

**MICROEMULSION FORMATION OF VEGETABLE OILS USING MIXED
EXTENDED SURFACTANT FOR CLEANING APPLICATIONS**

Siriluk Jariyawattanarat

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By: Siriluk Jariyawattanarat
Program: Petrochemical Technology
Thesis Advisors: Dr. Ampira Charoensaeng
Prof. David A. Sabatini

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

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

Thesis Committee:

.....
(Dr. Ampira Charoensaeng)

.....
(Prof. David A. Sabatini)

.....
(Assoc. Prof. Boonyarach Kitiyanan)

.....
(Dr. Sirinthip Kittisrisawai)

ABSTRACT

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Some vegetable oils and animal fats can form semi-solid crystalline. The formation of semi-solid fats or waxy soils results in weak interactions between the oil and surfactant during the cleaning process. In this study, the anionic extended surfactant (C_{14-15} , 8PO-SO₄) systems were employed to form a middle phase microemulsion with various vegetable oils (coconut, palm and soybean oil). The addition of nonionic extended surfactant (C_{16-18} , 2PO-4EO-OH) in the mixed surfactant systems was also evaluated to observe the solubility enhancement of oil and water phase. The IFT value of formulated surfactant systems was measured to determine the optimum salinity. The Hydrophilic-Lipophilic Deviation (HLD) concept was conducted to estimate the required Cc and K parameter for examination of the correlation with the experiment. It was found that the extended surfactant systems formed the middle phase microemulsion with coconut, palm and soybean oil at the optimum salinity of 7 wt%, 8 wt% and 9 wt% NaCl, respectively. For the mixed system with the nonionic surfactant, the middle phase microemulsion formed at lower optimum salinity than that of the single surfactant system. The negative Cc value that obtained from HLD equation indicated that the hydrophilic surfactant property. For hard surface cleaning, the oil removal efficiency of mixed surfactant system is higher than the single surfactant system alone. The results obtained in this study improve the better understanding of the surfactant selection for vegetable oil microemulsions as well as semi-solid fats in cleaning application.

บทคัดย่อ

สิริลักษณ์ จรรย์วัฒน์ : การเกิดไมโครอิมัลชันของน้ำมันพืช โดยใช้สารลดแรงตึงผิวผสมที่มีส่วนขยาย สำหรับการประยุกต์ใช้ในการซักล้าง (Microemulsion Formation of Vegetable Oils Using Mixed Extended Surfactant for Cleaning Applications) อ. ที่ปรึกษา : ดร. อัมพิรา เจริญแสง และ ศ.ดร. David A. Sabatini 73 หน้า

น้ำมันพืชและไขมันสัตว์บางชนิดสามารถเกิดเป็นรูปผลึกน้ำมันกึ่งของแข็ง การเกิดน้ำมันกึ่งสภาพของแข็งหรือสภาพเป็นไขเป็นผลให้น้ำมันทำปฏิกิริยาได้น้อยกับสารลดแรงตึงผิวในระหว่างกระบวนการทำความสะอาด ในการศึกษาครั้งนี้ ระบบสารลดแรงตึงผิวประจุลบที่มีส่วนขยาย (C_{14-15} , $8PO-SO_4$) ได้นำมาใช้ในการสร้างไมโครอิมัลชันวิภูภาคกึ่งกลางกับน้ำมันพืชต่างชนิด (น้ำมันมะพร้าว, น้ำมันปาล์ม และ น้ำมันถั่วเหลือง) ด้วยวัตถุประสงค์เพื่อปรับปรุงปฏิกิริยาในวิภูภาคน้ำมัน การเติมสารลดแรงตึงผิวไม่มีประจุที่มีส่วนขยาย (C_{16-18} , $2PO-4EO-OH$) ในระบบสารลดแรงตึงผิวผสมได้นำมาศึกษาเพื่อเพิ่มการละลายในวิภูภาคน้ำมันและน้ำ ค่าแรงตึงผิวของระบบสารลดแรงตึงผิวได้นำมาศึกษาเพื่อหาระดับเกลือที่เหมาะสม แนวคิดค่าเบี่ยงเบนในการชอบน้ำและน้ำมัน (HLD) ได้นำมาใช้เพื่อประมาณค่าตัวแปร C_c และ K ที่ต้องการสำหรับการหาความสัมพันธ์กับค่าจากการทดลอง พบว่าระบบสารลดแรงตึงผิวที่มีส่วนขยายสร้างไมโครอิมัลชันวิภูภาคกึ่งกลางกับน้ำมันมะพร้าว น้ำมันปาล์ม และน้ำมันถั่วเหลือง ที่ระดับเกลือที่เหมาะสมคือ 7, 8 และ 9 ร้อยละของความเข้มข้นเกลือตามลำดับ สำหรับระบบผสมกับสารลดแรงตึงผิวไม่มีประจุ ไมโครอิมัลชันวิภูภาคกึ่งกลางเกิดที่ระดับเกลือที่เหมาะสมต่ำกว่าระบบสารลดแรงตึงผิวเดียว ค่า C_c ที่เป็นลบซึ่งได้จากการสมการค่าเบี่ยงเบนในการชอบน้ำและน้ำมัน บ่งชี้ถึงความชอบน้ำของสารลดแรงตึงผิว สำหรับการทำความสะอาดน้ำมันกึ่งของแข็งบนพื้นผิว พบว่าประสิทธิภาพการกำจัดน้ำมันของระบบสารลดแรงตึงผิวผสมมากกว่าระบบสารลดแรงตึงผิวเดี่ยว ผลที่ได้รับจากการศึกษาในครั้งนี้จะช่วยเพิ่มความเข้าใจของการเลือกใช้สารลดแรงตึงผิวไมโครอิมัลชันสำหรับน้ำมันพืชเช่นเดียวกับน้ำมันกึ่งของแข็งในการทำความสะอาด

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CHAPTER I

INTRODUCTION

Triglyceride is the main component of vegetable oil which has low solubilization capacity because of their large structure. Some vegetable oils have a melting point below the water washing temperature that can form semi-solid fat. The semi-solid fat results weak interactions between the oil and surfactant which make them difficult to remove from surface during a cleaning process (Do *et al.*, 2014). The surfactants are useful in detergent and cleaning applications that they can reduce the interfacial tension (IFT) between the washing solution and the surface and the washing solution and the oil. Microemulsions are thermodynamically stable mixtures of water oil and surfactant, which are divided into four types, Winsor Type I (oil-in-water), Winsor Type II (water-in-oil), Winsor Type III (bicontinuous phase) and Winsor Type IV (single phase). The middle phase microemulsion or Winsor Type III can provide not only high oil solubilization but also low interfacial tension (Do *et al.*, 2009).

The extended surfactants have intermediate ethylene oxide (EO) and propylene oxide (PO) groups inserted between the hydrophilic head and hydrophobic tail. Due to their unique structure, the extended surfactants can improve the solubilization of oil in microemulsion and provide ultralow IFT (Phan *et al.*, 2010). This study interested in the extended surfactants to form microemulsions with long chain triglycerides oil at ambient temperature ($25\pm 2^{\circ}\text{C}$) that can provide minimum IFT value with enhancing oil removal efficiency for cleaning application. The mixed system between the extended surfactants and nonionic extended surfactant as a co-surfactant was investigated.

The HLD (Hydrophilic-Lipophilic Deviation) values have been used to explain the microemulsion systems. $\text{HLD} < 0$ for Winsor type I microemulsion, $\text{HLD} > 0$ for Winsor type II microemulsion and $\text{HLD} = 0$ for Winsor type III microemulsion. The C_c value that obtained from HLD equation was used to indicate the hydrophilicity or hydrophobicity of surfactant (Salager *et al.*, 1979).

The anionic extended surfactant used in this study is alkyl polypropoxylate sulfate which contains eight PO groups (C_{14-15} , 8PO-SO_4) in the structure. The mid-

dle phase microemulsion formation together with IFT measurement is evaluated at different salinities and surfactant concentrations to confirm the optimum salinity at low interfacial tension. The addition of co-surfactant, C_{16-18} , 2PO-4EO-OH in the mixed surfactant system is evaluated to observe the solubility enhancement. The HLD is conducted to estimate the required C_c and K values. In application, hard surface cleaning or the oil solubilization test with palm stearin as a semi/solid fat is studied to find the optimum condition of each formulated surfactant system for maximizing oil removal efficiency.

CHAPTER II

LITERATURE REVIEW

2.1 Surfactant

A surfactant (a contraction of term surface-active agent) is a substance which can adsorb onto the surface or interface of the system and can change a marked degree the surface or interfacial free energies of those surface or interface when show at low concentration in a system. The surfactants contain two groups in the molecule, one being hydrophobic (water-hating) in nature and one being hydrophilic (water-loving) in nature (Rosen, 2004) as show in Figure 2.1.

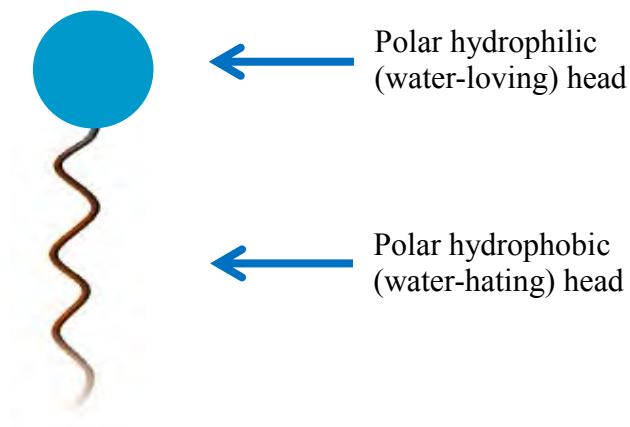


Figure 2.1 General structure of a surfactant molecule.

The hydrophilic group or head group is generally a polar or ionic group; the hydrophobic group or tail group is a long-chain hydrocarbon residue, and less often a halogenated or siloxane chain or oxygenated hydrocarbon. The surfactant can be classified into four groups based on the nature of the hydrophilic group.

2.1.1 Surfactant Classification

2.1.1.1 *Anionic Surfactant*

The surface-active portion is a negative charge. This surfactant is used widely for many applications in detergency, for example, $\text{CH}_3(\text{CH}_2)_{11}\text{SO}_4^-$

Na^+ (Sodium dodecylsulfate), $\text{RCOO}^- \text{Na}^+$ (soap), $\text{RC}_6\text{H}_4\text{SO}_3^- \text{Na}^+$ (alkylbenzene sulfonate).

2.1.1.2 Cationic Surfactant

The surface-active portion is a positive charge. This surfactant is used mainly for softener application in detergency, for example, $\text{RNH}_3^+\text{Cl}^-$ (salt of a long-chain amine), CTAB (Cetyl Trimethylammonium Bromide), $\text{RN}(\text{CH}_3)_3^+\text{Cl}^-$ (quaternary ammonium chloride).

2.1.1.3 Amphoteric Surfactant or Zwitterionic Surfactant

Both positive and negative charges may be presented in the surface-active portion. This surfactant typically is used in baby cleaner, soap and shampoo product, for example, Dodecyl Dimethyl Amine Oxide, $\text{RN}^+(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{SO}_3^-$ (sulfobetaine).

2.1.1.4 Nonionic Surfactant

The surface-active portion bears no apparent ionic charge. The nonionic surfactant is cleaner and sterilizer products, for example, polyoxyethylenated alkylphenol, $\text{RCOOCH}_2\text{CHOHCH}_2\text{OH}$ (monoglyceride of long-chain fatty acid), $\text{R}(\text{OC}_2\text{H}_4)_x\text{OH}$ (polyoxyethylenated alcohol).

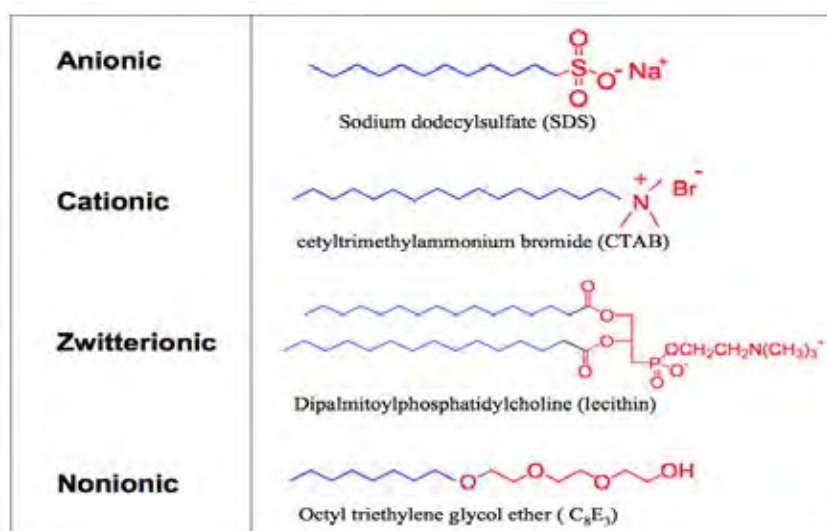


Figure 2.2 Surfactant classifications according to the nature of the hydrophilic group (Paroor, 2012).

2.1.2 Extended Surfactants

Extended surfactants have intermediate ethylene oxide (EO) and propylene oxide (PO) groups inserted between the hydrophilic head and hydrophobic tail. The extended surfactants are different from conventional surfactants. Due to their unique structure, the extended surfactants can improve not only high oil solubilization for cleaning application but also provide an ultralow IFT (Attaphong *et al.*, 2012).

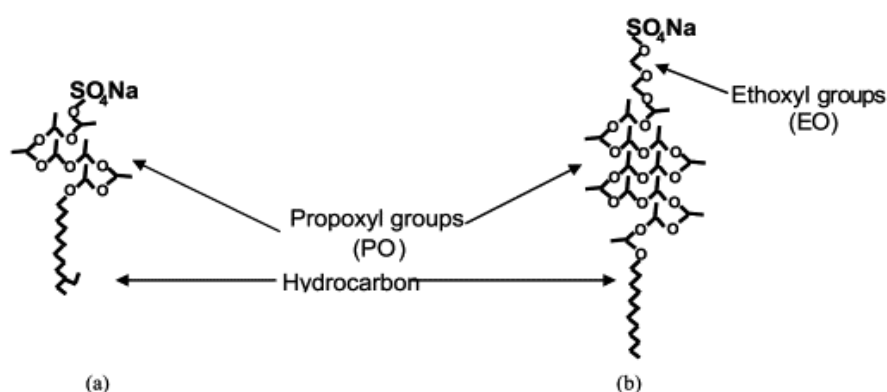


Figure 2.3 Schematics of anionic extended surfactant, (a) $R-(PO)_x-SO_4Na$, (b) $R-(PO)_y-(EO)_2-SO_4Na$ (Witthayapanyanon *et al.*, 2008).

Do and co-workers (2009) formed microemulsions at ambient conditions with soybean, sunflower, canola, peanut and olive oils using extended surfactants, linear alkyl polypropoxylated ethoxylated sulfate (LAPES) surfactants and linear alkyl polypropoxylated sulfate (LAPS) surfactants. They found that Winsor Type III and IV microemulsions can form with the vegetable oils at ambient conditions without the adding of co-surfactant and at low electrolyte concentrations. The extended surfactant studied in their work can produce ultralow IFT. Phan and co-workers (2011) studied the effect of extended surfactant structure on microemulsion formation and IFT values. They found that microemulsion formation with vegetable oils can be achieved using extended surfactants with at least eight PO groups.

2.1.3 Co-surfactant

The surfactants that apply to improve the efficiency of microemulsion surfactant system are called co-surfactants. They can increase the oil solubilization capacity of microemulsion surfactant systems (Rosen, 2004). A single surfactant system form well at a liquid/liquid boundary, which effects to quite stiff interfaces or even liquid-crystal phases. In this work, the co-surfactant is added to achieve high oil solubilization capacity and ultralow IFT. An example of such a co-surfactant is a long-chain alcohol.

2.2 Vegetable Oils

The vegetable oils are widely used as a cooking oil in households. The main component of vegetable oils is triglycerides which consist of glycerol group and three hydrocarbon chain. Because of their bulky structure, triglycerides are highly hydrophobic nature that effects low solubulization capacity. Some vegetable oils have a melting point above the water washing temperature that can form semi-solid fat or waxy soils. The semi-solid fat which composes of solid fat and liquid oil results weak interactions between the oil and surfactant (Do *et al.*, 2014).

Table 2.1 Properties of vegetable oils (Karmakar *et al.*, 2010 and Singh *et al.*, 2010)

| Vegetable oils | Density kg/m³ at 15 °c | Kinematic viscosity (cS) | Melting point (°c) | Flash point (°c) |
|-----------------------|--|---------------------------------|---------------------------|-------------------------|
| Coconut | 918 | 27 | 25 | - |
| Corn | 910 | 31-35 | -40 | 277 |
| Cottonseed | 915 | 34 | -15 | 234 |
| Palm | 918 | 40-45 | 35 | 267 |
| Peanut | 903 | 40 | -7 | 271 |
| Soybean | 914 | 29-33 | -12 | 254 |
| Sunflower | 916 | 34-36 | -15 | 274 |

Table 2.2 Fatty acid distributions of vegetable oils (Ramos *et al.*, 2008)

| Saturated fatty acid | | | | | | |
|-----------------------------------|-------------|--------------|---------------|----------------|----------------|-------------|
| Fatty acid | Palm | Olive | Peanut | Soybean | Coconut | Corn |
| Myristic (C14:0) | 0.7 | - | 0.1 | - | 18.0 | - |
| Palmitic (C16:0) | 36.7 | 11.6 | 8.0 | 11.3 | 9.0 | 6.5 |
| Stearic (C18:0) | 6.6 | 3.1 | 1.8 | 3.6 | 3.0 | 1.4 |
| Others | 0.7 | 1.0 | 5.7 | 0.4 | 62.0 | 0.1 |
| Total | 44.7 | 15.7 | 15.6 | 15.3 | 92.0 | 8.0 |
| Monounsaturated fatty acid | | | | | | |
| Fatty acid | Palm | Olive | Peanut | Soybean | Coconut | Corn |
| Oleic (C18:1) | 46.4 | 76.0 | 55.7 | 25.6 | 6.0 | 66.4 |
| Polyunsaturated fatty acid | | | | | | |
| Fatty acid | Palm | Olive | Peanut | Soybean | Coconut | Corn |
| Linoleic (C18:2) | 8.6 | 7.8 | 28.4 | 53.0 | 2.0 | 25.2 |
| Linolenic (C18:3) | 0.3 | 0.6 | 0.3 | 6.1 | - | 0.1 |
| Total | 8.9 | 8.4 | 28.7 | 59.1 | 2.0 | 25.3 |

The melting point of palm oil (35 °C) is higher than room temperature (25 ± 2 °C). In addition, palm oils have highly monounsaturated fatty acids that make them difficult to remove from surface because they turn to be a semi-solid fat at room temperature.

Table 2.3 Fatty acid composition of various palm oils (Che *et al.*, 1999)

| Fatty acid composition (%) | | | | | |
|-----------------------------------|------------------------|---------------------|------------------|--------------------|-------------------|
| Fatty acid | CPO^a | RBD palm oil | RBD olein | RBD stearin | Superolein |
| Saturated | | | | | |
| M | 0.93 | 0.92 | 0.89 | 1.21 | 0.81 |
| P | 45.48 | 46.30 | 41.54 | 61.21 | 38.47 |
| S | 3.49 | 3.52 | 3.51 | 4.00 | 3.14 |
| Total | 49.91 | 50.74 | 45.94 | 66.42 | 42.42 |
| Unsaturated | | | | | |
| O | 40.17 | 39.58 | 43.63 | 27.54 | 45.77 |
| L | 9.92 | 9.68 | 10.43 | 6.05 | 11.81 |
| Total | 50.09 | 49.26 | 54.06 | 33.59 | 57.78 |

^aCPO, crude palm oil; RBD, refined, bleached, deodorized; M, myristic; P, palmitic; S, stearic; O, oleic; L, linoleic.

Table 2.4 Glyceride composition of various palm oils (Che *et al.*, 1999)

| Glyceride composition (%) | | | | | |
|----------------------------------|------------------------|---------------------|------------------|--------------------|-------------------|
| Fatty acid | CPO^a | RBD palm oil | RBD olein | RBD stearin | Superolein |
| Diglyceride | 6.32 | 5.20 | 5.55 | 5.15 | 6.24 |
| Triglyceride | 93.60 | 94.80 | 94.45 | 94.85 | 93.76 |
| Triunsaturated | | | | | |
| OOO | 3.90 | 4.40 | 4.61 | 2.14 | 5.25 |
| OOL | 1.22 | 0.58 | 0.66 | 1.81 | 0.77 |
| Total | 5.12 | 4.98 | 5.27 | 3.95 | 6.02 |
| Glyceride composition (%) | | | | | |
| Fatty acid | CPO^a | RBD palm oil | RBD olein | RBD sterin | Superolein |
| Monosaturated | | | | | |
| PLO | 10.02 | 9.68 | 10.63 | 4.53 | 12.56 |
| POO | 21.39 | 23.26 | 25.60 | 9.40 | 29.13 |
| OOS | 2.78 | 2.24 | 2.58 | 2.47 | 3.17 |
| Total | 34.10 | 35.18 | 38.81 | 16.40 | 44.86 |
| Disaturated | | | | | |
| MPL | 3.03 | 2.20 | 2.52 | 2.22 | 2.99 |
| PPL | 9.37 | 9.23 | 9.61 | 7.18 | 10.14 |
| PPO | 27.39 | 29.62 | 29.64 | 23.36 | 22.46 |
| POS | 5.29 | 4.90 | 5.11 | 3.85 | 3.97 |
| SOS | 1.36 | - | 0.68 | - | 0.51 |
| Total | 46.43 | 45.95 | 47.56 | 36.61 | 40.07 |
| Trisaturated | | | | | |
| MMM | 0.76 | 0.42 | 0.46 | 0.93 | 0.54 |
| MMP | 2.38 | 1.70 | 1.85 | 2.05 | 2.27 |
| PPP | 4.81 | 5.51 | 0.50 | 27.16 | - |
| PPS | - | 1.06 | - | 5.06 | - |
| Total | 7.95 | 8.69 | 2.81 | 35.20 | 2.81 |
| Unknown | - | - | - | 2.69 | - |

^aSee Table 2.3 for abbreviations.

Palm oil can separate into two phases; liquid phase is known as palm olein or superolein generally used in household cooking oil, semi-solid fats or palm stearin normally use in margarine and soap production. Fatty acid composition and glyceride composition of the palm oil are tabulated in Table 2.3 and Table 2.4, respectively. Palm stearin has more saturated fatty acids and trisaturated fatty acids than palm olein.

2.3 Microemulsion

Microemulsions are thermodynamically stable mixtures consist of oil, water and surfactant. They are transparent dispersions composing of two immiscible liquids with particles of 10–100 nm (or 0.01–0.1 mm) diameters that are typically acquired by mixing the components tenderly. Types of microemulsions can be classified into oil-external (W/O), water-external (O/W), or both.

Microemulsions are divided into four types depending on microemulsion phases. Winsor Type I microemulsion is normal micelles solubilizing oil in equilibrium with the excess oil phase. Winsor Type II microemulsion is reverse micelles solubilizing water in equilibrium with an excess water phase and having oil as the continuous media. Winsor Type III microemulsion is a bicontinuous phase that has three presented phases, excess water and oil phases in equilibrium with a middle phase containing a surfactant, water, and oil. When the surfactant concentration of the middle phase increase resulting the volume of middle phase increases up to the point that water and oil do not occur, is leads to a Winsor Type IV or single phase microemulsion (Attaphong *et al.*, 2015).

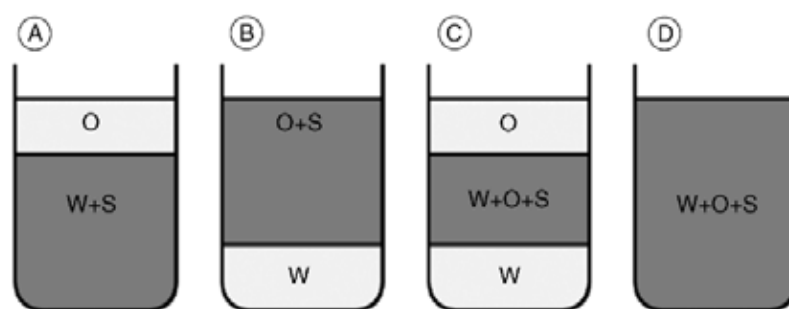


Figure 2.4 Winsor types I - IV microemulsion. A) Winsor type I; B) Winsor type II; C) Winsor type III; D) Winsor type IV (Matthia *et al.*, 2015).

The fish diagram presents the microemulsion transition from Type I to type III to type II microemulsion that shows in Figure 2.5. The diagram plots between the total surfactant concentration and a tuning parameter, which can be surfactant

mixture, electrolyte concentration for ionic surfactants or temperature for nonionic surfactants. At high surfactant concentrations, Winsor type IV (single-phase microemulsion) is formed. This area is also called a fishtail. When decreasing the surfactant concentration, the multiphase systems are formed. The Winsor type I, which forms normal micelles is occurred in the left region of the fish diagram. While Winsor type II, which forms reverse micelles is occurred in the right region of the fish diagram. Winsor type III is a bicontinuous phase or middle phase with excess both oil and water phase that appear in the middle region of the diagram. This common pattern is significant for the targeted interpretation of experimental data and improvement of microemulsion formation (Matthia *et al.*, 2015).

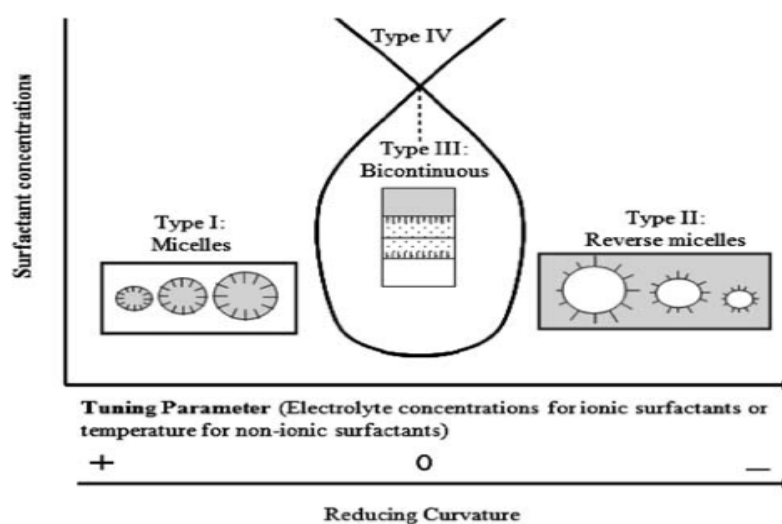


Figure 2.5 Microemulsion phase behavior presented as a fish diagram parameter (Do *et al.*, 2009).

Tanthakit and co-workers (2010) formed microemulsions using the extended surfactant, sodium alkyl polypropylene oxide sulfate with palm oil. They were able to form a Winsor Type III microemulsion at 0.2 w% surfactant concentrations and the range of salinities is from 1.22 to 3.75% NaCl. Do and co-workers (2014) studied microemulsion phase behavior. They formed microemulsions using extended surfactants $C_{10-18}PO-2EO-NaSO_4$ with four vegetable oils (i.e., jojoba oil, coconut oil,

palm kernel and canola oil). They found that the middle phase microemulsions of coconut oil and palm kernel oil were obtained at 1 % and 1.5 % NaCl, respectively.

2.4 IFT Measurement

Interfacial tension or IFT is the surface free energy per unit area. The molecules at the surface of a liquid have potential energies more than those of similar molecules in the interior of the liquid, because of the attractive interaction of molecules at the surface. At the interface between two condensed phases, the different molecules in the adjacent layers facing each other across the interface also have potential energies different from those in their respective phase (Rosen *et al.*, 2012).

In this work, IFT value was measured by spinning drop tensiometer (SITE 04, Krüss GmbH, Hamburg). IFT values indicated the phase transition of the microemulsions as shown in the fish diagram plot. The plot between IFT value and NaCl concentration can show the minimum IFT of the microemulsion at the optimum salt as shown in the work of Nguyen and Sabatini (2004). They plotted the IFT value against NaCl concentration of SBDHS mixed with JBR (0.05 M: 0.05 M) with limonene as shown in Figure 2.6.

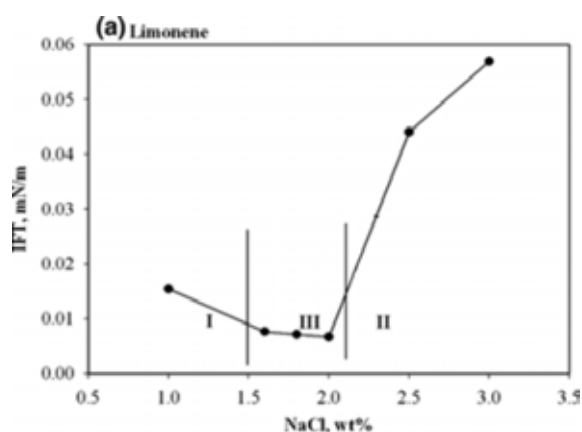


Figure 2.6 Microemulsion formulations (Winsor type I, II and III) with limonene (Nguyen and Sabatini, 2009).

Figure 2.6 shows the plot between IFT values and NaCl concentrations. The Winsor type I appeared in the left area of the plot (<1.5 wt% NaCl concentration) and Winsor type II occurred in the right area of the plot (>2.0 wt% NaCl concentration). While the ultralow IFT (<0.01 mN/m) (Nguyen and Sabatini, 2004) occurred in the middle phase region at the range of 1.5 wt% to 2.0 wt% NaCl concentration.

2.5 Hydrophilic Lipophilic Deviation (HLD) Concept

The HLD concept which was developed by Salager and coworkers (1979) is the thermodynamically derived correlation to explain microemulsion systems at the formulation conditions. Although there are other correlations such as HLB (Hydrophilic-lipophilic balance) equation and Winsor R ratio to explain emulsion and microemulsion systems as well as the overall hydrophilic-lipophilic attraction of the surfactants, there are some limitations of HLB equation and Winsor R ratio. For example, the HLB concept has its own limitations of not taking into account of both equilibrium and formulation conditions. HLB number cannot examine the effect of formulation variables on surfactant such as surfactant structure, surfactant concentration, salinity concentration, temperature and so on. HLB technique is still widely used for estimating the hydrophilic-lipophilic characteristic of surfactants and oils. For Winsor R ratio, the parameters are difficult to determine.

The HLD equation can overcome the limitations of both the Winsor R ratio and HLB equation. It can be used with mixed surfactant system and receive the optimum salinity of surfactant system. The HLD method is easy to use and is more effective than HLB and Winsor R ratio method for microemulsion (Acosta *et al.*, 2003). The HLD values are used to determine the microemulsion types. The negative value of HLD equation indicates Winsor Type I microemulsion and the positive value represents Winsor Type II microemulsion. For Winsor Type III microemulsion, the HLD value equal to zero. The HLD equation has two forms, one form of the HLD equation is for ionic surfactants and the other form of the HLD equation is for nonionic surfactants. Because the surfactant used in this research is an anionic surfactant, the HLD equation is written as:

$$\text{HLD} = \ln(S) - K \times (\text{EACN}) - f(A) + C_c - \alpha_T \Delta \quad (1)$$

where S (g/100 mL) is the salt or electrolyte concentration, K is a constant parameter in the range of 0.1 to 0.16 depending on surfactant head group. EACN is the number of carbons atoms in the oil molecules as known in alkane carbon number (ACE) for alkane oil or equivalent alkane carbon number for other oils, $f(A)$ represent the influence of alcohol, co-surfactant or co-solvent for alcohol free equal to zero. C_c is the characteristic curvature of the surfactant molecule. The C_c value for ionic surfactant has been found to correlate with the packing factor for those surfactants. α_T is the temperature coefficient and has a value of 0.01 for the most ionic surfactants, ΔT is the temperature difference between the studied surfactant and the reference temperature equal 25 °C. For Winsor type III microemulsions, $\text{HLD} = 0$, the HLD equation can be rewritten as:

$$\ln S^* = K(\text{EACN}) - C \quad (2)$$

According to the HLD concept, C_c and K are important parameters for evaluating the hydrophilic-lipophilic nature of surfactant. C_c value correlates with the hydrophobicity of the surfactant and K depends on the hydrophilicity of a surfactant. Witthayapanyanon and co-workers (2008) formed middle phase using the anionic surfactant, twin-tail sodium dihexyl sulfosuccinate surfactant (AMA). They determined the C_c and k value by the plot between optimum salinity and EACN. The optimum salinity (S^*) of AMA-oil system was determined by measuring the phase volume and the minimum interfacial tension (IFT^*). The S^* and IFT^* values of the oils are shown in Table 2.5. They obtained the C_c value at -0.93 ± 0.10 from the y-intercept of the plot between $\ln S^*$ (optimum salt) and EACN number.

Table 2.5 Summary of the optimum salinity (S^*) and the minimum equilibrium interfacial tension (IFT*) of the 0.07 M sodium dihexyl sulfosuccinate (AMA) with many of oils (Witthayapanyanon *et al.*, 2008)

| Oil | EACN | S^* (wt%) | IFT* |
|----------|------------------|-------------|--------|
| Benzene | 0 | 2.5 | 0.2920 |
| Pentane | 5 | 6.8 | 0.0450 |
| Limonene | 5.7 ^a | 6.8 | 0.0538 |
| Heptane | 7 | 8.0 | 0.0593 |
| Octane | 8 | 9.0 | 0.0803 |
| Decane | 10 | 15.5 | 0.273 |

^aCalculated at optimum salinity (S^*)

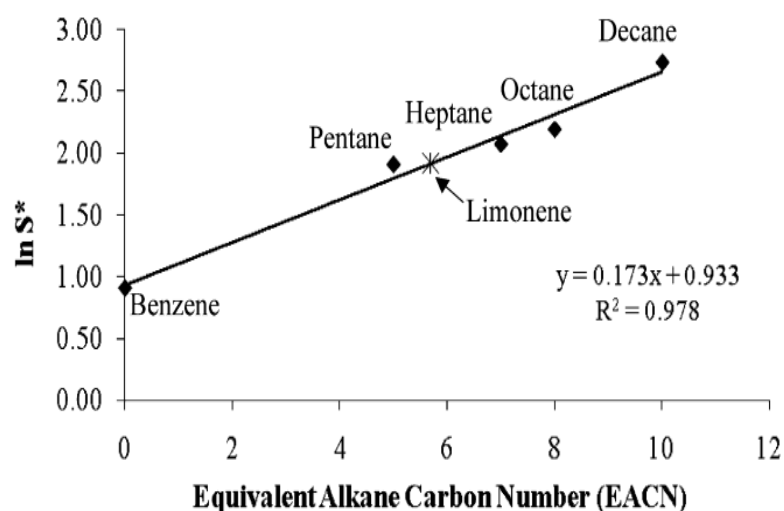


Figure 2.7 Determination of the K_{AMA} , C_{cAMA} , and EACN of limonene using a HLD equation of 0.07 M AMA surfactant at the optimum salinity (see Table 2.3) at 25 °C and no additives (Witthayapanyanon *et al.*, 2008).

Based on the HLD equation, a negative C_c value refers to a hydrophilic surfactant that forms micelles; and a positive C_c value refers to a hydrophobic surfactant that produces reverse micelles (Nguyen and Sabatini, 2009). The work of Witthaya-

panyanon and coworkers (2008) achieved the C_c value at -0.93 ± 0.10 , therefore this (AMA) surfactant is a hydrophilic surfactant.

2.6 Hard Surface Cleaning

In application, hard surface cleaning is used for determining the efficiency of the microemulsion systems in percentages of oil removal or detergency test as Eq. (4). Acosta and coworkers (2008) evaluated the hard surface cleaning power of Type I limonene microemulsions containing a total of 0.1 M of a surfactant mixture of 20% SDS and 80% SDHS. They plotted the percentage of fat removal from the surface of the glass as a function of the inverse value of the HLD as shown in Figure 2.8. They found that the fat removal and the solubilization of limonene in these Type I microemulsions increase as the inverse of the HLD increases.

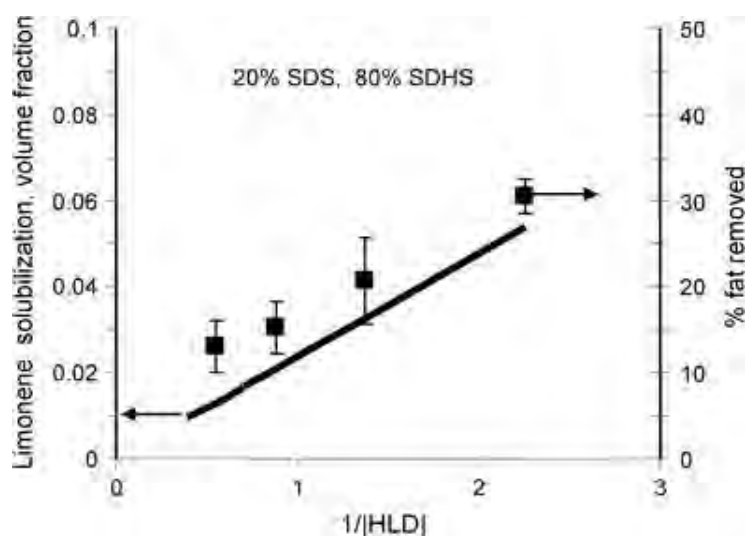


Figure 2.8 Limonene solubilization and fat removal from glass test tubes obtained with Type I microemulsions formulated with 0.1 M total surfactant and saturated with limonene at room temperature.

Tanthakit and coworkers (2010) studied palm oil removal using microemulsion-based formulations. They calculated the percentage of oil removal and plotted between microemulsion types and oil removal efficiency at different salt

concentrations. They found that the maximum oil removal was achieved in type III region as shown in Figure 2.9.

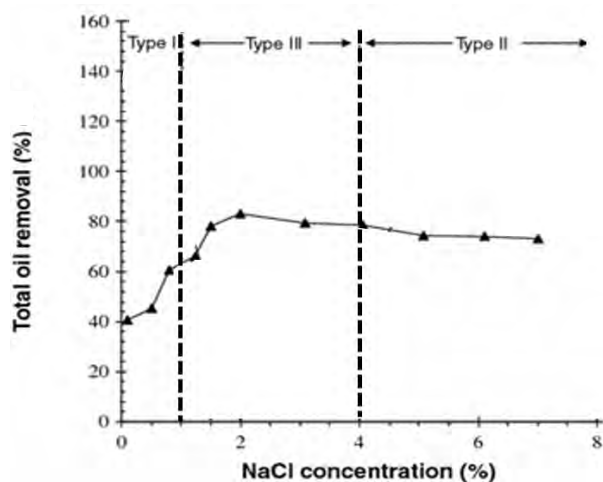


Figure 2.9 Correlation between microemulsion types and oil removal efficiency at various salinities.

$$\text{Oil removal (\%)} = \frac{(A-B)}{(A)} \times 100 \quad (4)$$

Where A is the average concentration before washing and B is the average concentration after washing with limonene for 24 hours.

CHAPTER III

METHODOLOGY

3.1 Chemicals

3.1.1 Anionic Surfactant

3.1.1.1 C_{14-15} , 8PO-SO₄ (obtained from Sasol North America)

3.1.1.2 $C_{18}H_{29}NaO_3S$ (purchased from Aldrich)

3.1.2 Co-surfactant

3.1.2.1 C_{16-18} , 2PO-4EO-OH (purchased from Sasol North America)

3.1.3 Oils

3.1.3.1 Palm Oil (Food-grade, Morakot industries Public Company Limited)

3.1.3.2 Coconut Oil (Food-grade, Nature Life industries Public Company Limited)

3.1.3.3 Soybean Oil (Food-grade, Yok industries Public Company Limited)

3.1.3.4 n-Hexane (95% purity AR-grade, purchased from Merck)

3.1.3.5 n-Dodecane (99% purity AR-grade, purchased from Merck)

3.1.3.6 n-Hexadecane (99% purity AR-grade, purchased from Merck)

3.1.4 Other chemical

3.1.4.1 Sodium Chloride (99% purity, RCL Labscan)

3.2 Equipments

- Spinning Drop Tensionmeter (Dataphysics, Model SVT20)
- 20-mL Flat-bottom Screw-up Tubes
- Orbital Shaker
- Ventilated Hood
- Incubator (BINDER, KB400/E2)
- UV/VIS Spectrophotometer (Shimadzu 1800)
- Beaker
- Auto Pipet
- Dropper
- Oven
- Hot Plate

Table 3.1 Properties of chemicals

| Type | Chemical | Formula | Molecular Weight (g/mol) | Active Matter |
|---------------|---------------------|--------------------------------|--------------------------|---------------|
| Surfactants | Anionic surfactant | $C_{14-15}, 8PO-SO_4$ | 787 | 30 |
| | Anionic surfactant | $C_{18}H_{29}NaO_3S$ (SDBS) | 186 | 99 |
| Co-surfactant | Nonionic surfactant | $C_{16-18}, 2PO-4EO-OH$ | 535 | 99 |

Table 3.2 Properties of oils

| Oil | Type | Active Matter | EACN | Melting Point (°C) |
|----------------|--------------|---------------|-------------------|--------------------------|
| Vegetable oils | Coconut oil | Food grade | 12 ^a | 23-25 ^d |
| | Palm olein | Food grade | 14 ^b | 24 ^e |
| | Palm stearin | Food grade | 14 ^b | 34.8-58.8 ^f |
| | Soybean oil | Food grade | 17.7 ^c | (-10)-(-16) ^g |
| Alkane oils | Hexane | 95 | 6 | - |
| | Dodecane | 99 | 12 | - |
| | Hexadecane | 99 | 16 | - |

^aThe data from Do *et al.*, 2009

^bThe data from Witthayapanyanon *et al.*, 2006

^cThe data from Do *et al.*, 2014

^dThe data from Gunstone, 2011

^eThe data from Gee, 2007

^fThe data from Ghosh and Bhattacharyya, 1997

^gThe data from Liu, 1997

3.3 Methodology

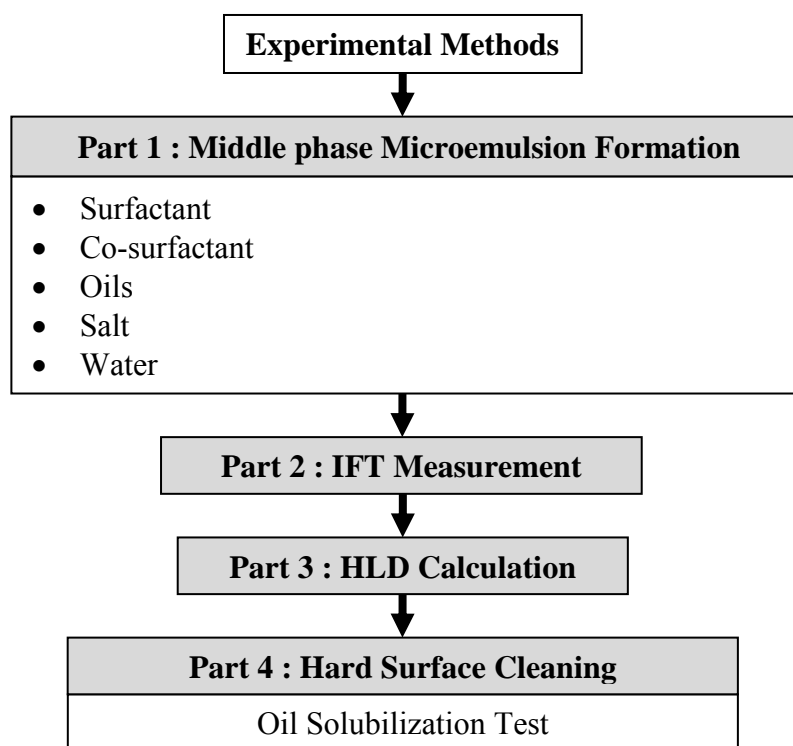


Figure 3.1 Experimental methods flow diagram.

3.3.1 Middle Phase Microemulsion Formation

Microemulsion phase scan experiments were conducted by varying surfactant concentrations from 1 to 4 wt% and the salinity concentrations from 1 to 10 wt%. A total of 5 mL oil phase and 5 mL of the aqueous phase containing a mixture of surfactant, co-surfactant, salt and water were added into a 15 ml with PTFE screwed cap vial. The solutions were mixed well to form a microemulsion under room temperature ($25\pm 2^\circ\text{C}$). After 48 hrs, the samples were observed the microemulsion by visual and then they were left for a month to ensure equilibrium.

3.3.2 IFT Measurement

The dynamic interfacial tension (IFT) experiments were performed using a spinning drop tensiometer (SITE 04, Krüss GmbH, Hamburg). The IFT meas-

measurements were made using 1-2 μL of oil injected into 300 μL . The diameter of the oil drop was measured after 20 min, whereas the rotational velocity was 7000 rpm. In this study, the interfacial tension at the middle phase formed is typically the minimum IFT value, where below 10^{-2} mN/m is defined as the ultralow IFT (Nguyen *et al.*, 2009), and this point the required salinity is called as the optimum salt.

3.3.3 HLD Calculation

In this study, the HLD was conducted to estimate K and Cc values. The HLD equation is as follow;

$$\text{HLD} = \ln(S^*) - K \times (\text{EACN}) - f(A) + Cc - \alpha_T \Delta T \quad (3.1)$$

Where salinity or S is the salt or electrolyte concentration at middle phase microemulsion, f(A) represents alcohol or alcohol-free f(A) equal to 0, α_T is the temperature coefficient and has a value of 0.01 for most ionic surfactants, ΔT is the temperature difference between the studied surfactant (25 ± 2 °C) and the reference temperature equal to 25 °C. The HLD equation indicates K and Characteristic curvature (Cc) values of each surfactant and oil. For Winsor type III microemulsions, the HLD equals to zero. Therefore, the HLD equation can be rewritten as shown in Eq. 3.2.

$$\ln(S^*) = K \times (\text{EACN}) - Cc \quad (3.2)$$

The plot between the optimum salt and EACN of alkane oils is represented by calibration curve. K and Cc values are determined by the slope and y-intercept of the plot between $\ln S^*$ (optimum salt) and EACN number, respectively. The reference alkane oil used to construct the HLD plot were hexane (C6), dodecane (C12) and hexadecane (C16).

3.3.4 Hard Surface Cleaning

Palm stearin was dyed by Oil-red-O and kept in incubator at 65 °C. Semi-solid fat or waxy solid 0.2 g was added into the 15mL flat-bottom PTFE screw-up tubes. The oil solubilization test was conducted at the optimum condition. Then, the aqueous phase containing 3wt% of C₁₄₋₁₅, 8PO-SO₄ and containing different NaCl concentrations was applied in tube. The sample was placed in a horizontal position shaker operated at 120 rpm. After that the surfactant solution containing any emulsified fat was removed and the sample was washed by DI water and DI water was evaporated in an incubator at 105 °C. The oil (fats) which is leftover in the bottom of the tube was the remaining oil. 5mL limonene was used to remove the dyed oil in the tubes. Amount of the remaining oil (dye oil) in the tube was measured by a UV/VIS spectrophotometer (1800 Shimadzu, liquid) for absorbance at λ_{max} (Acosta *et al.*, 2008). The concentration of the remaining oil was calculated throughout the material balance equation. The percentage of oil removal was calculated followed by the Eq. 3.3.

$$\text{Oil removal (\%)} = \frac{(A-B)}{(A)} \times 100 \quad (3.3)$$

Where A is the average concentration before washing and B is the average concentration after washing with limonene after 24 hours.

CHAPTER IV

RESULT AND DISCUSSION

In this study, the middle phase microemulsion was formulated with vegetable oils using the extended surfactant (C_{14-15} , 8PO-SO₄) and the co-surfactant (C_{16-18} , 2PO-4EO-OH) for enhance oil removal efficiency for semi-solid fat cleaning application. The addition of nonionic surfactant as a co-surfactant was conducted to enhance the solubilization of the vegetable oil. The anionic extended surfactant, C_{14-15} , 8PO-SO₄ and the nonionic extended surfactant, C_{16-18} , 2PO-4EO-OH were selected as a mixed surfactant system by varying the ratios between anionic and nonionic surfactants. Three vegetable oils (soybean, coconut and palm oil) were selected due to their different fatty acid composition and their EACN. For the experiments, the middle phase microemulsion formation was performed to determine the optimum salinity. The IFT measurement was conducted to confirm the optimum salinity. The HLD equation was conducted to estimate the Cc and K values of surfactant. For application study, the hard surface cleaning experiment using palm stearin as a semi-solid fat was performed to determine the oil removal efficiency, the results of each experiment are reported and discussed as following.

4.1 Middle Phase Microemulsion Formation

The vegetable oil based microemulsion systems were formed by the mixture of anionic extended surfactant, C_{14-15} , 8PO-SO₄, and nonionic extended surfactant, C_{16-18} , 2PO-4EO-OH. The surfactant properties are shown in Table 4.1. The vegetable oils used in this study were soybean oil, coconut oil and palm oil. Generally, the middle phase or Winsor type III microemulsions form at the optimum salinity (Do *et al.*, 2014). At Winsor type III, micelles form a bicontinuous phase or middle phase which places in the middle level of the solution between the oil phase (upper level) and the aqueous phase (lower level).

Table 4.1 Surfactant properties

| Surfactants | Alkyl C# | # of EOs | # of POs | Mw (g/mol) | Active (wt%) | CMC (mM) | HLB ^b |
|---|-------------|-------------|-------------|---------------|-----------------|--------------------|------------------|
| C ₁₄₋₁₅ , 8PO-SO ₄ (Alfoterra® 145-8S) | 14-15 | - | 8 | 787 | 30 | 0.015 ^a | 37.85 |
| C ₁₆₋₁₈ , 2PO-4EO-OH (MARLOX RT42) | 16-18 | 4 | 2 | 535 | 99 | - | 2.32 |

^aThe data from Archawapanich *et al.*, 2012

^bDavies's HLB equation from Davies, 1957

The microemulsion phase scan was conducted in 15 ml flat-bottom test tubes to examine the middle phase. The appropriate ratios between anionic extended and nonionic extended surfactant select based on the presence of middle phase formation. The microemulsion phase scan was conducted at ratio of 1:1, 8:2 and 9:1 (wt% of C₁₄₋₁₅, 8PO-SO₄: wt% of C₁₆₋₁₈, 2PO-4EO-OH). Then, the ratio of 9:1 (wt%:wt%) was selected for further the middle phase microemulsion formation experiments.

In this work, the microemulsion phase scan was performed with different vegetable oils deviated by both their fatty acid content and EACN. It was found that the middle phases were clearly observed with soybean oil, coconut oil and palm oil as showed in Table 4.2.

Table 4.2 Summarize the optimum salinities of $C_{14-15}, 8PO-SO_4$ and $C_{14-15}, 8PO-SO_4/ C_{16-18}, 2PO-4EO-OH$ with coconut, palm and soybean oils

| Vegetable oil | | Optimum Salinity (S*) | | |
|---------------|--|-----------------------|-----------------|-----------------|
| | | Soybean | Palm | Coconut |
| EACN | | 17.7 ^a | 14 ^b | 12 ^c |
| Single | $C_{14-15}, 8PO-SO_4$ | 9 | 8 | 7 |
| Mixed | $C_{14-15}, 8PO-SO_4/ C_{16-18}, 2PO-4EO-OH$ | 8 | 7 | 6 |

^a The data from Do *et al.*, 2014

^b The data from Witthayapanyanon *et al.*, 2006

^c The data from Do *et al.*, 2009

The middle phase microemulsion of the single anionic extended surfactant, $C_{14-15}, 8PO-SO_4$ alone, with soybean oil (EACN=17.7) was visually observed at 9 wt% NaCl concentration, while the system with palm oil (EACN=14) was appeared at 8 wt% NaCl and coconut oil (EACN=14) was observed at 7 wt% NaCl. It can be seen that the optimum salinity (S*) of the microemulsion system decreases with decreasing EACN of the vegetable oils.

Table 4.2 presents the optimum salinity (S*) of the single anionic extended surfactant system with three types of vegetable oil. The middle phase microemulsions of the system with soybean oil, palm oil and coconut oil obtained at different salinity are shown in Figures 4.1 to 4.3, respectively. The microemulsion formation of the $C_{14-15}, 8PO-SO_4$ alone with the vegetable oils was able to produce Type I, III and II microemulsions. This trend is in accordance with the work of Do and co-workers (2014) that they were able to form Type I, III and II microemulsions using $C_{10,18PO-2EO-SO_4}$ alone with various vegetable oils (i.e., coconut, palm kernel, canola and jojoba oil).

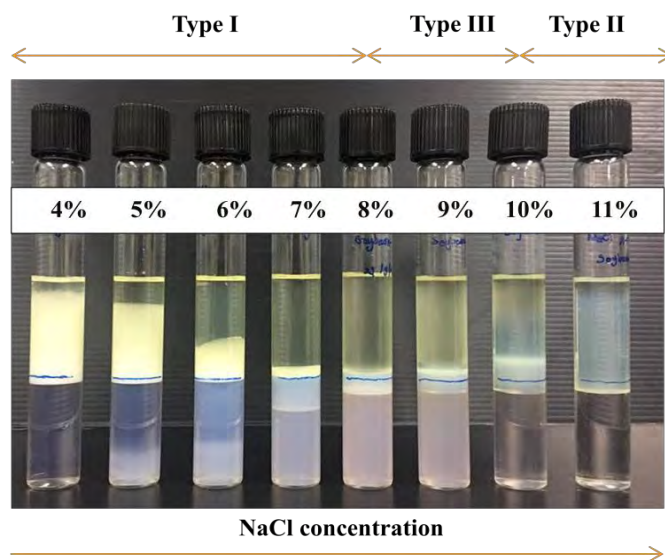


Figure 4.1 The phase scan of the microemulsion system using 3 wt% C₁₄₋₁₅, 8PO-SO₄ with soybean oil as an oil phase.

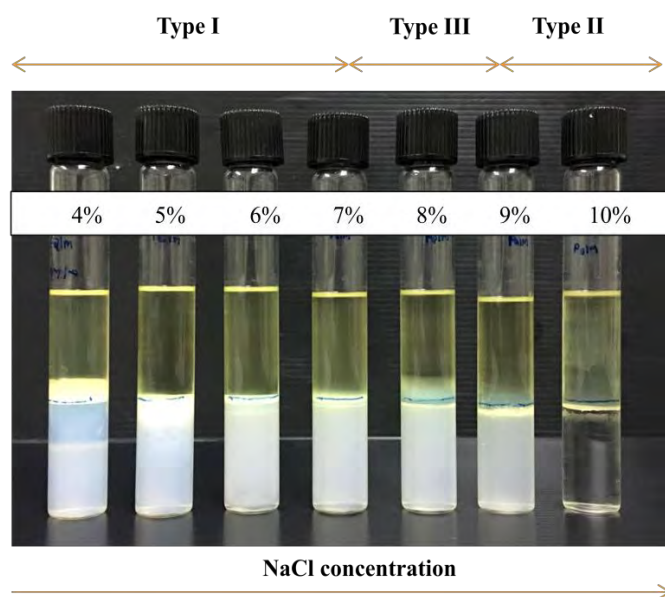


Figure 4.2 The phase scan of the microemulsion system using 3 wt% C₁₄₋₁₅, 8PO-SO₄ with palm oil as an oil phase.

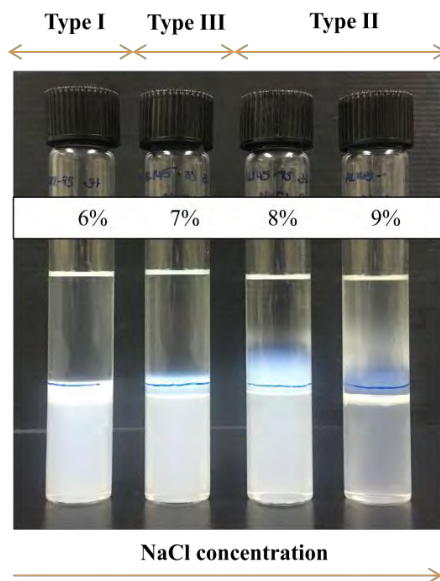


Figure 4.3 The phase scan of the microemulsion system using 3 wt% C_{14-15} , 8PO-SO₄ with coconut oil as an oil phase.

For the microemulsion phase scan at 3 wt% C_{14-15} , 8PO-SO₄ with the vegetable oils, the presence of middle phase (optically transparent solution) required about at least two weeks for soybean and coconut oil and four weeks for palm oil. The middle phase microemulsions of coconut, palm and soybean oils were optically transparent solution and occurred in the middle level of the solution as shown in Figures 4.1 to 4.3, respectively. At lower salt concentration (4 wt% NaCl), the milky viscous white phase or sponge phase was observed in the oil phase, indicating low oil solubilization and weak interactions with oil phase (Do *et al.*, 2009).

For mixed surfactant system, the optimum salinity of the anionic system mixed with C_{16-18} , 4EO-2PO-OH as a co-surfactant at 9:1 (wt%) decreased from 9 wt% to 8 wt% NaCl for soybean oil (EACN=17.7), from 8 wt% to 7 wt% NaCl for palm oil (EACN=14) and from 7 wt% to 6 wt% NaCl for coconut oil (EACN=12). When compared the mixed surfactant system and single surfactant system, it can be observed that the middle phase microemulsions form at lower optimum salinity due to an increasing of the hydrophobicity of the nonionic surfactant (HLB=2.32).

4.1.1 Effect of Salt Concentration

Salt or electrolyte is an important parameter for the middle phase microemulsion formation of ionic surfactants. As the microemulsion phase inversion from Winsor type I to III to II microemulsions is changed by increasing salt concentration for ionic surfactants or increasing temperature for nonionic surfactants. The phase volume was determined by scaling the level of phase (Do *et al.*, 2009). Figure 4.4 shows the plot of the phase volume of the microemulsion systems versus different salt concentrations.

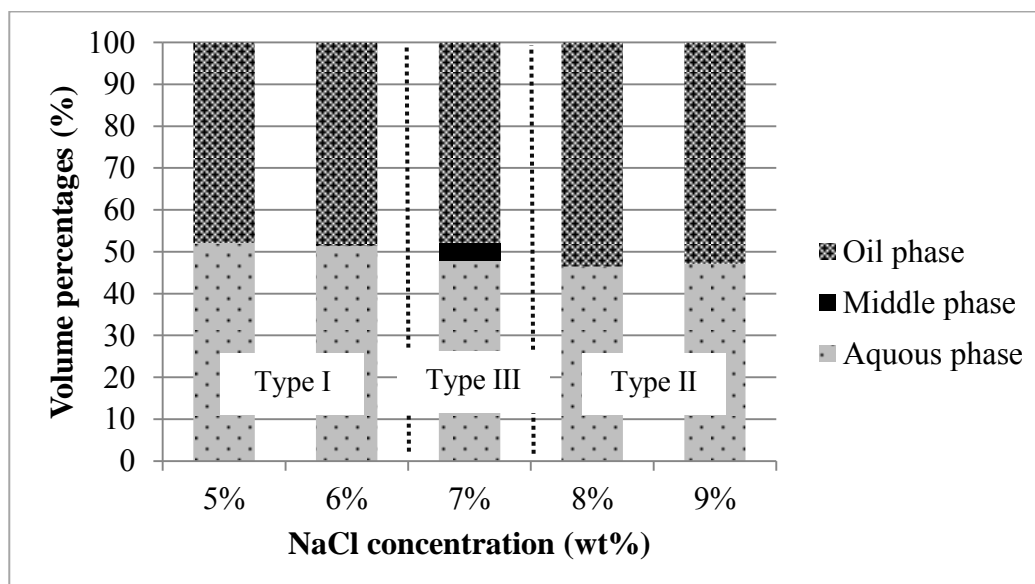


Figure 4.4 The microemulsion systems prepared by C_{14-15} , 8PO-SO₄ alone 3 wt% with coconut oil at various salt concentrations.

The results showed that the microemulsion Type I-II-II transition of 3 wt% C_{14-15} , 8PO-SO₄ with coconut oil was appeared by increasing the salt concentration from 5 wt% to 9 wt% NaCl. For Winsor type I microemulsions, surfactant form normal micelles with excess oil phase (W/O), formed at 5 wt% to 6 wt% NaCl. The Winsor type III microemulsions or middle phase occurred at 7 wt% NaCl. When the salt concentrations further increased up to 8 wt%, the system formed Winsor type II microemulsions, the surfactants form reverse micelles with excess water phase (O/W). This phase transition is similar to the result obtained by Phan and co-workers

(2010) that they were able to form the microemulsions using C_{14-15} , 8PO-SO₄Na with a canola oil. They found that Winsor type I microemulsion was occurred at the ranges of 0 wt% to 6 wt% NaCl concentrations. The Winsor type I microemulsions turned to middle phase or Winsor type III microemulsions when the salinity was increased to 10 wt%. The microemulsion system turned into Winsor type II microemulsions when the salinity was increased from 14 wt% to 16 wt% NaCl.

4.1.2 Effect of Surfactant Concentration

Surfactant concentration is one of the important parameters to formulate a middle phase microemulsion. The minimum surfactant concentration required for the middle phase is called Critical Microemulsion Concentration ($C_{\mu}C$) (Rosen, 2004). The $C_{\mu}C$ is defined as the efficiency of the surfactant as the lowest surfactant concentration requires to form the middle phase. In this work, the microemulsion systems prepared by C_{14-15} , 8PO-SO₄ alone at various surfactant concentrations were investigated. Each minimum surfactant concentrations at an optimum salt for the oils with different fatty acid composition was determined. In addition, it can be also seen that the surfactant concentration increases with volume fraction of the middle phase increases for all microemulsion systems.

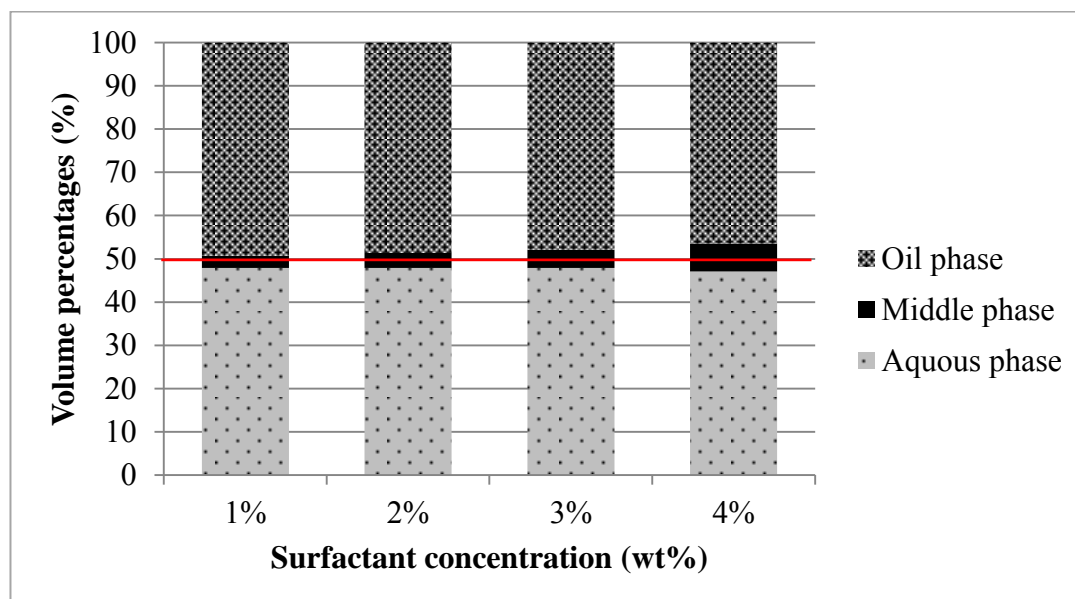


Figure 4.5 The microemulsion systems prepared by C_{14-15} , 8PO-SO₄ alone and coconut oil at the optimum salt of 7wt% with varying various surfactant concentration.

Figure 4.5 shows the plot of volume percentages of the oil phase, water phase and middle phase of the microemulsion systems prepared by the C_{14-15} , 8PO-SO₄ alone at different surfactant concentrations. At the optimum salt of the microemulsion system with coconut oil (7 wt%), the surfactant concentration increased from 1 wt% to 4 wt%, the volume of the middle phase where bicontinuous micellar solubilizes of which oil and water phase increases. This because more additional surfactant molecules solubilize both oil and water and form more volume of middle phase. On the other hand, if the surfactant concentration is lower than $C_{\mu C}$, there is not enough surfactant to form a middle phase or bicontinuous phase. This work, 1 wt% of the C_{14-15} , 8PO-SO₄ surfactant was the minimum surfactant concentration required to form the middle phase microemulsion. Similar to Do and coworkers (2014) that they formed the middle phase with coconut oil using 1wt% of $C_{10-18}PO-2EO-NaSO_4$ and SDOSS at 0.26/0.74 mole fraction. According to the economic point of views, the concentration of surfactant is an important not only factor maintaining the microemulsion formation or efficiency of the system, but also affecting the cost in the detergency application.

4.1.3 Effect of Co-surfactant

The co-surfactant was employed to improve the solubilization capacity and reduce the optimum salinity of the microemulsion system. The nonionic extended surfactant, C₁₆₋₁₈, 2PO-4EO-OH was used as a co-surfactant in this study. The C₁₆₋₁₈, 2PO-4EO-OH which has intermediate 4 polyethylene oxide (EO) groups and 2 polypropylene (PO) groups is classified as a hydrophobic surfactant (HLB = 2.32, as mentioned in Table 4.1). The mixture of C₁₄₋₁₅, 8PO-SO₄ and C₁₆₋₁₈, 2PO-4EO-OH was prepared at ratio 9:1(%wt: %wt). The microemulsion systems prepared by mixed surfactant system at various salt concentrations are showed in Figure 4.6.

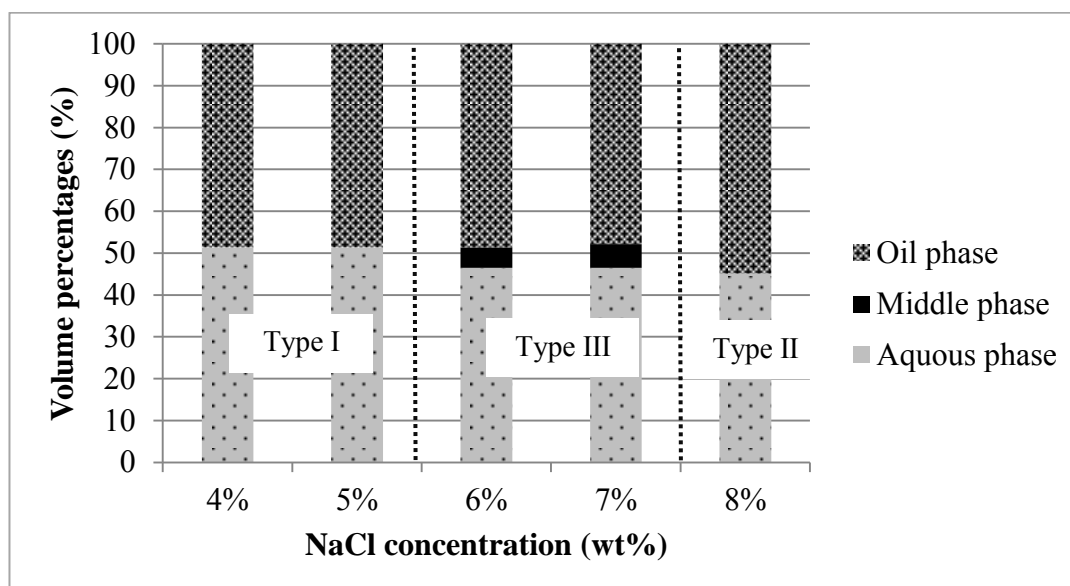


Figure 4.6 Microemulsion phase scan of the system using C₁₄₋₁₅, 8PO-SO₄ mixed with C₁₆₋₁₈, 2PO-4EO-OH as a surfactant system in coconut oil at various salt concentrations.

From Figure 4.6, the middle phases of mixed surfactant system and coconut oil were occurred at 6 wt% and 7 wt% NaCl. In comparison, the C₁₄₋₁₅, 8PO-SO₄ mixed with C₁₆₋₁₈, 2PO-4EO-OH presents a lower optimum salinity than the C₁₄₋₁₅, 8PO-SO₄ system alone because C₁₆₋₁₈, 2PO-4EO-OH can improve the oil solubilization capacity due to its having higher hydrophobic moiety in the molecule. Acosta and coworkers (2008) formed the middle phase microemulsion using anionic

surfactant, sodium dihexyl sulfosuccinate (SDHS) mixed with a small amount of nonionic surfactant (C_{12-13} alcohol ethoxylate-6.5EO) with limonene oil. They reported that the addition of nonionic surfactant can reduce the optimum salinity.

To ensure the optimum salinity obtained by the phase scan, the optimum salt that obtained from the middle phase scan experiment was confirmed by IFT measurement.

4.2 IFT Measurement

The dynamic IFT or dynamic interfacial tension was measured by a spinning drop tensiometer (SITE 04, Krüss GmbH, Hamburg). The diameter of the oil drop was measured at equilibrium after 20 min at 7000 rpm of rotational velocity. The plot of dynamic IFT value versus times is shown in Figure 4.7. The result shows that the dynamic IFT value reached to its equilibrium within 15 min, indicated by the constant IFT value.

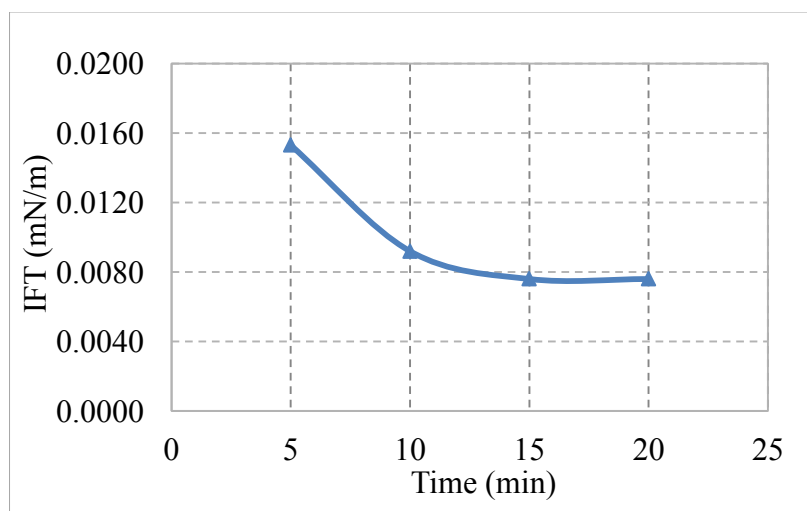


Figure 4.7 The dynamic IFT value of the microemulsion using 0.50 wt% C_{14-15} , 8PO-SO₄ alone with soybean oil.

Generally, the middle phase occurs at the minimum IFT value or ultralow IFT value (Do *et al.*, 2009). The optimum salinity was determined by the obtained

minimum IFT from the plot between the IFT value versus NaCl concentration. In addition, the ultralow IFT value that occurred at the middle phase is defined at the IFT value less than 0.01 mN/m (Nguyen *et al.*, 2009).

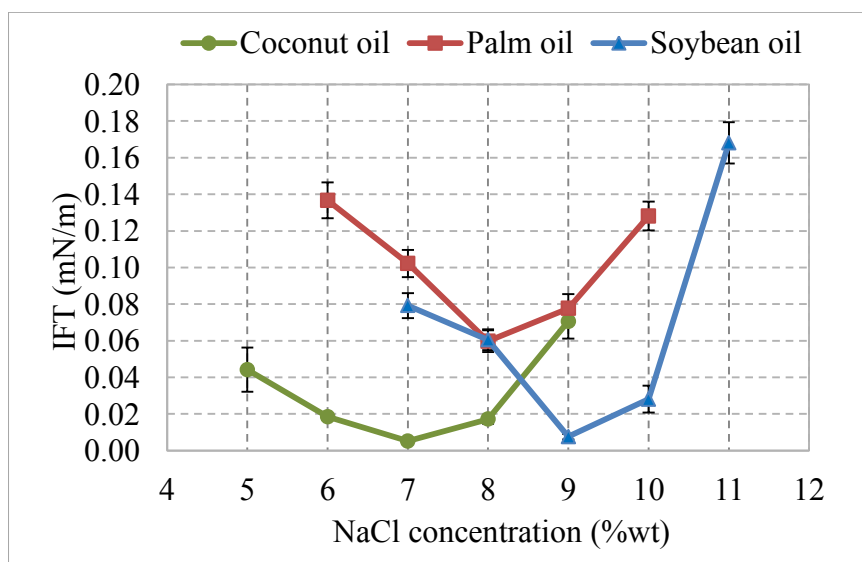


Figure 4.8 The IFT value of the microemulsion using 0.50 wt% C_{14-15} , 8PO-SO₄ alone with coconut, palm and soybean oil.

From Figure 4.8, the minimum IFT values of the microemulsion systems with 0.5 wt% C_{14-15} , 8PO-SO₄ in coconut oil and soybean oil were achieved at 7 wt% and 9 wt% NaCl concentrations, respectively. The minimum IFTs are obtained at the ultralow IFT and correlate with the results that obtained from the middle phase microemulsion formation study. For the system of 0.5 wt% C_{14-15} , 8PO-SO₄ with palm oil, the minimum IFT values was achieved at 8 wt%. This result is similar to NaCl concentration that obtained by the microemulsion phase scan study.

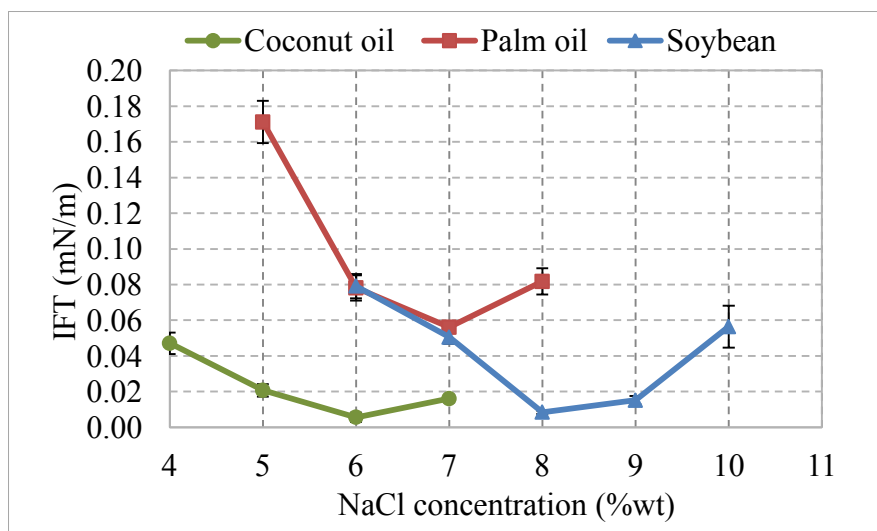


Figure 4.9 The IFT value of the microemulsion using 0.50 wt% C_{14-15} , $8PO-SO_4/C_{16-18}$, $2PO-4EO-OH$ with coconut, palm and soybean oil.

From Figure 4.9, the minimum IFT value of 0.5 wt% C_{14-15} , $8PO-SO_4$ with C_{16-18} , $2PO-4EO-OH$ at 9:1 (wt%) were achieved at 6, 7 and 8 wt% for coconut, palm and soybean oil, respectively. The minimum IFT of mixed surfactant systems present a lower optimum salinity than the C_{14-15} , $8PO-SO_4$ system alone that correlates with the result obtained from middle phase formation experiment. The minimum IFTs of the microemulsion system with anionic and nonionic extended surfactant for soybean and coconut oil were obtained at the ultralow IFT, while the obtained minimum IFT of palm oil did not occur at the ultralow IFT. Similar to the results of Tanthakit and coworkers (2019) that the minimum dynamic IFT value of palm oil using anionic surfactant mixed with nonionic surfactant was more than ultralow IFT (0.01 mN/m) but the equilibrium IFT value occurred at ultralow IFT. In our work, the equilibrium IFT value did not measure because the aqueous phase appeared to be a white milky phase that makes it difficult to measure by the instrument.

In this study, the minimum IFT scans for microemulsion systems using 0.5 wt% C_{14-15} , $8PO-SO_4$ alone with three types of vegetable oil (i.e., coconut oil, soybean oil and palm oil) and three alkane oils (i.e., hexane (C_6), dodecane (C_{12}), and hexadecane (C_{16})) were used to determine the optimum salinity. Table 4.3

summarizes the minimum IFT values at the optimal salinity of the alkane oils and vegetable oils.

Table 4.3 Summary of the optimum salinity (S^*) and the minimum equilibrium interfacial tension (IFT*) of 0.5 wt% C_{14-15} , 8PO-SO₄ alone and C_{14-15} , 8PO-SO₄/ C_{16-18} , 2PO-4EO-OH with a wide range of oils.

| Surfactant | Oils | EACN | S^* (wt%) | IFT*(mN/m) |
|---|------------|-------------------|-------------|---------------|
| C_{14-15} , 8PO-SO ₄ | Hexane | 6.0 | 3 | 0.0524±0.0124 |
| | Dodecane | 12.0 | 5 | 0.0027±0.0005 |
| | Hexadecane | 16.0 | 7 | 0.0032±0.0008 |
| C_{14-15} , 8PO-SO ₄ | Coconut | 12.0 ^a | 7 | 0.0051±0.0012 |
| | Palm | 14.0 ^b | 8 | 0.0597±0.0060 |
| | Soybean | 17.7 ^c | 9 | 0.0076±0.0015 |
| C_{14-15} , 8PO-SO ₄ / C_{16-18} , 2PO-4EO- OH (9:1) | Hexane | 6.0 | 2 | 0.0831±0.0097 |
| | Dodecane | 12.0 | 4 | 0.0084±0.0009 |
| | Hexadecane | 16.0 | 6 | 0.0178±0.0050 |

^a The data from Do *et al.*, 2014

^b The data from Witthayapanyanon *et al.*, 2006

^c The data from Do *et al.*, 2009

4.3 Determination of K and Cc Values

Hydrophilic-Lipophilic Deviation (HLD) developed by Salager and coworkers (1979) was conducted to estimate the Cc and K values at which the middle phase microemulsion formed or minimum IFT is achieved. The single anionic extended surfactant, C_{14-15} , 8PO-SO₄ and its mixed systems with C_{16-18} , 2PO-4EO-OH were investigated. The HLD equation used in this study as shown in Eq. (4.1) (Salager *et al.*, 1979).

$$\text{HLD} = \ln(S) - K \times (\text{EACN}) - f(A) + C_c - \alpha_T \Delta T \quad (4.1)$$

This study, the formulated microemulsions were conducted at room temperature (25 ± 2 °C), therefore ΔT is equal to 0. $f(A)$ is the term of an alcohol or linker, if the system without alcohol is used the i.e. $f(A) = 0$. The optimum salinity is represented as S^* . Based on the HLD equation, the middle phase typically is occurred at the optimum salinity at which the HLD is equal to 0. The simplified HLD equation is shown in Eq. (4.2)

$$\ln(S^*) = K \times (\text{EACN}) - C_c \quad (4.2)$$

The K and C_c values of specific surfactant system were calculated from the plot between $\ln(S^*)$ and EACN which K is obtained from the slope of the plot and C_c is acquired by y-intersection of the plot. The alkane oils applied for C_c and K values determination were hexane (C_6), dodecane (C_{12}), and hexadecane (C_{16}), and their EACN values are presented in Table 4.3. The plot between $\ln(S^*)$ and EACN are shown in Figure 4.8.

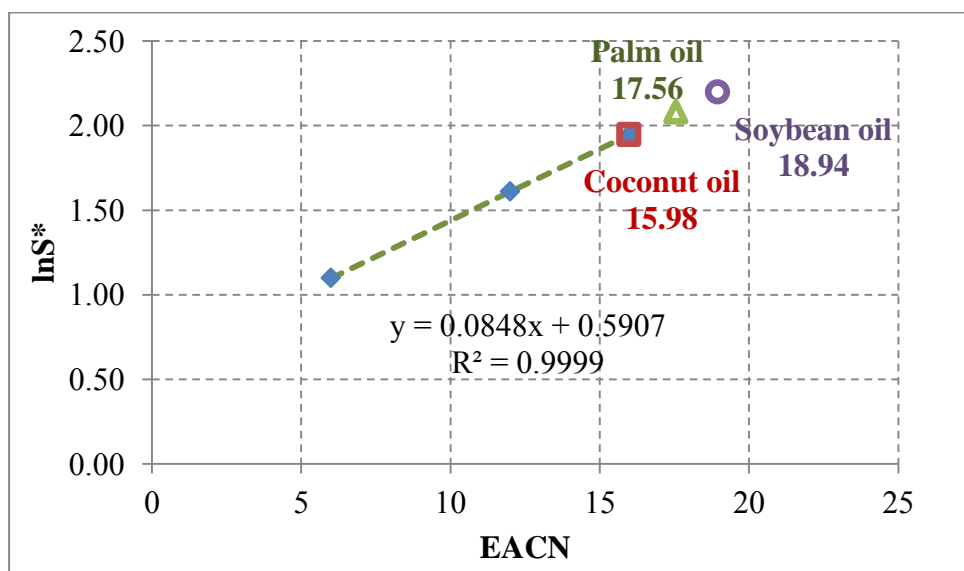


Figure 4.10 The plot of the optimum salt versus EACN for the system with C_{14-15} , 8PO-SO₄.

From Figure 4.10, the linear plot between $\ln(S^*)$ versus EACN is corresponded to a linear equation as shown in Eq. (4.3)

$$y = 0.0848x + 0.5907 \quad (4.3)$$

From Eq. (4.3), the y-intercept is the Cc value and the slope of the plot is the K value. The R^2 value of the plot has more than 0.99 indicated that the linear fitting is in agreement with the trend in data. The obtained K and Cc values from the plot were 0.0848 and -0.5907, respectively.

In this work, we added the co-surfactant at low concentration in the mixed surfactant system to improve the solubilization capacity, thus the simplified HLD equation used for determine the Cc and K calculation of the mixed surfactant system is applied for single anionic surfactant system as show in Eq. (4.2).

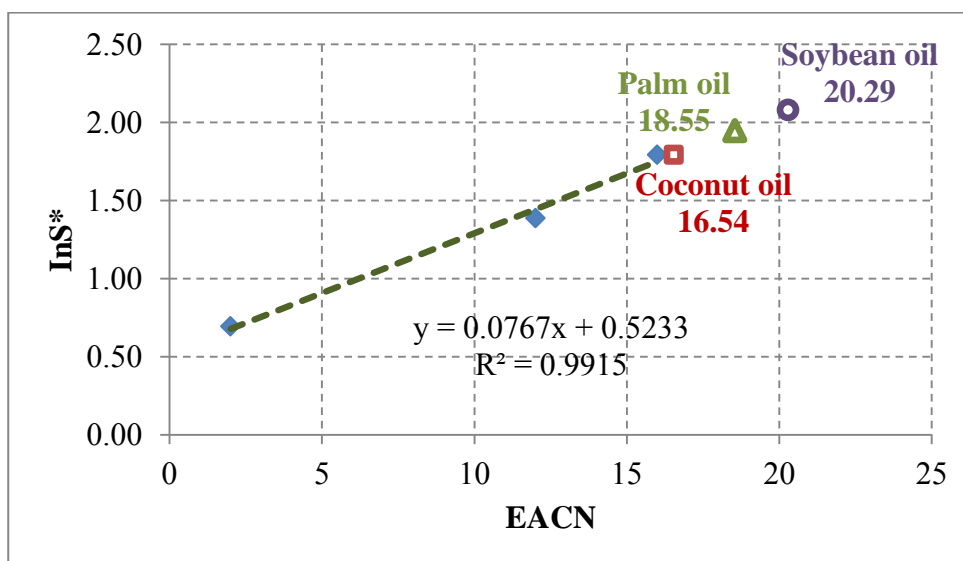


Figure 4.11 The plot of the optimum salt versus EACN for the system with C_{14-15} , $8PO-SO_4/C_{16-18}$, $2PO-4EO-OH$.

Figure 4.11 shows the plot between $\ln(S^*)$ versus EACN is corresponded to a linear equation as shown in Eq. (4.4)

$$y = 0.0767x + 0.5233 \quad (4.4)$$

From Eq. (4.4), the y-intercept is the Cc value and the slope of the plot is the K value. The R² value of is 0.99 suggesting that the linear fitting is in agreement with the trend in data. The obtained K and Cc values from the linear plot were 0.0767 and -0.5233, respectively.

Table 4.4 K-values and Cc-values of the surfactant systems obtained from HLD calculation

| Surfactant | K | Cc |
|--|--------|---------|
| C ₁₄₋₁₅ , 8PO-SO ₄ | 0.0848 | -0.5907 |
| C ₁₄₋₁₅ , 8PO-SO ₄ / C ₁₆₋₁₈ , 2PO-4EO-OH (9:1 wt%) | 0.0767 | -0.5233 |

For the HLD equation, the Cc value has been used to determine the hydrophobicity of a surfactant. From Table 3, the calculated Cc and K values of extended surfactant, C₁₄₋₁₅, 8PO-SO₄ alone were -0.5907 and 0.0848, respectively. While the calculated Cc and K values of mixed surfactant system were -0.5233 and 0.0767, respectively. The obtained K value from experiment is in the similar ranges of K value (0.07-0.12) of extended surfactant family that reported in previous literature (Velásquez *et al.*, 2010). For Cc value of the extended surfactant system that obtained from the experiment, it is in agreement with the Cc value of C₁₄₋₁₅, 8PO-SO₄Na from Witthayapanyanon and coworkers (2006) which reported that the Cc value of -0.52. When compared the anionic extended surfactant system alone with the anionic extended surfactant mixed with nonionic extended surfactant as a co-surfactant, the anionic extended surfactant, C₁₄₋₁₅, 8PO-SO₄alone system was achieved more negative Cc value than the system with co-surfactant indicated that the C₁₄₋₁₅, 8PO-SO₄ system with C₁₆₋₁₈, 2PO-4EO-OH is more hydrophobicity.

4.3.1 EACN Determination

The EACN is determined to indicate the oil' hydrophobicity (Do *et al.*, 2009). The plot of optimum salt versus each EACN of alkane oil as shown in Figure 4.10 and Figure 4.11. In this study, the optimum salt of each vegetable oil is obtained from the IFT measurement.

Table 4.5 Summary of the EACN of vegetable oils using extended surfactant alone and mixed surfactant system.

| Vegetable oil | EACN from literature | EACN from extended surfactant alone | EACN from mixed surfactant |
|---------------|----------------------|-------------------------------------|----------------------------|
| Coconut oil | 12 ^a | 15.98 | 16.54 |
| Palm oil | 14 ^b | 17.56 | 18.55 |
| Soybean oil | 17.7 ^c | 18.94 | 20.29 |

^a The data from Do *et al.*, 2014

^b The data from Witthayapanyanon *et al.*, 2006

^c The data from Do *et al.*, 2009

From Table 4.4, the EACN of vegetable oils using anionic extended surfactant alone are in the range of 15-19, which indicates that the vegetable oils studied in this work are very hydrophobic (Do *et al.*, 2009). The EACN of each vegetable oil obtained from the microemulsion system with anionic extended surfactant alone are in agreement with the trend of EACN obtained from the previous literature. For the mixed surfactant system, EACN of vegetable oils are not well agreed with EACN obtained from the previous literature. The result showed that the HLD model of extended surfactant alone did not fit well for the mixture of anionic surfactant and nonionic surfactant system. For the mixed surfactant of anionic extended surfactant and nonionic surfactant as a co-surfactant system, however the HLD of mixed system have still investigation and a few works have been done with limited result. Acosta and coworkers (2008) studied the HLD-NAC model for the mixture of ionic and nonionic surfactants. The temperature factor was examined in their work, this is the interesting variable parameter that will be further investigation.

4.4 Hard Surface Cleaning

In cleaning application, the hard surface cleaning or oil solubilization test was performed to determine the efficiency of the formulated surfactant systems for semi-solid fat removal at room temperature ($25\pm 2^\circ\text{C}$). In this study, palm stearin was used as a semi-solid fat in hard surface cleaning experiment. The melting point of palm stearin is about $34.8\text{-}58.8^\circ\text{C}$ (Ghosh and Bhattacharyya, 1997) that above the room temperature ($25\pm 2^\circ\text{C}$). The anionic extended surfactant (C_{14-15} , 8PO-SO_4) with/without C_{16-18} , 2PO-4EO-OH systems were conducted and compared with the conventional surfactant (SDBS). The NaCl concentration was varied to maintain the cleaning efficiency.

Palm stearin was dyed by Oil-red-O. The 0.2 g red palm stearin was deposited in the 15mL flat-bottom PTFE. Then, the sample was added with the aqueous phase containing 3 wt% either C_{14-15} , 8PO-SO_4 or C_{14-15} , $8\text{PO-SO}_4/\text{C}_{16-18}$, 2PO-4EO-OH (9:1) at the optimum salinity. The percentages of oil removal were calculated through material balance equation as represented in Eq. (4.6) for determined the efficiency of surfactant system.

$$\text{Oil removal (\%)} = \frac{(A-B)}{(A)} \times 100 \quad (4.6)$$

Where, A is the average concentration before washing and B is the average concentration after washing with limonene for 24 hours.

Note that palm stearin dot not solubilize in water.

4.4.1 The Effect of Extended Surfactant

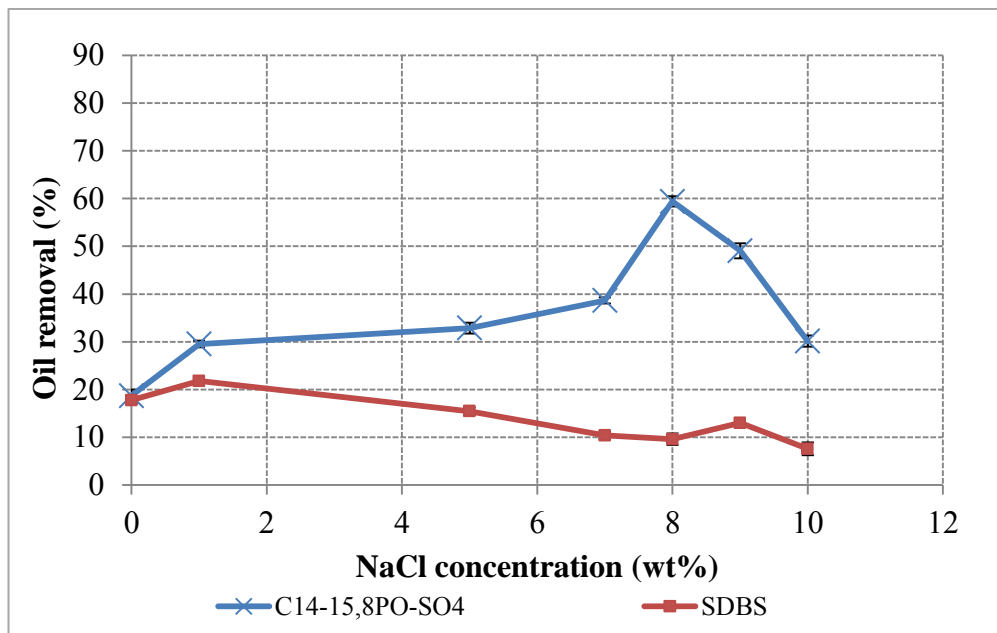


Figure 4.12 The oil removal efficiency of $C_{14-15}, 8PO-SO_4$ alone and SDBS using palm oil as semi-solid fat.

Figure 4.12 shows the comparisons of oil removal efficiency between the single anionic extended surfactant system, $C_{14-15}, 8PO-SO_4$ and the conventional surfactant, SDBS. The maximum oil removal of $C_{14-15}, 8PO-SO_4$ was about 59% at 8 wt% NaCl. While the maximum oil removal of conventional surfactant was about 21% at 1 wt% NaCl. The efficiency of extended surfactant system alone is obviously higher than the conventional surfactant by 38%, since the extended surfactant containing an intermediate PO group can improve the interactions between surfactant and oil (Witthayapanyanon *et al.*, 2008).

4.4.2 The Effect of Co-surfactant

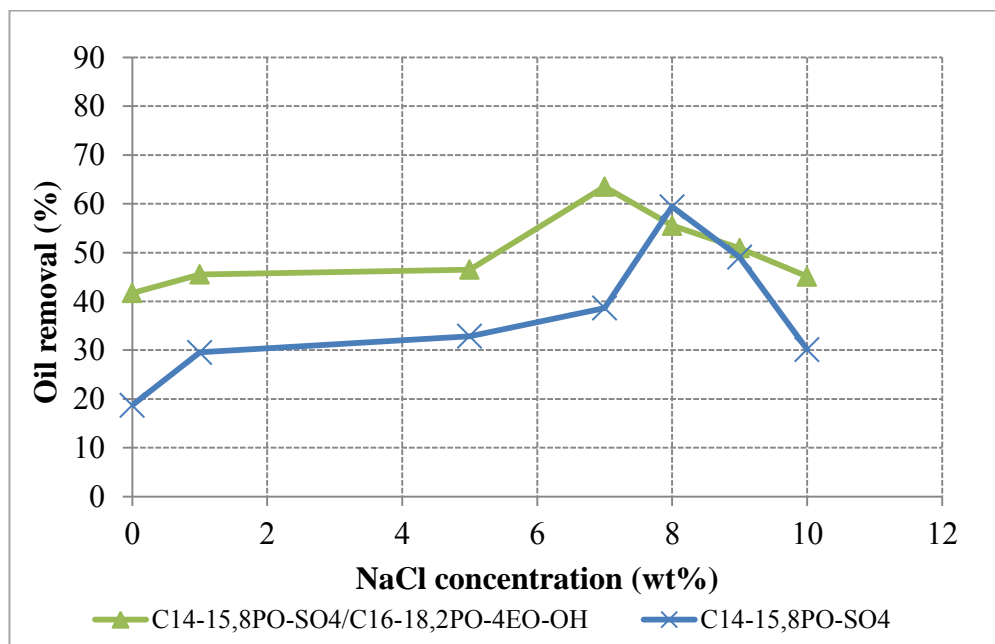


Figure 4.13 The oil removal efficiency of $C_{14-15}, 8PO-SO_4$ mixed with $C_{16-18}, 2PO-4EO-OH$ and $C_{14-15}, 8PO-SO_4$ alone using palm oil as semi-solid fat.

Figure 4.13 shows the comparison of oil removal efficiency between the extended surfactant, $C_{14-15}, 8PO-SO_4$ alone and $C_{14-15}, 8PO-SO_4$ mixed with $C_{16-18}, 2PO-4EO-OH$ systems. The maximum oil removal of $C_{14-15}, 8PO-SO_4$ mixed with $C_{16-18}, 2PO-4EO-OH$ system was about 63% at 7 wt% NaCl. For the anionic extended surfactant alone, the maximum oil removal was achieved about 59% at 8 wt% NaCl. The oil removal efficiency of the anionic extended surfactant mixed with nonionic surfactant is more than the extended surfactant system alone about 4%. This result indicated that the addition of co-surfactant can slightly enhance the solubilization capacity.

4.4.3 The Effect of Microemulsion Types

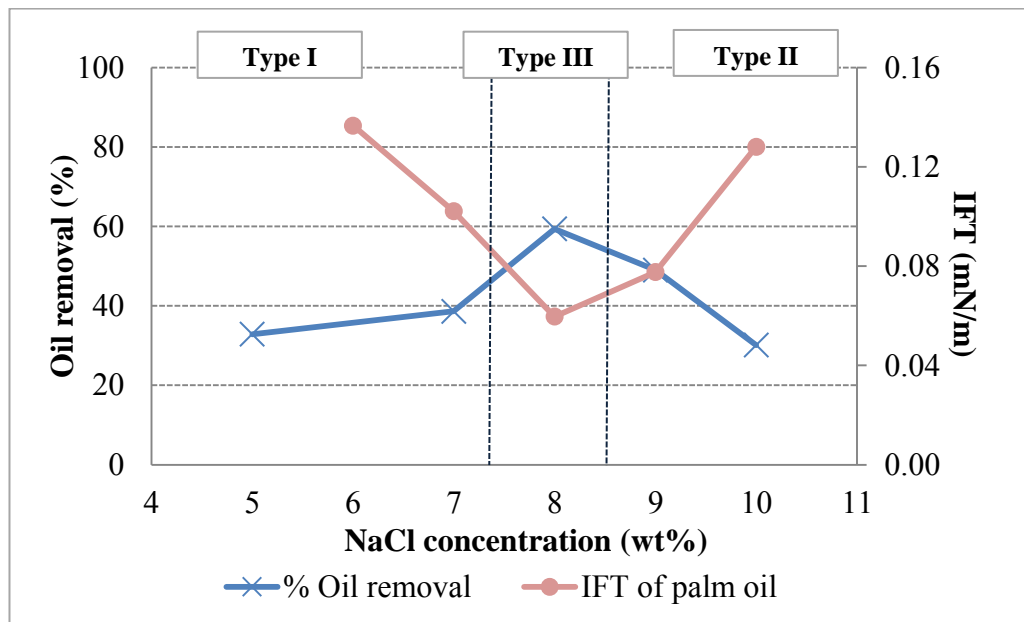


Figure 4.14 Correlations between the oil removal efficiency and microemulsion types using 3 wt% C_{14-15} , 8PO-SO₄ with palm olein and palm stearin, respectively.

Figure 4.14 presents the maximum oil removal by C_{14-15} , 8PO-SO₄ alone with palm stearin oil obtained at the optimum salt (8 wt% NaCl concentration). The middle phase that occurred at the optimum salt can provide high oil solubilization, so the middle phase could be applied for semi-solid fat removal. This result similar to Tanthakit and coworkers (2010) that they formed the middle phase microemulsion using the mixed surfactant systems, $C_{14-15}(PO)_3SO_4$ and $C_{12-14}O(EO)_5$ with palm oil. They found that the maximum oil removal efficiency of palm oil was achieved at the optimum salinity.

This study, the middle phase microemulsion was formed at the optimum salinity. The IFT measurement was conducted to confirm the optimum salinity that obtained from microemulsion phase scan. The IFT indicates the optimum salinity of the system at the minimum IFT that the middle phase was formed. The HLD was applied to predict K and C_c values of the systems; K is a constant value for specific surfactant of the surfactant calculation system and C_c value indicates the presence of

hydrophobicity or hydrophilicity of the surfactant which can help predict optimum salinity of the surfactant system and oils. For application, the hard surface cleaning of semi-solid fats provided the removal efficiency of the selected surfactant formulation. The result indicated that the addition of co-surfactant system was more efficiency.

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

This study, the middle phase microemulsions were formulated with soybean, coconut, and palm oil using the extended surfactant C_{14-15} , 8PO-SO₄ alone and their mixed system with C_{16-18} , 2PO-4EO-OH as co-surfactant. The middle phase microemulsions were occurred with C_{14-15} , 8PO-SO₄ alone and mixed C_{14-15} , 8PO-SO₄ with soybean oil (9 wt% and 8 wt%), palm oil (8 wt% and 7 wt%) and coconut oil (7 wt% and 6 wt%). When increasing EACN of the oil, the middle phase was appeared at higher NaCl concentration. The addition of nonionic surfactant as a co-surfactant can slightly improve the solubilization capacity due to increasing the hydrophobicity of the surfactant system. The parameters which affect to the middle phase formation are salt concentration, surfactant concentration and co-surfactant.

For IFT measurement, the obtained minimum IFT value of the microemulsion containing the extended surfactant, C_{14-15} , 8PO-SO₄ were achieved at the optimum salinity that is correlate with the obtained optimum salinity from the middle phase formation experiment.

The Hydrophilic-Lipophilic Deviation (HLD) was conducted to determine the C_c and K values. The C_c values indicated the hydrophilicity or hydrophobicity of surfactant and K value is a constant value of the surfactant system. The C_c values of the C_{14-15} , 8PO-SO₄ alone and mixed with C_{16-18} , 2PO-4EO-OH were -0.5907 and -0.5233, respectively. The K values of the C_{14-15} , 8PO-SO₄ alone and mixed with C_{16-18} , 2PO-4EO-OH were 0.0848 and 0.0767, respectively. The result indicated that the C_{14-15} , 8PO-SO₄ is a hydrophilic surfactant.

The hard surface cleaning experiment was conducted to determine the oil removal efficiency of the formulated surfactant systems at room temperature ($25 \pm 2^\circ\text{C}$). The comparison between C_{14-15} , 8PO-SO₄ alone and the C_{14-15} , 8PO-SO₄ mixed with C_{16-18} , 2PO-4EO-OH systems indicated that the presence of nonionic surfactant, C_{16-18} , 2PO-4EO-OH could enhances the solubilization capacity of the oil and thus improve the interactions between the surfactant and oil phase.

5.2 Recommendations

The HLD model for mixed surfactant system between anionic surfactant and nonionic surfactant could be further investigated.

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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 and water. For oil phase, the oils were varied (i.e., vegetable oils and other oils)

Table A1 Microemulsion formation

| Batch | Oil | EACN | Surfactant | Surfactant Concentration (wt%) | Co-surfactant | Middle phase point (wt%) |
|-------|------------|------|---|--------------------------------|---------------|--------------------------|
| 1 | Soybean | 17.7 | C ₁₄₋₁₅ , 8PO-SO ₄ | 1, 2 | - | - |
| 2 | Mineral | 16 | C ₁₄₋₁₅ , 8PO-SO ₄ | 1, 2 | - | - |
| 3 | Coconut | 12 | C ₁₄₋₁₅ , 8PO-SO ₄ | 1, 2, 3, 4 | - | - |
| 4 | Soybean | 17.7 | C ₁₄₋₁₅ , 8PO-SO ₄ | 3,4 | - | - |
| 5 | Palm olein | 14 | C ₁₄₋₁₅ , 8PO-SO ₄ | 3 | - | - |
| 6 | Limonene | 5.7 | C ₁₄₋₁₅ , 8PO-SO ₄ | 3 | - | - |
| 7 | Soybean | 17.7 | C ₁₄₋₁₅ , 8PO-SO ₄ | 1, 2, 3 | - | 9 |
| 8 | Palm olein | 14 | C ₁₄₋₁₅ , 8PO-SO ₄ | 1,2 | - | - |

| Batch | Oil | EACN | Surfactant | Surfactant Concentration (wt%) | Co-surfactant | Middle phase point (wt%) |
|-------|------------|------|---|--------------------------------|--|--------------------------|
| 9 | Palm olein | 14 | C ₁₄₋₁₅ , 8PO-SO ₄ | 3,4 | - | 8 |
| 10 | Coconut | 12 | C ₁₄₋₁₅ , 8PO-SO ₄ | 1, 2 | - | 7 |
| 11 | Limonene | 5.7 | C ₁₄₋₁₅ , 8PO-SO ₄ | 2 | - | - |
| 12 | Mineral | 16 | C ₁₄₋₁₅ , 8PO-SO ₄ | 1, 2 | - | - |
| 13 | Coconut | 12 | C ₁₄₋₁₅ , 8PO-SO ₄ | 3, 4 | - | 7 |
| 14 | Limonene | 5.7 | C ₁₄₋₁₅ , 8PO-SO ₄ | 3 | - | - |
| 15 | Mineral | 16 | C ₁₄₋₁₅ , 8PO-SO ₄ | 1, 2 | - | - |
| 16 | Coconut | 12 | C ₁₄₋₁₅ , 8PO-SO ₄ | 3,4 | - | 7 |
| 17 | Soybean | 17.7 | C ₁₄₋₁₅ , 8PO-SO ₄ | 1,2 | C ₁₆₋₁₈ , 2PO-4EO- OH | - |
| 18 | Soybean | 17.7 | C ₁₄₋₁₅ , 8PO-SO ₄ | 3 | C ₁₆₋₁₈ , 2PO-4EO- OH | 8 |
| 19 | Palm olein | 17.7 | C ₁₄₋₁₅ , 8PO-SO ₄ | 3 | C ₁₆₋₁₈ , 2PO-4EO- OH | 7 |

| Batch | Oil | EACN | Surfactant | Surfactant Concentration (wt%) | Co-surfactant | Middle phase point (wt%) |
|-------|------------|------|---|--------------------------------|--|--------------------------|
| 20 | Palm olein | 17.7 | C ₁₄₋₁₅ , 8PO-SO ₄ | 3 | C ₁₆₋₁₈ , 2PO-4EO- OH | 7 |
| 21 | Palm olein | 14 | C ₁₄₋₁₅ , 8PO-SO ₄ | 2 | C ₁₆₋₁₈ , 2PO-4EO- OH | - |
| 22 | Mineral | 16 | C ₁₄₋₁₅ , 8PO-SO ₄ | 1, 2 | C ₁₆₋₁₈ , 2PO-4EO- OH | - |
| 23 | Mineral | 16 | C ₁₄₋₁₅ , 8PO-SO ₄ | 3,4 | C ₁₆₋₁₈ , 2PO-4EO- OH | - |
| 24 | Coconut | 12 | C ₁₄₋₁₅ , 8PO-SO ₄ | 1,2 | C ₁₆₋₁₈ , 2PO-4EO- OH | - |
| 25 | Coconut | 12 | C ₁₄₋₁₅ , 8PO-SO ₄ | 3,4 | C ₁₆₋₁₈ , 2PO-4EO- OH | 6 |
| 26 | Palm olein | 14 | C ₁₄₋₁₅ , 8PO-SO ₄ | 3 | C ₁₆₋₁₈ , 2PO-4EO- OH | 7 |
| 27 | Coconut | 12 | C ₁₄₋₁₅ , 8PO-SO ₄ | 3,4 | C ₁₆₋₁₈ , 2PO-4EO- OH | 6 |

For the middle phase formation occur the C₁₄₋₁₅, 8PO-SO₄ alone and the C₁₄₋₁₅, 8PO-SO₄ mixed with C₁₆₋₁₈, 2PO-4EO-OH using soybean, palm and coconut oil.

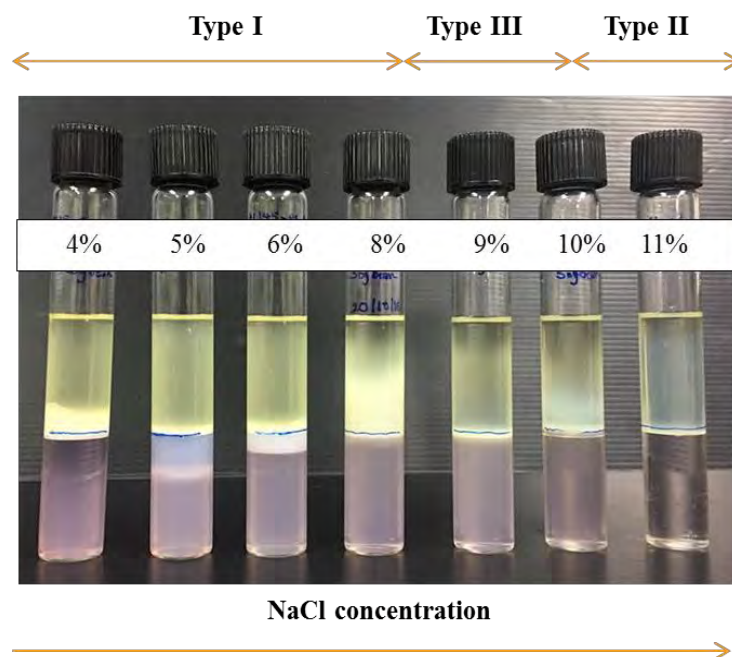


Figure A1 Microemulsion phase scan of the microemulsion system using 1 wt% C_{14-15} , 8PO- SO_4 and soybean oil as an oil phase.

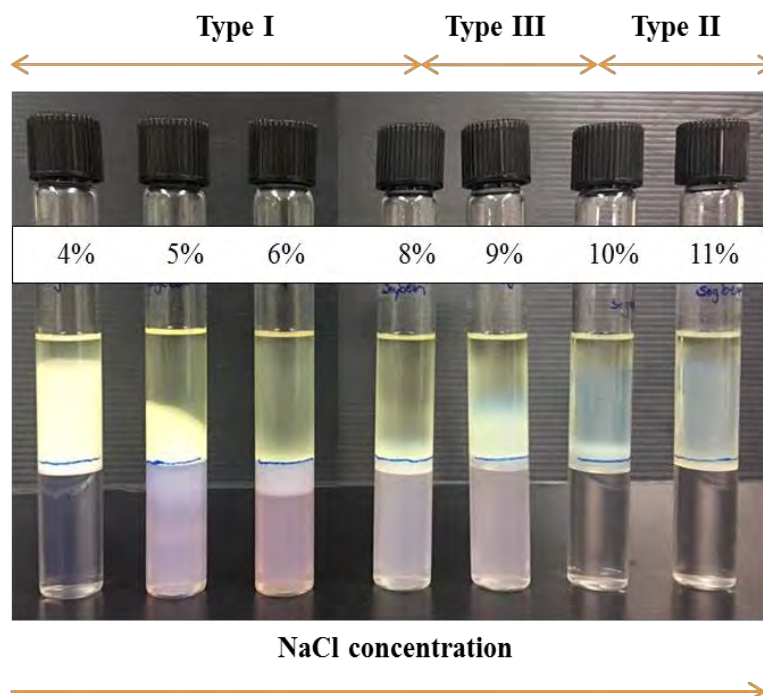


Figure A2 Microemulsion phase scan of the microemulsion system using 2 wt% C_{14-15} , 8PO- SO_4 and soybean oil as an oil phase.

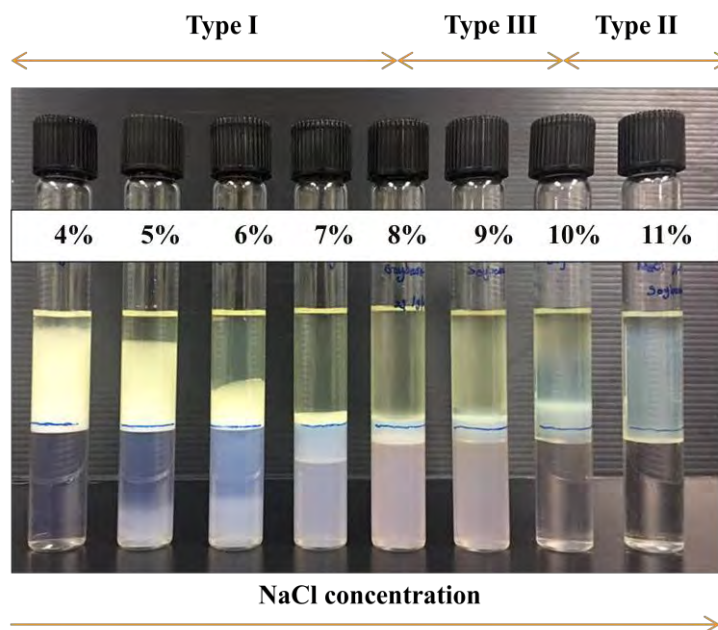


Figure A3 Microemulsion phase scan of the microemulsion system using 3 wt% C_{14-15} , 8PO-SO₄ and soybean oil as an oil phase.

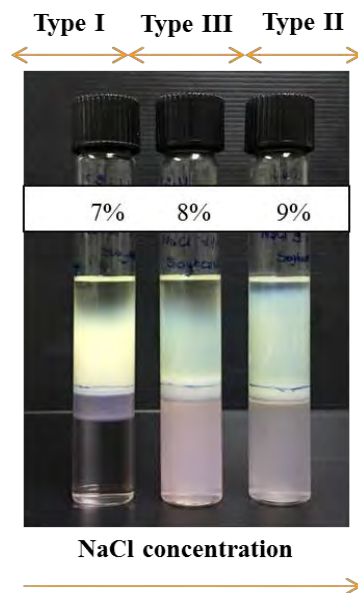


Figure A4 Microemulsion phase scan of the microemulsion system using 3 wt% C_{14-15} , 8PO-SO₄ mixed with C_{16-18} , 2PO-4EO-OH and soybean oil as an oil phase.

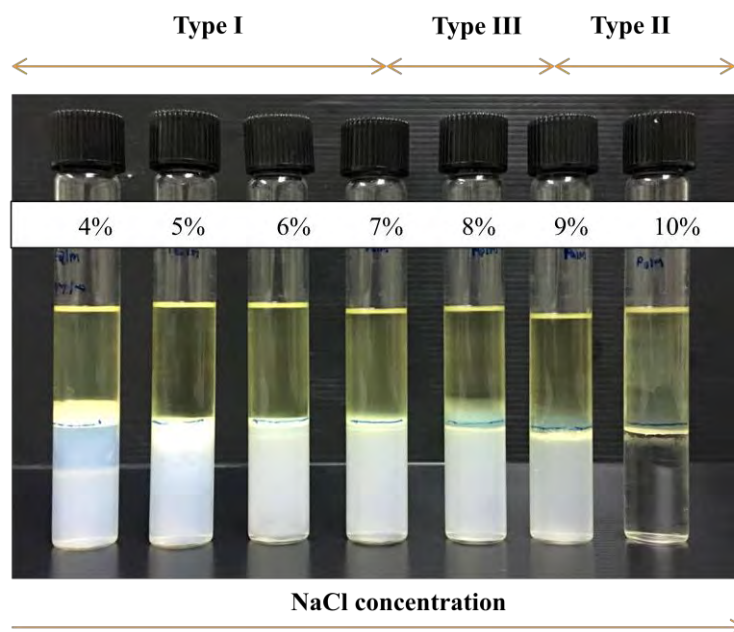


Figure A5 Microemulsion phase scan of the microemulsion system using 3 wt% C_{14-15} , 8PO-SO₄ and palm oil as an oil phase.

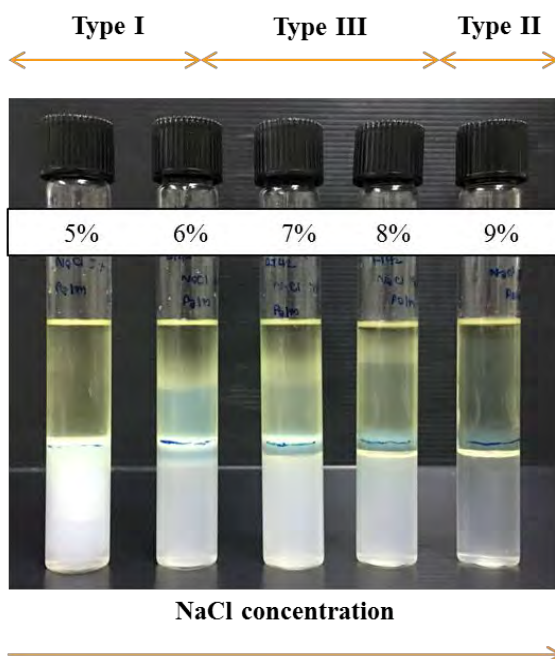


Figure A6 Microemulsion phase scan of the microemulsion system using 3 wt% C_{14-15} , 8PO-SO₄ mixed with C_{16-18} , 2PO-4EO-OH and palm oil as an oil phase.

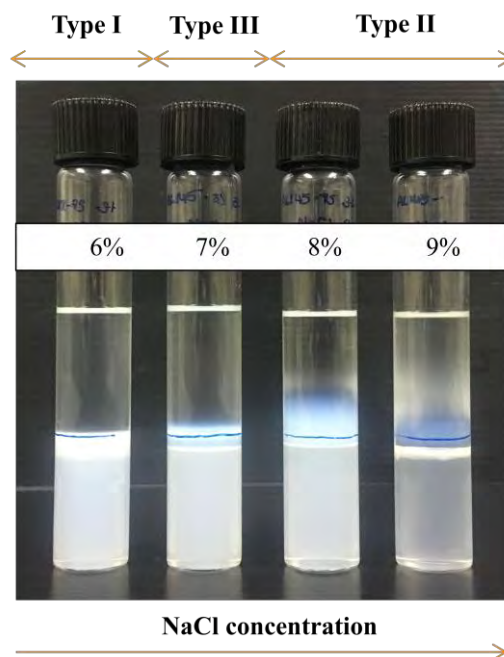


Figure A7 Microemulsion phase scan of the microemulsion system using 3 wt% C_{14-15} , 8PO-SO₄ and coconut oil as an oil phase.

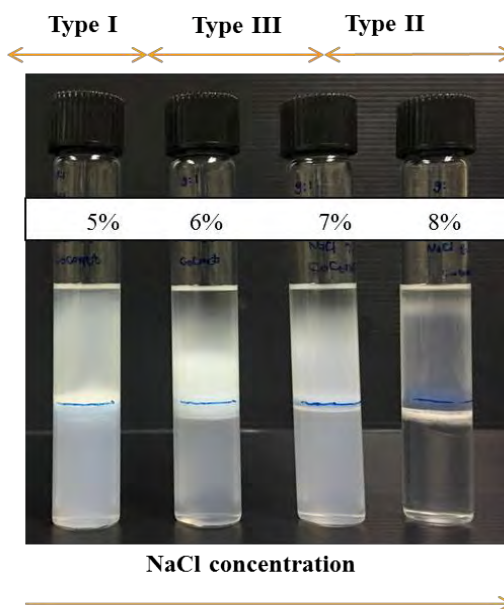


Figure A8 Microemulsion phase scan of the microemulsion system using 3 wt% C_{14-15} , 8PO-SO₄ mixed with C_{16-18} , 2PO-4EO-OH and coconut oil as an oil phase.

Appendix B IFT Measurement

The study measured the IFT values 2 part, The vegetable oils (i.e., soybean and coconut oil) with the $C_{14-15}, 8PO-SO_4$ alone system and the alkane oils (i.e., hexane (C_6), dodecane (C_{10}) and hexadecane (C_{16})) the $C_{14-15}, 8PO-SO_4$ with/without $C_{16-18}, 2PO-4EO-OH$. For the experiments did triplicate of each values.

Table B1 IFT values of 0.50 wt% $C_{14-15}, 8PO-SO_4$ and coconut oil as an oil phase

| NaCl (wt%) | IFT1 | IFT2 | IFT3 | Avg | SD |
|------------|--------|--------|--------|--------|--------|
| 5 | 0.0524 | 0.0498 | 0.0303 | 0.0442 | 0.0121 |
| 6 | 0.0171 | 0.0185 | 0.0196 | 0.0184 | 0.0013 |
| 7 | 0.0063 | 0.0040 | 0.0051 | 0.0051 | 0.0012 |
| 8 | 0.0196 | 0.0147 | 0.0171 | 0.0171 | 0.0025 |
| 9 | 0.0604 | 0.0790 | 0.0724 | 0.0706 | 0.0094 |

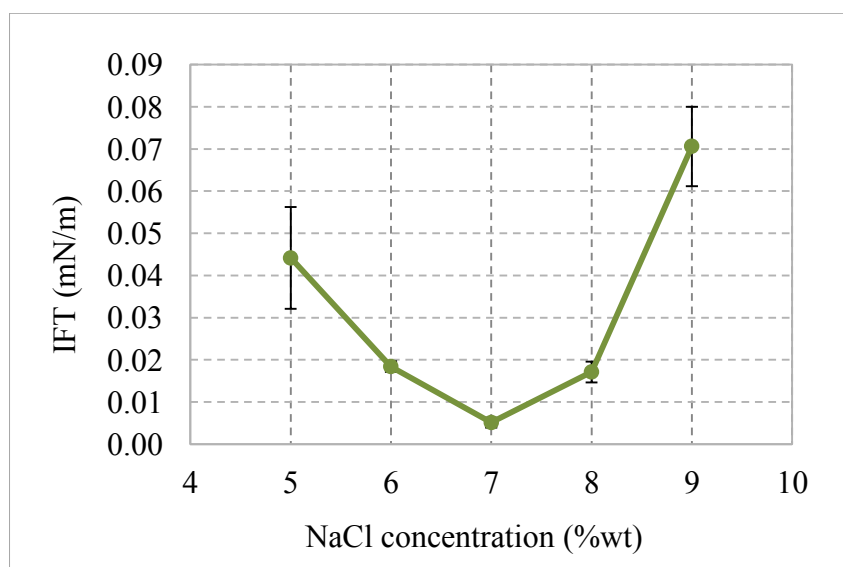
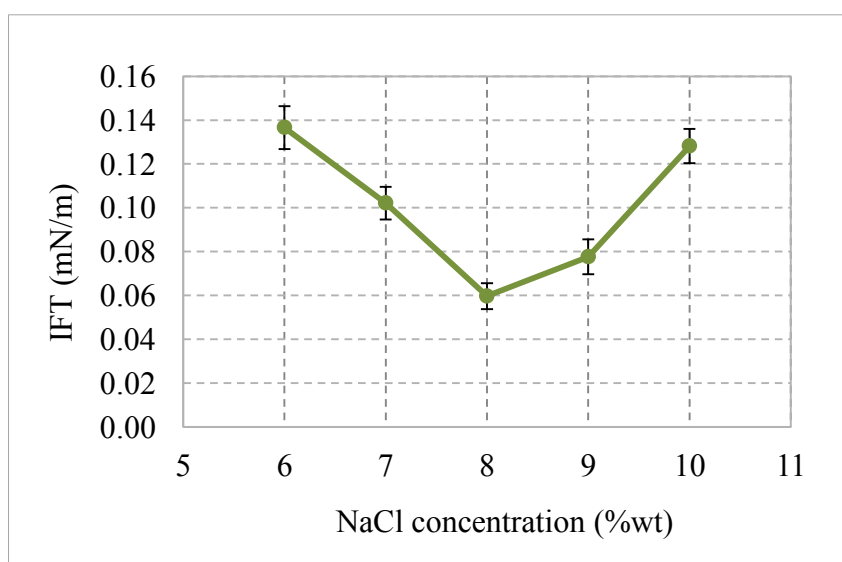


Figure B1 The IFT value of the microemulsion formulate 0.50 wt% $C_{14-15}, 8PO-SO_4$ alone and coconut oil as an oil phase.

Table B2 IFT values of 0.50 wt% C₁₄₋₁₅, 8PO-SO₄ and palm oil as an oil phase

| NaCl (wt%) | IFT1 | IFT2 | IFT3 | Avg | SD |
|------------|--------|--------|--------|--------|--------|
| 6 | 0.1465 | 0.1269 | 0.1365 | 0.1366 | 0.0098 |
| 7 | 0.0946 | 0.1024 | 0.1095 | 0.1022 | 0.0075 |
| 8 | 0.0538 | 0.0596 | 0.0657 | 0.0597 | 0.0060 |
| 9 | 0.0739 | 0.0867 | 0.0723 | 0.0776 | 0.0079 |
| 10 | 0.1365 | 0.1269 | 0.1210 | 0.1281 | 0.0078 |

**Figure B2** The IFT value of the microemulsion formulate 0.50 wt% C₁₄₋₁₅, 8PO-SO₄ alone and palm oil as an oil phase.**Table B3** IFT values of 0.50 wt% C₁₄₋₁₅, 8PO-SO₄ and soybean oil as an oil phase

| NaCl (wt%) | IFT1 | IFT2 | IFT3 | Avg | SD |
|------------|--------|--------|--------|--------|--------|
| 7 | 0.0860 | 0.0724 | 0.0792 | 0.0792 | 0.0068 |
| 8 | 0.0604 | 0.0662 | 0.0549 | 0.0605 | 0.0057 |
| 9 | 0.0091 | 0.0075 | 0.0062 | 0.0076 | 0.0015 |
| 10 | 0.0224 | 0.0255 | 0.0363 | 0.0281 | 0.0073 |
| 11 | 0.1679 | 0.157 | 0.1794 | 0.1681 | 0.0112 |

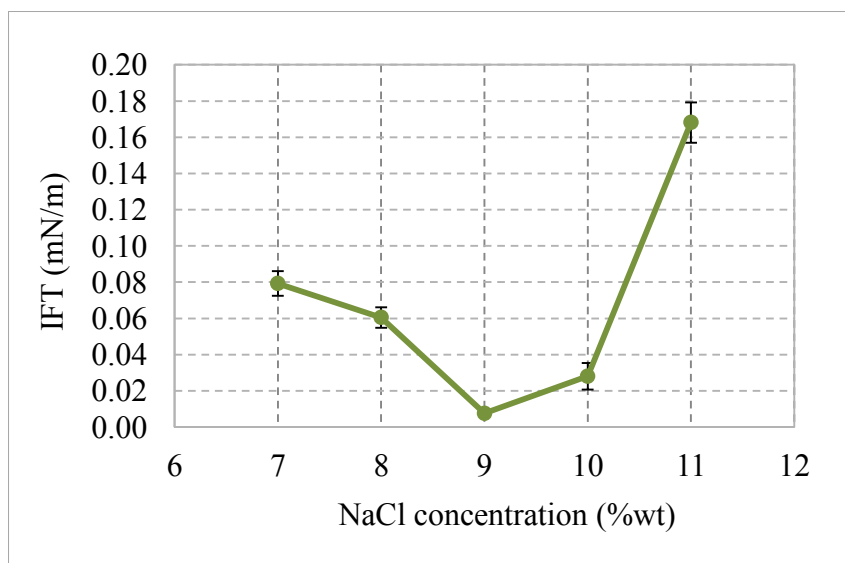


Figure B3 The IFT value of the microemulsion formulate 0.50 wt% C_{14-15} , 8PO-SO₄ alone and soybean oil as an oil phase.

Table B4 IFT values of 0.50 wt% C_{14-15} , 8PO-SO₄ and hexane (C_6) as an oil phase

| NaCl (wt%) | IFT1 | IFT2 | IFT3 | Avg | SD |
|------------|--------|--------|--------|--------|--------|
| 1 | 0.4749 | 0.4486 | 0.5108 | 0.4781 | 0.0255 |
| 2 | 0.2907 | 0.2749 | 0.3536 | 0.3064 | 0.0340 |
| 3 | 0.0548 | 0.0662 | 0.0362 | 0.0524 | 0.0124 |
| 4 | 0.3988 | 0.3792 | 0.3602 | 0.3794 | 0.0158 |
| 5 | 0.4486 | 0.5024 | 0.4749 | 0.4753 | 0.0220 |

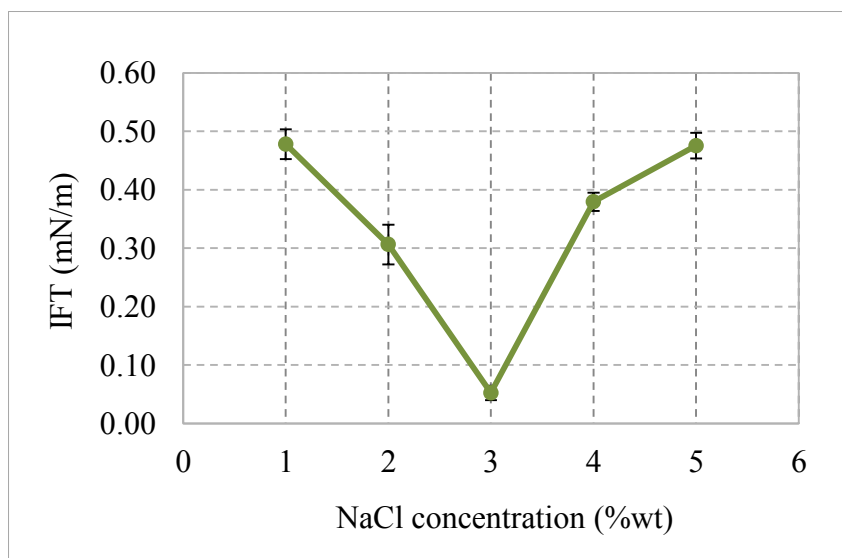


Figure B4 The IFT value of the microemulsion formulate 0.50 wt% C_{14-15} , 8PO-SO₄ alone and hexane (C₆) as an oil phase.

Table B5 IFT values of 0.50 wt% C_{14-15} , 8PO-SO₄ and dodecane (C₁₂) as an oil phase

| NaCl (wt%) | IFT1 | IFT2 | IFT3 | Avg | SD |
|------------|--------|--------|--------|--------|--------|
| 3 | 0.2591 | 0.1269 | 0.1465 | 0.1775 | 0.0713 |
| 4 | 0.0790 | 0.0860 | 0.0724 | 0.0791 | 0.0068 |
| 5 | 0.0032 | 0.0023 | 0.0025 | 0.0027 | 0.0005 |
| 6 | 0.0255 | 0.0224 | 0.0255 | 0.0245 | 0.0018 |
| 7 | 0.1011 | 0.1093 | 0.1465 | 0.1190 | 0.0242 |
| 8 | 0.1365 | 0.2743 | 0.208 | 0.2063 | 0.0689 |

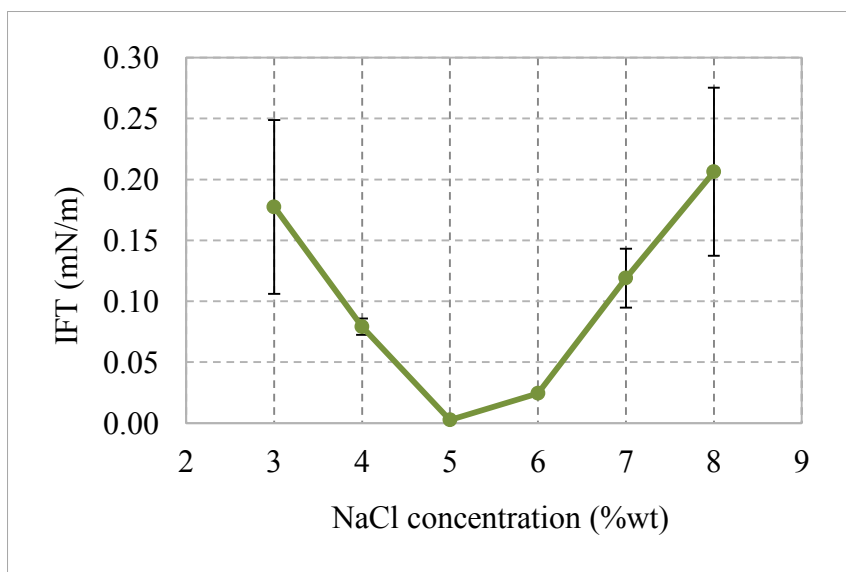


Figure B5 The IFT value of the microemulsion formulate 0.50 wt% C_{14-15} , 8PO-SO₄ alone and dodecane (C_{12}) as an oil phase.

Table B6 IFT values of 0.50 wt% C_{14-15} , 8PO-SO₄ and hexadecane(C_{16}) as an oil phase

| NaCl (wt%) | IFT1 | IFT2 | IFT3 | Avg | SD |
|------------|--------|--------|--------|--------|--------|
| 5 | 0.0405 | 0.0449 | 0.0355 | 0.0403 | 0.0047 |
| 6 | 0.0062 | 0.0075 | 0.0051 | 0.0063 | 0.0012 |
| 7 | 0.0040 | 0.0025 | 0.0032 | 0.0032 | 0.0008 |
| 8 | 0.0363 | 0.0405 | 0.0324 | 0.0364 | 0.0041 |
| 9 | 0.0549 | 0.0449 | 0.0323 | 0.0440 | 0.0113 |
| 10 | 0.1465 | 0.1093 | 0.0950 | 0.1169 | 0.0266 |

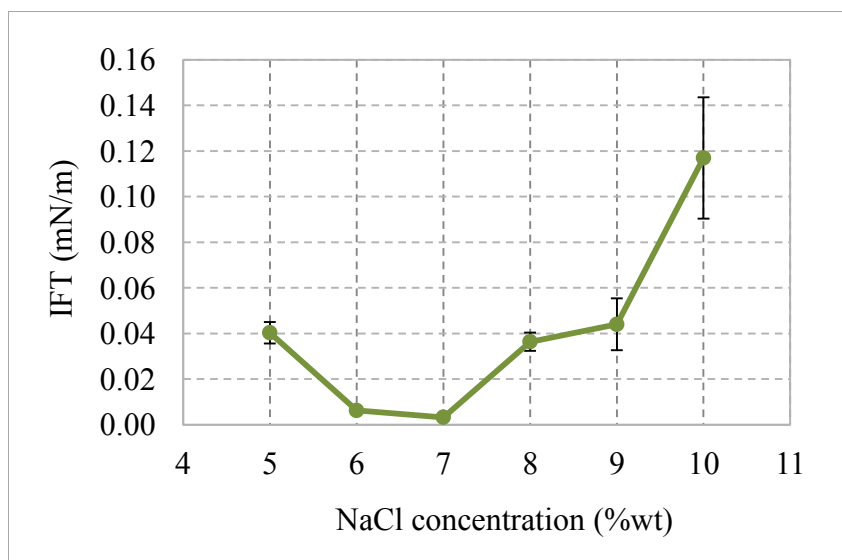


Figure B6 The IFT value of the microemulsion formulate 0.50 wt% C_{14-15} , 8PO-SO₄ alone and hexadecane (C_{16}) as an oil phase.

Table B7 IFT values of 0.50 wt% C_{14-15} , 8PO-SO₄ mixed with C_{16-18} , 2PO-4EO-OH and hexane (C_6) as an oil phase

| NaCl (wt%) | IFT1 | IFT2 | IFT3 | Avg | SD |
|------------|--------|--------|--------|--------|--------|
| 1 | 0.2536 | 0.2907 | 0.2536 | 0.2660 | 0.0214 |
| 2 | 0.0723 | 0.0910 | 0.0860 | 0.0831 | 0.0097 |
| 3 | 0.3602 | 0.3103 | 0.2907 | 0.3204 | 0.0358 |

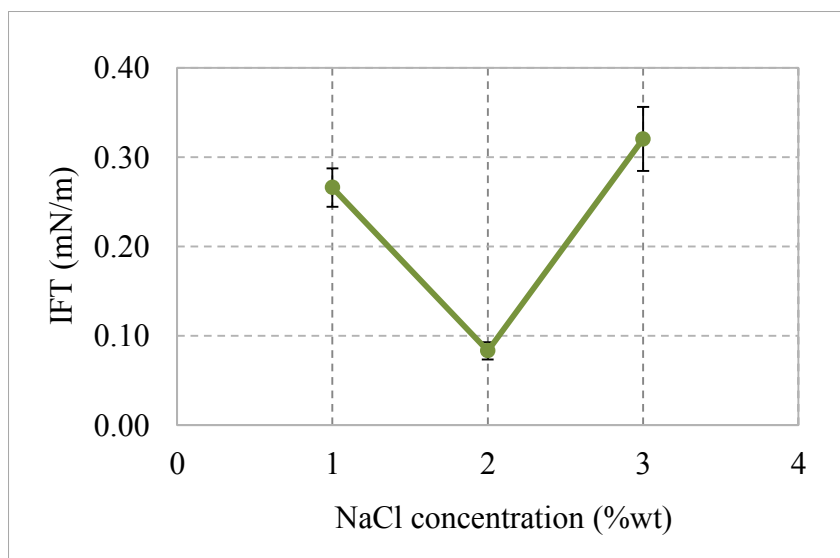


Figure B7 The IFT value of the microemulsion formulate 0.50 wt% C₁₄₋₁₅, 8PO-SO₄ mixed with C₁₆₋₁₅, 2PO-4EO-OH and hexane (C₆) as an oil phase.

Table B8 IFT values of 0.50 wt% C₁₄₋₁₅, 8PO-SO₄ mixed with C₁₆₋₁₈, 2PO-4EO-OH and dodecane (C₁₂) as an oil phase

| NaCl (wt%) | IFT1 | IFT2 | IFT3 | Avg | SD |
|------------|--------|--------|--------|--------|--------|
| 2 | 0.1749 | 0.2536 | 0.1749 | 0.2011 | 0.0454 |
| 3 | 0.0860 | 0.0946 | 0.0790 | 0.0865 | 0.0078 |
| 4 | 0.0074 | 0.0086 | 0.0091 | 0.0084 | 0.0009 |
| 5 | 0.0204 | 0.0255 | 0.0204 | 0.0221 | 0.0029 |

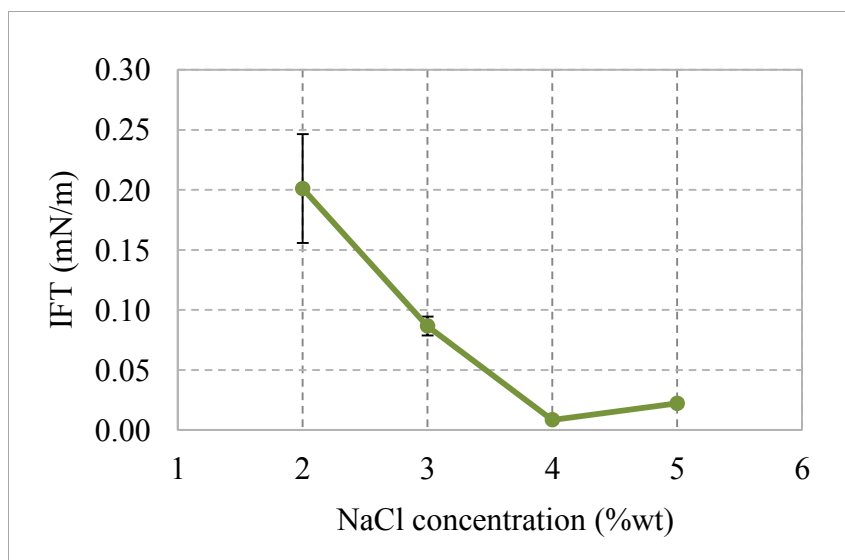


Figure B8 The IFT value of the microemulsion formulate 0.50 wt% C_{14-15} , 8PO- SO_4 mixed with C_{16-15} , 2PO-4EO-OH and dodecane (C_{12}) as an oil phase.

Table B9 IFT values of 0.50 wt% C_{14-15} , 8PO- SO_4 mixed with C_{16-18} , 2PO-4EO-OH and hexadecane (C_{16}) as an oil phase

| NaCl (wt%) | IFT1 | IFT2 | IFT3 | Avg | SD |
|------------|--------|--------|--------|--------|--------|
| 4 | 0.1570 | 0.1011 | 0.2080 | 0.1554 | 0.0535 |
| 5 | 0.0449 | 0.0549 | 0.0604 | 0.0534 | 0.0079 |
| 6 | 0.0185 | 0.0124 | 0.0224 | 0.0178 | 0.0050 |
| 7 | 0.0790 | 0.0604 | 0.0790 | 0.0728 | 0.0107 |

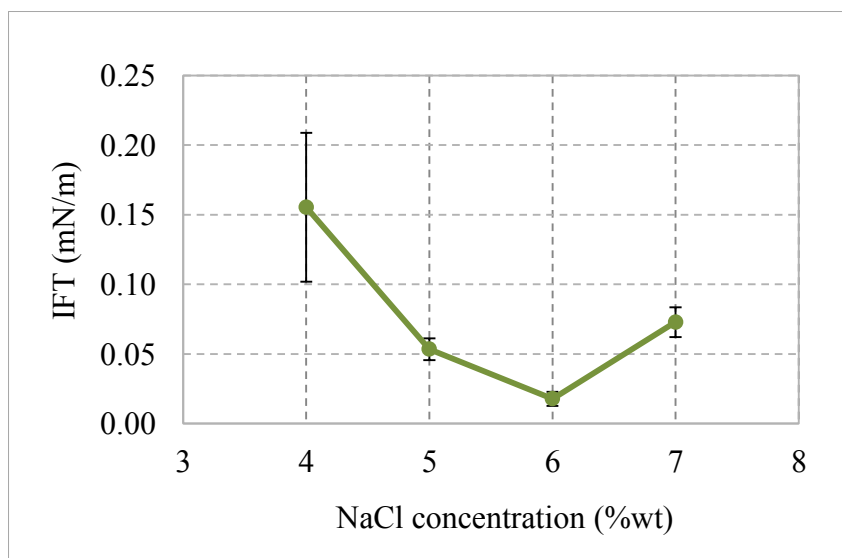


Figure B9 The IFT value of the microemulsion formulate 0.50 wt% C_{14-15} , 8PO-SO₄ mixed with C_{16-18} , 2PO-4EO-OH and hexadecane (C_{16}) as an oil phase.

Appendix C K and Cc Values Determination

For K and Cc values were determined by the plot between $\ln S^*$ (optimum salt) and EACN of the alkane oils (i.e., hexane(C_6), dodecane (C_{12}) and hexadecane (C_{16})). K values were the slope and Cc values were the y-interception of the plot.

Table C1 The data of the plot with C_{14-15} , 8PO-SO₄ system

| Oil | S^* | $\ln S^*$ | EACN |
|-------------|-------|-----------|-------|
| Hexane | 3 | 1.09861 | 6 |
| Dodecane | 5 | 1.60944 | 12 |
| Hexadecane | 7 | 1.94591 | 16 |
| Coconut oil | 7 | 1.94591 | 15.98 |
| Palm oil | 8 | 2.07944 | 17.56 |
| Soybean oil | 9 | 2.19722 | 18.94 |

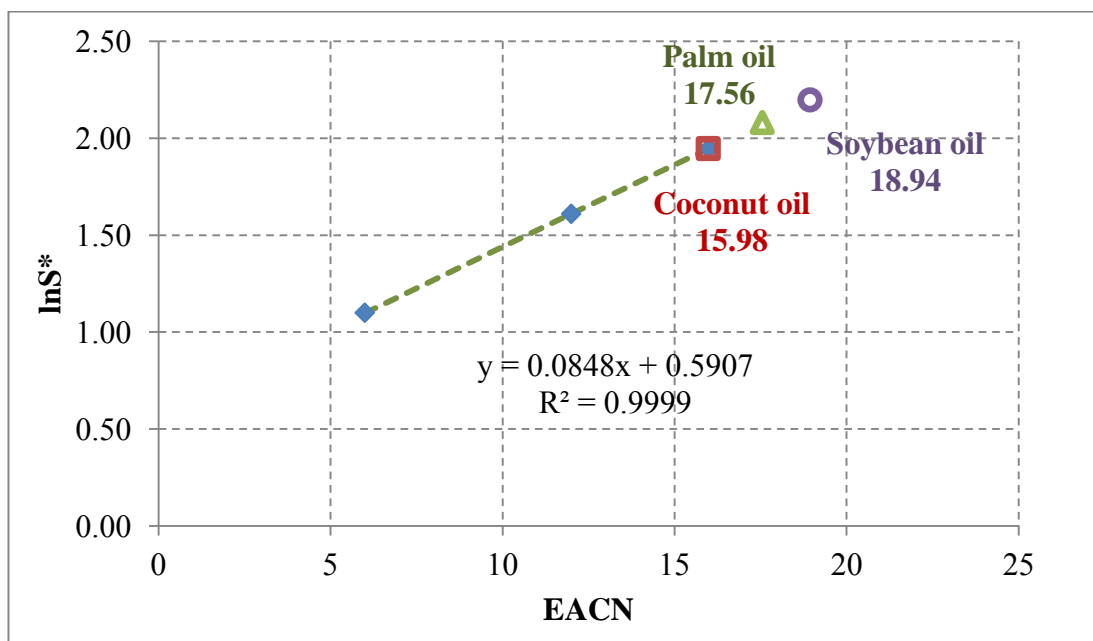


Figure C1 Plot of optimum salt versus EACN for the C₁₄₋₁₅, 8PO-SO₄.

Table C2 The data of the plot with C₁₄₋₁₅, 8PO-SO₄ /C₁₆₋₁₈, 2PO-4EO-OH system

| Oil | S* | ln S* | EACN |
|-------------|----|--------|---------|
| Hexane | 2 | 0.6931 | 2.0000 |
| Dodecane | 4 | 1.3863 | 12.0000 |
| Hexadecane | 6 | 1.7918 | 16.0000 |
| Coconut oil | 6 | 1.7918 | 16.5379 |
| Palm oil | 7 | 1.9459 | 18.5477 |
| Soybean oil | 8 | 2.0794 | 20.2887 |

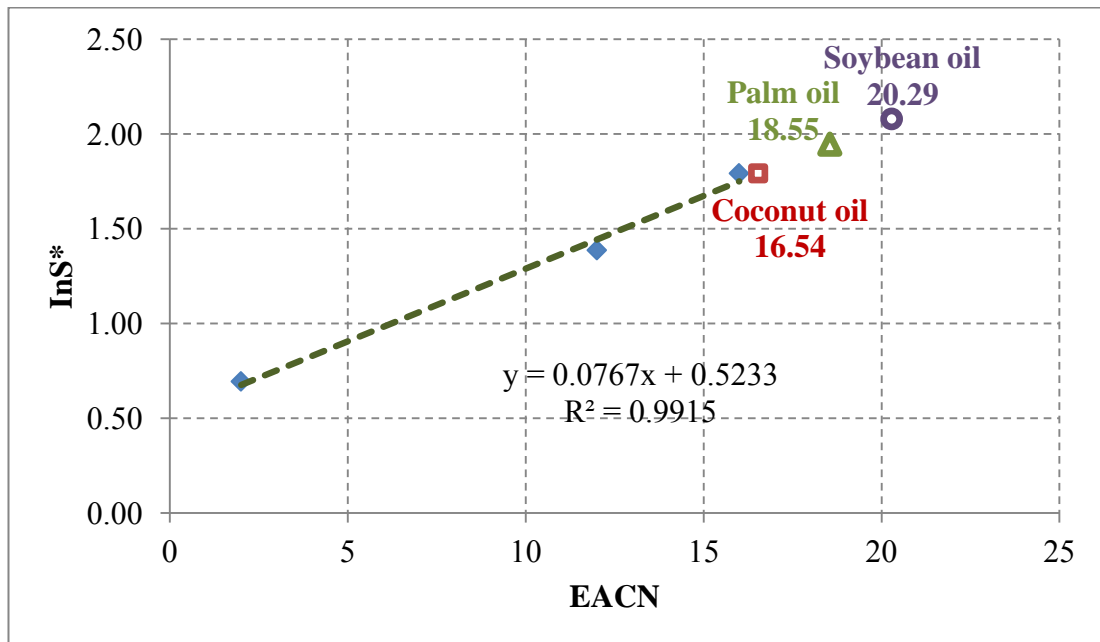


Figure C2 Plot of optimum salt versus EACN for the C₁₄₋₁₅, 8PO-SO₄/C₁₆₋₁₈, 2PO-4EO-OH.

Appendix D EACN Calculation

For EACN calculation of the oils; follow by HLD equation;

$$\text{HLD} = \ln(S) - K \times (\text{EACN}) - f(A) + C_c - \alpha_T \Delta T$$

| | |
|-----------------------------------|----------|
| Where, the middle phase formation | HLD = 0 |
| S is optimum salinity. | S = S* |
| Alcohol free | f(A) = 0 |
| Occur at room temp (25 °C) | ΔT = 0 |

$$\ln(S^*) = K \times (\text{EACN}) - C_c$$

| | |
|------------------|--------------------------------------|
| From Figure C1, | y = 0.0848x + 0.5907 |
| Then | K = 0.0848, C _c = -0.5907 |
| For, Coconut oil | (S* = 7) |

Palm oil (S* = 8)

Soybean oil (S* = 9)

Replace K, Cc and S* of Coconut, Palm and Soybean oil in equation;

$$\ln(S^*) = K \times (\text{EACN}) - C_c$$

Then EACN of Coconut oil = 15.98

EACN of Palm oil = 17.56

EACN of Soybean oil = 18.94

From Figure C2, $y = 0.0767x + 0.5233$

Then $K = 0.0767, C_c = -0.5233$

For, Coconut oil (S* = 6)

Palm oil (S* = 7)

Soybean oil (S* = 8)

Replace K, Cc and S* of Coconut, Palm and Soybean oil in equation;

$$\ln(S^*) = K \times (\text{EACN}) - C_c$$

Then EACN of Coconut oil = 16.54

EACN of Palm oil = 18.55

EACN of Soybean oil = 20.29

Appendix E Hard Surface Cleaning

For hard surface cleaning, the cleaning efficiency of the microemulsion system was indicated by oil removal percentages. The percentages of oil removal followed;

$$\text{Oil removal (\%)} = \frac{(A-B)}{(A)} \times 100$$

Where A is the average concentration before washing and B is the average concentration after washing with limonene for 24 hours.

Table E1 The average beginning sample

| Sample | C |
|----------|---------|
| starter1 | 53.5031 |
| starter2 | 52.9223 |
| starter3 | 53.2445 |
| Avg | 53.2233 |

Table E2 The average oil removal with the C₁₄₋₁₅, 8PO-SO₄ alone

| NaCl | C1 | C2 | C3 | C,avg | %remove | SD |
|------|---------|---------|---------|---------|---------|--------|
| 0 | 41.8012 | 44.0883 | 43.9021 | 43.2639 | 18.7125 | 1.2701 |
| 1 | 36.7231 | 37.6468 | 38.1350 | 37.5016 | 29.5391 | 0.7171 |
| 5 | 34.8381 | 37.0189 | 35.3132 | 35.7234 | 32.8801 | 1.1468 |
| 7 | 32.7827 | 33.2295 | 31.9521 | 32.6548 | 38.6457 | 0.6482 |
| 8 | 20.5991 | 21.4804 | 22.7573 | 21.6123 | 59.3932 | 1.0851 |
| 9 | 27.8390 | 25.2871 | 28.2115 | 27.1125 | 49.0589 | 1.5918 |
| 10 | 38.0819 | 37.6245 | 35.8397 | 37.1820 | 30.1396 | 1.1848 |

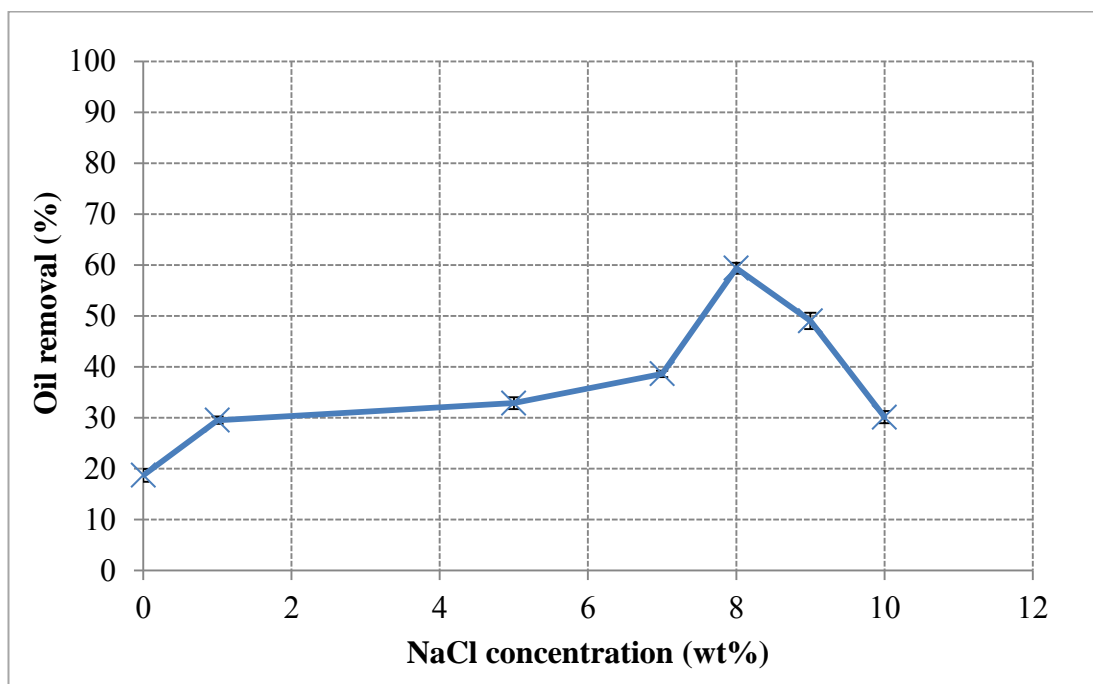


Figure E1 The average oil removal with the C₁₄₋₁₅, 8PO-SO₄ alone.

Table E3 The average oil removal with the C₁₄₋₁₅, 8PO-SO₄ mixed with C₁₆₋₁₈, 2PO-4EO-OH

| NaCl | C1 | C2 | C3 | C _{avg} | %remove | SD |
|------|---------|---------|---------|------------------|---------|--------|
| 0 | 32.0983 | 29.9123 | 31.0513 | 31.0206 | 41.7161 | 1.0933 |
| 1 | 30.6247 | 28.4561 | 27.9012 | 28.9940 | 45.5239 | 1.4392 |
| 5 | 27.7371 | 29.0912 | 28.5612 | 28.4632 | 46.5212 | 0.6824 |
| 7 | 18.9851 | 19.4312 | 19.8723 | 19.4295 | 63.4943 | 0.4436 |
| 8 | 23.6712 | 24.5123 | 22.8112 | 23.6649 | 55.5366 | 0.8506 |
| 9 | 25.6481 | 25.7081 | 27.0198 | 26.1253 | 50.9137 | 0.7752 |
| 10 | 30.4981 | 28.0181 | 29.1278 | 29.2147 | 45.1093 | 1.2423 |

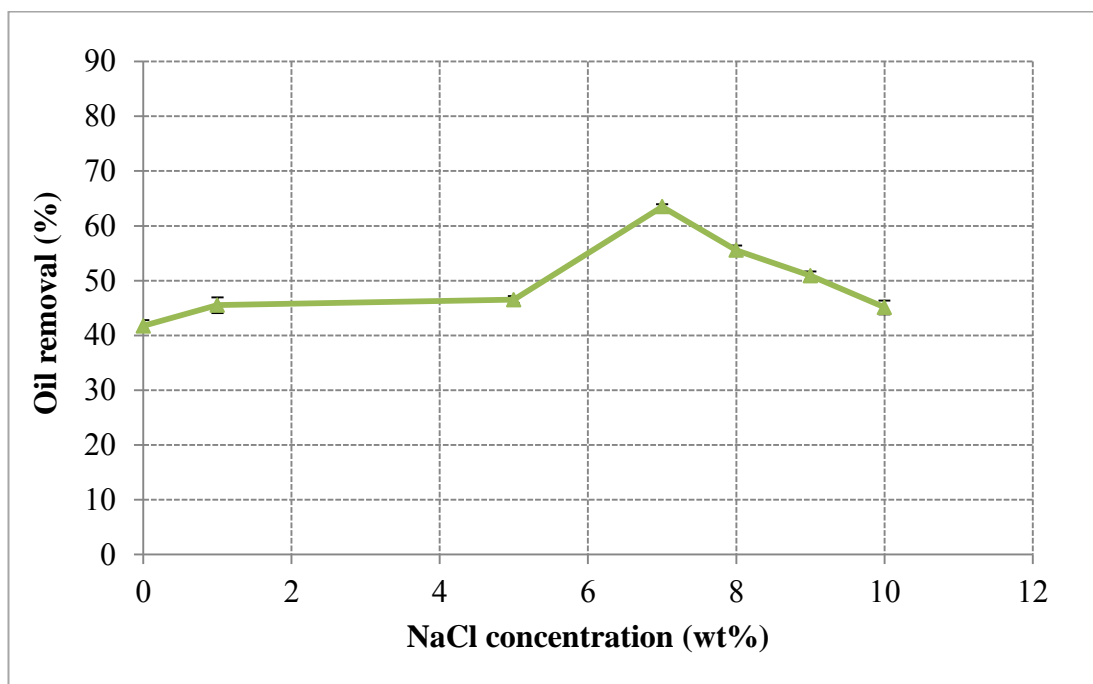


Figure E2 The average oil removal with the C₁₄₋₁₅, 8PO-SO₄ mixed with C₁₆₋₁₈, 2PO-4EO-OH.

Table E4 The average oil removal with SDBD alone

| NaCl | C1 | C2 | C3 | C _{avg} | %remove | SD |
|------|---------|---------|---------|------------------|---------|--------|
| 0 | 43.6862 | 44.5812 | 43.0314 | 43.7663 | 17.7686 | 0.7780 |
| 1 | 40.5981 | 41.9312 | 42.3452 | 41.6248 | 21.7921 | 0.9130 |
| 5 | 45.8095 | 45.0389 | 44.1672 | 45.0052 | 15.4408 | 0.8217 |
| 7 | 47.8672 | 46.8923 | 48.3452 | 47.7016 | 10.3747 | 0.7405 |
| 8 | 49.4357 | 47.9026 | 47.0167 | 48.1183 | 9.5916 | 1.2238 |
| 9 | 47.0124 | 46.5534 | 45.3218 | 46.2959 | 13.0158 | 0.8742 |
| 10 | 50.0395 | 49.8789 | 47.6428 | 49.1871 | 7.5836 | 1.3398 |

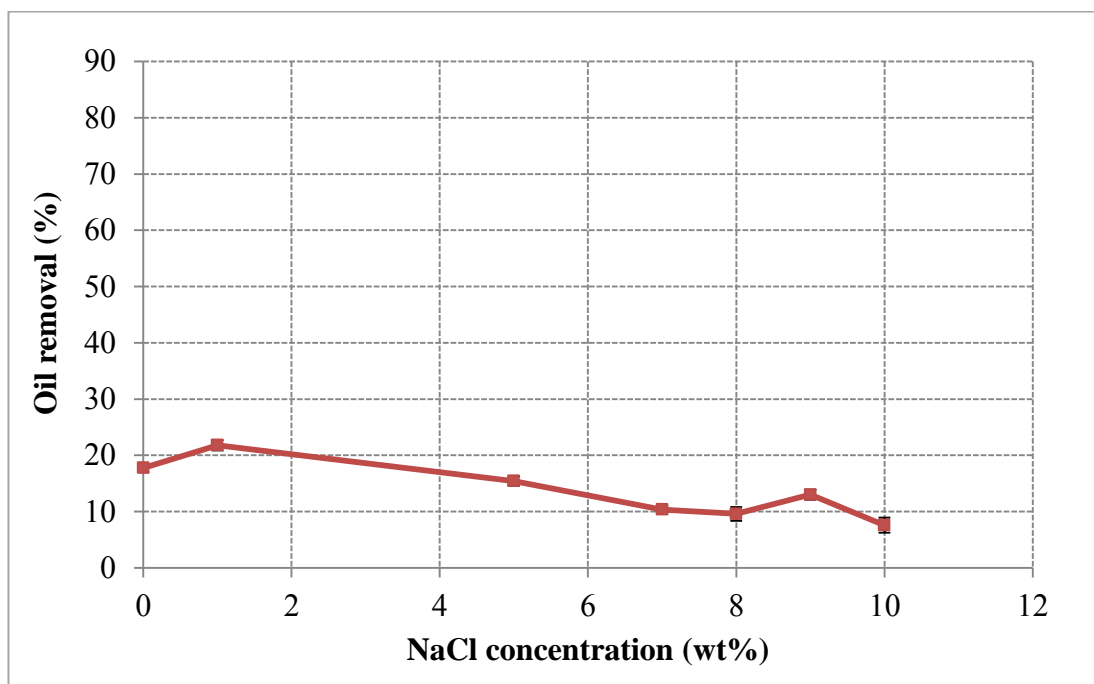


Figure E3 The average oil removal with SDBD alone.

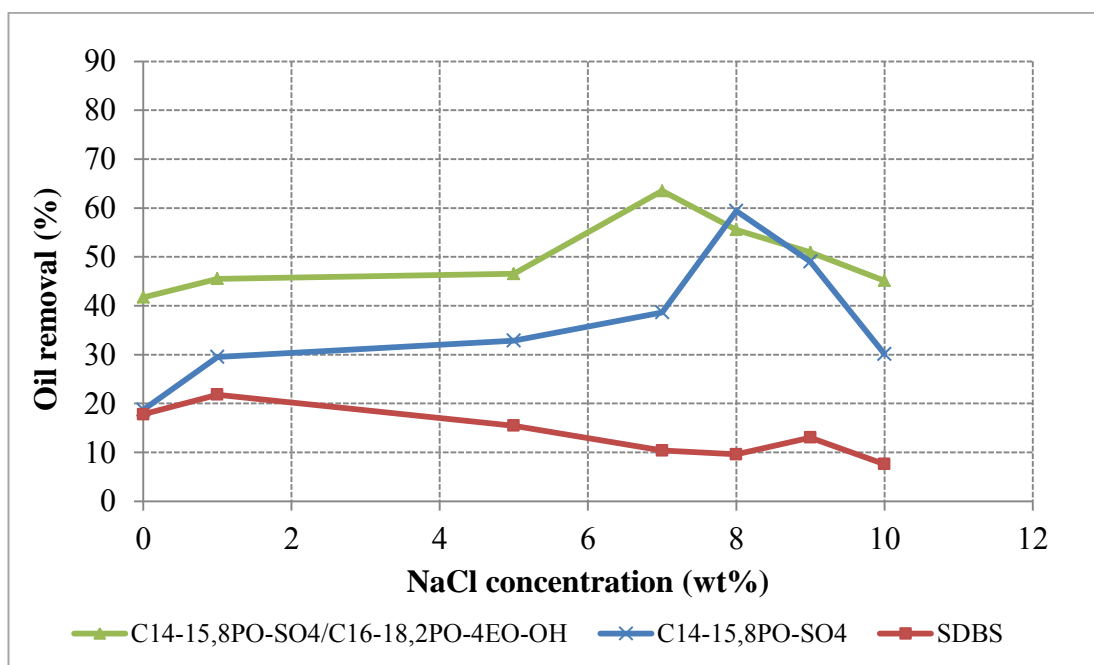


Figure E4 The average oil removal with the $C_{14-15}, 8PO-SO_4$ alone, the $C_{14-15}, 8PO-SO_4$ mixed with $C_{16-18}, 2PO-4EO-OH$ and SDBD alone.

CURRICULUM VITAE

Name: Ms. Siriluk Jariyawattanarat

Date of Birth: September 5, 1992

Nationality: Thai

University Education:

2011-2015 Bachelor Degree of Engineering (Petrochemicals and Polymeric Materials), Faculty of Engineering and Industrial Technology, Silpakorn University, Nakornphathom, Thailand

Work Experience:

2014 Position: Student Internship

Company name: Vatchara Packing Products Company Limited

Proceedings:

Jariyawattanarat, S., Chodchanok, A., Sabatini, D.A., Scamehorn, J., and Charoensaeng, A. (2017, May 23) Microemulsion formation of vegetable oils using mixed extended surfactant for cleaning applications. Proceedings of The 8th Research Symposium on Petroleum, Petrochemicals and Advanced Materials and The 23rd PPC Symposium on Petroleum, Petrochemicals, and Polymers, Bangkok Thailand.

Presentation:

Jariyawattanarat, S., Chodchanok, A., Sabatini, D.A., Scamehorn, J., and Charoensaeng, A. (2017, June 18) Microemulsion formation of semi-solid fats and vegetable oils based on HLD concept for cleaning applications. Poster presented at 7th International Colloids Conference, Sitges, Spain.