

**DESIGNING BINARY LOW IFT SURFACTANT SYSTEM USING HLD  
CONCEPT FOR OIL RECOVERY**

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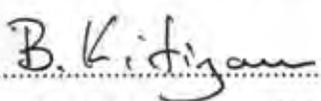
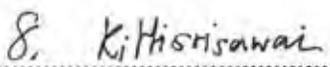
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**ABSTRACT**

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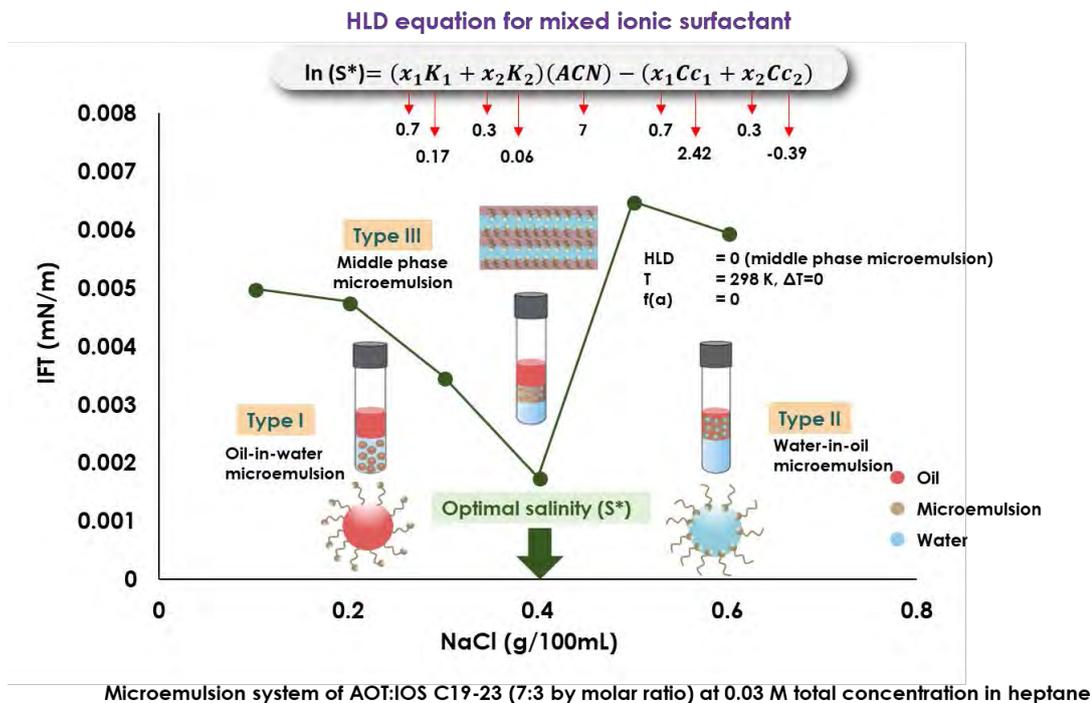
Surfactant-based microemulsion technology is widely used in tertiary enhanced oil recovery applications (EOR). The formulation of suitable surfactant system is a key success in production and economic feasibility of this technology. The middle phase or Winsor Type III microemulsions, employed for selecting appropriate surfactant system, can offer an optimal salinity at which the high oil solubilization capacity and minimum interfacial tension (IFT) or ultralow IFT ( $<0.01$  mN/m) are obtained. By this technology, more remaining oil in the reservoir can be solubilized and mobilized which leads to an improvement of oil recovery. This study aims to formulate surfactant systems for the oil recovery through microemulsion formulation. The novel mixed anionic surfactant system of a sodium dioctyl sulfosuccinate (AOT) and an internal olefin sulfonates (IOS) with different alkyl chain lengths (C15-18, C19-23, C24-28) were used due to its mixture avoiding the surfactant precipitation. The result found that the binary mixture of AOT and (IOS C15-18 and IOS C19-23) can form the middle phase at the mixing ratios of 5:5 to 9:1 (by molar ratio) with heptane and decane. When the fraction of IOS increased in the mixed AOT/IOS system, the optimal salinity ( $S^*$ ) also increased. For the effects of a carbon tail length of IOS surfactant was observed that the tail length increased with decreasing the optimal salinity. The hydrophilic-lipophilic deviation (HLD) for the mixed surfactant system was investigated to individually determine the  $K$  and  $C_c$  values for the IOS surfactants. The finding from this work provided a guide for surfactant selection through HLD concept to formulate microemulsion-based surfactant flooding for EOR application.

## บทคัดย่อ

ตุ๊กตา แจ่มประโคน : การออกแบบระบบสารลดแรงตึงผิวแบบสองตัวโดยใช้แนวคิดเฮชแอลดีสำหรับการผลิตน้ำมัน (Designing Binary Low IFT Surfactant System Using HLD Concept for Oil Recovery) อ. ที่ปรึกษา : ดร. อัมพิกา เจริญแสง, รศ.ดร.บอร์ เจียร์ เซาร์ และ ผศ.ดร. อุทัยพร สุริยาประภาติลก 74 หน้า

เทคโนโลยีไมโครอิมัลชันถูกนำมาใช้งานอย่างกว้างขวางในการผลิตน้ำมันขั้นตติยภูมิ (Tertiary enhanced oil recovery) ส่วนผสมของสารลดแรงตึงผิวที่เหมาะสมเป็นกุญแจสำคัญในด้านการผลิต ไมโครอิมัลชันวิภาคกึ่งกลาง (middle-phase microemulsion) หรือ วินเซอร์ (Winsor) ประเภทที่ 3 ถูกใช้เพื่อเลือกระบบสารลดแรงตึงผิวที่เหมาะสม โดยค่าเกลือที่เหมาะสม (optimal salinity) ซึ่งมีความสามารถในการละลายน้ำมันได้สูงสุด และมีค่าแรงตึงผิวระหว่างน้ำมันกับน้ำต่ำที่สุด เทคโนโลยีนี้ส่งผลให้น้ำมันส่วนที่ตกค้าง (remaining oil) สามารถละลายและเคลื่อนที่ออกจากแหล่งผลิตน้ำมันได้มากขึ้น จึงนำไปสู่การปรับปรุงการผลิตน้ำมันขั้นตติยภูมิให้มีประสิทธิภาพมากขึ้น งานวิจัยนี้มีวัตถุประสงค์เพื่อสร้างสูตรสารลดแรงตึงผิวสำหรับการผลิตน้ำมันขั้นตติยภูมิ โดยผ่านการก่อตัวแบบไมโครอิมัลชันระบบสารลดแรงตึงผิวชนิดประจุลบผสมกันแบบใหม่ (novel Mixed anionic surfactant system) ระหว่าง โซเดียมไดออกทิลซัลโฟซักซิเนต (Sodium dioctyl sulfosuccinate (AOT)) กับ อินเทอโนลโอเลฟินซัลโฟเนต (Internal Olefin Sulfonate (IOS)) ด้วยความยาวหางที่ต่างกัน (C15-18, C19-23, C24-28) ถูกนำมาใช้เนื่องจากสามารถหลีกเลี่ยงการตกตะกอนของสารลดแรงตึงผิวได้ โดยจากผล เราพบว่า ระบบสารลดแรงตึงผิวแบบผสม AOT และ (IOS C15-18 และ IOS C19-23) สามารถเกิดไมโครอิมัลชันวิภาคกึ่งกลางในอัตราส่วน 5: 5 ถึง 9:1 (อัตราส่วนโดยโมลาร์) ในเฮปเทน (heptane) และ เดกเคน (decane) เมื่ออัตราส่วนของ IOS มากขึ้นในระบบสารลดแรงตึงผิวแบบผสม ค่าเกลือที่เหมาะสม (optimal salinity) จะมากขึ้น ผลกระทบของการเพิ่มความยาวหางของสารลดแรงตึงผิว IOS พบว่าเมื่อความยาวหางมากขึ้น ค่าเกลือที่เหมาะสม (optimal salinity) จะน้อยลง สมการ (Hydrophilic-Lipophilic difference (HLD)) สำหรับระบบสารลดแรงตึงผิวชนิดประจุลบแบบผสม (mixed anionic surfactant) ถูกใช้กำหนดหาตัวแปรที่สนใจในการศึกษา คือ ค่า K และค่า Cc ของสารลดแรงตึงผิวประจุลบ (Internal Olefin Sulfonate (IOS)) การค้นพบจากงานนี้จะเป็นแนวทางไปสู่การใช้เลือกสารลดแรงตึงผิวที่เหมาะสม โดยผ่านวิธี HLD สำหรับการผลิตน้ำมันขั้นตติยภูมิ

## GRAPHICAL ABSTRACT



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## **CHAPTER I**

### **INTRODUCTION**

Crude oil reserve is a limited resource that naturally comes from organic materials comprising of hydrocarbons and other organic compounds. Crude oil is one of the foremost energy sources which most of their products are used to produce fuels such as gasoline, diesel, and valuable intermediate and downstream petrochemical products. In recent years, the demand for crude oils has rapidly been increasing due to the population growth. Primary and secondary recovery can recover the oils only about 20-40 percent of original oil in place (OOIP) while tertiary recovery well known as Enhanced Oil Recoveries (EOR) can recover crude oils about 30-60 percent of OOIP (Elmofty, 2012). The Enhanced Oil Recovery can be divided into three methods; thermal recovery, gas injection and chemical injection. Among those methods, the chemical injection can make desirable mobility ratio by way of improving the mobility ratio through substitution phase (water).

Surfactant flooding is the most extensively used method of chemical injections. In EOR application, the phase behavior in the reservoir is operated efficiently through the injection with surfactant formulations either single or mixed surfactant. The surfactants can create favorable conditions for solubilizing and mobilizing trapping oils, thus resulting in enhanced oil recovery.

Microemulsions are an isotropic transparent thermodynamically stable phase of oil (non-polar) and water (polar) which can be formed by the combination of surfactants with and without co-surfactant(s) that can reduce the interfacial tension (IFT) of the water and oil. Consequently, the residual oil is solubilized and mobilized by surfactant flooding that leads to improving oil recovery.

The formulation of appropriate surfactant systems for high brine conditions has been rising in attention due to most of the onshore and offshore reservoirs operating with brine and usable water source from the produced reservoirs such as seawater in the offshore. Because monovalent or divalent cations dissolved in the reservoir's water can make an improper environment for anionic surfactants that result in surfactant precipitation. Surfactant precipitation is a problem that can occur in high brine condition.

For improving surfactant formulations for EOR in high brine conditions, selecting surfactant systems should be carried out carefully with proper surfactant structures. Many of researchers have widely studied on optimum microemulsion formulations with different reservoir conditions.

Finally, this study aims to improve and develop surfactant system based on microemulsion formulation for the enhanced oil recovery application. A novel surfactant system is used to conduct the middle-phase scan study in different oil types. The mixed of anionic surfactant systems will be formulated by avoiding precipitation. The effects of oil types deviated by their EACN on middle phase behaviors are investigated. The Hydrophilic-Lipophilic Deviation (HLD) equation is used to estimate an optimal salinity at first, at which can form middle-phase microemulsions. The capability of the microemulsion formation through solubilization and interfacial tension are investigated at different surfactant structures and mixed molar ratios and salinities. In addition, the effect of mixed surfactant systems are investigated by measuring CMC of mixed surfactant systems.

## **CHAPTER II**

### **LITERATURE REVIEW**

#### **2.1 Enhanced oil recovery (EOR)**

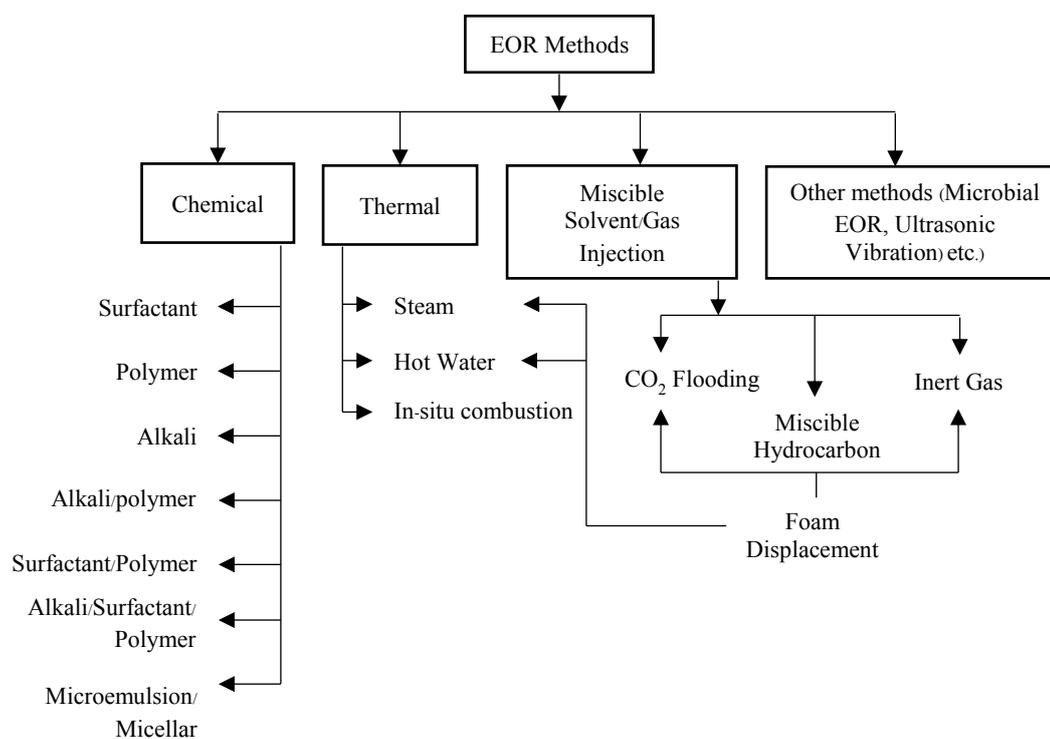
The energy demand is found by a global energy, which is undergoing the shift from the presently outstanding of fossil fuels to increase the balance of energy sources. Although the demand for crude oils has been increased for many years, discoveries of conventional oil fields are slow down. Normally, the oil production, called oil recovery is the hydrocarbon flow from the reservoir due to the pressure difference between the production well and reservoir. Oil recovery can be divided into three levels: primary recovery, secondary recovery and tertiary recovery. Primary recovery is the first step that oil can be produced by natural force with recovering 5-30 percent of the original oil in place (OOIP). Then, Secondary recovery is usually applied after primary recovery decreases and can improve recovering up to 20-35 percent of the OOIP. Both primary and secondary recovery have still remained crude oil in the reservoir

Therefore, several advanced technologies have been developed to improve the yield of recovered oil, which known as enhanced oil recovery (EOR) or Tertiary recovery methods that can produce oil up to 30-60 percent of the OOIP or more. The EOR or Tertiary recovery is the technique or process, which is an important method to increase the amount of crude oil. There are three main categories of enhanced oil recovery (EOR) as follows;

- Thermal recovery method implicates with the established heat such as injection of steam, which can decrease the viscosity of the crude oil and then increase the mobility of residual oil. If the oil mobility increases, the mobility ratio will approach the more desirable displacing process.

- Gas injection method utilizes gases for instance hydrocarbon, nitrogen, carbon dioxide (CO<sub>2</sub>) or other gases. They can be expanded in the reservoir to drive supplementary oil from the reservoirs to the production wellbores and can be dissolved the oil in the reservoir for creating less viscosity and enhancing flow rate of oil.

- Chemical injection is to create the desirable mobility ratio by way of adapting mobility through substituting phase (water). The methods of chemical injection are classified into three methods that are polymer flooding, alkali flooding, alkali/polymer flooding and surfactant flooding. Polymer and surfactant flooding create the emulsion, which hydrocarbon molecules in the reservoir are dispersed in aqueous phase. Alkaline flooding utilizes KOH or NaOH to inject into the reservoir for producing surfactant by reaction with organic acids that are naturally existed in the reservoir. This work focuses on the surfactant flooding which is one of the chemical injections.



**Figure 2.1** Categories of Enhanced Oil Recovery methods (Bera and Mandal, 2014).

### 2.1.1 Surfactant flooding

Surfactant flooding is EOR method. The phase behavior in reservoirs is operated through the injection by either single or mixed surfactant system. It can create favorable conditions for trapping oil. Surfactant systems together with the crude oil can create microemulsions with crude oil and water. The residual oil is mobilized by surfactant flooding; therefore, it can improve the volume of their efficiency. Surfactant flooding is a challenging area due to many factors affecting such as types of surfactants, mixed surfactant systems, oils, brines, rocks or media and conditions in the reservoir. The surfactant must be enduring and active in severe reservoir conditions such as high pressure, temperature and brine condition. Surfactant flooding is one of the remarkable enhance oil recovery methods because of the unique characteristics of surfactants including wettability to modification of oil-wet rocks and interfacial tension (IFT) reduction between oil and water. At undesirable conditions, surfactant flooding has considerable concerns in environmental and economic perspectives.

The factors in surfactant flooding have been deliberated in EOR, are the capillary number and mobility ratio (Daghlian Sofla *et al.*, 2016). First, the capillary number is a factor associating with the residual oil saturation. The addition of surfactants can create the microemulsions which lead to the reduction of the oil/water interfacial tension (Sheng, 2015). Second, mobility ratio for enhanced oil recovery is the association of the related permeability for water to oil ratio (Muggeridge *et al.*, 2014). Mobility ratio can be enriched by removing the residual oil in the reservoir, enlarging oil permeability and reducing water permeability. At the same time, the IFT is reduced by adsorbed surfactant molecule at the movement of oil efficiently (Sheng, 2015)

## 2.2 Surfactants

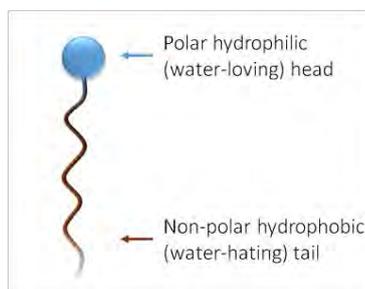
### 2.2.1 Definition Structure and Types

A surfactant is well known as a surface active agent that is favorable to adsorb or accumulate at the surface or interface. It can create a new molecular surface, which can bring about a significant alteration in the surface or interfacial tension (IFT). Thus it can lead to resist the rupture by stabilizing the thin film (Berg, 2010).

Surfactants are amphiphilic molecules composing of two parts; a hydrophilic head, which is soluble in water and has a polar that is a cationic, anionic, dipolar, or nonpolar type and a hydrophobic tail, which is soluble in liquid phases and is typically composed of a straight or branched hydrocarbon chain (Berg 2010).

The lowering surface tension or interfacial tension is one of the surfactant properties. The area between a condensed phase and gas phase is called surface area such as solid-air, or liquid-air, but the area between two condensed phases can be called interface area such as solid-solid, and liquid-liquid. Millinewton per meter (mN/m) is the unit of the surface and interfacial tension (IFT).

Surfactant molecules in the solution can self-assemble into a group so called a micelle. Critical micelle concentration (CMC) is the minimum surfactant concentration to form the first micelle. The surface tension (SFT) or interfacial tension (IFT) will be reduced until the first micelle is formed and then will become a constant at higher concentration. Above the CMC, the oil solubilization increases as the surfactant concentration increases. The factors affecting a CMC value are surfactant structure, temperature, salinity, and alcohol (co-solvent). The higher oil solubility can be achieved by increasing temperature, salinity, and alcohol concentration.



**Figure 2.2** Surfactant structure([www.bristol.ac.uk/chemistry/research/eastoe/what-are-surfactants/](http://www.bristol.ac.uk/chemistry/research/eastoe/what-are-surfactants/)).

Surfactants can be classified into four types, which depend on the nature of the head group.

- Anionic surfactants

Sulfate, sulfonate, carboxylate, and phosphate are the polar head groups, which can be found in anionic surfactants. Anionic surfactants are utilized more than other surfactant types and are mostly utilized in detergent formulation. The main cause of attracting is that they are inexpensive. The cations that are generally used as counterions are alkaline metals such as  $\text{Na}^+$ ,  $\text{K}^+$ . Negative charges are carried by the surface active portion such as detergents, soaps, foaming agents, etc.

- Cationic surfactants

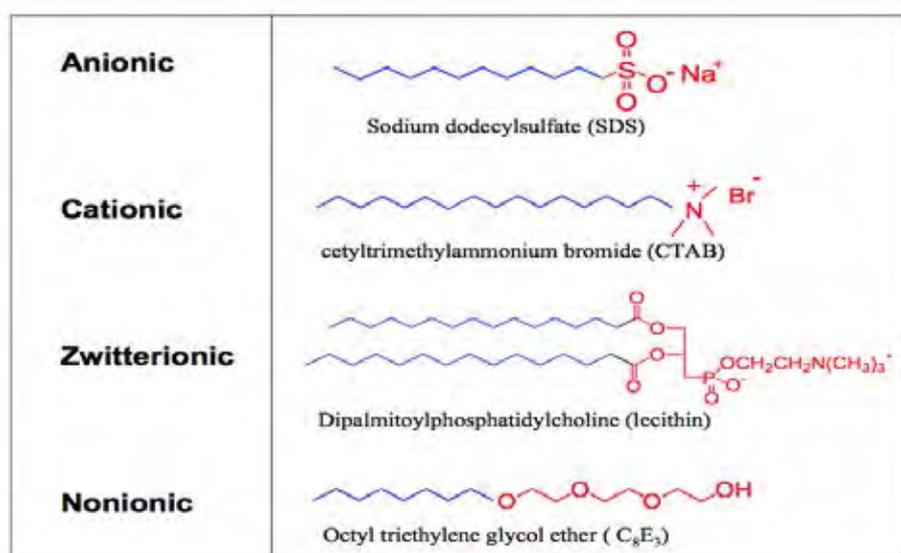
Cationic surfactants are not usually used because they are more expensive than others. Nitrogen atoms are used widely for the counterion parts in the cationic surfactants that are carried cationic charge. Cationic surfactants are generally utilized for softeners, bactericide and anticorrosion materials.

- Zwitterionic or Amphoteric Surfactants

Zwitterionic or amphoteric surfactants consist of two different groups that are anion and cation portion. As the cation portion (positive charge) uses ammonium, an anionic portion (negative charge) is varied such as sulfobetaine, amino acid and phospholipids.

- Nonionic surfactant

The second widely used surfactant type is nonionic surfactants. Nonionic surfactants are utilized in many applications, such as detergents, wetting agents, etc. Nonionic surfactants are non-association groups that mean no charge in the hydrophilic (head) part). Many hydrophilic parts of nonionic surfactants are ethoxylate, polypropylene glycol, diethanolamine, polyether, alcohol, amide group, etc. Hydrophilic compounds are generally discovered in the nonionic surfactants which are ethylene oxide ( $C_2H_4O$ ), propylene oxide ( $CH_3CHCH_2O$ ), or association between ethylene oxide and propylene oxide.



**Figure 2.3** Surfactant classification according to the nature of the hydrophilic group and examples. The red colored part represents the hydrophilic head and the blue colored part represents the hydrophobic chains of the surfactant. (Harsha Mohan Paroor, 2012).

**Table 2.1** Hydrophilic compounds of each surfactant type

Surfactant type	Hydrophilic compound	Structure
Anionic	Sulfate	$-\text{OSO}_2\text{O}^-$
	Sulfonate	$-\text{SO}_2\text{O}^-$
	Ether sulfate/ Alkyl ethoxy ester sulfate	$-(\text{O}-\text{CH}_2-\text{CH}_2)_n-\text{O}-\text{SO}_2\text{O}^-$
	Ether phosphate	$-(\text{CH}_2-\text{CH}_2\text{O})_n-\text{P}(\text{O})\text{O}^-$
	Ether carboxylate	$-(\text{CH}_2-\text{CH}_2\text{O})_n-\text{CO}_2^-$
	Carboxylate	$-\text{C}(\text{O})\text{O}^-$
Cationic	Primary ammonium	$-\text{N}^+\text{H}_3$
	Secondary ammonium	$-\text{N}^+(\text{R})\text{H}_2$
	Tertiary ammonium	$-\text{N}^+(\text{R})_2\text{H}$
	Quaternary ammonium	$-\text{N}^+(\text{R})_3$
Zwitterionic	Amine oxide	$-\text{N}^+(\text{R})_3\text{O}^-$
	Betaine	$-\text{N}^+(\text{R})_3(\text{CH}_2)_n\text{C}(\text{O})\text{O}^-$
	Aminocarboxylates	$-\text{N}^+\text{H}(\text{R})_3(\text{CH}_2)_n\text{C}(\text{O})\text{O}^-$
Nonionic	Polyoxyethylene/ ethoxylate/ ethoxylated alcohols	$-(\text{O}-\text{CH}_2-\text{CH}_2)_n-\text{OH}$
	Acetylenic	$-\text{CH}(\text{OH})\text{C}\equiv\text{CH}(\text{OH})-$
	Monoethanolamine	$-\text{NHCH}_2\text{CH}_2\text{OH}$
	Polyoxypropylene/ Polypropylene glycol	$-\text{H}-(\text{CH}_3\text{CHCH}_2\text{O})_n-\text{OH}$

**Table 2.2** Example of surfactants that used in EOR applications (Negin *et al.*, 2017)

Types	Common use in surfactant EOR process
Anionic surfactant	Alkyl Aryl Sulfonates, Alkyl Benzene Sulfonate, Alkyl Sulfate, N-Ethoxy Sulfonate, Sodium Dodecyl Sulfate, Alcohol Propoxy Sulfate, Alpha-Olefin Sulfonate, Alpha-Olefin Sulfate, Alkyl Ethoxy Sulfate, Sodium Petroleum Sulfonate, Gemini Anionic Surfactant
Nonionic surfactant	Alkyl Ethoxy Carboxylated, Alkyl Polyglycoside, Neodol, Tweens, Spans, Tridecyl Alcohol, Triphenylmethane
Cationic surfactant	Cetyl Trimethyl Ammonium Bromide, Dodecyl Trimethyl Ammonium Bromide, Ethoxylated Alkyl Amine

### 2.2.2 Surfactant Properties in EOR

#### - Critical Micelle Concentration (CMC)

At the high concentration of the surfactant solution, surfactant molecules will self-assemble to form spherical aggregate structure, which is so called micelle. The critical micelle concentrations (CMC) are the lowest concentration of surfactants that the first micelle structures are formed.

#### - Interfacial tension (IFT)

Interfacial tension (IFT) is studied as the free energy per unit surface area. This parameter is advantageous for enhanced oil recovery. The parameters, which affect in the interfacial tension between the non-polar and polar group for EOR methods, are oil type, surfactant type and concentration, water-oil ratio in mixed surfactant condition, brine or electrolyte, temperature and pressure. Surfactant concentration and brine (salinity) are more influential than other parameters. The lowest interfacial tension can be generated by adding the proper surfactant concentration that is more than its CMC and the suitable salinity, which is called an optimal salinity.

#### - Solubility

The solubility is important for microemulsion formation of surfactant. The surfactant solubility is depended on structure and micelle solubility. It is different in the ionic and nonionic surfactant systems. The solubility of ionic surfactant increases with increasing temperature. On the other hand, nonionic surfactants generally comprise of ethoxylate group that leads to decrease in the solubility with increasing temperature.

#### - Krafft point

Krafft point is the significant property of ionic surfactants. The solubility of ionic surfactants is increased by increasing temperature. Krafft point is the minimum temperature for each surfactant to generate micelle structure. The temperature at which is less than the Krafft point temperature is worthless because it cannot generate micelle. If the temperature of the system is reduced below this point, the concentration of surfactant in the system will be less than critical micelle concentration (CMC). This condition will affect the solubility of surfactant.

### **2.3 Crude oil**

Crude oil is an important resource, which used widely for many applications. The crude oils contain wide range of compositions, which are light to heavy crude oil, a combination for the various atoms such as nitrogen, oxygen and sulfur and traces of metal such as nickel and vanadium. Therefore, the characteristics of each crude oil should be specified for proper refinery process.

Crude oils consist of hydrocarbon components and other organic compounds (e.g. metallic elements). The characteristics of crude oils are different based on boiling point (i.e. density, viscosity, volatility and color). The crude oils are classified into four classes.

**Table 2.3** Types of crude oils with API (American Petroleum Institute) gravity

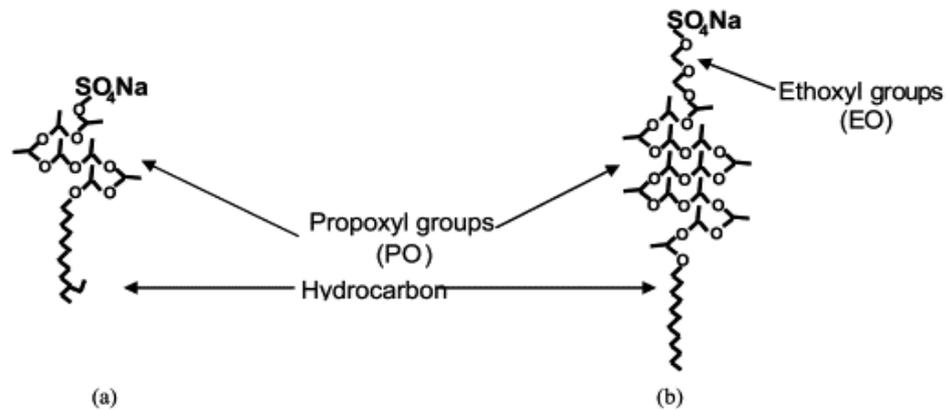
<b>Oil class</b>	<b>°API</b>
Light	°API < 31
Medium	22 < °API < 31
Heavy	10 < °API < 22
Extra-heavy	°API < 10

Table 3 exhibits the type of crude oils, which are light, medium, heavy and extra-heavy crude oil according to API.

The light compound in crude oils is mainly methane (CH<sub>4</sub>) or one carbon atom (C1). The compositions of crude oil can extend to C200. Nevertheless, crude oils with C7 and heavier fractions (C7+) are generally more complex than light fractions (methane, ethane, propane and others) (Tharanivasan, 2012). The C7+ fractions can be investigated as the heavy and extra-heavy fractions, which are not easy to separate from conventional oil refinery process.

#### **2.4 Extended surfactant**

The extended surfactants are a new class of surfactants that have intermediate polar groups (i.e., polypropylene oxides and polyethylene oxides), added to the hydrophilic (head) and hydrophobic (tail) part of the surfactant molecule. They are interesting for microemulsion systems because they can improve both hydrophilic and hydrophobic interaction of the oil and water interface film. Thus, the presence of intermediate group can enhance the surfactant properties by creating ultralow of interfacial tension (IFT) and reduction in an optimal salinity that leads to higher oil solubility (Witthayapanyanon *et al.*, 2008).



**Figure 2.4** The structure of extended surfactants, (a)  $R-(PO)_x-SO_4Na$ , (b)  $R-(PO)_y-(EO)_2-SO_4Na$  (Witthayapanyanon *et al.*, 2008).

## 2.5 Mixed surfactant

Mixed surfactant systems are the combination of the conventional or primary surfactant with additional surfactants to improve the efficiency of the surfactant system. The mixed surfactant can increase the oil solubility in the systems (Schlumberger, 2015).

The alcohols are used as a co-surfactant that can facilitate the primary surfactant forming micelles at lower surfactant concentration. It can improve phase behavior and operate under the amount of brine or hydrocarbon (oil) in the systems that lead to forming microemulsions. The viscosity of the oil can enhance by a suitable co-surfactant or mixed surfactant for mobility control. Association between mixed surfactant system and several parameters including electrolyte, oil (hydrocarbon) type, temperature and pressure have been investigated for formulating microemulsion systems.

Binary mixtures of extended surfactants and ethoxy sulfate surfactant have been investigated for high brine conditions in EOR. Extended surfactants with polypropylene oxide (POs) or polyethylene oxides (EOs) or combination between polyethylene oxides (EOs) and polyethylene oxides (POs) added between the hydrophilic (head) parts and lipophilic (tail) parts which bring about enhancing

surfactant systems. The method for selecting an optimal middle phase microemulsion is known as Winsor's R ratio. For Winsor's R ratio, Type III (middle phase). The Winsor R is termed as the equal of solubilized oil and water that leads to having the lowest IFT and improving surfactant-oil and surfactant-water interaction. The conventional surfactants (SDS, SDBS) may be lost water solubility due to increasing hydrophobic (tail) part and are not satisfying for enhanced oil recovery processes. On the other hand, the extended surfactants can sustain great interactions of water and oil phase and can create an ultralow interfacial tension without losing water solubility because of the available of polar groups such as polypropylene oxide (POs) or polyethylene oxide groups (Budhathoki *et al.*, 2016).

Sodium alkyl ethoxy sulfates, an extended surfactant, presented great results in high brine conditions for EOR application. This surfactant group was utilized as a co-surfactants or additional surfactant in mixed surfactant system to improve oil recovery (Budhathoki *et al.*, 2016).

Acharya and coworkers (2016) studied the effect of co-surfactants or co-solvents using iso-butanol (branch alkyl chains) and n-butanol for forming microemulsion systems. The system consisted of the mixtures of diesel and kerosene at varying part as the oil phase and non-ionic surfactant (Tween-80), co-solvents (alcohols) and water as the aqueous phase. They found the branch of alkyl chains (iso-butanol) as a co-surfactants or co-solvents showed that the inappropriate formation of microemulsion systems because they did not create strong intermolecular cohesive forces and the short alkyl chain in their structure can lead to ineffective molecules.

They also found that the mixture of surfactants has been used in surfactant flooding process to improve oil-recovery ability because the synergism of the binary surfactant system can facilitate the surfactant behavior to stabilize the aqueous and oil phases. Surfactant types, oil types, brine conditions, temperatures and pressures were considered for optimal phase behavior. Mixing surfactants were interesting to comprehend the effectiveness of mixed surfactants on the phase behavior. The mixing rules should properly blend for the formulation of the microemulsion systems with an ultralow IFT. The combinations of anionic with non-ionic surfactants are widely utilized for the mixing rules. These combinations are more advantageous for high brine conditions than single anionic surfactants that are sensitive to brine conditions.

However, the binary surfactant system contains a non-ionic surfactant need to consider the effect of temperature because it affects the surfactant property.

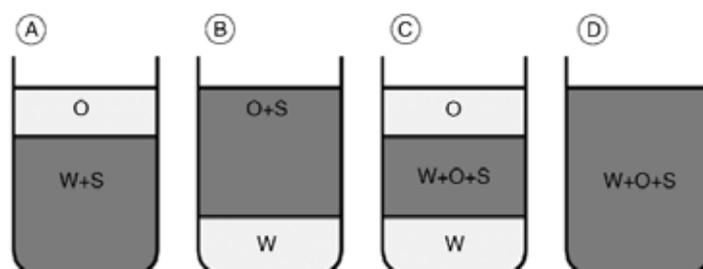
## 2.6 Microemulsion

The microemulsion is the important mechanism for selecting the appropriate optimum formulation of the surfactant flooding. The middle phase formation can improve the efficiency of oil solubilization by reducing the salinity required and generating an ultralow interfacial tension (Bera *et al.*, 2014).

The microemulsions are composed of polar (water) phase, non-polar (oil) phase and thermodynamically stabilized by a surfactant or mixed surfactant phase. It is isotropic transparent dispersion solution that includes two immiscible liquids where a dispersed micelle solubilized an oil droplet in the continuous water phase, which is similar a separated colloid in the system. Microemulsions can be classified into two types, which are oil in water (O/W) that is micelle structure and water in oil (W/O) that is reverse micelle structure (Malik *et al.*, 2012)

The Winsor type system is conducted to study the surfactant selection for microemulsion formations, which can be divided into four types as shown in Figure 5. Winsor type I microemulsions, oil-in-water micelle formation (O/W), are generated with the excess of oil phase. The micellar aggregates are present regular micelle at equilibrium in low brine condition. On the other hand, Winsor Type II microemulsions, water-in-oil micelle formation (W/O), are generated with the excess of a water phase. The surfactant aggregates in the form of reverse micelle at equilibrium in higher brine condition. If brine is suitably increased from Winsor Type I, the middle-phase of microemulsion formations will occur. Winsor Type III microemulsions have three phases, which are the excess of an oil and water phase at equilibrium by middle-phase comprised of oil, water, and surfactant. For creating middle-phase microemulsions, it can be achieved by increasing surfactant concentration above critical microemulsion concentration (CMC). The more volume of middle-phase microemulsion until both oil and water can completely miscible to be known as Winsor Type IV or a single phase microemulsion (Baran, 2001, Kumar *et*

*al.*, 2016). In this study, Winsor type III or middle-phase microemulsions are desired because it exhibits the lowest interfacial tension (IFT).

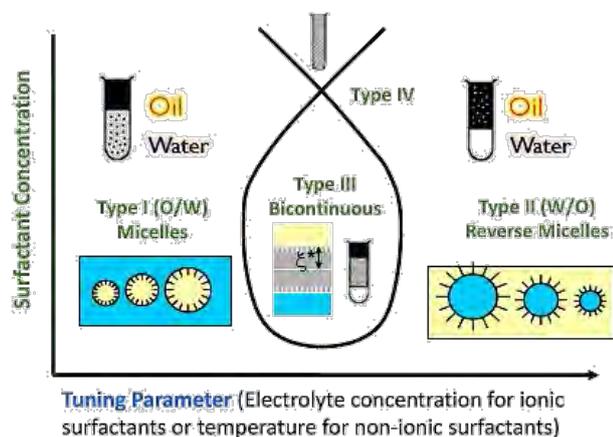


**Figure 2.5** Winsor types of microemulsion formations with oils (O), waters (W) and surfactants (S). There are A) Winsor type I (oil-in-water), B) Winsor type II (water-in-oil), C) Winsor type III (middle-phase) and D) Winsor type IV (Winsor, 1948).

Microemulsion phase inversions are related to the types of surfactants. For ionic surfactant systems, brine (electrolyte) is the tuning parameter in different type of microemulsion formations. Addition of brine affects the microemulsion formation from type I to III to II (o/w to w/o). The presence of brine can decrease electrostatic repulsion between the hydrophilic head group of ionic surfactants. The addition of brine does not affect to non-ionic surfactants, but they are affected by temperature. When the temperature of the microemulsion system increases, non-ionic surfactants have more hydrophobicity due to less interaction of their ethylene oxide (EO) head groups. Thus, they can simply dissolve in an oil phase.

Fish diagram representing the microemulsion phases is shown in Figure 6. When the brine (electrolyte) concentration or temperature is changed, the phase behavior of microemulsions is also changed at the same surfactant concentration. If the surfactant concentration is added in excess, Winsor type IV (single phase) microemulsion formation, which is fish-tail, will be formed (Figure 5). Winsor types (I, II and III) can be generated by surfactant concentration at below the minimum concentration of Winsor type IV (Baran, 2001, Kumar *et al.*, 2016). The shape of fish diagram is varied depending on types, structures, temperatures or other factors of each

surfactant system. Fish diagram has advantageous for the targeted improvement of microemulsion formations and the analysis of experimental data.



**Figure 2.6** Fish diagram of surfactant systems that the curvature is changed with surfactant concentrations and tuning parameters (Withayapanyanon *et al.*, 2009).

Tanthakit and coworkers (2010) found that the middle phase microemulsion formations of palm oil were achieved using extended surfactants, sodium alkyl polypropylene oxide sulfate. The surfactant system can form Winsor Type III (middle-phase) microemulsions at 0.2 % by weight of surfactant concentration and 1.22 to 3.75 % by weight of NaCl concentration as a brine or salinity. Do and co-workers (2014) investigated microemulsion phase behavior using the extended surfactant,  $C_{10-18}PO-2EO-NaSO_4$ , with four vegetable oils, jojoba oil, coconut oil, palm kernel and canola oil. The middle-phase microemulsions of coconut oil and palm kernel oil occurred at 1 % and 1.5 by weight of NaCl concentration, respectively.

Withayapanyanon and coworkers (2008) studied the microemulsion formation conditions using 0.07 M of sodium dihexyl sulfosuccinate (AMA) as an anionic surfactant. The results were concluded that the optimal salinities (%wt) for benzene, pentane, heptane, octane, decane, and limonene were 2.5, 6.8, 8.0, 9.0, 15.5, and 6.8, respectively. They also concluded that the optimum salinities increased with increasing the EACN of oils.

Acosta and coworkers (2009) investigated the microemulsion phase behavior of mixed surfactant with the total surfactant concentration of 0.1 M, using anionic-nonionic ratio of 9:1 by weight and limonene as an oil phase at the ratio of 5:5 by volume, at controlled temperature and pressure (25 °C and 1 atm). The anionic surfactant was SDHS and nonionic surfactants were NPE2, NPE5, NPE9, C11.5E5, and C12E6.5. They found that the middle phase formation occurred at 5.5, 6.5, 9, 7, and 7 g NaCl/100 ml, respectively.

Budhathoki and co-workers (2016) studied the optimal salinity of the microemulsion systems prepared by anionic extended surfactants including  $C_8-(PO)_4-(EO)_1-SO_4Na$ ,  $C_8-(PO)_4-SO_4Na$ ,  $C_{10}-(PO)_4-(EO)_1-SO_4Na$ ,  $C_{10}-(PO)_4-SO_4Na$ , at the total concentration of 0.1 M. Hexane and octane were used as an oil phase. The optimal salinities for the hexane system were 16.2, 16.5, 13.5, and 12.9 wt%, respectively and 18.3, 18.7, 15.6, and 15.1 wt%, respectively for octane. Their results revealed that increasing EACN of oils increased optimal salinities. The tail length of the surfactant decreased with the optimal salinity decreased. The lowest IFT ( $<10^{-3}$  mN/m) was obtained from binary mixtures of extended surfactants and Steol Cs460 with the reservoir crude oil at 52°C. The binary mixture of  $C_{10}-(PO)_4-(EO)_1-SO_4Na$  and Steol Cs460 was lower than the binary mixture of  $C_8-(PO)_4-(EO)_1-SO_4Na$  and Steol Cs460 due to the longer chain of surfactant resulting in the stronger interaction between surfactant and oil.

## 2.7 Surfactant precipitation

A limitation of using surfactants in the EOR is the losses by surfactant precipitation with the monovalent or divalent cations in the reservoirs. Then, the efficiency of oil removal can be significantly reduced. Otherwise, the more surfactant dosage is required to compensate the interactions. Surfactant precipitation mainly depends on types of surfactants. Anionic surfactants generally tend to precipitate by electrolyte or salt ions (e.g.,  $Ca^{2+}$ ,  $Mg^{2+}$ ) and in some cases by hydrophobic interactions.

Surfactant precipitation is a formation of precipitated surfactant molecules as crystal-like form, which depends on type, structure, solubilization of surfactants and temperatures. Crystal formation can occur, especially at the high concentration (above CMC) of surfactants. Adding low CMC-nonionic surfactants, increasing temperature and decreasing alkyl chain length of the hydrophobic tails can reduce precipitation.

## 2.8 Hydrophilic lipophilic deviation (HLD) concept

Hydrophilic-lipophilic difference (HLD) method is the correlation of thermodynamically formulated equation to explain about microemulsion behaviors at formulation conditions (Salager *et al.*, 1979). This equation has been developed by Salager and co-workers (1987). HLD exhibits the parameters, which are the efficiency of transferring surfactants from oil phase to aqueous phase that depends on several factors (temperature, oil, water and salt) for the oil-water-surfactant system. Moreover, HLD can help to define the optimum formulation of systems, which are related to a variety of alcohols and divalent ions (Salager *et al.*, 1979, Acosta *et al.*, 2012, Budhathoki *et al.*, 2016). Eq. 1 and Eq. 2 are the HLD equations for ionic surfactants and non-ionic surfactants, respectively (Castellino *et al.*, 2011).

HLD equation for ionic surfactants,

$$\text{HLD} = \ln(S) - K \cdot \text{EACN} - f(A) - \alpha \Delta T + C_c \quad \text{Eq. 1}$$

HLD equation for non-ionic surfactants,

$$\text{HLD} = b(S) - K \cdot \text{EACN} - \varphi(A) + c \Delta T + C_{cn} \quad \text{Eq. 2}$$

The factor of salinity concentration (S), which is added into the aqueous phases for g/100mL, is  $\ln(S)$  and  $b(S)$ . The nonionic surfactant systems are not considered b parameter. K is the slope of the logarithm pattern, the indicator of surfactant properties (hydrophilic part). The equivalent alkane carbon numbers that are depending on the used oils is EACN parameter. The  $f(A)$  and  $\varphi(A)$  are the alcohol functions, which rely on type and concentration of used alcohols. The parameters  $\alpha$  and  $c$  are the temperature coefficient at the optimum salinity.  $\Delta T$  is the temperature

difference from the reference temperature (typically 298 K).  $C_c$  and  $C_{cn}$  are the characteristic curvatures.

For binary mixtures of surfactants, HLD equation for this condition is combined effect with both surfactant (1) and surfactant (2). Acosta et al. studied the HLD equation for mixed surfactant in the systems, the equation 3 is HLD equation for ionic-ionic surfactant systems. For ionic-nonionic surfactant systems, HLD equation is equation 4 (Acosta *et al.*, 2008).

$$\text{HLD}_{\text{mix}} = X_1(\text{HLD}_1) + X_2(\text{HLD}_2) \quad \text{Eq. 3}$$

$$\text{HLD}_{\text{mix}} = X_i \times \text{HLD}_i + X_{ni} \times \text{HLD}_{ni} + G_{\text{EX}}/RT \quad \text{Eq. 4}$$

Where,

$\text{HLD}_1, \text{HLD}_2$	=	HLD value of surfactant 1 and 2
$X_1, X_2$	=	mole fraction of surfactant 1 and 2
$G_{\text{EX}}$	=	excess free energy
$i, n_i$	=	ionic and non-ionic surfactant
$R$	=	gas constant
$T$	=	temperature (kelvin)

HLD value is associated with Winsor type microemulsion formation. For HLD value, Winsor type I (oil-in-water) microemulsion formation shows the negative value. Winsor type III (middle-phase) microemulsion formation shows zero value. Finally, Winsor type II (water-in-oil) microemulsion formation shows positive value (Salager *et al.*, 1979). The shift of microemulsion phase, which changes of Winsor type I, type III and type II, is generated to relate to the changes in negative value, zero value and positive value for HLD value (Salager *et al.*, 1979).

In the EOR application, the estimation of parameters in HLD equation is determined such as optimal salinity ( $S^*$ ). Some of the researchers tried to determine the optimal condition leading to reducing the number of experiments and time that are currently being invested to phase behavior studies.

## **CHAPTER III**

### **EXPERIMENTAL**

#### **3.1 Objective**

The objective of this research is to formulate Winsor type III middle phase microemulsions using the mixed anionic surfactant system for EOR application. The sub-objectives of this research are;

1. To study the effects of surfactant structures and mixing ratios of the mixed anionic surfactants on the middle phase microemulsion formation.
2. To study the effects of alkane oil deviated their carbon numbers (ACN) on the middle phase microemulsions and their optimal conditions.
3. To formulate middle phase microemulsions with maximum solubilization at minimum interfacial tension (IFT).
4. To investigate the selection of the mixed surfactant system based on HLD concept for middle phase microemulsion formation.

#### **3.2 Scope of Research**

The scope of this research will cover the following:

1. The HLD calculation for anionic and mixed anionic surfactants is conducted at the middle phase or Winsor type III microemulsion formation.
2. Sodium dioctyl sulfosuccinate (AOT) and Internal olefin sulfonate (IOS) are used as a binary surfactant mixture; IOS surfactants with different numbers of carbon chain length are used to study the effect of the surfactant structure.
3. The mixed surfactant system for conducting the microemulsion study is selected based on avoiding surfactant precipitation.
4. All experimental studies were conducted at room temperature ( $25 \pm 2$  °C).

### 3.3 Materials and Equipment

#### 3.3.1 Equipment

- Spinning drop tensiometer (Dataphysics, Model SVT20)
- Wisemix Vortex Mixer (VM), WVM00010
- 15 ml Borosilicate Flat-bottom test tubes

#### 3.3.2 Chemicals

- Anionic surfactants

**Table 3.1** Surfactant properties

<b>Anionic Surfactants</b>	<b>No. of carbon atoms</b>	<b>Molecular weight (g/mol)</b>	<b>%Active matter</b>	<b>CMC (wt%)</b>
Internal olefin sulfonate (IOS15-18)	15-18	350.00	28.03	0.030
Internal olefin sulfonate (IOS19-23)	19-23	411.90	30.30	0.060
Internal olefin sulfonate (IOS24-28)	24-28	498.10	69.40	0.189
Sodium dioctyl sulfosuccinate (AOT)	-	444.56	>97	0.055

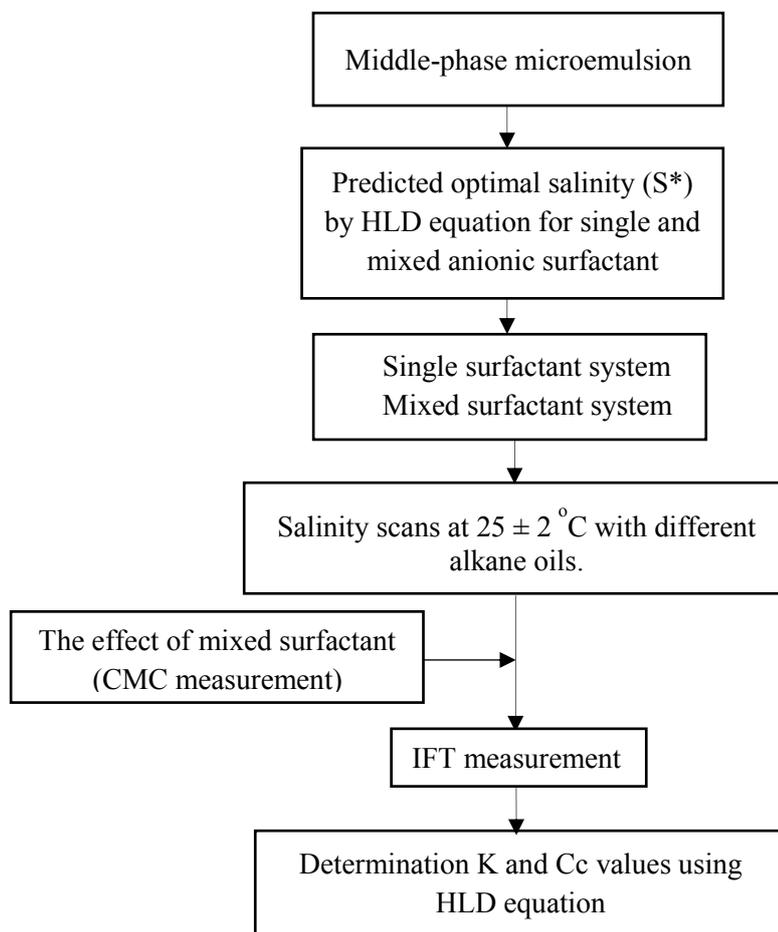
#### - Oils

- Heptane
- Octane
- Decane
- Dodecane
- Hexadecane

#### - Others

- Sodium Chloride (purity 99% AR grade)

### 3.4 Experimental Procedures



#### 3.4.1 Middle-phase Microemulsion Formation

The microemulsion phase behavior was conducted through the phase scan by varying the salinity (NaCl) concentrations. The middle phase formation of the single and mixed anionic surfactant systems was investigated in this study; the effects of surfactant mixing ratios of AOT/IOS mixed system. Number of carbon tails of IOS surfactants, number of ACN of oils were also investigated. For the phase or salinity scan experiment, a total of 5 mL oil phase and 5 mL of the aqueous phase containing a mixture of surfactants, salinity (NaCl) and DI water were added into a vial. The solutions were gently mixed to form microemulsions under a room temperature (25±2°C) and after that, the microemulsions were left for a month to ensure their equilibrium.

### 3.4.2 IFT measurement

The interfacial tension (IFT) measurement was performed using a spinning drop tensiometer (SITE 04, Krüss GmbH, Hamburg). The IFT measurement was made using 1-2  $\mu\text{L}$  of oil injected into 300  $\mu\text{L}$ . The diameter of the oil drop was measured every 5 min until 20 min, whereas the rotational velocity was kept constant at 5000 rpm. In this study, the minimum IFT or below  $10^{-2}$  mN/m (ultralow IFT) was indicated as the optimal conditions, the middle phase microemulsions, and the salinity at which the minimum IFT achieved is the optimum salinity ( $S^*$ ) of the surfactant system (Nguyen *et al.*, 2009).

### 3.4.3 Critical micelle concentration (CMC) measurement

Surface tension measurement is commonly used to determine the CMC value. The plot of surfactant concentrations against surface tension values is used to determine the CMC. The unit of surface tension can be described in mN/m. The CMC values were found by the point of the intersections of the plot. This study, the total concentrations of the surfactant were varied from 0.001 to 1 % by weight.

## **CHAPTER IV**

### **RESULTS AND DISCUSSION**

In this study, the middle phase microemulsions were formed with the alkane oils using the binary mixture of anionic surfactants, which are sodium dioctyl sulfosuccinate (AOT) as a primary surfactant and internal olefin sulfonate (IOS) as a secondary surfactant. AOT can be mixed with IOS surfactant without precipitation at the desired mixing ratio. The middle phase microemulsions of the anionic mixed surfactants were investigated by varying mixing surfactant ratios at 0.03 M of total surfactant concentration under the room temperature ( $25\pm 2$  °C). Three IOS surfactants (IOS<sub>15-18</sub>, IOS<sub>19-23</sub>, IOS<sub>24-28</sub>) were selected to study the effect of their alkyl chain lengths on the microemulsion formation. The microemulsion phase scan or salinity scan was performed to determine the phase behavior and the optimal condition also known as an optimal salinity ( $S^*$ ). The IFT measurement was conducted to study the effect of mixed surfactant ratios and surfactant structures on their interfacial tension property. Three alkane oils with deviated by carbon chain lengths, heptane, decane and hexadecane were selected as a model oil to investigate the effect on the optimal salinity ( $S^*$ ). In the experimental approach, the HLD equation of anionic mixed surfactant system was used to estimate the optimal salinity ( $S^*$ ) values. In comparisons, the obtained parameters, K and  $C_c$  values, from the experiment also reported and discussed as follows;

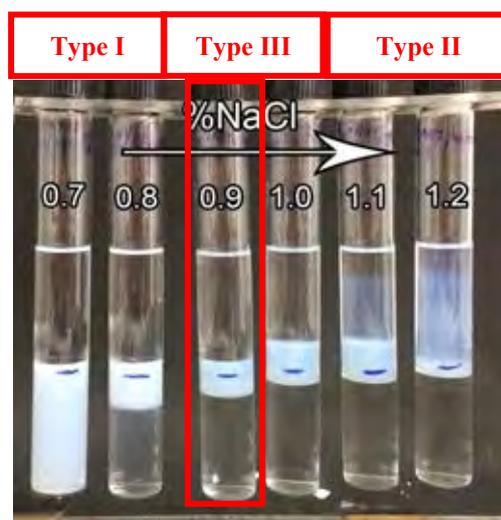
#### **4.1 The Microemulsion Phase Study**

The microemulsion phase scan was conducted in 15 ml flat-bottom test tubes to examine the formation of the middle phase. A total of 5 mL oil phase and 5 mL of the aqueous phase contained a mixture of surfactants, salinity (NaCl) and DI water are added into a vial. The solutions are gently mixed to form microemulsions under a room temperature ( $25\pm 2$ °C) and leave for a month to ensure its equilibrium.

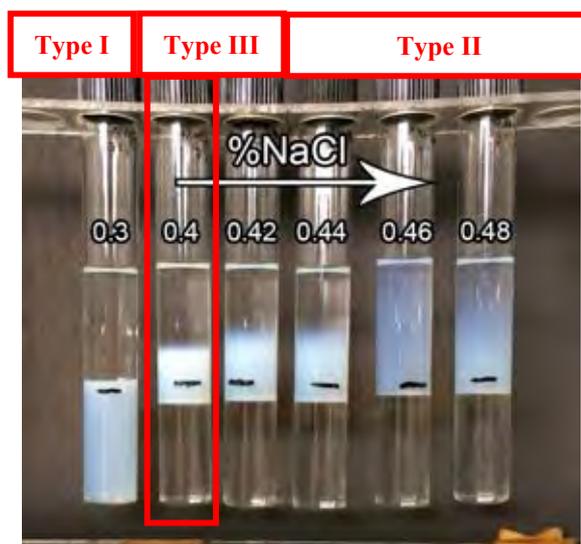
The appropriate ratios of the mixed anionic surfactants, sodium dioctyl sulfosuccinate (AOT) and internal olefin sulfonates (IOS), were varied by mixed molar

ratio ranging from 1:1 to 9:1 AOT: IOS of 0.03 M of total surfactant concentration. In this work, the microemulsion phase scan was performed with different carbon tails of IOS surfactants series (IOS<sub>15-18</sub>, IOS<sub>19-23</sub>, IOS<sub>24-28</sub>) in three alkane oils. It was found that the middle phases of AOT: IOS mixed surfactant systems were clearly observed with heptane and decane as an oil phase. The salinity scan and the middle phase of the microemulsion system of AOT: IOS C15-18 (6: 4 by molar ratio) mixed surfactant system with heptane shows in Figure 4.1.

Generally, the optimum condition, also known as the optimal salinity ( $S^*$ ) when using salinity as a tuning parameter, can be observed at the middle phase microemulsion. At a middle phase microemulsion or Winsor Type III, micelles form a bicontinuous phase structure, which places in the middle level of the solution between the oil phase (upper level) and the aqueous phase (lower level) (Do *et al.*, 2014).

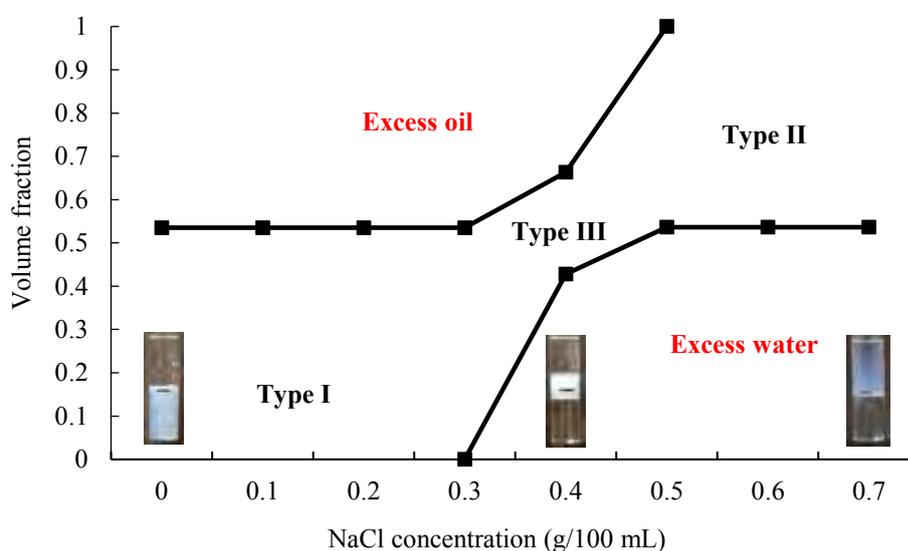


**Figure 4.1** The microemulsion phase scans of AOT: IOS C15-18 (6: 4 by molar ratio) mixed surfactant system for heptane as an oil phase under room temperature ( $25\pm 2$  °C) 0.03 M total surfactant concentration.



**Figure 4.2** The microemulsion phase scans of AOT: IOS C19-23 (7: 3 by molar ratio) mixed surfactant system for heptane as an oil phase under room temperature ( $25\pm 2$  °C) at 0.03 M total surfactant concentration.

For ionic surfactant systems, salinity (e.g. NaCl) is an important parameter for tuning the microemulsion phase formation. As the microemulsion phase inversion can occur from Winsor type I to III and to II by increasing salinity concentration. Figures 4.1-4.2 show the phase transition of AOT: IOS C15-18 (6: 4 by molar ratio) and AOT: IOS C19-23 (7: 3 by molar ratio) systems at different salinity (NaCl) concentrations in heptane as an oil phase. It can be observed that the microemulsion phase was transitioned from Winsor type I to type III and to type II when the salinity increased. It can be implied from Winsor type I microemulsions (o/w), that the surfactants formed normal micelles at 0.7-0.8 and 0.3 (g/100 mL) NaCl concentration for AOT: IOS C15-18 (6: 4 by molar ratio) and AOT: IOS C19-23 (7: 3 by molar ratio), respectively. While, the Winsor type III microemulsions or middle phase microemulsion occurred at 0.9 and 0.4 (g/100 mL) NaCl concentration, respectively. When the salinity concentrations further increased up to 1.0 and 0.42 (g/100 mL) NaCl concentration, respectively, the microemulsion systems were transitioned from Winsor type III to II microemulsions (w/o).

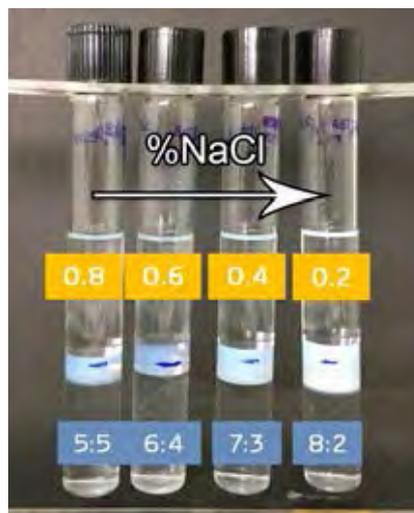


**Figure 4.3** The relationship between phase volume fraction of AOT: IOS C19-23 (7: 3 by molar ratio) mixed surfactant system and salinity (NaCl) concentrations with heptane as an oil phase under room temperature ( $25 \pm 2$  °C) at 0.03 M total surfactant concentration.

For each surfactant system, the relationship between phase volume fraction of the microemulsion system was plotted against the salinity to compare the microemulsion phase behavior as shown in Figure 4.3. Figure 4.3 shows the microemulsion phase volume fraction of AOT: IOS19-23 (7: 3 by molar ratio) mixed surfactant system with heptane. It can be observed that when the salinity of the system increase, the surfactants prefer to soluble in the oil phase resulting in the microemulsion phase transition. For Winsor type I microemulsions, the surfactants formed normal micelles (O/W) up to 0.3 (g/100 mL) NaCl. The Winsor type III microemulsions, the bicontinuous phase or middle phase with excess both oil and water phase occurred at 0.4 (g/100 mL) NaCl. When the salinity concentrations further increased up to 0.5 g/100 mL) NaCl, the systems formed Winsor type II microemulsions of which the surfactants form reverse micelles (W/O).

#### 4.1.1 Effect of mixed surfactant ratios

The mixed surfactant systems were employed to not only for avoiding the precipitation of the IOS surfactant at high salinity concentration, but also for improving the system by reducing salinity required to achieve the optimum salinity ( $S^*$ ) of the microemulsions. The AOT: IOS (C15-18, C19-23) at 5: 5 to 9: 1 by molar ratio mixed surfactant systems can form the middle phase microemulsions in heptane and decane as an oil phase. It can be seen that the middle phase microemulsions can form in AOT riched-systems. The optimal salinity ( $S^*$ ) of AOT: IOS C19-23 mixed surfactant system at various molar ratio for heptane are showed in Figure 4.4.

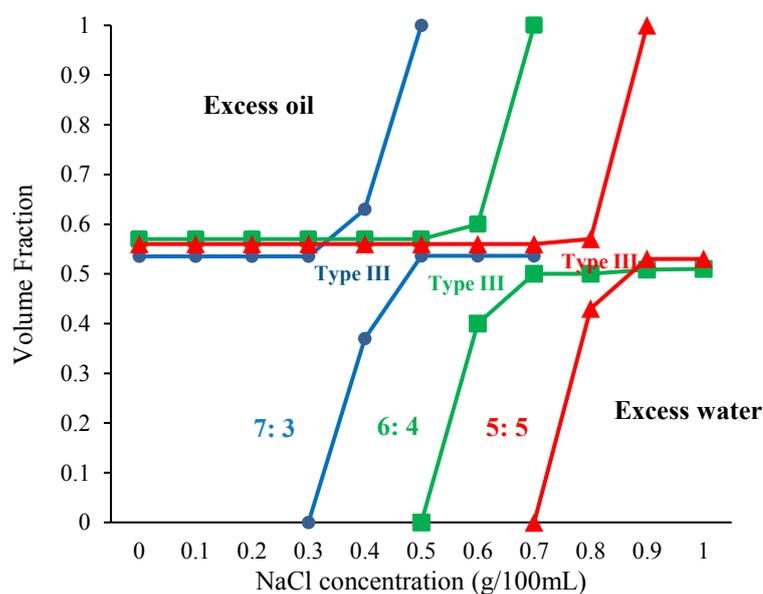


**Figure 4.4** The middle-phase microemulsions or optimal salinity ( $S^*$ ) of AOT: IOS C19-23 mixed surfactant system at various molar ratio for heptane as an oil phase under room temperature ( $25\pm 2$  °C) 0.03 M total surfactant concentration.

**Table 4.1** Summarizes the optimal salinities of AOT: IOS (by various molar ratio) mixed surfactant systems for heptane as an oil phase under room temperature ( $25\pm 2$  °C) at 0.03 M total surfactant concentration

Surfactant			
Primary	Secondary	Ratio by molar	Optimal salinity $S^*$
AOT	IOS C19-23	9:1	0.10
AOT	IOS C19-23	8:2	0.20
AOT	IOS C19-23	7:3	0.40
AOT	IOS C19-23	6:4	0.60
AOT	IOS C19-23	5:5	0.80

Table 4.1 showed the optimal salinity of AOT: IOS mixed surfactant systems at various molar ratios of 0.03 M total surfactant concentration for heptane. The results indicated that the molar ratio of IOS C19-23 increased, the optimal salinity ( $S^*$ ) increased. In other words, the molar ratio of AOT in AOT: IOS mixed surfactant systems decreased, the optimal salinity ( $S^*$ ) increased.



**Figure 4.5** The relationship between phase volume fraction and salinity (NaCl) concentrations of AOT: IOS C19-23 mixed surfactant systems at various molar ratio for heptane as an oil phase under room temperature ( $25 \pm 2$  °C) at 0.03 M total surfactant concentration.

Figure 4.5 shows the plot of phase volume fraction and salinity (NaCl) concentrations of AOT: IOS C19-23 mixed surfactant systems at various molar ratio with heptane. AOT: IOS C19-23 mixed surfactant systems at molar ratio of 7: 3 had the optimal salinity ( $S^*$ ) at 0.4 g/100mL, indicating the highest volume of the middle phase compared to those of the other systems. The lowest middle phase volume was obtained from AOT: IOS C19-23 mixed surfactant system at 5: 5 by molar ratio which

had optimal salinity ( $S^*$ ) at 0.8 g/100mL. For AOT: IOS C19-23 mixed surfactant system at 6: 4 by molar ratio, the volume of the middle was between AOT: IOS C19-23 at 7: 3 by molar ratio and AOT: IOS C19-23 at 5: 5 by molar ratio which had optimal salinity ( $S^*$ ) at 0.6 g/100mL. It can be seen from the AOT: IOS C19-23 mixed surfactant system that when the fraction of IOS C19-23 decreased, the volume fraction of the middle phase decreased.

#### 4.1.2 Effect of surfactant structures

The mixed anionic surfactant systems of sodium dioctyl sulfosuccinate (AOT) can be mixed well with individual internal olefin sulfonate (IOS C15-18, IOS C19-23, IOS C24-28) at any ratio without precipitation. The effects of increasing in the carbon tail length of IOS surfactant on their optimal salinity ( $S^*$ ) were investigated in this study.

**Table 4.2** Summarizes the optimal salinities of AOT: IOS (C15-18, C19-23, C24-28) at 7: 3 by molar ratio for decane as an oil phase under room temperature ( $25 \pm 2$  °C) at 0.03 M total surfactant concentration

Surfactants	Molar ratio	Decane Optimal salinity ( $S^*$ )
AOT: IOS C15-18	7: 3	0.90
AOT: IOS C19-23	7: 3	0.70
AOT: IOS C24-28	7: 3	0.40

Table 4.2 showed the effect of numbers of carbon tail length of IOS surfactant on their optimal salinity ( $S^*$ ) in the AOT: IOS mixed surfactant system at fixed the molar ratio of 7: 3 for decane. It can be seen that the carbon tail length of IOS increases, the optimal salinity ( $S^*$ ) decreases. This trend can discuss with Winsor R concept that the ratio of net surfactant-oil interactions,  $A_{co}$ , to the net surfactant-water interaction,  $A_{cw}$ . As the carbon tail length of surfactants increases, the net surfactant-oil interactions increase. The balance of this effect can be explained by the increased

$A_{cw}$ , which decreases salinity to obtain the middle phase because the addition of salt reduces  $A_{cw}$  by compressing the electrical double layer of the surfactant head group. It can be applied to describe the effect of an increase in carbon tail length of the surfactant with decreasing the optimal salinity (Budhathoki *et al.*, 2016).

#### 4.1.3 Effect of alkane oils

The mixed anionic surfactant systems of sodium dioctyl sulfosuccinate (AOT) and internal olefin sulfonate (IOS C15-18, IOS C19-23) can form the middle phase with heptane, decane and hexadecane. The effects of an increase in EACN of alkane oil on their optimal salinity ( $S^*$ ) of the mixed surfactant system were investigated in this study.

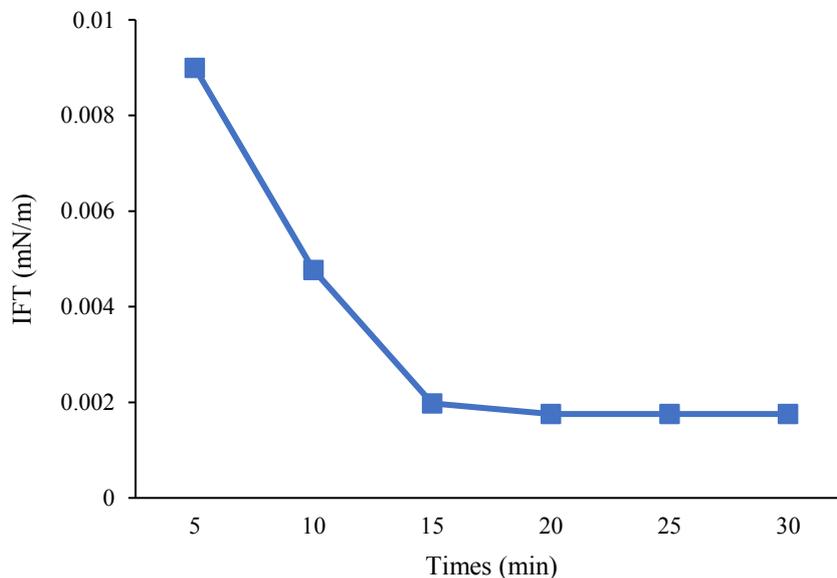
**Table 4.3** Summarizes the optimal salinities of AOT: IOS C19-23 at 5: 5 by molar ratio for heptane, decane and hexadecane as an oil phase under room temperature ( $25 \pm 2$  °C) at 0.03 M total surfactant concentration

Alkane oils	EACN	Optimal salinity ( $S^*$ )
Heptane	7	0.50
Decane	10	0.45
Hexadecane	16	0.30

Table 4.3 showed the effect of an increase in EACN of alkane oil on the optimal salinity ( $S^*$ ) of the mixed surfactant system at 5: 5 by molar ratio for heptane, decane and hexadecane. It can be observed that the EACN of IOS increased, the optimal salinity ( $S^*$ ) increased. The observation is in line with Winsor R concept that defines the ratio of net surfactant-oil interactions,  $A_{co}$ , to the net surfactant–water interaction,  $A_{cw}$ . As the EACN of the oil increase, the net surfactant-oil interactions decrease. The balance of this effect can be explained by the  $A_{cw}$  decrease by adding salinity to obtain the middle phase.

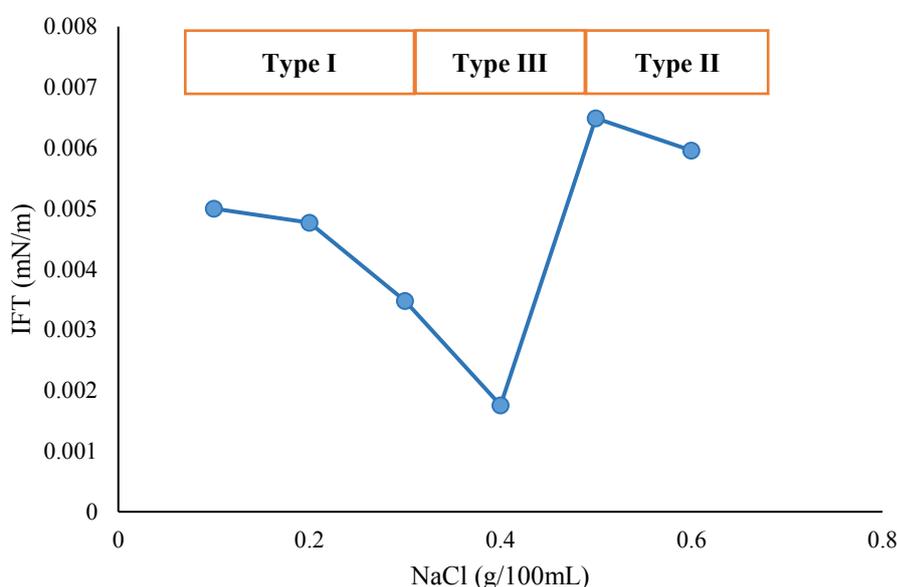
## 4.2 IFT Measurement

One of the unique characteristics of using surfactants in enhanced oil recovery is the reduction of interfacial tension between oil and water, indicating by IFT values. In this study, the equilibrium IFT were measured by a spinning drop tensiometer (SITE 04, Krüss GmbH, Hamburg). The IFT measurement was conducted to ensure the minimum IFT or ultralow IFT at the middle phase microemulsion obtained from the phase behavior study. In the experiment, the diameter of the oil drops was measured at every 5 minutes, whereas the rotational velocity was kept constant at 5000 rpm. Notwithstanding from the literature, an ultralow IFT is defined at the IFT value below 0.01 mN/m (Nguyen *et al.*, 2009). In this study, the optimum salinity ( $S^*$ ) was determined by the obtained minimum IFT from the plot between the IFT value versus NaCl concentration.



**Figure 4.6** The equilibrium IFT measurement as a function of time of the microemulsion system using AOT:IOS C19-23 mixed surfactant system (7:3 by molar ratio of 0.03 M total surfactant concentration) at the optimal salinity (0.4 g/100 mL) for heptane as an oil phase under room temperature ( $25\pm 2$  °C)

The plot of the equilibrium IFT values versus times is shown in Figure 4.6. The result showed that the equilibrium IFT value reached to its equilibrium within 15 min, indicated by the constant IFT value. The minimum IFT value of AOT: IOS C19-23 mixed surfactant systems at 7:3 by molar ratio with heptane was 0.00176 mN/m at 0.4 g/100 mL NaCl. The optimum salinity of the microemulsion system is obtained at the minimum IFT value. From Figure 4.6, the minimum IFT of the mixed surfactant system is in line with an ultralow IFT ( $< 0.01$  mN/m).



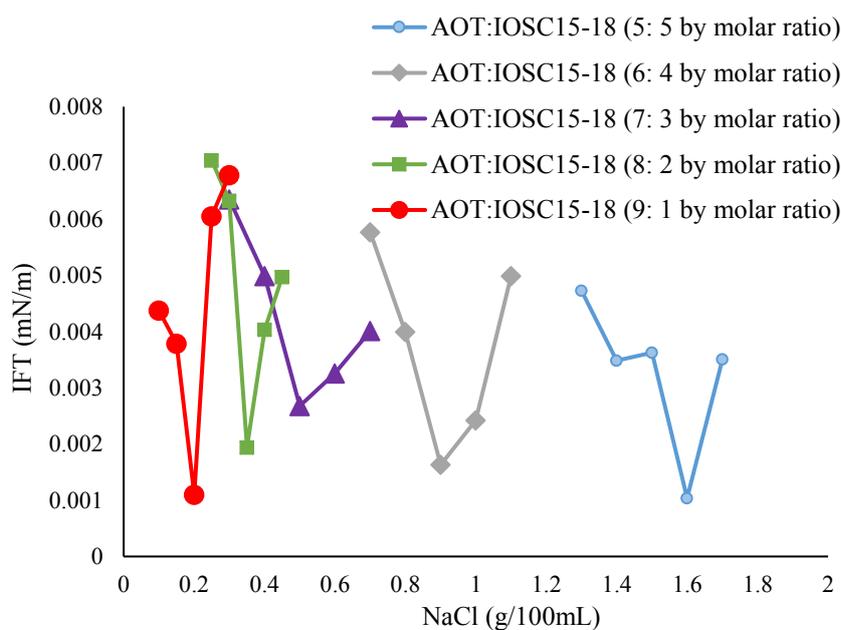
**Figure 4.7** The equilibrium IFT measurement of AOT: IOS C19-23 mixed surfactant system at 7:3 by molar ratio of 0.03 M total surfactant concentration for heptane as an oil phase under room temperature ( $25 \pm 2$  °C).

From Figure 4.7, the IFT values of the microemulsion system of AOT: IOS C19-23 at 7:3 by molar ratio with heptane decrease with increasing the salinity concentration at the Type I microemulsion, until the IFT reached to the minimum value at the Type III and then the IFT sharply increased when the microemulsions transition to the Type II. The minimum IFT value (0.00176 mN/m) was obtained at 0.4 g/100 mL NaCl concentration which is defined as the optimal salinity ( $S^*$ ) of the surfactant

system. It can be noted that the optimal salinity ( $S^*$ ) obtained from the IFT measurement is similar with the result obtained from the phase behavior study.

#### 4.2.1 Effect of mixed surfactant ratios

This study, the IFT values of the microemulsion system with heptane prepared by AOT: IOS C15-18 mixed surfactant systems at varying mixing ratios were investigated. The results showed that the minimum interfacial tension values of AOT: IOS C15-18 mixed surfactant systems were obtained at the middle phase microemulsions or Winsor type III at the mixing molar ratios of 5: 5 to 9: 1 as shown in Figure 4.8.

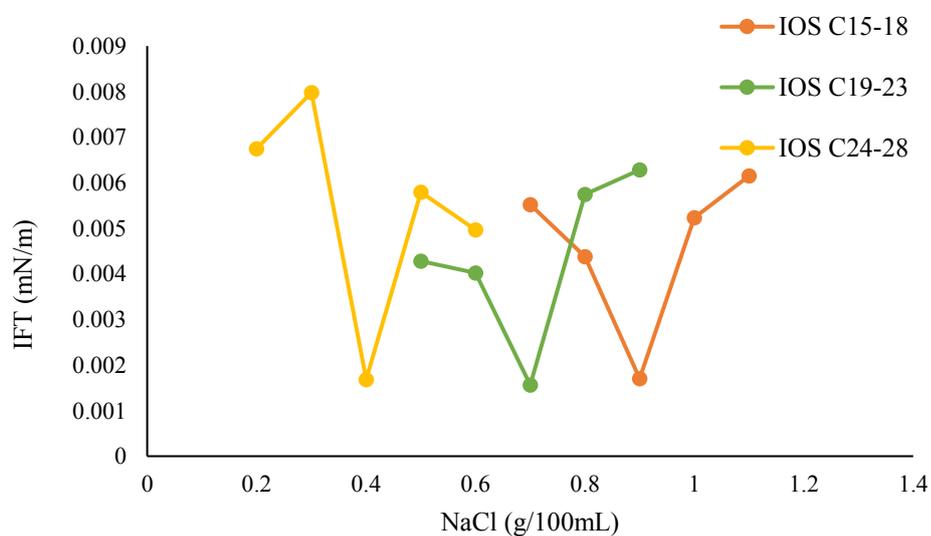


**Figure 4.8** The IFT values of the microemulsion system using AOT: IOS C15-18 mixed surfactant system at varying mixing molar ratio of 5: 5 to 9:1 AOT: IOS with heptane as an oil phase under room temperature ( $25\pm 2$  °C).

**Table 4.4** Summarizes the equilibrium IFT values at optimal salinity ( $S^*$ ) of AOT:IOS C15-18 at varying mixing molar ratio from 5: 5 to 9: 1 for the microemulsion system with heptane as an oil phase under room temperature ( $25\pm 2$  °C) at 0.03 M total surfactant concentration

AOT: IOS C15-18 (by molar ratio)	Optimal salinity (g/100mL)	IFT values (mN/m)
5: 5	1.60	0.001037
6: 4	0.90	0.001630
7: 3	0.50	0.002677
8: 2	0.35	0.001941
9: 1	0.20	0.001098

#### 4.2.2 Effect of surfactant structures



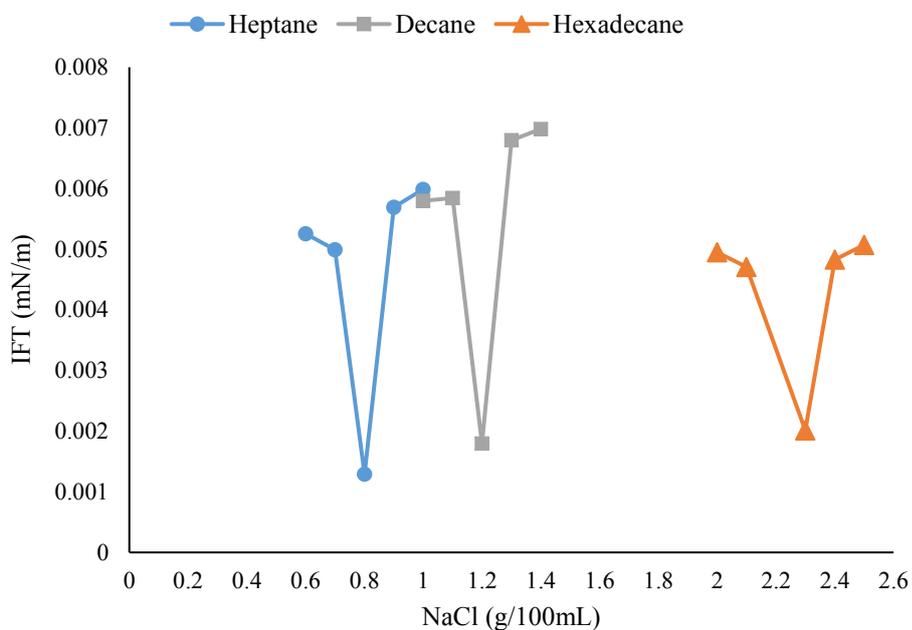
**Figure 4.9** The equilibrium IFT measurement of AOT: IOS C15-18, IOS C19-23, IOS C24-28 (7: 3 by molar ratio) microemulsion system with decane as an oil phase under room temperature ( $25\pm 2$  °C) at 0.03 M total surfactant concentration.

From Figure 4.9, the IFT values of the microemulsion system using the mixed systems of the mixed surfactant systems of AOT with varying numbers of alkyl chain length, IOS C15-18, IOS C19-23, IOS C24-28 at the fixed molar ratio of 7: 3 AOT: IOS with decane were investigated. The minimum IFT values of the mixed surfactant system with IOS C15-18, IOS C19-23, and IOS C24-28 were achieved at 0.9 g/100mL, 0.7 g/100mL and 0.4 g/100mL NaCl concentrations, respectively. The minimum IFT value of each system is obtained at the optimal salinity that was obtained from the microemulsion phase scan study.

**Table 4.5** Summarizes the equilibrium IFT values at optimal salinity ( $S^*$ ) of AOT: IOS C15-18, IOS C19-23, IOS C24-28 (7: 3 by molar ratio) for decane as an oil phase under room temperature ( $25\pm 2$  °C) at 0.03 M total surfactant concentration

Surfactants	AOT: IOS (by molar ratio)	Optimal salinity (g/100mL)	IFT values (mN/m)
AOT: IOS C15-18	7: 3	0.95	0.001703
AOT: IOS C19-23	7:3	0.70	0.001534
AOT: IOS C24-28	7: 3	0.40	0.001685

### 4.2.3 Effect of alkane oils



**Figure 4.10** The IFT values of AOT:IOS C19-23 (5: 5 by molar ratio) microemulsion systems with heptane, decane and hexadecane as an oil phase under room temperature ( $25\pm 2$  °C) at 0.03 M total surfactant concentration.

From Figure 4.10, the minimum IFT values of microemulsion systems using AOT:IOS C19-23 mixed systems at the molar ratio 5:5 AOT: IOS C19-23 with heptane, decane and hexadecane were attained at 0.8 g/100mL, 1.2 g/100mL and 2.3 g/100mL NaCl concentrations, respectively. The minimum IFTs are obtained at the optimal salinity that obtained from the middle phase microemulsion formation study.

**Table 4.6** Summarizes the equilibrium IFT values at optimal salinity ( $S^*$ ) of AOT: IOS C19-23 (5: 5 by molar ratio) for heptane, decane and hexadecane as an oil phase under room temperature ( $25\pm 2$  °C) at 0.03 M total surfactant concentration

Alkane oil	EACN	Optimal salinity	IFT values (mN/m)
Heptane	7	0.8	0.001290
Decane	10	1.2	0.001794
Hexadecane	16	2.3	0.002010

### 4.3 Hydrophilic-Lipophilic Deviation (HLD) Calculation

#### 4.3.1 Determination of K and Cc Values using a reference surfactant

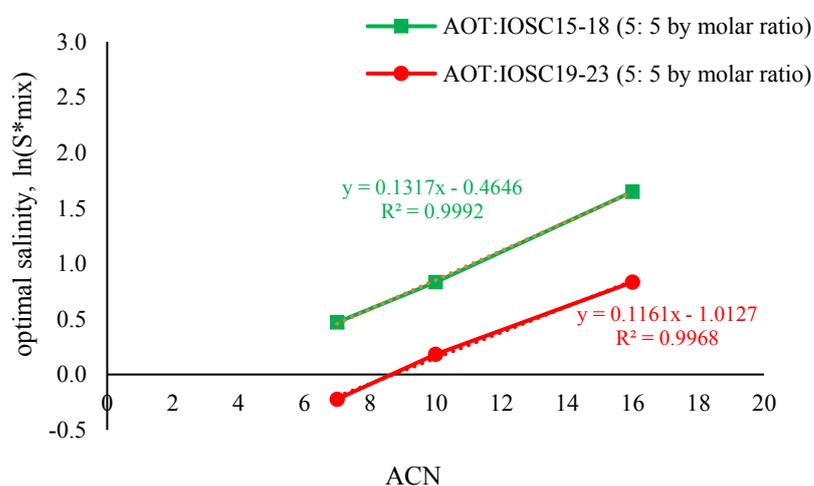
Hydrophilic-Lipophilic Deviation (HLD) developed by Salager and coworkers (1979), was conducted to estimate the  $C_c$  and  $K$  values of the surfactant systems. It is noted that the  $K$  and  $C_c$  values of the single surfactant systems of an internal olefin sulfonate (IOS C15-18, C19-23) surfactants cannot be determined by the middle phase scan because the IOS surfactant alone are unable to form a middle phase with the selected alkanes. In this effort, the alternative approach was used to determine the  $K$  and  $C_c$  values of the IOS surfactants. Two sets of the surfactant, the selected reference surfactant, sodium dioctyl sulfosuccinate (AOT), was mixed with the IOS surfactants, IOS C15-18 and IOS C19-23, in order to form a middle phase with all three reference oils deviated by their alkane carbon number (ACN), i.e., heptane, decane, and hexadecane.

The HLD equation combined the linear mixing rule has been developed for mixed anionic surfactant systems (Salager et al., 1979). Based on the mixing rule, the HLD equation for the mixed surfactant system are described in Eq. (4.1) as below:

$$\ln(S_{mix}^*) = (x_1K_1 + x_2K_2)(ACN) - (x_1Cc_1 + x_2Cc_2) \quad (4.1)$$

Where, the subscripts 1 and 2 represent the reference surfactant, AOT, and the test surfactant, IOS series. For example,  $x_1$  and  $x_2$  are the mole fractions for the reference surfactant and test surfactant of the mixed surfactant systems. This study, the formulated microemulsions were conducted at room temperature ( $25 \pm 2$ ) °C without adding alcohol. The optimum salinity is represented as  $S^*$ . To determine  $\ln(S_{mix}^*)$  in Eq. (4.1), the salinity (NaCl) scan was carried out for each surfactant mixture used in this study.

The K and Cc values of the test surfactant systems were calculated from the plots of  $\ln(S_{mix}^*)$  against ACN for each surfactant mixture, AOT mixed with IOS C15-18 and IOS C19-23 surfactant. For all samples, the total surfactant concentrations were maintained at 0.03 M. The mixing ratio of AOT and each IOS surfactant was fixed at 5:5 (by molar ratio). The plots between  $\ln(S_{mix}^*)$  and ACN are shown in Figure 4.13.



**Figure 4.11** The plots of  $\ln(S_{mix}^*)$  against ACN for two mixed surfactant systems of the reference surfactant, AOT, and each IOS (IOS C15-18, IOS C19-23).

According to Figure 4.11, the optimal salinity decreases with increasing alkyl chain length of the IOS surfactants. The result showed that the optimal salinity of the microemulsions containing IOS C15-18 with heptane (ACN=7) was higher than that containing IOS C19-23. The explanation for this observation is similar to the fact that the optimal salinity increases with increasing the ACN of oil. The surfactant with longer carbon chain length has the stronger interaction with oil, resulting in lower salinity needed to weaken the interactions between the surfactant head group and aqueous phase for maintaining the balance of the water and oil phase.

In Figure 4.11, the linear regression was applied to each set of data. All the correlation factors,  $R^2$  are greater than 0.99, which indicates the linear trend has a good agreement with each set of data. According to Eq. (4.1), the slopes and intercepts of the individual curve corresponded to their  $(x_1K_1 + x_2K_2)$  and  $(x_1Cc_1 + x_2Cc_2)$  values, respectively. The values of  $K_1$  and  $Cc_1$  of the reference surfactant, AOT, were verified previously to be 0.17 and 2.42, respectively. The mole fractions,  $x_1$  for AOT and  $x_2$  for IOS surfactant added, are also known. Thus, the two unknown HLD parameters of the IOS surfactants,  $K_2$  and  $Cc_2$ , can be solved simultaneously. For example, the results of linear regression for 50% IOS C15-18 and 50% AOT are listed below,

$$\ln(S_{mix}^*) = 0.1317(ACN) - (0.4646) \quad (4.2)$$

Where, 0.1317 is equal to  $(x_1K_1 + x_2K_2)$  and 0.4646 is equal to  $(x_1Cc_1 + x_2Cc_2)$ .

Thus,  $K_2$  and  $Cc_2$  can be calculated as follows:

$$K_2 = \frac{0.1317 - (0.5 \times 0.17)}{0.5} = 0.0934 \quad (4.3)$$

$$Cc_2 = \frac{0.4646 - (0.5 \times 2.42)}{0.5} = -1.49 \quad (4.4)$$

Based on the example calculated above, the resulted  $K$  and  $Cc$  values for IOS surfactants are summarized in Table 4.7

**Table 4.7** Summary of the  $K$  and  $C_c$  values of IOS C15-18 and IOS C19-23 surfactants

Surfactant	IOS C15-18	IOS C19-23
$K$	$0.0934 \pm 0.02$	$0.0622 \pm 0.02$
$C_c$	$-1.49 \pm 0.16$	$-0.3946 \pm 0.16$
$C_c/K$	-15.95	-6.34

In Table 4.7, the  $C_c$  value increases (i.e., less negative) with the increase of carbon chains in IOS surfactants. The carbon chain length of IOS C15-18 is shorter than IOS C19-23, which is a negative  $C_c$  value (-1.49); IOS C19-23 has the longer carbon chain and more positive  $C_c$  value (-0.71). This value is consistent with the definition of the  $C_c$  that corresponds to the hydrophobicity of surfactants (Acosta et al., 2008). For example, a more negative  $C_c$  value corresponds to a more hydrophilicity of the surfactants of which tend to form normal oil-swollen micelles, whereas a more positive  $C_c$  value corresponds to a more hydrophobic surfactant that tends to form water-swollen reverse micelles. In general, the surfactants with longer carbon chains tend to have more hydrophobicity, indicating a more positive  $C_c$  value.

Table 4.7 also shows the  $K$  values of the IOS surfactants, which is in the range of 0.039 to 0.1. The  $K$  value for the common sulfonate head group has been reported to be 0.16 (J. Salager, Bourrel, et al., 1979; J. Salager, Morgan, et al., 1979; Baran et al., 1994; Witthayapanyanon et al., 2008; Hammond & Acosta, 2012). Notwithstanding, the reported  $K$  value is slightly different from the  $K$  values obtained from the experiment. The explanation given for this difference is that the head groups of the IOS surfactants are sulfonate, di-sulfonate and hydroxyl groups that have contributions on the  $K$  values.

### 4.3.2 Determination of predicted optimal salinity ( $S^*$ )

**Table 4.8** K and Cc values of the surfactants.

Surfactants	K	Cc	Reference
IOS15-18	0.083	-2.130	Harwell et al., 2017
IOS19-23	0.114	-1.390	Harwell et al., 2017
IOS24-28	0.127	-0.650	Harwell et al., 2017
AOT	0.170	2.42	Witthayapanyanon et al., 2008

**Table 4.9** Predicted optimum salinity ( $S^*$ ) for AOT: IOS C15-18 with heptane (EACN=7) as an oil phase under room temperature ( $25 \pm 2$  °C) at 0.03 M total surfactant concentration at 25 °C

Primary SFT	Secondary SFT	Ratio	$C_{c_{mix}}$	$K_{mix}$	$S^*_{mix}$
AOT	IOS15-18	9:1	1.965	0.161	0.433
AOT	IOS15-18	8:2	1.510	0.153	0.643
AOT	IOS15-18	7:3	1.055	0.144	0.953
AOT	IOS15-18	6:4	0.600	0.135	1.414
AOT	IOS15-18	5:5	0.145	0.127	2.097
AOT	IOS15-18	4:6	-0.310	0.118	3.110
AOT	IOS15-18	3:7	-0.765	0.109	4.612
AOT	IOS15-18	2:8	-1.220	0.100	6.840
AOT	IOS15-18	1:9	-1.675	0.092	10.144

**Table 4.10** Predicted optimum salinity ( $S^*$ ) for AOT: IOS C19-23 with heptane (EACN=7) as an oil phase under room temperature ( $25\pm 2$  °C) at 0.03 M total surfactant concentration at 25 °C

Primary SFT	Secondary SFT	Ratio	$C_{mix}$	$K_{mix}$	$S^*_{mix}$
AOT	IOS19-23	9:1	2.039	0.164	0.411
AOT	IOS19-23	8:2	1.658	0.159	0.579
AOT	IOS19-23	7:3	1.277	0.153	0.815
AOT	IOS19-23	6:4	0.896	0.148	1.147
AOT	IOS19-23	5:5	0.515	0.142	1.614
AOT	IOS19-23	4:6	0.134	0.136	2.272
AOT	IOS19-23	3:7	-0.247	0.131	3.198
AOT	IOS19-23	2:8	-0.628	0.125	4.501
AOT	IOS19-23	1:9	-1.009	0.120	6.336

**Table 4.11** Predicted optimum salinity ( $S^*$ ) for AOT: IOS C15-18 with decane (EACN=10) as an oil phase under room temperature ( $25\pm 2$  °C) at 0.03 M total surfactant concentration at 25 °C

Primary SFT	Secondary SFT	Ratio	$C_{mix}$	$K_{mix}$	$S^*_{mix}$
AOT	IOS15-18	9:1	1.965	0.161	0.703
AOT	IOS15-18	8:2	1.510	0.153	1.016
AOT	IOS15-18	7:3	1.055	0.144	1.468
AOT	IOS15-18	6:4	0.600	0.135	2.121
AOT	IOS15-18	5:5	0.145	0.127	3.065
AOT	IOS15-18	4:6	-0.310	0.118	4.428
AOT	IOS15-18	3:7	-0.765	0.109	6.398
AOT	IOS15-18	2:8	-1.220	0.100	9.244
AOT	IOS15-18	1:9	-1.675	0.092	13.356

**Table 4.12** Predicted optimum salinity ( $S^*$ ) for AOT: IOS C19-23 with decane (EACN=10) as an oil phase under room temperature ( $25\pm 2$  °C) at 0.03 M total surfactant concentration at 25 °C

Primary SFT	Secondary SFT	Ratio	$C_{mix}$	$K_{mix}$	$S^*_{mix}$
AOT	IOS19-23	9:1	2.039	0.164	0.674
AOT	IOS19-23	8:2	1.658	0.159	0.932
AOT	IOS19-23	7:3	1.277	0.153	1.290
AOT	IOS19-23	6:4	0.896	0.148	1.786
AOT	IOS19-23	5:5	0.515	0.142	2.472
AOT	IOS19-23	4:6	0.134	0.136	3.421
AOT	IOS19-23	3:7	-0.247	0.131	4.735
AOT	IOS19-23	2:8	-0.628	0.125	6.554
AOT	IOS19-23	1:9	-1.009	0.120	9.070

**Table 4.13** Summarize of the optimum salinities ( $S^*$ ) for AOT: IOS C15-18 with heptane (EACN=7) as an oil phase under room temperature ( $25\pm 2$  °C) at 0.03 M total surfactant concentration at 25 °C

Primary SFT	Secondary SFT	Ratio by molar	$S^*_{mix}$ Predicted	$S^*_{mix}$ Experiment
AOT	IOS15-18	9:1	0.433	0.20
AOT	IOS15-18	8:2	0.643	0.35
AOT	IOS15-18	7:3	0.953	0.50
AOT	IOS15-18	6:4	1.414	0.90
AOT	IOS15-18	5:5	2.097	1.60
AOT	IOS15-18	4:6	3.110	No middle phase
AOT	IOS15-18	3:7	4.612	No middle phase
AOT	IOS15-18	2:8	6.840	No middle phase
AOT	IOS15-18	1:9	10.144	No middle phase

**Table 4.14** Summarizes the optimum salinities for AOT: IOS C19-23 with heptane (EACN=7) as an oil phase under room temperature ( $25\pm 2$  °C) at 0.03 M total surfactant concentration at 25 °C

Primary SFT	Secondary SFT	Ratio by molar	$S^*_{mix}$ Predicted	$S^*_{mix}$ Experiment
AOT	IOS19-23	9:1	0.411	0.10
AOT	IOS19-23	8:2	0.579	0.20
AOT	IOS19-23	7:3	0.815	0.40
AOT	IOS19-23	6:4	1.147	0.60
AOT	IOS19-23	5:5	1.614	0.80
AOT	IOS19-23	4:6	2.272	No middle phase
AOT	IOS19-23	3:7	3.198	No middle phase
AOT	IOS19-23	2:8	4.501	No middle phase
AOT	IOS19-23	1:9	6.336	No middle phase

**Table 4.15** Summarizes the optimum salinities for AOT: IOS C15-18 with decane (EACN=10) as an oil phase under room temperature ( $25\pm 2$  °C) at 0.03 M total surfactant concentration at 25 °C

Primary SFT	Secondary SFT	Ratio by molar	$S^*_{mix}$ Predicted	$S^*_{mix}$ Experiment
AOT	IOS15-18	9:1	0.703	0.30
AOT	IOS15-18	8:2	1.016	0.50
AOT	IOS15-18	7:3	1.468	0.85-0.95
AOT	IOS15-18	6:4	2.121	1.50
AOT	IOS15-18	5:5	3.065	1.90-2.50
AOT	IOS15-18	4:6	4.428	No middle phase
AOT	IOS15-18	3:7	6.398	No middle phase
AOT	IOS15-18	2:8	9.244	No middle phase

**Table 4.15** Summarizes the optimum salinities for AOT: IOS C15-18 with decane (EACN=10) as an oil phase under room temperature ( $25\pm 2$  °C) at 0.03 M total surfactant concentration at 25 °C (continued)

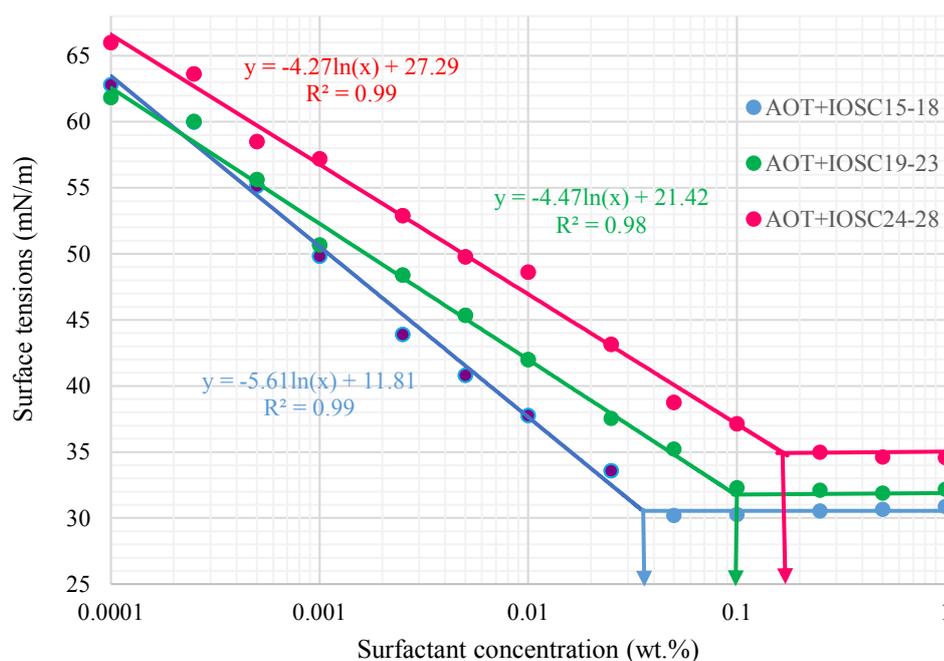
<b>Primary SFT</b>	<b>Secondary SFT</b>	<b>Ratio by molar</b>	<b>S*<sub>mix</sub> Predicted</b>	<b>S*<sub>mix</sub> Experiment</b>
AOT	IOS15-18	1:9	13.356	No middle phase

**Table 4.16** Summarizes the optimum salinities for AOT: IOS C19-23 with decane (EACN=10) as an oil phase under room temperature ( $25\pm 2$  °C) at 0.03 M total surfactant concentration at 25 °C

<b>Primary SFT</b>	<b>Secondary SFT</b>	<b>Ratio by molar</b>	<b>S*<sub>mix</sub> Predicted</b>	<b>S*<sub>mix</sub> Experiment</b>
AOT	IOS19-23	9:1	0.674	0.30
AOT	IOS19-23	8:2	0.932	0.45
AOT	IOS19-23	7:3	1.290	0.70
AOT	IOS19-23	6:4	1.786	0.90
AOT	IOS19-23	5:5	2.472	1.20
AOT	IOS19-23	4:6	3.421	No middle phase
AOT	IOS19-23	3:7	4.735	No middle phase
AOT	IOS19-23	2:8	6.554	No middle phase
AOT	IOS19-23	1:9	9.070	No middle phase

The results from Tables 4.13 to 4.16 show that the mixed surfactant systems of AOT: IOS at 9:1 to 5:5 by molar ratio can form the middle-phase microemulsions (Type III). Apart from this, AOT: IOS mixed surfactant systems 4:6 to 1:9 by molar ratio cannot form the middle phase with both heptane and decane. It can be observed that the AOT/IOS mixed surfactant system can form the middle-phase microemulsions at low salinity (NaCl). The optimal salinity ( $S^*$ ) obtained from the microemulsion phase scan experiment is presented in Table 4.13-4.16. It can be seen

that the optimum salinity from the HLD prediction using  $K$  and  $C_c$  values from the literature published elsewhere is slightly shifted, compared with that obtained from the phase scan experiment. The reason for this phenomenon could be because the IOS surfactants obtained from the manufacturer is a mixed component, leading to different  $K$  and  $C_c$  values of IOS. However, the reason for the shifting of the optimal salinity ( $S^*$ ) of the mixed surfactant system on HLD calculation needs further investigation. The synergism effect of the mixed surfactant systems was conducted to support the linear mixing rule applied for HLD calculation. The CMC of single and mixed surfactant systems were determined. The CMC of the mixed surfactant systems are shown in Figure 4.12



**Figure 4.12** Critical micelle concentration (CMC) measurement of mixed surfactant systems.

Figure 4.12 shows the plots of the surface tension values of the mixed surfactant systems (AOT: IOS C15-18, AOT: IOS C19-23, AOT: IOS C24-28) against the surfactant concentration at room temperature (25°C). In each plot, the breakpoint is used to determine the CMC of each surfactant system. It can be seen that AOT mixed

with IOS C24-28 had the CMC value at 0.18 wt% which is the highest CMC value compared to those of the other systems. The lowest CMC value is obtained from AOT mixed with IOS C15-18 which is equal to 0.038 wt%. Whereas the CMC of AOT mixed with IOS C19-23 is 0.1 wt%. It can be observed that the CMC values of mixed surfactant systems were higher than its single systems (see Table 4.17). This indicates that there is no synergism between two anionic surfactants with asymmetric molecular structures.

**Table 4.17** Summarize of the CMCs of single surfactants and AOT: IOS (5: 5 by molar ratio) mixed surfactant systems at room temperature ( $25\pm 2^\circ\text{C}$ )

Surfactant system	CMC (wt%)	Slope	Area per molecule (nM/mole)
AOT	0.055	-	-
IOS C15-18	0.030	-	-
IOS C19-23	0.060	-	-
IOS C24-28	0.189	-	-
AOT: IOS C15-18	0.038	-5.61	0.73
AOT: IOS C19-23	0.1	-4.47	0.92
AOT: IOS C24-28	0.18	-4.27	0.96

## CHAPTER V

### CONCLUSIONS AND RECOMMENDATIONS

#### 5.1 Conclusions

This study aims to formulate the appropriate the surfactant systems through HLD concept for applying in EOR application using the binary mixture of a sodium dioctyl sulfosuccinate (AOT) and an internal olefin sulfonate (IOS). The surfactant precipitation study showed that IOS can be mixed with AOT without precipitation at any desired ratios. Three model oils used in the microemulsion formation were heptane, decane and hexadecane as an oil phase. The middle phase microemulsions of the binary mixtures of AOT and IOS C15-18 and IOS C19-23 were observed in AOT rich system (at mixing molar ratios of 5: 5 to 9: 1 (AOT: IOS) with both heptane and decane. When the fraction of IOS in the mixed surfactant of AOT rich side increased, the optimal salinity ( $S^*$ ) also increased. In other words, the molar ratio of AOT in the mixed system decreased, the optimal salinity ( $S^*$ ) increased.

For the numbers of carbon tail length of IOS surfactants, the optimal salinity ( $S^*$ ) decreased when the chain length of IOS's tail increased. In addition, the effects of an increase in EACN of the alkane oils on optimal salinity of the microemulsions indicated that the EACN of the oil increased, the salinity required to achieve the optimal also increased.

The minimum IFT values of the formulated microemulsions using the mixed AOT/IOS system were achieved at the optimum salinity obtained from the microemulsion phase scan experiment. The IFTs for the mixed surfactant system with the three model oils were in the range of 0.001-0.005 mN/m which are an ultralow IFT. However, no trend was observed when varying the ratio of AOT and IOS in the surfactant mixture.

The HLD equation for mixed anionic-anionic surfactant system could be used to determine the K and Cc values of the mixture AOT and IOS surfactant containing different alkyl chain length. The Cc values of IOS C15-18 and IOS C19-23 are  $-1.49 \pm 0.16$  and  $0.71 \pm 0.16$ , respectively. Due to the fact that the carbon chain of IOS C15-18 is shorter than IOS C19-23, the Cc values of IOS C15-18 is more negative Cc value

than IOS C19-23. This behavior is consistent with the definition of the  $C_c$  that corresponds to the hydrophobicity of surfactants.

However, the optimum salinity ( $S^*$ ) predicted from the HLD method and conducted from the microemulsion phase scan experiment are slightly shifted. This could be due to the fact that the surfactants used in this study are the mixed component of the different alkyl chain (i.e. C15 to 18).

## **5.2 Recommendations**

This study, the HLD equation to predict the optimal condition of the mixed anionic-anionic surfactant system was applied based on the linear mixing rule. Notwithstanding, a binary surfactant mixture can present synergism effect.

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## APPENDICES

### Appendix A Middle Phase Microemulsion Formation

The middle phase microemulsion consisted of the aqueous phase and oil phase. The aqueous phase composed of surfactant, co-surfactant, salt (NaCl) and water. For oil phase, the alkane oils were varied (i.e., heptane oils and decane oils).

**Table A1** Summarize of the optimum salinities , $S^*$ , of the binary mixtures of sodium dioctyl sulfosuccinate, AOT, and internal olefin sulfonate, IOS 15-18, 0.03 M total surfactant concentration with heptane at 25 °C

Primary SFT	Secondary SFT	Ratio by molar	$S^*_{mix}$ Predicted	$S^*_{mix}$ Experiment
AOT	IOS15-18	9:1	0.433	0.20
AOT	IOS15-18	8:2	0.643	0.35
AOT	IOS15-18	7:3	0.953	0.50
AOT	IOS15-18	6:4	1.414	0.90
AOT	IOS15-18	5:5	2.097	1.60
AOT	IOS15-18	4:6	3.110	No middle phase
AOT	IOS15-18	3:7	4.612	No middle phase
AOT	IOS15-18	2:8	6.840	No middle phase
AOT	IOS15-18	1:9	10.144	No middle phase

**Table A2** Summarizes the optimum salinities of binary mixtures of sodium dioctyl sulfosuccinate, AOT, and internal olefin sulfonate, IOS 19-23, 0.03 M total surfactant concentration with heptane at 25 °C

Primary SFT	Secondary SFT	Ratio by molar	S* <sub>mix</sub> Predicted	S* <sub>mix</sub> Experiment
AOT	IOS19-23	9:1	0.411	0.10
AOT	IOS19-23	8:2	0.579	0.20
AOT	IOS19-23	7:3	0.815	0.40
AOT	IOS19-23	6:4	1.147	0.60
AOT	IOS19-23	5:5	1.614	0.80
AOT	IOS19-23	4:6	2.272	No middle phase
AOT	IOS19-23	3:7	3.198	No middle phase
AOT	IOS19-23	2:8	4.501	No middle phase
AOT	IOS19-23	1:9	6.336	No middle phase

**Table A3** Summarizes the optimum salinities of binary mixtures of sodium dioctyl sulfosuccinate, AOT, and internal olefin sulfonate, IOS 15-18, 0.03 M total surfactant concentration with decane at 25 °C

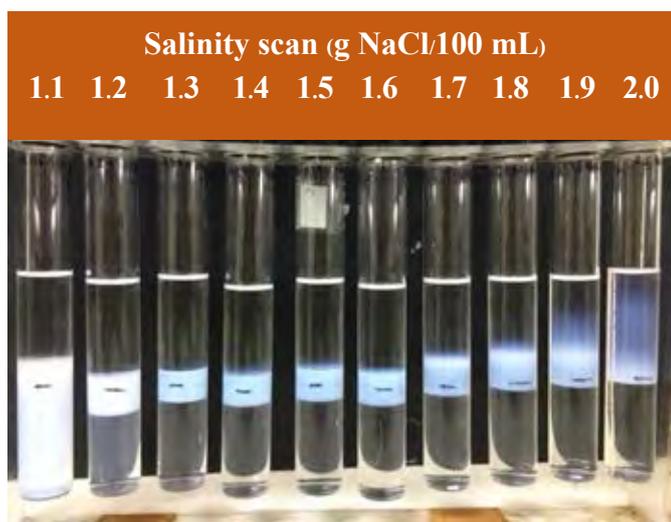
Primary SFT	Secondary SFT	Ratio by molar	S* <sub>mix</sub> Predicted	S* <sub>mix</sub> Experiment
AOT	IOS15-18	9:1	0.703	0.30
AOT	IOS15-18	8:2	1.016	0.50
AOT	IOS15-18	7:3	1.468	0.85-0.95
AOT	IOS15-18	6:4	2.121	1.50
AOT	IOS15-18	5:5	3.065	1.90-2.50
AOT	IOS15-18	4:6	4.428	No middle phase
AOT	IOS15-18	3:7	6.398	No middle phase
AOT	IOS15-18	2:8	9.244	No middle phase

**Table A3** Summarizes the optimum salinities of binary mixtures of sodium dioctyl sulfosuccinate, AOT, and internal olefin sulfonate, IOS 15-18, 0.03 M total surfactant concentration with decane at 25 °C (continued)

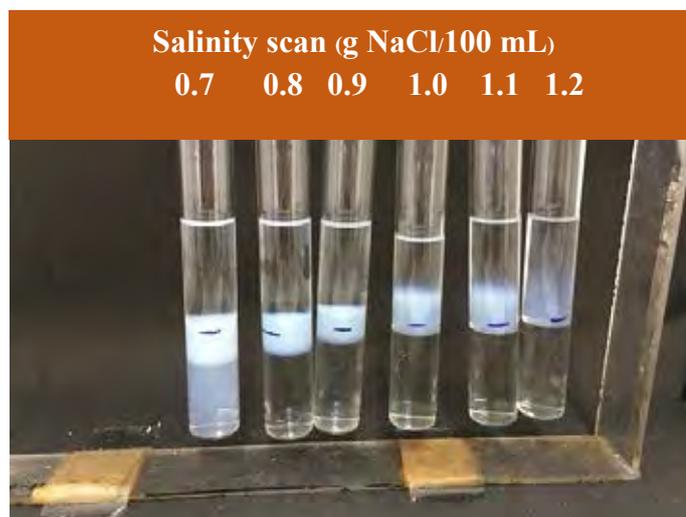
<b>Primary SFT</b>	<b>Secondary SFT</b>	<b>Ratio by molar</b>	<b>S*<sub>mix</sub> Predicted</b>	<b>S*<sub>mix</sub> Experiment</b>
AOT	IOS15-18	1:9	13.356	No middle phase

**Table A4** Summarizes the optimum salinities of binary mixtures of sodium dioctyl sulfosuccinate, AOT, and internal olefin sulfonate, IOS 19-23, 0.03 M total surfactant concentration with decane at 25 °C

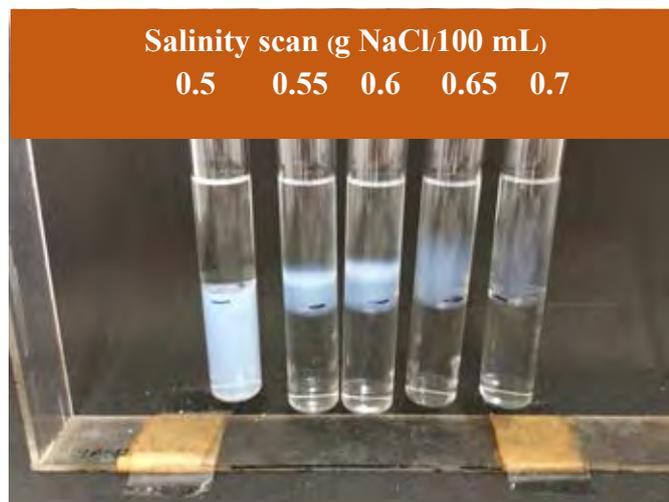
<b>Primary SFT</b>	<b>Secondary SFT</b>	<b>Ratio by molar</b>	<b>S*<sub>mix</sub> Predicted</b>	<b>S*<sub>mix</sub> Experiment</b>
AOT	IOS19-23	9:1	0.674	0.30
AOT	IOS19-23	8:2	0.932	0.45
AOT	IOS19-23	7:3	1.290	0.70
AOT	IOS19-23	6:4	1.786	0.90
AOT	IOS19-23	5:5	2.472	1.20
AOT	IOS19-23	4:6	3.421	No middle phase
AOT	IOS19-23	3:7	4.735	No middle phase
AOT	IOS19-23	2:8	6.554	No middle phase
AOT	IOS19-23	1:9	9.070	No middle phase



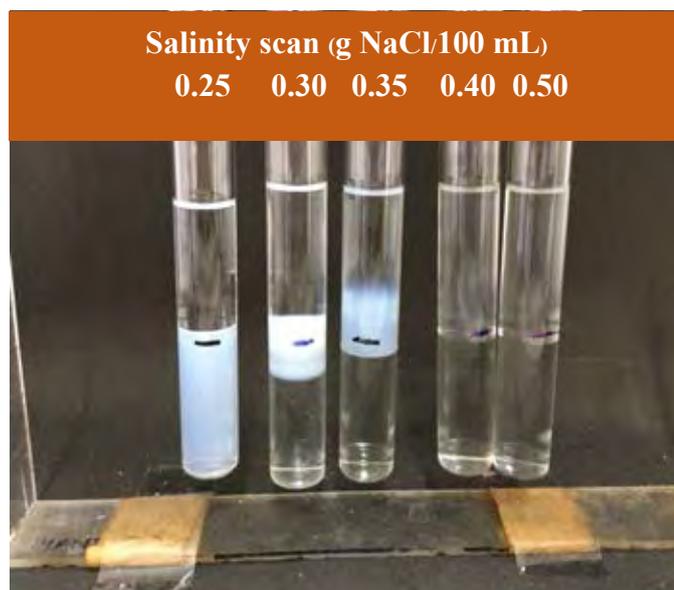
**Figure A1** Phase behavior of 5:5 by molar ratio of sodium dioctyl sulfosuccinate ,AOT, and internal olefins sulfonate ,IOS C<sub>15-18</sub>, using heptane as an oil phase.



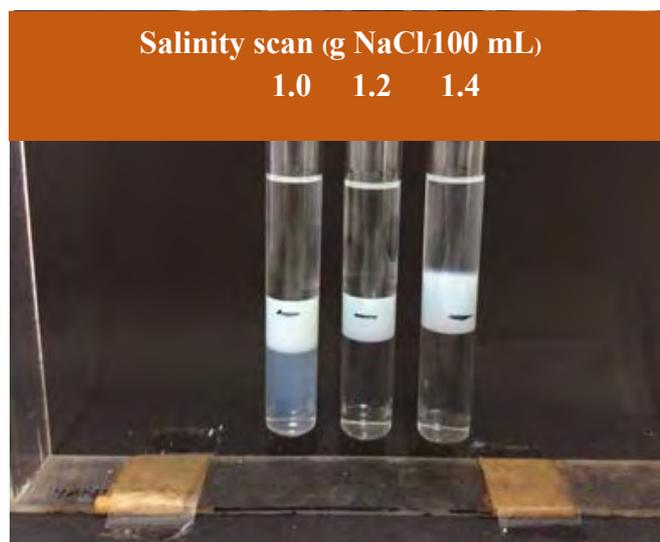
**Figure A2** Phase behavior of 6:4 by molar ratio of sodium dioctyl sulfosuccinate ,AOT, and internal olefins sulfonate ,IOS C<sub>15-18</sub>, using heptane as an oil phase.



**Figure A3** Phase behavior of 7:3 by molar ratio of sodium dioctyl sulfosuccinate ,AOT, and internal olefins sulfonate ,IOS C<sub>15-18</sub>, using heptane as an oil phase.



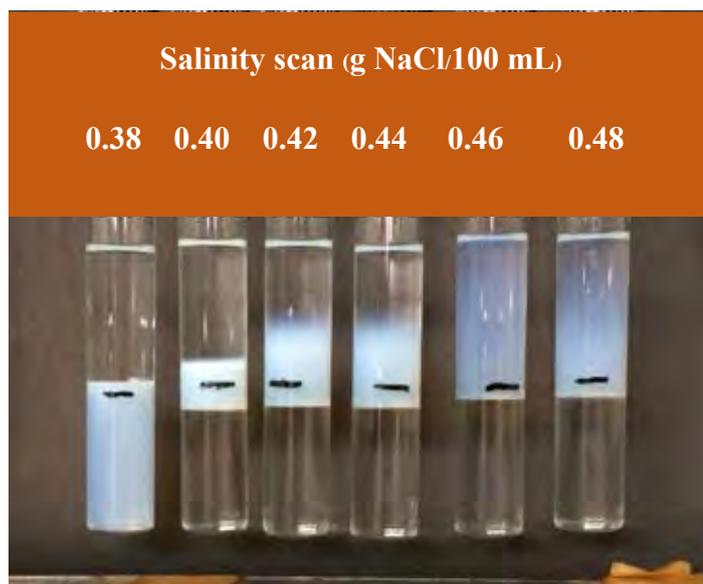
**Figure A4** Phase behavior of 8:2 by molar ratio of sodium dioctyl sulfosuccinate ,AOT, and internal olefins sulfonate ,IOS C<sub>15-18</sub>, using heptane as an oil phase.



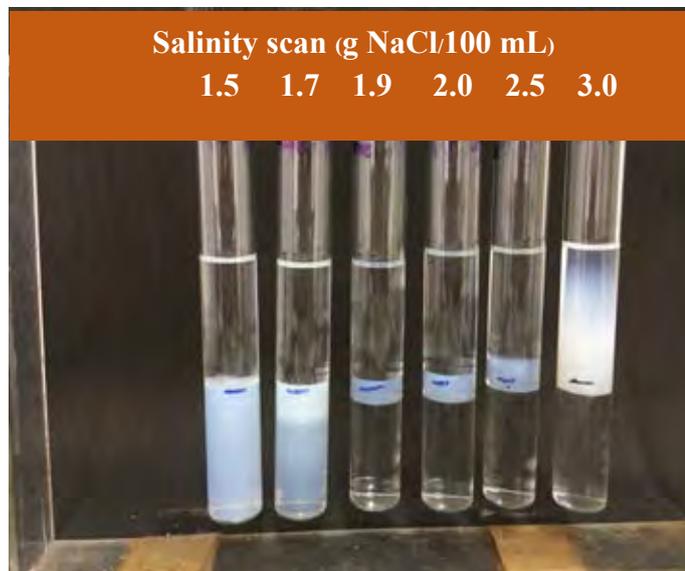
**Figure A5** Phase behavior of 5:5 by molar ratio of sodium dioctylsulfosuccinate ,AOT, and internal olefins sulfonate ,IOS C<sub>19-23</sub>, using heptane as an oil phase.



**Figure A6** Phase behavior of 6:4 by molar ratio of sodium dioctyl sulfosuccinate ,AOT, and internal olefins sulfonate ,IOS C<sub>19-23</sub>, using heptane as an oil phase.



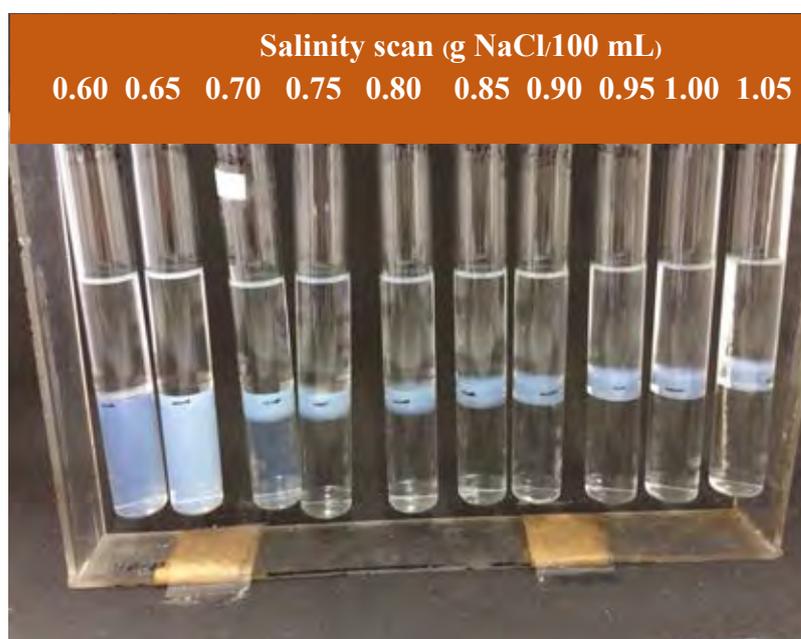
**Figure A7** Phase behavior of 7:3 by molar ratio of sodium dioctyl sulfosuccinate ,AOT, and internal olefins sulfonate ,IOS C<sub>19-23</sub>, using heptane as an oil phase.



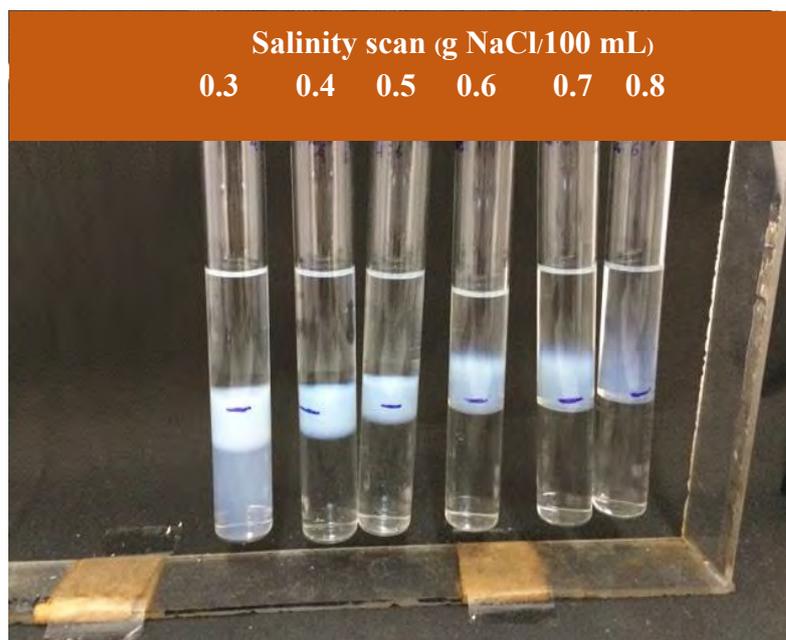
**Figure A8** Phase behavior of 5:5 by molar ratio of sodium dioctyl sulfosuccinate ,AOT, and internal olefins sulfonate ,IOS C<sub>15-18</sub>, using decane as an oil phase.



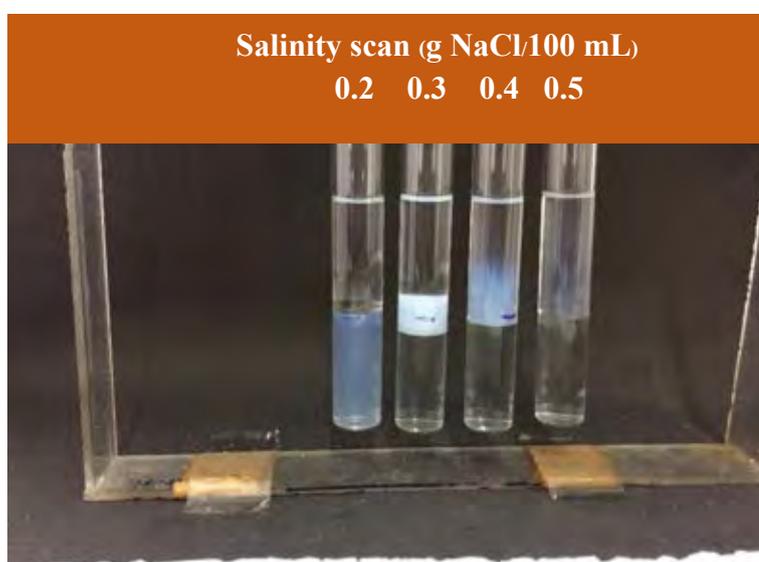
**Figure A9** Phase behavior of 6:4 by molar ratio of sodium dioctyl sulfosuccinate ,AOT, and internal olefins sulfonate ,IOS C<sub>15-18</sub>, using decane as an oil phase.



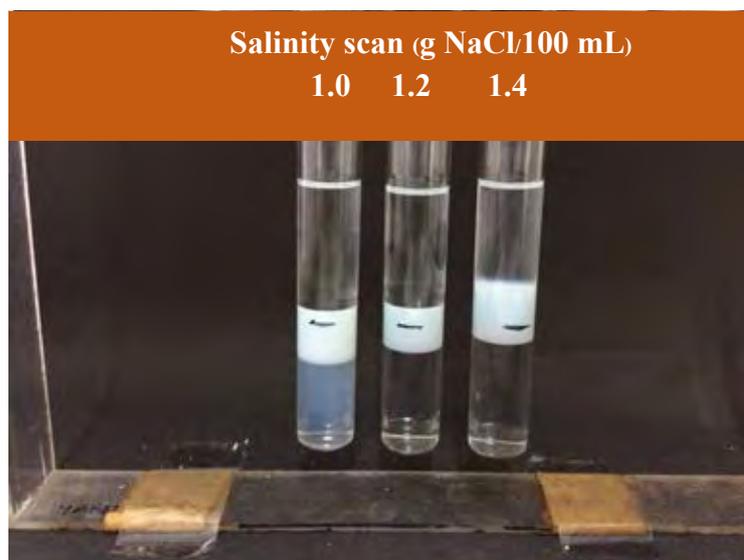
**Figure A10** Phase behavior of 7:3 by molar ratio of sodium dioctyl sulfosuccinate ,AOT, and internal olefins sulfonate ,IOS C<sub>15-18</sub>, using decane as an oil phase.



**Figure A11** Phase behavior of 8:2 by molar ratio of sodium dioctyl sulfosuccinate ,AOT, and internal olefins sulfonate ,IOS C<sub>15-18</sub>, using decane as an oil phase.



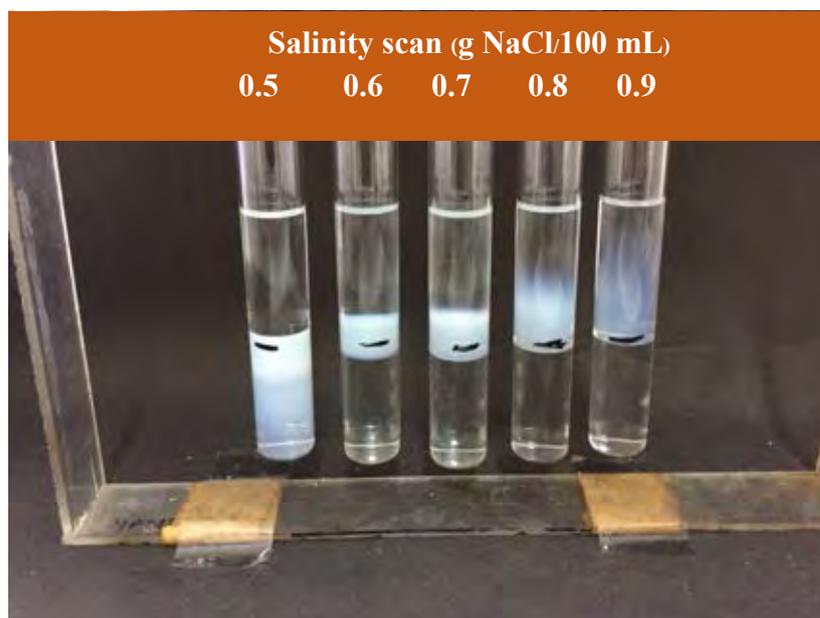
**Figure A12** Phase behavior of 9:1 by molar ratio of sodium dioctyl sulfosuccinate ,AOT, and internal olefins sulfonate ,IOS C<sub>15-18</sub>, using decane as an oil phase.



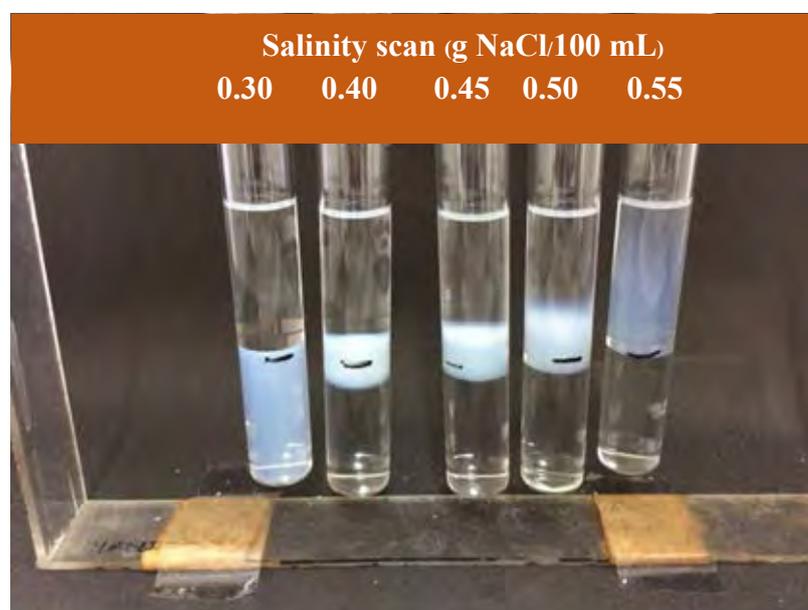
**Figure A13** Phase behavior of 5:5 by molar ratio of sodium dioctyl sulfosuccinate, AOT, and internal olefins sulfonate, IOS C<sub>19-23</sub>, using decane as an oil phase.



**Figure A14** Phase behavior of 6:4 by molar ratio of sodium dioctyl sulfosuccinate, AOT, and internal olefins sulfonate, IOS C<sub>19-23</sub>, using decane as an oil phase.



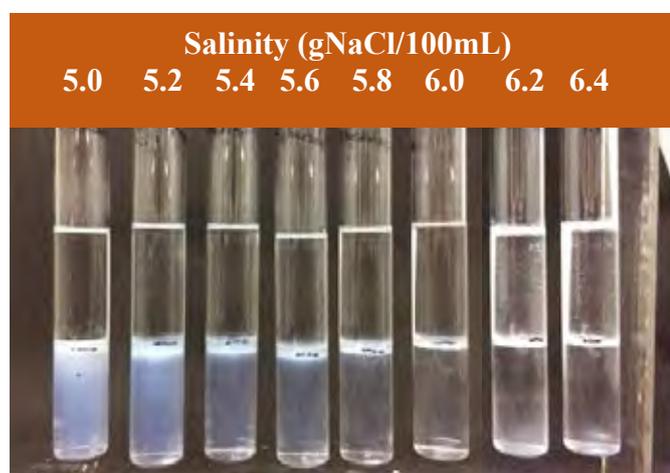
**Figure A15** Phase behavior of 7:3 by molar ratio of sodium dioctyl sulfosuccinate ,AOT, and internal olefins sulfonate ,IOS C<sub>19-23</sub>, using decane as an oil phase.



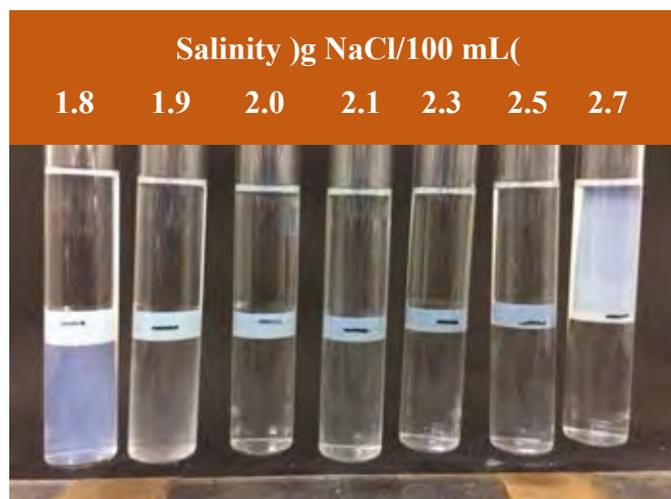
**Figure A16** Phase behavior of 8:2 by molar ratio of sodium dioctyl sulfosuccinate ,AOT, and internal olefins sulfonate ,IOS C<sub>19-23</sub>, using decane as an oil phase.



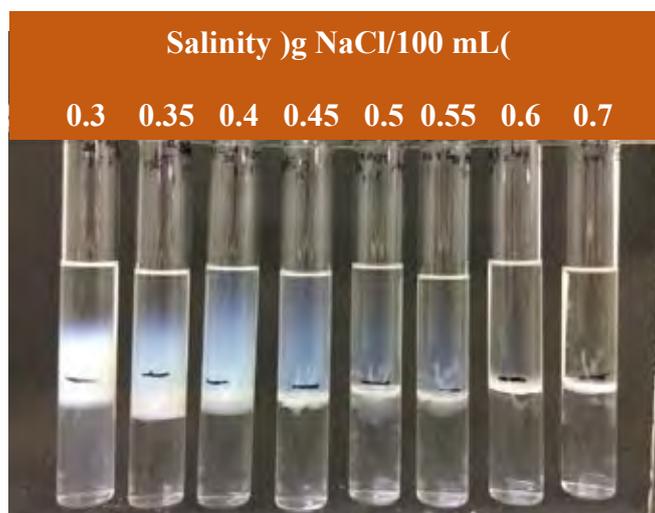
**Figure A17** Phase behavior of 9:1 by molar ratio of sodium dioctyl sulfosuccinate ,AOT, and internal olefins sulfonate ,IOS C<sub>19-23</sub>, using decane as an oil phase.



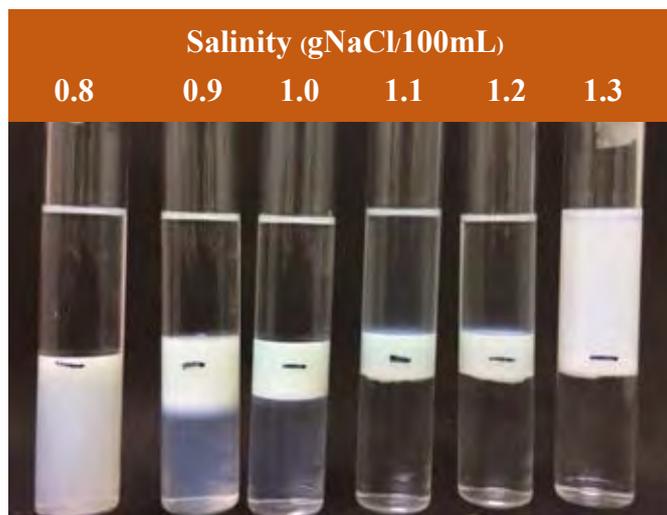
**Figure A18** Phase behavior of 5:5 by molar ratio of sodium dioctyl sulfosuccinate ,AOT, and internal olefins sulfonate ,IOS C<sub>15-18</sub>, using hexadecane as an oil phase.



**Figure A19** Phase behavior of 5:5 by molar ratio of sodium dioctyl sulfosuccinate ,AOT, and internal olefins sulfonate ,IOS C<sub>19-23</sub>, using hexadecane as an oil phase.



**Figure A20** Phase behavior of 5:5 by molar ratio of sodium dioctyl sulfosuccinate ,AOT, and internal olefins sulfonate ,IOS C<sub>24-28</sub>, using heptane as an oil phase.



**Figure A21** Phase behavior of 5:5 by molar ratio of sodium dioctyl sulfosuccinate ,AOT, and internal olefins sulfonate ,IOS C<sub>24-28</sub>, using hexadecane as an oil phase.

#### **B1. Predicted optimum salinity (S\*) from HLD equation**

**Table B1** Predicted optimum salinity, S\*, for single surfactants with heptane as an oil phase at 25 °C at surfactant concentration 0.03 M

Surfactant	K	Cc	EACN	S*	Reference
<b>IOS15-18</b>	0.083	-2.130	7	15.044	<b>Harwell and coworkers, 2017</b>
<b>IOS19-23</b>	0.114	-1.390	7	8.917	<b>Harwell and coworkers, 2017</b>
<b>IOS24-28</b>	0.127	-0.650	7	4.659	<b>Harwell and coworkers, 2017</b>
<b>AOT</b>	0.170	2.42	7	0.292	<b>Witthayapanyanon, 2008</b>

**Table B2** Predicted optimum salinity,  $S^*$ , for the binary mixtures of sodium dioctyl sulfosuccinate, AOT, and internal olefin sulfonate, IOS C15-18, with heptane at 25 °C

Primary SFT	Secondary SFT	Ratio	$C_{mix}$	$K_{mix}$	$S^*_{mix}$
AOT	IOS15-18	9:1	1.965	0.161	0.433
AOT	IOS15-18	8:2	1.510	0.153	0.643
AOT	IOS15-18	7:3	1.055	0.144	0.953
AOT	IOS15-18	6:4	0.600	0.135	1.414
AOT	IOS15-18	5:5	0.145	0.127	2.097
AOT	IOS15-18	4:6	-0.310	0.118	3.110
AOT	IOS15-18	3:7	-0.765	0.109	4.612
AOT	IOS15-18	2:8	-1.220	0.100	6.840
AOT	IOS15-18	1:9	-1.675	0.092	10.144

**Table B3** Predicted optimum salinity,  $S^*$ , for the binary mixtures of sodium dioctyl sulfosuccinate, AOT, and internal olefin sulfonate, IOS C19-23, with heptane at 25 °C

Primary SFT	Secondary SFT	Ratio	$C_{mix}$	$K_{mix}$	$S^*_{mix}$
AOT	IOS19-23	9:1	2.039	0.164	0.411
AOT	IOS19-23	8:2	1.658	0.159	0.579
AOT	IOS19-23	7:3	1.277	0.153	0.815
AOT	IOS19-23	6:4	0.896	0.148	1.147
AOT	IOS19-23	5:5	0.515	0.142	1.614
AOT	IOS19-23	4:6	0.134	0.136	2.272
AOT	IOS19-23	3:7	-0.247	0.131	3.198
AOT	IOS19-23	2:8	-0.628	0.125	4.501
AOT	IOS19-23	1:9	-1.009	0.120	6.336

**Table B4** Predicted optimum salinity for single surfactants with decane as an oil phase at 25 °C at surfactant concentration 0.03 M

Surfactant	K	Cc	EACN	S*	References
IOSC15-18	0.083	-2.130	10	19.297	Harwell and coworker,2017
IOSC19-23	0.114	-1.390	10	12.553	Harwell and coworker,2017
IOSC24-28	0.127	-0.650	10	6.820	Harwell and coworker,2017
AOT	0.17	2.42	10	0.487	Withayapanyanon, 2008

**Table B5** Predicted optimum salinity ,S\*, for the binary mixtures of sodium dioctyl sulfosuccinate ,AOT, and internal olefin sulfonate ,IOS C15-18, with decane at 25 °C

Primary SFT	Secondary SFT	Ratio	Cc <sub>mix</sub>	K <sub>mix</sub>	S* <sub>mix</sub>
AOT	IOS15-18	9:1	1.965	0.161	0.703
AOT	IOS15-18	8:2	1.510	0.153	1.016
AOT	IOS15-18	7:3	1.055	0.144	1.468
AOT	IOS15-18	6:4	0.600	0.135	2.121
AOT	IOS15-18	5:5	0.145	0.127	3.065
AOT	IOS15-18	4:6	-0.310	0.118	4.428
AOT	IOS15-18	3:7	-0.765	0.109	6.398
AOT	IOS15-18	2:8	-1.220	0.100	9.244
AOT	IOS15-18	1:9	-1.675	0.092	13.356

**Table B6** Predicted optimum salinity ,S\*, for the binary mixtures of sodium dioctyl sulfosuccinate ,AOT, and internal olefin sulfonate ,IOS C19-23, with decane at 25 °C

Primary SFT	Secondary SFT	Ratio	C <sub>mix</sub>	K <sub>mix</sub>	S* <sub>mix</sub>
AOT	IOS19-23	9:1	2.039	0.164	0.674
AOT	IOS19-23	8:2	1.658	0.159	0.932
AOT	IOS19-23	7:3	1.277	0.153	1.290
AOT	IOS19-23	6:4	0.896	0.148	1.786
AOT	IOS19-23	5:5	0.515	0.142	2.472
AOT	IOS19-23	4:6	0.134	0.136	3.421
AOT	IOS19-23	3:7	-0.247	0.131	4.735
AOT	IOS19-23	2:8	-0.628	0.125	6.554
AOT	IOS19-23	1:9	-1.009	0.120	9.070

### Appendix C Calculation of Solution Preparation

#### C1. Salinity (NaCl) solution preparation

The total concentration of all experiments was 0.03 M. In phase behavior experiments, the twice concentration of salinity (NaCl) solution and surfactant solution should be considered when combined together. The example of calculation is shown below;

Assume 1000mL of 10 gNaCl/100mL solution

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

$$\text{Desired NaCl weight (g)} = \frac{10 \text{ gNaCl}}{100\text{mL solution}} \times 1000\text{mL solution}$$

$$\text{Desired NaCl weight (g)} = 100 \text{ g}$$

Assume 2.5 mL of 2 gNaCl/100mL mixing with surfactant solution in salinity scan

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

$$\text{Stock solution volume} \times \frac{10 \text{ gNaCl}}{100\text{mL solution}} = 2 \times \frac{2 \text{ gNaCl}}{100\text{mL solution}} \times 2.5\text{mL}$$

## C2. Surfactant solution preparation

**Table C1** Active mass and molecular weight of surfactants in this study

Surfactant	Active content )%(	Molecular weight
AOT	>97.00	444.56
IOS C <sub>15-18</sub>	28.03	350.00
IOS C <sub>19-23</sub>	31.30	414.90
IOS C <sub>24-28</sub>	69.40	498.10

Assume 250 mL of 0.03 M AOT solution

$$\text{Surfactant weight (g)} = 2 \times \frac{0.03 \text{ mol}}{\text{L}} \times \frac{\text{g Mw}_{\text{surfactant}}}{1 \text{ mol}} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times \frac{1}{\% \text{active}} \times \text{Stock Volume (mL)}$$

The desired surfactant weight for preparing stock solution in each surfactant can be calculated as following

$$\text{AOT weight (g)} = 2 \times \frac{0.03 \text{ mol}}{\text{L}} \times \frac{444.56 \text{ g}}{1 \text{ mol}} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times \frac{1}{0.97} \times 250 \text{ mL} = 6.8746 \text{ g}$$

$$\text{IOS}_{\text{C}_{15-18}} \text{ weight (g)} = 2 \times \frac{0.03 \text{ mol}}{\text{L}} \times \frac{350 \text{ g}}{1 \text{ mol}} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times \frac{1}{0.2803} \times 250 \text{ mL} = 18.7299 \text{ g}$$

$$\text{IOS}_{\text{C}_{19-23}} \text{ weight (g)} = 2 \times \frac{0.03 \text{ mol}}{\text{L}} \times \frac{414.9 \text{ g}}{1 \text{ mol}} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times \frac{1}{0.313} \times 250 \text{ mL} = 19.8834 \text{ g}$$

$$\text{IOS}_{\text{C}_{24-28}} \text{ weight (g)} = 2 \times \frac{0.03 \text{ mol}}{\text{L}} \times \frac{498.1 \text{ g}}{1 \text{ mol}} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times \frac{1}{0.694} \times 250 \text{ mL} = 10.7659 \text{ g}$$

## CURRICULUM VITAE

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**Proceedings:**

1. Jamprakhon, T., Charoensaeng, A., and Suriyapraphadilok, U., (2018, June 5) Microemulsion formulation of Novel Mixed Anionic Surfactant systems using Hydrophilic Lipophilic Deviation (HLD) method for Enhanced Oil Recovery. Proceedings of The 24<sup>th</sup> PPC Symposium on Petroleum, Petrochemicals, and Polymers and The 9<sup>th</sup> Research Symposium on Petrochemicals and Materials Technology, Bangkok, Thailand.
2. Jamprakhon, T., Charoensaeng, A., and Suriyapraphadilok, U., (2017, Oct 18-20) Binary Low IFT Surfactant System Using HLD Concept for Oil Recovery. Proceedings of The 7<sup>th</sup> International Thai Institute of Chemical Engineering and Applied Chemistry Conference 2017 (ITChE 2017), Bangkok, Thailand.