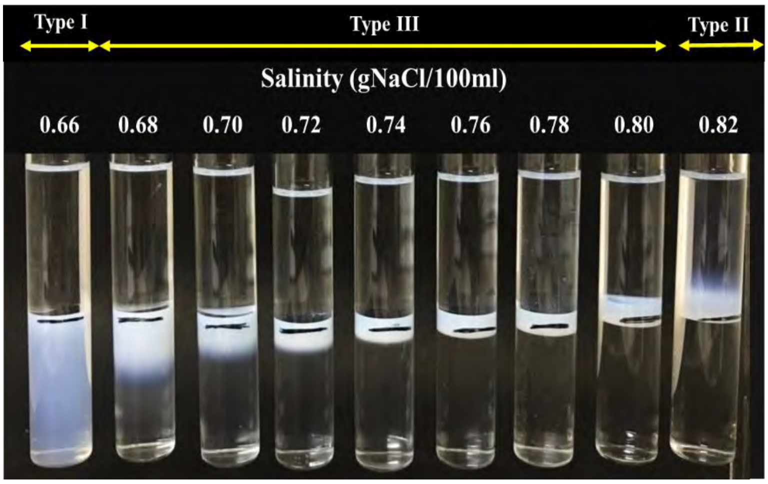


Figure B8 The microemulsion phase behavior of AOT : $C_{13}(EO)_4COO^-$ (9:1 by molar ratio) mixed surfactant system with decane as an oil phase at 0.015 M total surfactant concentration under room temperature (25±2°C).

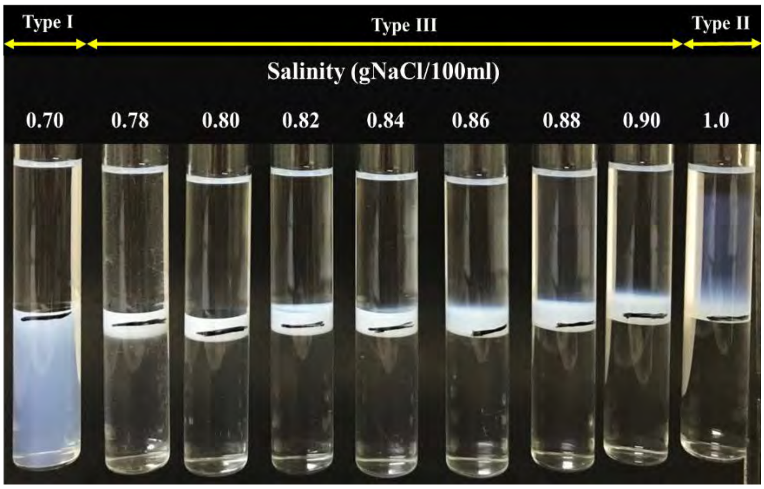


Figure B9 The microemulsion phase behavior of AOT : $C_{13}(EO)_6COO^-$ (9:1 by molar ratio) mixed surfactant system with decane as an oil phase at 0.015 M total surfactant concentration under room temperature (25±2°C).

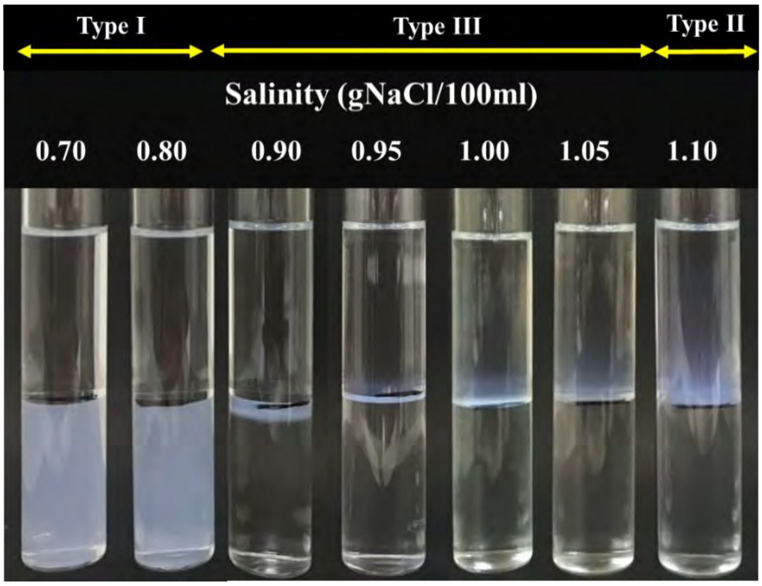


Figure B10 The microemulsion phase behavior of AOT : $C_{13}(EO)_2COO^-$ (9:1 by molar ratio) mixed surfactant system with dodecane as an oil phase at 0.015 M total surfactant concentration under room temperature (25±2°C).

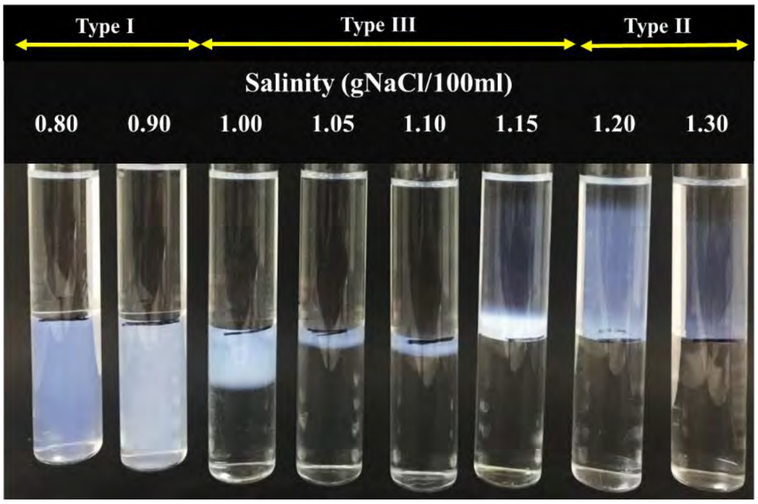


Figure B11 The microemulsion phase behavior of AOT : $C_{13}(EO)_4COO^-$ (9:1 by molar ratio) mixed surfactant system with dodecane as an oil phase at 0.015 M total surfactant concentration under room temperature (25±2°C).

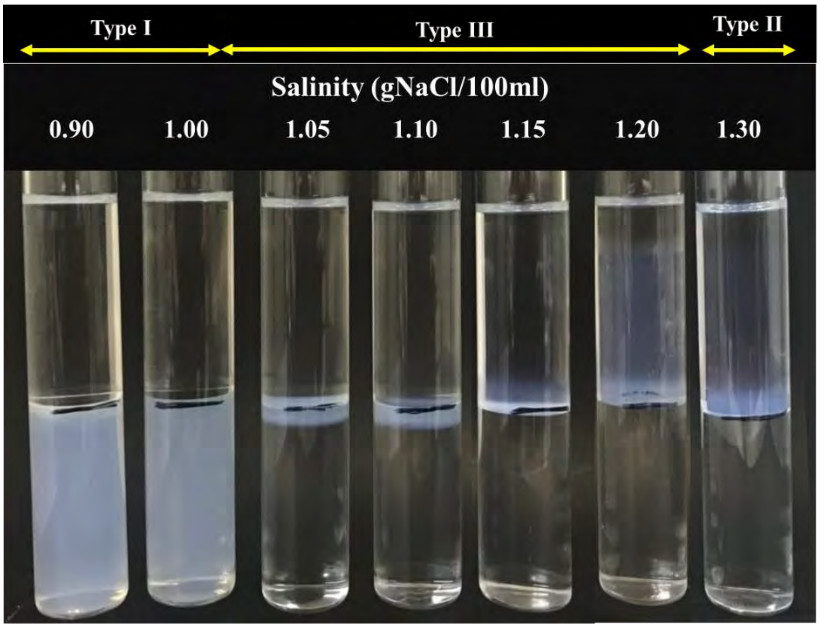


Figure B12 The microemulsion phase behavior of AOT : $C_{13}(EO)_6COO^-$ (9:1 by molar ratio) mixed surfactant system with dodecane as an oil phase at 0.015 M total surfactant concentration under room temperature (25±2°C).

Appendix C Surfactant Adsorption

The batch adsorption of carboxylate based extended surfactant onto quartz sand surface was investigated at pH 9 ± 0.5 and room temperature (25±2°C). The mixtures of 30 ml of surfactant solution and 3 g of quartz sand were shaken at 200 rpm for 24 hours and left them to equilibrium for 48 hours. The surfactant concentration was analyzed using total organic compound method (Shimadzu, TOCV-csh). The amount of adsorbed surfactant was calculated by a difference between the initial and final values of surfactant concentration by equation below;

$$\text{Amount of adsorbed surfactant} = \frac{(C_1\text{-}C_2) \times V}{m} \qquad (3.1)$$

where C_1 and C_2 are the surfactant concentration at before and after adsorption test, respectively. V is a volume of surfactant solution and m is mass of solid or adsorbent.

Table C1 Summarize the amount of adsorbed surfactant of carboxylate based extended surfactant onto quartz sand surface at pH 9 and room temperature (25±2 °C)

Surfactant	Equilibrium Concentration (M)	C_1 (mg/L)	C_2 (mg/L)	Adsorbed surfactant (mg/g)
$C_{13}(EO)_2COO^-$	0.0001	39.4	35.9	0.035
	0.0005	114.1	106.8	0.074
	0.001	238.7	228.2	0.105
	0.005	1065.7	1054.3	0.113
	0.01	2121.0	2105.7	0.153
	0.015	2557.0	2527.3	0.297
	0.02	2844.3	2822.7	0.217

Table C1 Summarize the amount of adsorbed surfactant of carboxylate based extended surfactant onto quartz sand surface at pH 9 and room temperature (25±2 °C) (Continued)

Surfactant	Equilibrium Concentration (M)	C_1 (mg/L)	C_2 (mg/L)	Adsorbed surfactant (mg/g)
$C_{13}(EO)_4COO^-$	0.0001	42.1	38.4	0.037
	0.0005	150.0	143.1	0.068
	0.001	256.3	247.4	0.089
	0.005	1532.7	1522.3	0.103
	0.01	2428.3	2414.0	0.143
	0.015	2721.7	2706.3	0.153
	0.02	2917.3	2905.3	0.120
$C_{13}(EO)_6COO^-$	0.0001	45.5	42.6	0.029
	0.0005	161.1	156.1	0.050
	0.001	311.5	301.8	0.097
	0.005	1675.7	1667.0	0.087
	0.01	2476.3	2466.7	0.097
	0.015	2845.3	2832.3	0.130
	0.02	3033.7	3021	0.127

CURRICULUM VITAE

Name:	Ms Suchawadee Kumkhuntod
Date of Birth:	May 24, 1995
Nationality:	Thai

University Education:

2017-2019 Master Degree of Petrochemical Technology, The Petroleum and Petrochemical College, Chulalongkorn University, Bangkok, Thailand

2013-2016 Bachelor Degree of chemical engineering, Mahidol university, Nakornpathom, Thailand

Work Experience:

2015	Position:	Trainee process engineer
	Company name:	TTCL public company limited

Proceedings:

1. Kumkhuntod, S., Charoensaeng, A., and Suriyapraphadilok, U., (2019, May 30) Novel Microemulsion Formation by the Hydrophilic-Lipophilic Deviation Concept using Carboxylate Extended surfactants for EOR application. Proceedings of The 25th PPC Symposium on Petroleum, Petrochemicals, and Polymers and The 10th Research Symposium on Petrochemicals and Materials Technology, Bangkok, Thailand.