# CHAPTER II
# THEORETICAL BACKGROUND AND LITERATURE REVIEW

## 2.1 Palm Oil

Crude palm oil (CPO) is extracted from the mesocrap (reddish pulp) of the oil palm fruits. CPO has naturally semi-solid characteristic at room temperature with a melting point between 36-50 °C. The CPO has to be refined for improving properties. The adsorption bleaching is one process for producing refined, bleached, and deodorized palm oil (RBD palm oil). This oil is separated liquid olein or superolein, mainly used in cooking oils in households, from solid stearin, largely used for margarines, shortening and soap industry. The CPO composes of equal level between saturated fatty acids and unsaturated fatty acids. The major triglycerides of CPO are palmitic acid (45.48%) and oleic acid (40.17%). The fatty acid composition of CPO and its production are shown in Table 2.1 (Mana *et al.*, 1999).

**Table 2.1** Fatty acids composition of various types palm oil

| Fatty acid | Fatty acid composition (%) | | | | |
|---|---|---|---|---|---|
| | CPO | 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 | 57.58 |

[a]CPO, crude palm oil; RBD, refined, bleached, deodorized; M, myristic; P, palmitic; S, stearic; O, oleic; L, linoleic

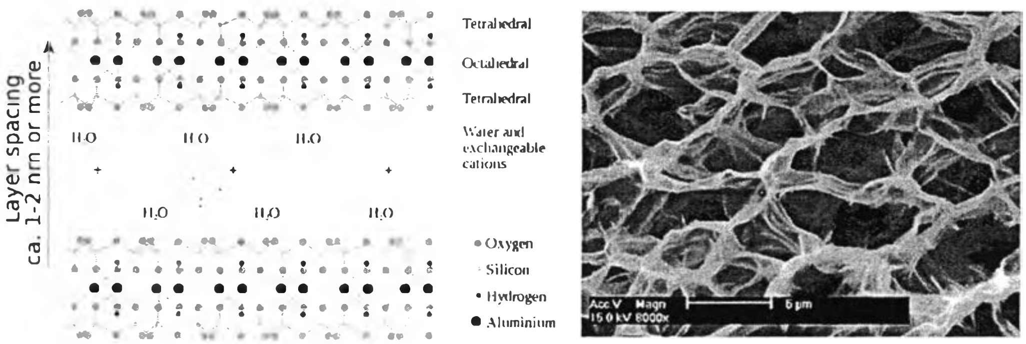
Palm oil can be used as a component blended with other fuels for biodiesel production due to high triglyceride content which is reacted through a transesterified process to obtain methyl ester (biodiesel).

## 2.2 Spent Bleaching Earth (SBE)

Spent bleaching earth is a solid waste generated as part of refining process in vegetable oil industry after removing certain pigments such as carotenoids and chlorophyll, oxidation products, contaminants such as soaps and trace metals, traces of phosphatides, polycyclic aromatic hydrocarbons and other pollutants. All of these substances have adverse effects on both the quality and stability of final product. The most common adsorbent used for bleaching process is the bleaching earth or clay. They have a naturally high affinity for adsorbing oil contaminants without any acid treatment. This nature is commonly referred to as natural clays. Acid or acid-activated clays require chemical treatment by acids to create the surface area and porosity for bleaching vegetable oils (http://lipidlibrary.aocs.org/processing/bleaching/index.htm).

### 2.2.1 Structure of Bleaching Earth

Bleaching earths are generally consisted of one or more of three types of clay minerals: calcium montmorillonite (commonly refered to as bentonite), attapulguite, and sepiolite. They are layer composed of tetrahedral silicate sheets ($SiO_4$) and octahedral hydroxide sheets ($AlO_4$). The tetrahedral silicate sheets are bonded with octahedral sheets and coordinated by six oxygen atoms. The oxygen atom located above the tetrahedral sheets is bonded with a hydrogen atom to form OH group. Some of lower valence ions such as magnesium, iron, manganese and lithium replace aluminium and silicon ions led to create charge on surfaces of each layer. The imbalanced negative charge is neutralized by hydratable cations (sodium and calcium). For example, Montmorillonites, the layer structure consists of central octahedral sheets sandwiched between two tetrahedral sheets which is known as 2:1 (tetrahedral : octahedral). Structure and microscopic view of (2:1 clay) is displayed in Figure 2.1 (http://en.wikipedia.org/wiki/Clay_minerals).



(a) (b)

**Figure 2.1** Montmorillonite with (a) structure view and (b) microscopic view (http://www.sorptive.org/minerals/montmorillonite/).

### 2.2.2 Application of Bleaching Earth in Vegetable Oil Refining Process

In the palm oil refining process, bleaching is one of significant stage for removing undesired color pigments (carotene and chlorophyll) and other impurities (e.g., phosphatides, trace metals, and peroxides) in order to improve the quality of palm oil. The use of strongly and high adsorbing capacity material is required for removal of these contaminants. Hence, bleaching earth is widely utilized as adsorbent in bleaching of palm oil because of high specific surface area, surface activity and porosity. After bleaching stage, a large amount of SBE is generated as a solid waste and disposed in landfills, which may present a fire hazard and cause pollution problem due to the residual oil in SBE. These substantial oil content should be recovered and regenerated for both economically and ecologically issues (Ngu and Twaiq, 2013).

### 2.2.3 Regeneration and Utilization of Spent Bleaching

Since SBE contained 20 to 40 % by weight oil, several studies considered recovering these residual oils and regenerating bleaching earth adsorbent for its utilization in bleaching process or other industrial applications. Al-Zahrani and Daous (2000) studied recovery of oil retained in SBE using organic solvent such as methylethylketone (MEK), acetone, petroleum ether and hexane at optimum conditions. The deoiled earths were reactivated by calcination. The percentage of extracted oil and percentage of bleaching were maximum for deoiled earths by MEK and minimum for hexane whereas the quality of oil had reversed trend. The result of deoiled earths after calcination could restore the bleaching power close to fresh earths. The amount of recovered oil (42-72% of the total oil content) was acceptable quality. These extracted oils could be recycled or used as raw material in the soap industry.

The results of Foletto and coworkers (2002) suggested that the extraction process using only solvent was not sufficient to recover the bleaching capacity of the treated SBE. The earths need additional treatment by thermal process at the temperature above 400 °C. However, when the temperature was too high (600°C), structure of clay was destructed or sintering. Hence, regeneration of spent bleaching earth involved two stages: recovery of oil from SBE and heat-regeneration of extracted SBE. This process can restore the adsorptive capacities of SBE without destructing original structure of earth, even more solve disposal problems, promote a zero-waste industry and reduce bleaching earth imports (Yoo and Lin, 2004).

Nursulihatimarsyila and coworkers (2010) reported that two types of regeneration process were performed such as solvent extraction followed by heat treatment, and direct heat treatment. The experimental results indicated that both acid-activated and natural clay accomplished the highest regeneration efficiency at 500 °C by direct heat treatment method, which was more efficient than that of heat treatment because of completely removal moisture, impurities and dirt. The physical properties of the regenerated SBE such as specific surface area and total pore volume decreased at high temperature due to pore collapse and damage in the structure, resulting in the reduction of regenerated efficiency for adsorbing color pigments and impurities.

After oil extraction from SBE, recovered residual oils contained high free fatty acids (more than 10%) and peroxide value which exhibited poor quality of extracted oil. These oils could not be properly used for food applications. However, they were converted to methyl esters via transesterification process for biofuels applications (Kheang *et al.*, 2006). In biodiesel production, the triglycerides are reacted with an alcohol such as methanol through transesterification to form fatty acids methyl esters (FAME) known as biodiesel and glycerol in presence of catalyst such as sodium hydroxide, potassium hydroxide, and sodium methoxide as shown in Figure 2.2 (Mana *et al.*, 1999).

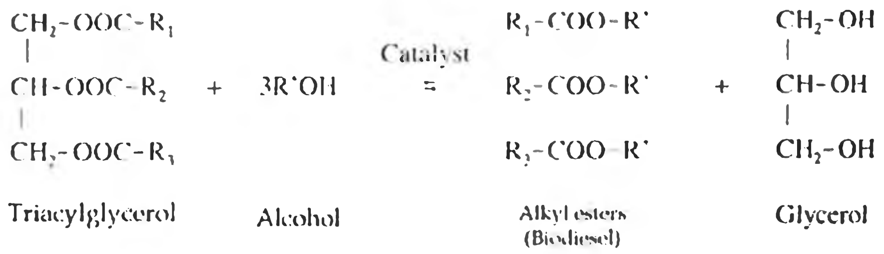


**Figure 2.2** Transesterification of triglyceride with alcohol.

Huang and Chang (2010) studied two processes for producing biodiesel such as esterification and tranesterification process. The FFAs content in the residual oil were converted to methyl esters via esterification with caustic soda to avoid the side reaction by saponification in the transesterification process. The properties of this residual oil were similar to those of diesel.

Additionally, SBE was found to contain sufficient quantity of nitrogen-phosphorous-potassium (NPK) contents, it could be converted into bio-organic fertilizer by co-composting with some agricultural and palm oil milling by-products. The nutrients in the SBE presented in terms of $P_2O_5$ had a positive effect on the growth of flowers and fruits, while nitrogen and magnesium affected leaves growth and potassium catalyzes photosynthesis. Thus, NPK was required in any form of fertilizer for overall plant growth (Loh *et al.*, 2013). Other options included using SBE as an alternative fuel in cement kilns or as a feedstock for the production of clay bricks.

### 2.2.4 Oil Extraction from SBE

Because of high amount of retained oil in SBE, it sounds reasonably to recover and reuse as raw material in suitable applications. Various methods have been used, some of which are listed below. To date, there are several methods to recover oil from SBE including, solvent extraction and supercritical fluid extraction (SC-$CO_2$).

#### *2.2.4.1* Solvent Extraction

Solvent extraction is the separation method of the compositions of a liquid by contacting with another insoluble liquid, also known as solvent. This method is widely used in recovering retained oil on solid surface because it provides a high yield and good properties of extracted oil. On the contrary, hexane is hazardous and high volatile solvent causing peripheral nerve damage, muscle wasting and atrophy. Therefore, High-priced equipment for handling and ensuring worker safety are required resulting in high cost of investment and operation.

Lee and coworkers (2000) found that the efficiencies of extraction by various hydrocarbons (e.g., petroleum ether, pentane, hexane, heptane) were higher than those of polar solvents (e.g., methanol, ethanol and isopropanol), but the extracted oils had lower in quality because of higher fatty acids concentration and Totox value. Ramasamy (2001) studied on the recovery of oil from SBE through the use of hydrocarbon solvents, hexane. The optimum contact time and ratio of spent earth to solvent (weight : volume) to obtain high oil recovery were 30 minutes and 1:3, respectively. The color of extracted oil was darker compared with the crude and bleached palm oil, but the quality of extracted oil was the same to those of the crude oil and bleached oil.

#### *2.2.4.2* Supercritical Fluid Extraction (SC-$CO_2$)

This method is separation of a component from another one using supercritical fluid as an extracting solvent. The process is operated at the temperature and pressure above its critical point, where the substance can exist as a vapor and liquid in equilibrium. It can diffuse through solid like a gas, and dissolve material like a liquid. Carbon dioxide ($CO_2$) is the most used supercritical fluid because of non-hazardous and non-flammable properties. Although this method is a clean and environmental-friendly technology, it requires high pressure causing high cost of operation.

Kheang and coworkers (2006) reported that the residual oils of two types of SBE were recovered via solvent and supercritical-fluid extraction (SC-$CO_2$). The extracted oils from SC-$CO_2$ were both lighter yellow and less impurity (lower peroxide value and total phosphorous content) in comparison with the extracted oil from hexane extraction. These oils with free fatty acids content could be converted to methyl esters as diesel substitute. Similarly to the study of King and coworkers (1992), the SC-$CO_2$ process was used in soybean oil extraction of both neutral and acidic earths. The recovered oil properties in terms of free fatty acids content, Lovibond color ratio, and phosphorous content from SC-$CO_2$ method were similar to those of degummed-bleached oils.

#### *2.2.4.3 Other Extraction Methods*

Oil removal from SBE by boil-off method is treated with a boiling aqueous solution of sodium hydroxide. Sodium chloride (1 to 8% of the earths weight) was also added to mixture in order to reduce the surface tension between the oil and the clay. The maximum oil recovery of 87% was obtained at optimum condition, 5wt% NaOH, 3wt% NaCl, water to clay ratio of 4 and a reaction time of 30 min. The bleaching capacity of reused earth was very low due to the inability of removal of strongly adsorbed coloring mater that blocks the adsorption sites on the clay surface (Alhamed and Al-Zahrani, 2002).

Subcritical water technology is used for extracting applications in the field of environment because it is a green alternative method to solvent extraction. The water is heated under enough pressure to maintain the liquid states. Many components could be easily extracted under these conditions because of its remarkable properties such as a low dielectric constant and a high ion product. The concluded results have been found that the optimum extraction temperature and time are 270 °C and 20 minutes, respectively (Fatta *et al.*, 2014).

In summary, solvent extraction and supercritical method could provide high yield of oil extraction and good quality of extracted oil from SBE. In addition, the disadvantage of solvent extraction is that organic solvent is a high volatile and hazardous solvent which can cause an impact on heath and production cost. In addition, the disadvantage of supercritical fluid method is a high operation cost.

Hence, extractions of oil in SBE using surfactant have been investigated because this method approaches both the environmental and economic concerns.

## 2.3 Surfactant

Surfactant is a surface active agent which can adsorb on the surface or interface resulting in changes the free energy of the system. The structure of surfactant molecule comprises of two parts. The first part is called hydrophilic (water-loving) or lyphobic (oil-hating) which can be charged or uncharged group. Another part is called hydrophobic or tail part (water-hating) or lyphilic (oil-loving) which consists of hydrocarbon chain. They also are amphiphilic molecules because of its structure which has dissimilar parts in a molecule of surfactant. A surfactant molecule in general is picturised in Figure 2.3.

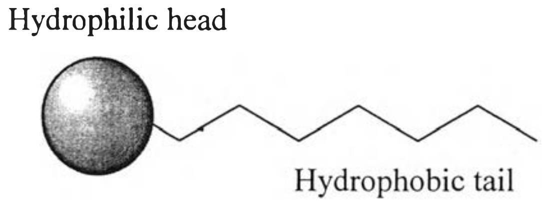


**Figure 2.3** Schematic diagram of a surfactant molecule.

A single molecule of surfactant is called a monomer. As the surfactant concentration in solution sufficiently increases, surfactant monomer will aggregate to form micelles. In other word, the micelle formation is an aggregation of surfactant in liquid which are formed when the surfactant concentration exceeds critical micelle concentration (CMC). This phenomenon is kwon as "micellization". The micelles are divided into two type; normal and reverse micelle. In aqueous medium, normal micelles are oriented with the hydrophobic tail part interior and the hydrophilic head group toward to aqueous phase. In contrast, reverse micelles are formed in non-polar medium or in oil with the hydrophilic head group interior and the hydrophobic tail group toward in non-aqueous phase. The formation of micelle is displayed in Figure 2.4.

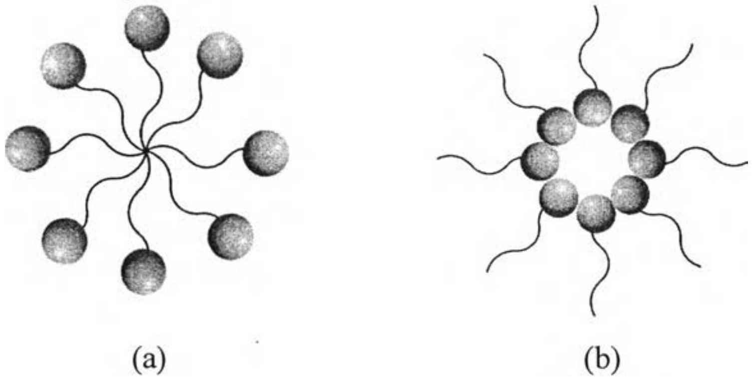

(a) (b)

**Figure 2.4** Schemetric representation of (a) normal and (b) reverse micelle.

2.3.1 Types of Surfactants

Surfactants are classified into four types depending on the nature of hydrophilic head group (see Figure 2.5).

*2.3.1.1 Anionic Surfactant:* The active surface part contains a negative charge such as sulfate, sulfonate, phosphate and carboxylates and tends to adsorb onto positively charged hydroplilic surface. This surfactant type is the largest class for useful application.

*2.3.1.2 Cationic Surfactant:* The active surface portion bears a positive charge and tends to adsorb onto negatively charged hydrophlilic surface. Due to strong adsorption onto most surfaces, this surfactant type is widely used for subsurface remediation.

*2.3.1.3 Zwitterionic Surfactant:* The active surface part has both positive and negative charge. Their properties generally depend on the pH of the solution. This surfactant type is compatible with other classes of surfactants.

*2.3.1.4 Nonionic Surfactant:* The active surface portion bears no charge tending to adsorb onto either hydroplilic or hydrophobic surface and orients toward the surface depending on the nature of surface. The important polar group of nonionic surfactants is ethylene oxide.

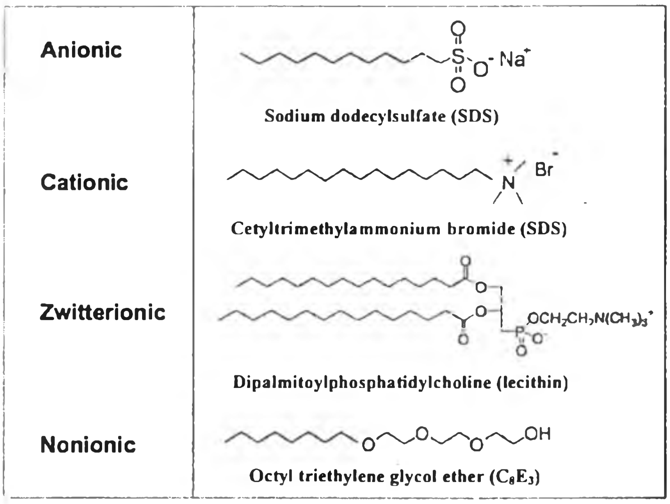


**Figure 2.5** Types of surfactant. (Paroor, 2012)

2.3.2 Extended Surfactant

A microemulsions formation requires a balanced and substantial interaction between surfactant-oil and surfactant-water phase. This concept was created by Winsor. The interfacial tension reduction and solubilization enhancement are adjusted by increasing individual interaction, which increases size of surfactant hydrophilic head group and hydrophobic tail. Nevertheless, a long hydrocarbon tail is limited by loss water solubility. Conventional surfactants could not produce ultralow interfacial tension with vegetable oil. Extended surfactants are an alternative surfactant to approach the Winsor concept without loss in soluble water because of theirs unique structure (Do and Sabatini, 2010).

Extended surfactants have intermediate polarity group, namely a polypropylene oxide (PO) and/or polypropylene-polyethylene oxide (PO-EO) chain, are placed between hydrophilic head and hydrophobic tail of the surfactant molecule to expand interaction of both polar phase and non-polar phase. The PO molecules are able to increase hydrophobic as well as extend the tail group. Therefore, the surfactant tail orients further into the non-aqueous phase with long hydrocarbon chain and avoiding water solubility. In conclusion, extended surfactants have unique characteristics, such as extended length, smooth transition between hydrophilic and hydrophobic regions at oil-water interface, water-soluble with large molecular weight and forming in high electrolyte concentration without surfactant precipitation (Witthayapanyanon *et al.*, 2006). The structure of extended surfactant is represented in Figure 2.6.

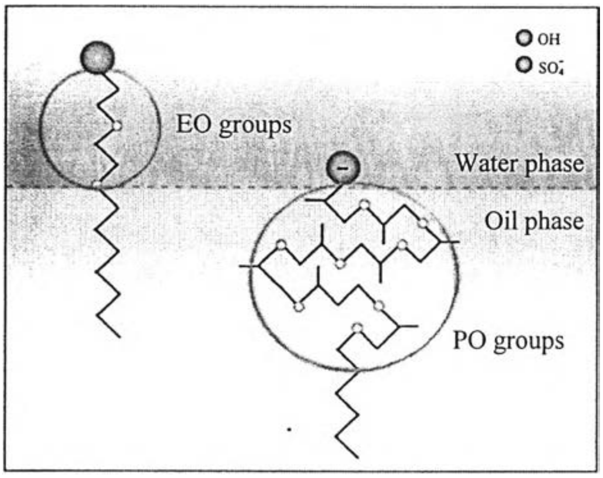


**Figure 2.6** Structure of extended surfactant.

The extended surfactant could form microemulsions (Winsor type I, II and III) with triglyceride oil which mainly contains in vegetable oil. Because structure of triglycerides is a long hydrocarbon chain which has high hydrophobic and polar natures in a molecule. It is difficult to form microemulsions. Nevertheless, the ultralow IFT and middle phase formation have been achieved at least eight propylene oxide groups of the extended surfactant (Phan *et al.*, 2011).

## 2.4 Microemulsions

Microemulsions are stable dispersion of two or partially miscible or more immiscible fluids stabilized by surfactant film, frequently in combination with a co-surfactant. The surfactants have to reduce adequate low interfacial tensions to form nanometer sizes. Thus, the visual appearance of microemulsions is a transparent or translucent and can be stable over time. In the other word, microemulsions are thermodynamically stable systems which are discriminated from emulsions. Emulsions are normally cloudy because of difference in their size and refractive index in continuous fluids as a result of light scattering from dispersed particle. Furthermore, the appearance of emulsion changes with time by visual observation. It can be concluded that emulsions are not thermodynamically stable.
(Eastoe *et al.*, 2013)

### 2.4.1 Types of Microemulsions

A classification of microemulsions is four general types of phase equilibrium, which is identified by Winsor: (Figure 2.7)

*2.4.1.1 Winsor Type I:* The two phases equilibrium, the lower phase contains mostly surfactant in water phase or oil in water (O/W) microemulsion phase with the upper excess oil phase (in case of oil is lighter than water). The oil droplet disperses in water phase and is solubilized in normal micelles.

*2.4.1.2 Winsor Type II*: The two phases equilibrium, the upper oil phase contains mostly surfactant or water in oil (O/W) microemulsion phase with the lower excess water phase. The water droplet disperses in oil phase and is solubilized in reverse micelles.

*2.4.1.3 Winsor Type III*: The three phases equilibrium consist of middle microemulsion phase which have mainly surfactant, with upper excess oil and lower excess water phase. This type corresponds to an oil and water phases that are stabilized by surfactant. This structure is called bicontinuous.

*2.4.1.4 Winsor Type IV*: The middle microemulsion phase expands into a single phase at high surfactant concentration, where the oil, water and surfactant phases homogeneously mix.

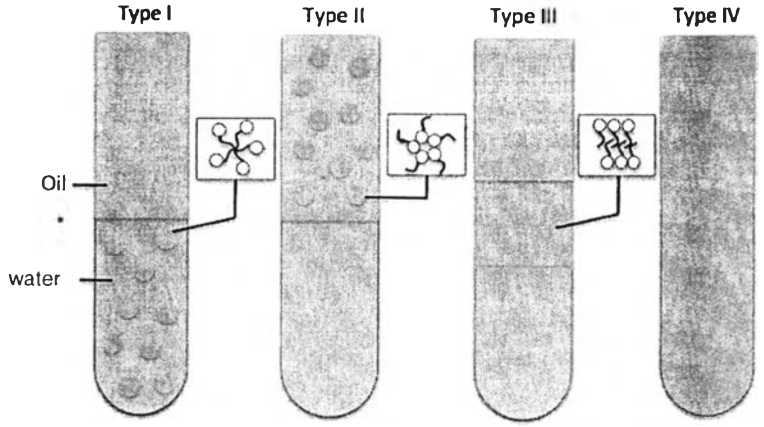


**Figure 2.7** Winsor type of phase equilibrium.

### 2.4.2 Transformation of Microemulsions Phase

Phase of microemulsions generally explain through the transition of microemulsion phase following Winsor phase diagram as illustrated in Figure 2.8. A single parameter is varied with changing microemulsion properties, the plot of the graph is known as a phase scan. For microemulsion systems in which ionic surfactants are presented, commonly used electrolyte concentration as the scan variable whereas nonionic surfactant systems often is used temperature. The transformation of microemulsion phase from Type I to Type II is related to its hydrophile-lipophile balance (HLB). This parameter indicates the partition of surfactant between oil phase and water phase correlative to surfactant hydrophobicity (For example, higher HLB shows more favorable water phase than oil phase or higher solubility). The phase transition represents in terms of interfacial tension (IFT) which is minimum tension between one phase dispersing into another phase. A high IFT could be implied that the polarity of two phases are very different.

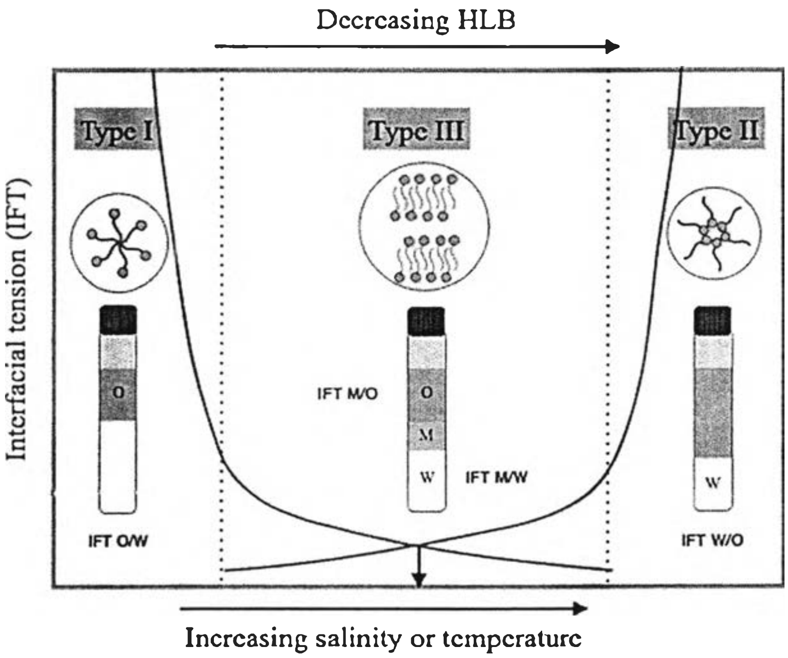


**Figure 2.8** Winsor phase diagram, where O is an excess oil phase; W is an excess water phase; M is middle phase.

At low salinity values (Figure 2.8, left side), Winsor type I microemulsion, the IFT between the upper excess oil phase and O/W microemulsion at the interface decreases as increasing the salinity. At an appropriate salinity, the systems approach to Winsor type III. The IFT value is often as low as $10^{-3}$ mN/m which is called ultralow IFT. The IFT between the middle phase and the excess oil phase (IFT M/O) as much as IFT between the middle phase and the excess water phase (IFT M/W) where is the lowest IFT at high oil solubilization. This point is known as an optimum condition. As the salinity further increases, the system transforms to a Winsor type II microemulsion as presented in right side of Figure 2.8 (Tongcumpou *et al.*, 2003).

In addition, IFT measurements are generally conducted as a function of surfactant concentrations in order to estimate the system attaining ultralow IFT. The graph follows two stages; (as shown in Figure 2.9) The first stage corresponds to the aggregation of surfactant monomer for micelle formation which occurs at the CMC point and another stage relates to the change in curvature of micelles, where the first droplet of microemulsion is formed. This concentration is known as critical microemulsion concentration (CμC) (Kadioglu *et al.*, 2011).

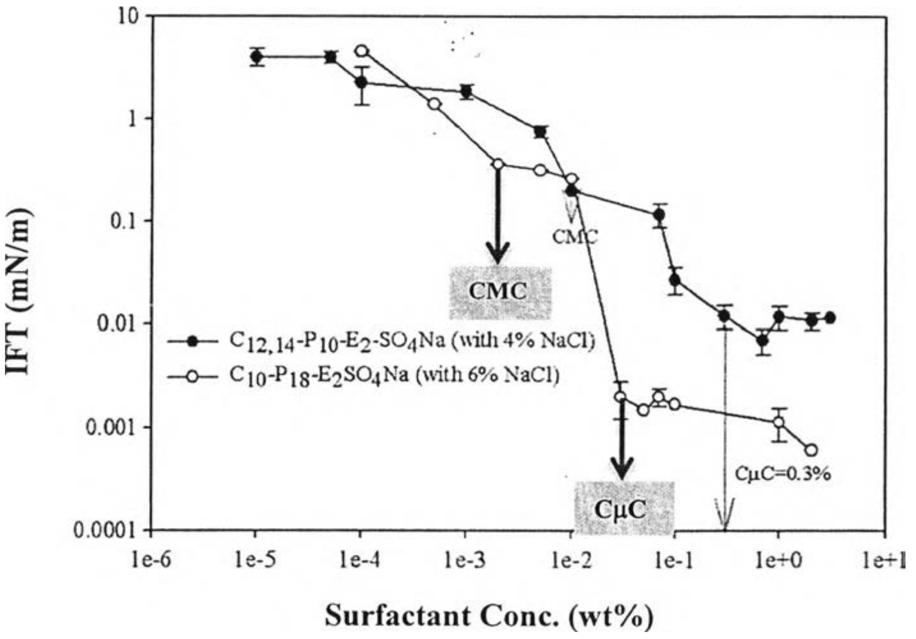


**Figure 2.9** IFT as a function of surfactant concentration.

2.4.3 Application of Microemulsion

Many researchers have significantly attended to microemulsions, especially middle phase microemulsions, can significantly reduce interfacial tension and enhance the solubilization of hydrophilic and lipophilic components. Thereby, these unique properties are used in various applications such as an enhance oil recovery, subsurface remediation, cleaning technology and vegetable oil extraction.

*2.4.3.1 Detergency*

The important mechanisms, related to oily soil removal from substrate, are roll up or rollback and snap-off or emulsification-solubilization mechanism (Figure 2.10). In the rollup mechanism, the IFT between the oil and surfactant solution and between the substrate and the surfactant solution decrease as a result of an increase in the contact angle of the attached oil droplet. The oil droplet completely detaches when the contact angel reaches 180°. As IFT attain to ultralow and high solubilization which can be related to microemulsion formation. Besides, the emulsification mechanism partially completes detachment of oil droplet. (Tongcumpou *et al.*, 2005).

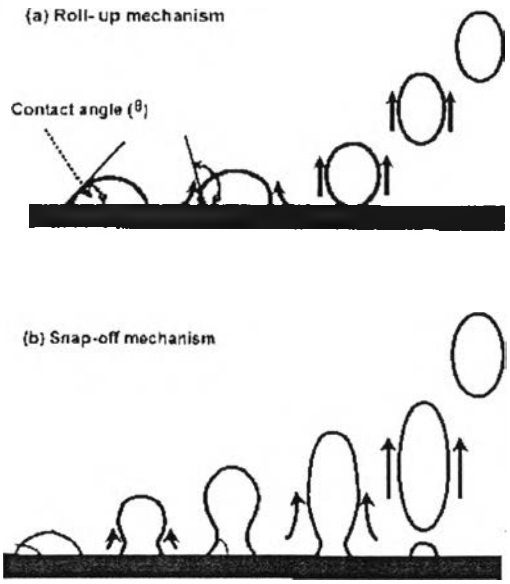


**Figure 2.10** Oily soil removal from substrate (a) roll up and (b) snap-off mechanism.

Phan and coworkers (2010) examined the use of the single extended surfactant ($C_{14-15}$-$(PO)_8$-$SO_4Na$) system for removal canola oil from the test fabric. Their result shown that the detergency efficiency was more than 80% at low temperature using low concentration surfactant. Tanthakit and coworkers studied the effect on detergency of palm oil using anionic extended surfactant mixed with nonionic surfactant. This surfactant system could produce an ultralow IFT in formation of microemulsions and the maximum oil removal (84%) reached approximately at 0.2% of total surfactant concentration.

### 2.4.3.2 *Vegetable Oil Extraction*

Microemulsions-based extraction has been evaluated as an alternative method instead hexane extraction for vegetable oil extraction. It can be claimed as a clean technology due to less toxic chemicals used during the process. In addition, low energy is required due to the microemulsions can be operated at room temperature. A major role of microemulsions is able to reduce IFT between aqueous phase and oil seeds resulting in liberation of oil droplet from seed. The IFT could be reduced to 0.001 mN/m (ultralow level) by incorporation of surfactant with co-surfactant or using extended surfactant. Thus, several research studies have been investigated microemulsions to extract vegetable oil.

Naksuk and coworkers (2009) studied the mixed surfactant system of 3 wt% nonionic coconut fatty acid diethanolamine (Comperlan KD) and either 0.1% extended anionic $C_{14\text{-}15}$-$(PO)_5$-$SO_4Na$ (Alfoterra145-5PO) or $C_{14\text{-}15}$-$(PO)_8$-$SO_4Na$ (Alfoterra145-8PO) to form microemulsions with palm kernel oil. The IFT measurements with increasing salt concentrations showed that the phase system transformed Winsor type I microemulsions toward Winsor type III microemulsions with ultralow IFT range ($10^{-2}$ to $10^{-3}$ mN/m) result in an increase in oil seed extraction. Palm kernel oil extraction efficiency for two aqueous surfactant systems were 93.99 and 94.13%. Other parameters had an impact of oil extraction efficiency including; grain size (between 0.212 and 0.425 mm) involving a larger surface area which ascended interaction between surfactant monomer and oil seed; contact time (30 min) was suitable for reducing IFT of oil and surface led oil to detach in the aqueous surfactant solution and another parameter was kernel loading (1 g). A higher mass of palm kernel oil loading descended contact of surfactant monomers with the kernel and coalition between surfactant and oil. The extracted oil from microemulsions had the same quality as from hexane extraction in terms of color, water content, surtactant content in oil phase and fatty acids composition.

Nguyen and coworkers (2010) found that reverse-micellar microemulsions (Winsor type II) was able to extract peanut oil from seed. This micelle formation had oil as the continuous phase and water as the interior of the micelles. As a result, peanuts oil was extracted directly into the oil phase and into the hydrophobic core of reverse micelles. The result indicated that an extraction efficiency of 95% was achieved at room temperature, extraction time of 10 min and single extraction step.

Do and Sabatini (2010) examined the aqueous anionic extended surfactants $C_{16}$-$(PO)_{10.7}$-$SO_4Na$, $C_{12}$-$(PO)_{14}$-$(EO)_2$-$SO_4Na$ and $C_{10}$-$(PO)_{18}$-$(EO)_2$-$SO_4Na$. These systems were able to achieve IFT value with triolein without adding co-oils and/or alcohol to extract peanut oil. They studied the effect of surfactant concentration, shaking speed, shaking time, salt concentration and solid-liquid ratio based on the fraction of oil extracted. Furthermore, the oil quality from aqueous extended-surfactant-based method was compared to those of hexane-based extraction. The results showed that $C_{10}$-$(PO)_{18}$-$(EO)_2$-$SO_4Na$ had the most performance for oil extraction due to producing the highest oil extraction efficiency of 95% at optimum condition (seed to liquid ratio of 1-5, 30 min extraction, 150 shakes/min, 8wt% NaCl). The IFT values as a function of surfactant concentration were observed at CμC value based on oil extraction efficiency. The CμC point was the highest fraction of oil extracted. Below the CμC value, IFT dramatically decreased as increasing extraction efficiency but above the CμC, oil extracted did not change with enhancing surfactant concentration. In addition, surfactant solution after first extraction could be easily recycled due to exhibiting the ultralow interfacial tension (less 0.02 mN/m) with fresh vegetable oil. Although the efficiency of alternative method is not as high as that of hexane method (98-99%), quality of extracted oil was better in terms of free fatty acid content, clear solution and fresh smell.

Kadioglu *et al.* (2011) investigated extraction of corn oil with anionic extended surfactants ($C_{12,14}$-$(PO)_{10}$-$(EO)_2$-$SO_4Na$ and $C_{10}$-$(PO)_{18}$-$(EO)_2$-$SO_4Na$) at room temperature (25±1°C). The system was able to produce ultralow IFT (<0.001 mN/m). They found that the extraction efficiency reaches a maximum (>80%) near the CμC where the IFT approaches a minimum. Additionally, IFT values around 0.1 mN/m is sufficiently low to provide high oil extraction. However IFT drop down to around 0.01 mN/m, oil droplet spread on oil seed making harder to remove the oil from corn germ. The chemical composition of the extracted corn oils from microemulsions method was similar to that of hexane. It contained mostly trigcylglycerols (98 wt%) with less level of free fatty acids (about 0.2 wt%).

Tuntiwiwattanapun and coworker (2013) studied that canola oil extraction using conventional surfactant (sodium dodecyl sulfate, SDS) was an alternative process instead of hexane extraction for useful biodiesel. The effects on extraction efficiency of surfactant concentration, contact time and solid to liquid ratio were 0.02 M, 45 min and 1/10 (g/ml), respectively. These conditions produced the highest extraction efficiency of 80%. In addition, the ability of reducing SDS solution needed to be succeeded by three stages extraction. The extracted oil from this method could approached biodiesel feedstock quality.

## 2.5 Research Motivation

Based on the literature reviews, the solvent extraction is a conventional method for recovery residual oil in SBE. This method exhibited good efficiency of extraction and provided a proper quality of extracted oil. However, organic solvents have a negative impact to human heath, environment and economy. Hence, the aqueous microemulsion based extraction is an appropiated method because of its extraction efficiency and extracted oil quality. Furthermore, a detachment mechanism of oil from SBE using surfactant is an influence mechanism to oily soil removal from substrate as shown in Figure 2.10 and a low IFT which is a key factor to extract residual oil adsorbed on SBE. Therefore, the most criterion of this method is the ability of lowering IFT between oil and aqueous surfactant solution in order to liberate oil from SBE.

Since the aqueous microemulsions based system has been proven for replacing hexane extraction in vegetable oil extraction, this research investigated the use of microemulsion extraction technique to recover residual oil adsorbed on SBE. The surfactant systems with different head groups (anionic extended and nonionic exthoxylate surfactant are selected for microemulsions formation with crude palm oil because of their charge interactions with SBE surface and theirs ability to formulate microemulsions with long chain fatty acid which are the main component of crude palm oil. The lowest IFT of surfactant systems is employed in oil extraction process. In oil extraction study, the effect of extraction parameters including surfactant concentration, salt concentration, shaking time and solid to liquid ratio are studied based on yield of extracted oil. Finally, the quality of extracted oil between microemulsion based versus hexane extraction is also compared.