

## CHAPTER II

### THEORETICAL BACKGROUND AND LITERATURE REVIEW

#### 2.1 Microemulsions

Microemulsions are one type of emulsions which are miscibility or suspension of a liquid in a second immiscible liquid with a role of emulsifying agent. They are classified by depending on the size of the dispersed particles (the particles that are dispersed in another liquid). Microemulsion has the size of dispersed particles < 100 nm (0.1  $\mu\text{m}$ ). At this research work, two immiscible liquids are oil and water, the emulsifying agent is surfactant.

Several special characteristics are present in microemulsions:

- (1) ultralow interfacial tension (water-oil interfacial tension  $\approx 10^{-3}$  mN/m which is lower than ordinary water-oil interfacial tension)
- (2) high solubilization (a number of oil can be hold in micelles, clusters of surfactant, to prevent oil redeposition)
- (3) spontaneous formation (requiring little or no input of mechanical energy for microemulsion formation)
- (4) thermodynamic stability
- (5) optically clear appearance
- (6) low viscosity

As a result of these special characteristics, uses and applications of microemulsions have been increased in several areas including in detergency, enhanced oil recovery, coatings, textile finishing, cosmetics, foods, and pharmaceuticals, (Kumar et al.)

##### 2.1.1 Types of microemulsions

Microemulsions can be classified into four types based on phase equilibrium (Winsor, 1954):

1. Winsor Type I: There are two phases in equilibrium which consists of an oil-in-water (o/w) phase, oil droplets (discontinuous or inner phase) dispersing in the water phase (continuous or outer phase), and an excess oil phase. Surfactant is preferentially soluble in the o/w microemulsion phase.

2. Winsor Type II: Two phases are present in this type. A water-in-oil (w/o) microemulsion, water droplets (discontinuous or inner phase) disperse in the oil phase (continuous or outer phase), exists in equilibrium with an excess water phase. Surfactant is preferentially soluble in oil.

3. Winsor Type III: This type consists of three phases. The middle phase (oil, water, and most of surfactant) is in equilibrium with both excess water and oil phases.

4. Winsor Type IV: This type has only one phase (single phase). Oil, water, and surfactant are homogeneously mixed into a single solution.

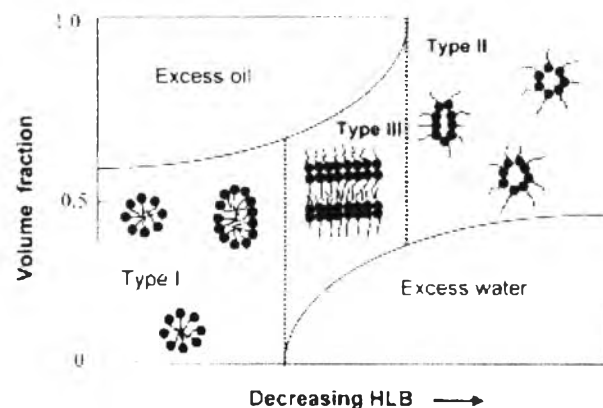
## **2.2 Phase Behavior and Microemulsion Formation**

In the phase transition behavior and formation of microemulsion are controlled by the hydrophile-lipophile balance (HLB) of the system. It means that to achieve any type of microemulsion, the HLB of the system must be changed to be suitable for forming that particular microemulsion. The HLB is the balance between the hydrophilic and lipophilic (hydrophobic) portions of surfactant. There are several factors that influence the HLB alteration: (1) nature of surfactant and nature of oil (each surfactant and oil has an individual HLB), and electrolyte concentration or salinity (for an anionic surfactant system), and temperature. When salinity is increased, the system HLB decreases because the reduction of the electrical interaction of the ionic head group can cause the surfactant to change from hydrophilic to lipophilic. On the other hand, if the salinity is decreased, the HLB increases. For a nonionic surfactant, if the temperature is raised, the HLB decreases due to the increased dyhydration of POE chains which increases the lipophilic. In contrast, the temperature is lowered, the HLB increase. The present of cosurfactants can also alter the HLB of the system, depending on the type of cosurfactant surfactants.

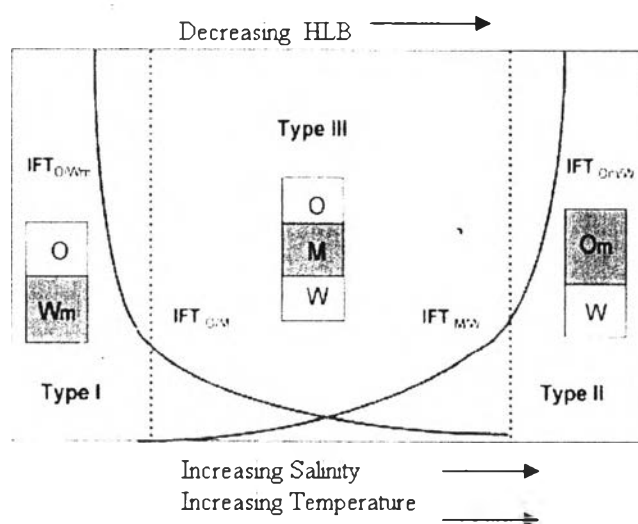
As known, the HLB can control the phase transition behavior and microemulsion formation. At high HLB values with low salinity or low temperature, (Fig 2.1 and 2.2 left side), the system become more hydrophilic and an oil-in-water microemulsion is formed in equilibrium with an excess oil. This is known as a Winsor Type I microemulsion or  $W_m$  or an O/W (oil-in-water) microemulsion. With further decreasing HLB or further decreasing temperature and increasing salinity, the POE chain nonionic surfactant becomes more and more dehydrate or the head group of ionic surfactant becomes less and less repulsive, the surfactant system becomes more lipophilic, causing the volume of the aqueous phase  $W_m$  increases and that of the oil phase decreases and a decrease in IFT between oil and water interface ( $IFT_{O/W_m}$ ). (the right side of Figure 2.2)

If the HLB is still decreasing or temperature is still decreasing or salinity is still increasing, the system will separate into three phase: an excess water phase (W) with low surfactant concentration, a middle phase (M) or microemulsion phase, and excess oil phase (O) with low surfactant concentration. This system is known as a Winsor Type III microemulsion. (see Figure 2.1) The IFT in the region of the middle phase or Winsor Type III is often as low as  $10^{-3}$  mN/m, so-called ultralow IFT. The lowest value of IFT where the IFT between the excess oil phase and the middle phase ( $IFT_{O/M}$ ) equals the IFT between the middle phase and the excess water phase ( $IFT_{M/W}$ ) (Figure 2.2 middle), is known as the optimum interfacial tension. In a non-ionic surfactant system, the temperature that can product the optimum interfacial tension knowing as the phase inversion temperature (PIT). For the anionic surfactant system, the salinity that can make the optimum interfacial tension knowing as optimum salinity.

If the HLB continues to decrease or temperature further decreases or salinity further increases, the surfactant system becomes more and more lipophilic and it preferably move to the oil phase, causing for reversing micelle in the excess oil phase. As a result, the volume of the oil phase ( $O_m$ ) increases while that of aqueous phase (W) decreases, the middle phase disappears, and the IFT between oil and water interface increases.



**Figure 2.1** Correlation between Typical phase behavior of microemulsion and HLB



**Figure 2.2** Correlation between interfacial tension (IFT) and HLB, Salinity, Temperature (Rosen, 2004)

### 2.3 Mechanism of Oily Soil Removal

There are several mechanisms involving in oily soil removal. However, the three primary mechanisms—roll-up, emulsification, and solubilization—were well accepted (Verma et al., 1998; Rosen, 2004)

### 2.3.1. Roll-up Mechanism

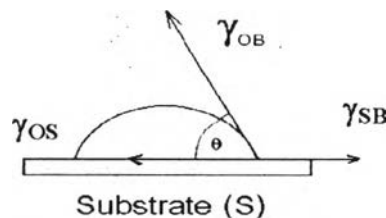
Roll-up or roll-back mechanism is the complete detachment of oily soil from substrate. The mechanism can remove oil droplets with two processes. First, an increase in the contact angle between the oil droplet and the substrate due to the reduction of interfacial tension (IFT) between oil and water. Second, the occurrence of repulsion force between the head groups of surfactant.

#### 2.3.1.1 *The increased contact angle process*

This process can be explained by Young's equation which is as follows:

$$\cos \theta = \frac{\gamma_{SB} - \gamma_{SO}}{\gamma_{OB}} \quad (1)$$

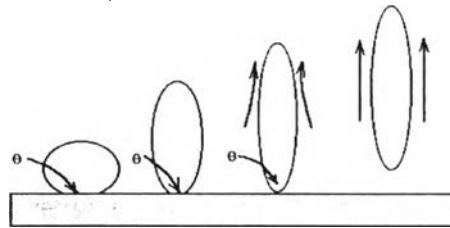
When  $\theta$  is the contact angle of the attached oil droplet with the substrate (see Figure 2.3 ),  $\gamma_{SB}$  is the interfacial tension between the substrate and the both aqueous phase),  $\gamma_{OS}$  is the interfacial tension between the substrate and the oil phase, and  $\gamma_{OB}$  is the interfacial tension between the oil phase and the bath.



**Figure 2.3** The contact angle between an oil droplet and substrate in bath (surfactant solution)

When surfactants are present in the bath (B) or surfactant solution, they will adsorb at two interfaces. The first interface is that between substrate and bath (SB). The another oil is the interface between oily soil and bath (OB). As a result, the interfacial tension (IFT) between the substrate and the bath ( $\gamma_{SB}$ ) and that between oily soil and bath ( $\gamma_{OB}$ ) are reduced, causing the decrease in  $\cos \theta$  and the increase in  $\theta$ , resulting oily soil detachment from substrate. However, this mechanism will be accomplished when the contact angle is more than  $90^\circ$ . The higher contact angle, the oily soil is more easily removed (Broze, 1994). If the contact angle is

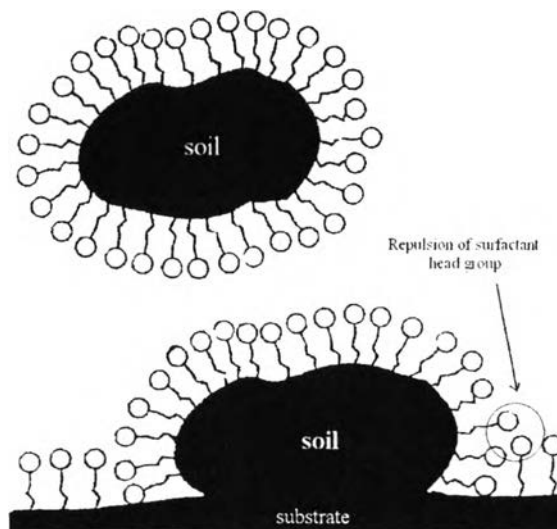
close to  $180^\circ$  ( $\cos \theta = 1$ ), which means that the soil will be spontaneously completely removed. If the contact angle is between  $90^\circ$  and  $180^\circ$ , the soil must be removed by hydraulic currents in the bath (Figure 2.4). In contrast, if the contact angle is less than  $90^\circ$ , the soil will not be completely removed which there is some part of the soil remaining in the substrate. To remove the residual soil, mechanical work or some mechanical (e.g. solubilization) will be used.



**Figure 2.4** Roll-up mechanism shows the complete removal of oil droplets from the substrate by hydraulic currents when  $\theta > 90^\circ$  (Rosen, 2004).

### 2.3.1.2 Surfactant head group repulsion process

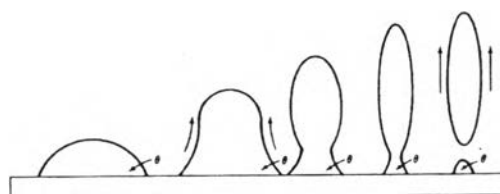
After the surfactants adsorb at substrate-bath interface (SB) and oily soil-bath interface (OB), the head group of surfactants which adsorb at substrate-bath interface repulsing with the head group of surfactants which adsorb at oily soil-bath interface. From this repulsion, the oil droplet can be raised from the substrate. (Figure 2.5)



**Figure 2.5** Repulsion force of surfactant head groups

### 2.3.2 Emulsification Mechanism

Emulsification, or snap-off, or necking mechanism, will take place when the contact angle between the oil droplet and the substrate is less than  $90^\circ$ . The principle of this mechanism is the same as the roll-up mechanism but the difference is the contact angle between the oil droplet and the substrate. Nevertheless, the disadvantage of this mechanism is some residual soil remaining on the substrate since the soil/bath interfacial tension is decreased, but the substrate/bath interfacial tension does not change substantially (Figure 2.6).

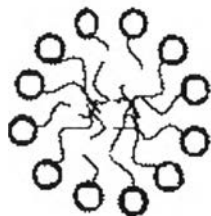


**Figure 2.6** Emulsification mechanism shows partial removal of oil droplets from substrate  $\theta < 90^\circ$  (Rosen, 2004).

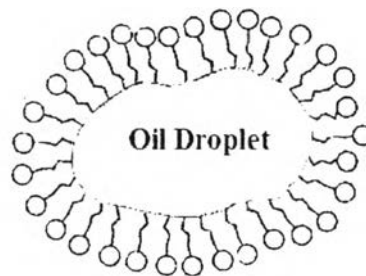
### 2.3.3. Solubilization Mechanism

Solubilization, or oil uptake capacity, is oil adsorption inside the core of the surfactant micelles. The roles of this mechanism are; (1) removal small amount of residual oil which cannot be removed by roll-up or emulsification and (2) prevention the redeposition of oil on the substrate. The solubilization depends on several factors, such as nature of oil and surfactant, surfactant concentration, electrolyte concentration, and temperature. The solubilization will substantially occur when the concentration of surfactant is above the critical micelle concentration (CMC), leading to the presence of micelles. The capacity of solubilized oil in the micelle core depends on the chemical structure of the surfactant, surfactant concentration, shape of the micelles and temperature. When the surfactant concentration is low, a small amount of oily soil can be solubilized. On the other hand, at high surfactant concentrations (10-100 time the CMC), a large amount of oily soil can adsorb in the micelle core which is similar to microemulsion formation (Figure 2.7 and 2.8) (Schwartz, 1972). The difference between solubilization and emulsification is the thermodynam-

ic stability of keeping all the oily soil from redepositing on the substrate which the emulsification cannot prevent all the redeposition of the oily soil on the substrate. An importance of solubilization is not only in detergency but also in polymerization, waste water treatment, separation of materials, etc.



**Figure 2.7** Solubilization



**Figure 2.8** Emulsification

#### 2.4 Application of Microemulsion for Detergency

Due to the unique characteristic properties of microemulsion namely, ultralow interfacial tension, high ability for solubilizing a compounds and etc, microemulsions can help to aid the detergency power for removal unwanted material.

There are several reports that encourage a use of microemulsion for detergency application. Solan et al. (1985) reported that high efficiency of oily soil removal from textile fabrics was found under microemulsion conditions compared with commercial liquid detergent. Azemar et al. (1993) They studied detergency using pure triolein as a triglyceride oil representative. They found that the Winsor Type III (middle phase) microemulsion condition provided a better for detergency. Bourrel and coworkers (1998) reported that the lowest oil/water IFT and highest oil solubilization were found to correspond to microemulsion formation using Aerosol OT (dioctyl sulfosuccinate) at 20°C in 100 ml of 25% (wt/vol) solution of Aerosol OT in carbon tetrachloride/paraffin mixture.

The maximum detergency performance was found to correspond to the Winsor Type III, middle phase, microemulsion, when sodium dioctyl sulfosuccinate (AOT), alkyl diphenyl oxide disulfonate (ADPODS), and sorbitan mono-



leate(span 80) were used for this studied formulation.(Tongcumpou, 2002; Korphol, 2003; and Pantipa, 2004)

## 2.5 Factors Affecting Oily Soil Detergency

In the study of detergency formulation and performance, Linfield et al. (1962) found that agitation speed, washing time and detergent concentration affected the detergency performance. Webb et al. (1998) suggested the oily soil removal from fibrous substrate was depended on the nature of the soil, the order of application, temperature, and the type of detergent formulation.

Recently, Germain (2002) conducted detergency experiment using a tergotometer and concluded that several factors such as agitation speed, temperature, and amount of detergent should be taken into consideration.

### 2.5.1. Surfactant System

Obendorf et al. (1982) found that the type of surfactant affected the detergency performance. An anionic detergent was found to remove oil from a cotton fabric more effectively than a nonionic detergent. As expected, anionic surfactants are effective on more polar fiber. However, there was little or no difference between the two studied detergents in total oil removal from the polyester/cotton fabric.

The effects of nonionic surfactant and temperature on detergency efficiency were studied by Solan et al. (1988) for nonpolar soils (hexadecane, squalene, mineral oil) on polyester/cotton fabric. It was found that the maximum detergency efficiency corresponded with the phase inversion temperature (PIT). Moreover, they reported that the optimum temperature was increased when the degree of ethoxylation of the surfactant increased.

The effect of ethoxylation numbers in nonionic surfactant to soil removal was also studied by Wormuth et al (1991). They found that the oily soil removal was influenced by the ethoxylation numbers in nonionic surfactant because when the ethoxylation numbers of the C<sub>12-14</sub> alkylpolyglycol ether was increased, the solubilization power of surfactant decreased which resulting the decrease in oily soil removal.

The advantages of using surfactant mixtures were reported by Ogino *et al.* (1992). They found that mixed surfactant systems generally exerted greater than single surfactant systems for enhancing of solubilization. However, this enhancement does not apply to all mixed surfactant systems.

Generally, a surfactant mixture that can exhibit a low oil-water interfacial tension is considered to provide superior oily soil detergency. Verma *et al.* (1998) measured the oil-water interfacial tension for a mixed anionic/nonionic surfactant system (NaLAS/C12EO3 and NaLAS/C12EO7) as a function of temperature and time. The oil-water interfacial tension was found to decrease as a function of time for all blends containing nonionic surfactant. It was proposed that the diffusivity of this hydrophobic fraction into phase lead to a decrease in oil-water interfacial tension.

The investigation conducted by Goel (1998) also gave similar results. It was reported the optimal EO moles (for maximal detergency) showed a monotonically increasing trend with increasing ratio of nonionic to anionic concentrations for a fixed level of electrolyte. The optimal EO moles' also increased with increasing level of electrolyte in the system. However, the effect of nonionic/anionic ratio was much stronger than the effect of electrolytes on the optimal EO moles.

In the same year, Goel investigated detergency performance at different ratios of nonionic to NaLAS concentrations. He found that the minimum value of interfacial tension was a function of EO moles in the nonionic surfactant. These minima were found to exhibit high solubilization of oily soil and related to corresponding to the maxima in detergency.

In 2003, Tongcumpou and coworker found that the formulation mixed surfactant system of sodium dioctyl sulfosuccinate (AOT, a surfactant of intermediate HLB), alkylidiphenyloxide disulfonate (ADPODS, very hydrophilic surfactant), and sorbitan monooleate (Span 80, very hydrophobic surfactant) was used for microemulsion formation with motor oil and hexadecane which can be considered as a temperature - insensitive system ( Salager *et al.*,1979 and Anton *et al.*,1992). They found that interfacial tension (IFT) value under the supersolubilization (SPS) condition was not substantially worse than that under the optimal condition in a Winsor Type III system (middle phase). In other words, quite low IFT could be attained

without formation of a middle phase supposed by the results of Wu et al. (2000). In addition, the supersolubilization region was found to give oil removal almost as high as that in the middle phase region. However, this microemulsion – based formulation required fairly high salinity (16 wt %) to achieve the supersolubilization condition or optimum conditions that it is not practical for real application.

In 2005, Tongcumpou and coworker found that, under the microemulsion conditions, the oil removal in the rinse step was almost as high as that in the wash step for both supersolubilization and Winsor type III region. This is because during the wash step, the spreading effect can occur which is supposed by other results (Thompson, 1994; Healy et al., 1976)

In addition, Korphol et al. (2004) further developed a mixed surfactant system of 1.5 wt% ADPODS, 5 wt% AOT, and 5 wt% Span 80 that exhibited a Winsor Type III microemulsion at a low salinity of 2.83 wt% for oily soil removal from fabrics.

#### 2.5.2 Nature of Oil

Scott (1963) found that the presence of polar oil enhanced the removal of nonpolar oil. Before aging, squalene was easier to remove when it was in a mixture rather than when it was present as a single soil. However, the effect of mixing on the removal of squalene was reversed after aging.

There were a number of research works about polar/nonpolar soils removal (Gordon, 1967; Powe, 1972; Morris et al., 1982). After washing, it was found that residual oily soil contained a greater percentage of nonpolar components than that in fresh oily soil. Polar soils was found to tend to be more easily removed in an aqueous detergent system.

Kissa (1987) found that oil viscosity affected oil removal. The oil with lower viscosity was usually removed more rapidly from the substrate than one with a higher viscosity. Interestingly, the viscosity of the emulsion of used motor oil and the aqueous detergent solution was found to be five times higher than that of the original used motor oil.

The effect of polar soil components on the phase inversion temperature and optimum detergency conditions was also studied by Raney and Benson (1990). They proposed that the snap-off of the oil drops resulted from the interfacial

tension reduction at the soil/water interface, thus influencing the removal of nonpolar/polar soil mixtures. It was also suggested that a minimum quantity of polar material in the soil might be necessary to attain a high soil removal.

Chi et al. (1998) found that highly unsaturated oily soil was easily oxidized upon aging, resulting in increasing removal whereas saturated oils is relatively stable. In addition, they reported that aging made oils to penetrate deeper into the fabric and fiber structures, resulting in removal more difficult.

### 2.5.3 Salt

Oil removal performance in the presence of electrolytes was reported by Webb et al. (1983). They found that, for the mineral oil, the removal time of the mixed system with 0.5 ml NaCl was about half that of the nonionic alone. They also found that an addition of a surface active compound having less active lead to a significant increase in the interfacial tension of the mixture and so adversely influenced the oil removal.

Moreover, detergent efficiency as a function of salt was observed to be independent on the temperature (Solan et al., 1992). An optimum of detergent efficiency was obtained at an optimum salinity of 10%wt NaCl which are favorable conditions for microemulsion formation.

The effect of temperature and salt concentration on detergency efficiency were investigated by Azemar *et al.* (1993). They concluded that detergency efficiency both with and without electrolyte increased with temperature in the same trends and reached an optimum. However, the optimum temperature for the maximum detergency efficiency was shifted to a lower temperature as the electrolyte concentration increased (effect of salinity out).

### 2.5.4 Substrate

The performance relating to soil removal is influenced markedly by the nature of the substrate (Christ *et al.*, 1994). Recently, Chi (2001) investigated the effect of the substrate on the removal of unaged oily soil and found it was higher for nylon than cotton or polyester. Squalene, a nonpolar hydrocarbon, was difficult to remove from polyester, a nonpolar substrate. On the other hand, cotton, a very polar substrate from polyester, a nonpolar substrate, might be expected to release oily soil fairly well in an aqueous detergent system, but this was not the case. The low

removal of squalene from the cotton was thought to be due to the morphological characteristics of cotton that makes oil difficult to be removed.

The soil removal from cotton fabrics that had been chemically modified by mercerization and carboxymethylation was studied by Obendorf (2001). It was proposed that the carboxymethylation changed the chemistry of the fiber by increasing the carboxyl group content, and this structure changed was believed to reduce the amount of soil deposited in the lumen of fiber. The mercerization was hypothesized to affect the chemical accessibility and hydrophilicity of the fiber structure, influencing both soil deposition and soil removal of lipid soil.

#### 2.5.5 Other Factors

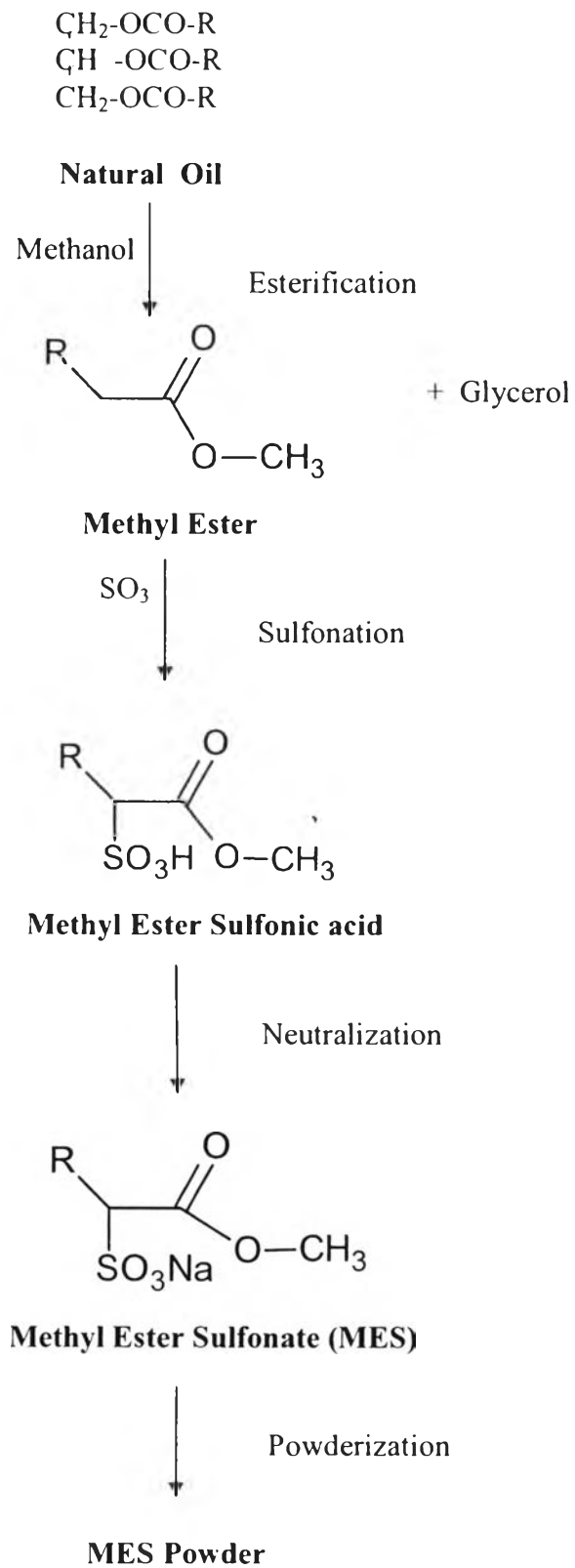
In the study of detergency formulation and performance, Linfield et al. (1962) found that an increase in agitation speed, washing time and detergent concentration, resulted in increasing detergency performance to the maximum levels. They reported that the maximum detergency was obtained at around 150-170 rpm and 15-20 min washing cycle. Obendorf et al. (1982) reported both mechanical action and detergent concentration affecting the soil removal. An increase in either mechanical action or detergent concentration resulted in increasing removal of triolein, but the surfactant residue in the cotton fiber remained high. In 1987, Raney and coworker studied the correlation of PIT with detergency performance. The maximum detergency in ternary systems was found to occur when the temperature was near the PIT of the system composed of water, the surfactant and the hydrocarbon soil itself. Webb et al. (1988) reported that builder is another influencing factor for enhancing the cleaning efficiency.

## 2.6 Methyl Ester Sulfonate (MES)

Methyl ester sulfonate (MES) is a new type of anionic surfactant. It is a derivative of methyl ester (ME) which is derived from natural fats and oils, renewable resources, such as palm oil or coconut oil. MES was first produced in the mid-1950s. since the U.S. Department of Agriculture wanted to find the uses of tallow. Since 1980s, MES has been gained more and more attention due to an increase in petroleum and petrochemical prices. In a near future, MES is expected to replace linear alkylbenzene sulfonate (LAS), which is the main component in most commercial detergents which is produced from petroleum, because all surfactants derived from petroleum feedstock will become more expensive which may make MES become more competitive. A second reason is that MES is a friendly environmental surfactant as it is produced from renewable resources. A third reason is the better properties of MES such as water solubility, water hardness stability, and high detergency power compared to other surfactants especially LAS.

### 2.6.1 MES Production Process

The production of MES is a complex process that consists of several steps. Figure 2.9 shows a schematic diagram of MES production. First, natural oil is used to produce methyl ester, known as biodiesel by esterification. Second, sulfur trioxide ( $\text{SO}_3$ ) is added to the alpha carbon of a methyl ester, known as the sulfonation to yield methyl ester sulfonic acid. Third, the methyl ester sulfonic acid is neutralized to obtain MES. Finally, MES is powdered by for easy handling.



**Figure 2.9** MES Production Process

### 2.6.2 MES Performance

In 1999, Cohen et al. studied the performance of MES compared to LAS. They found that some MES performance parameters were better than LAS performance such as surface tension, critical micelle concentration, viscosity, solubility and foaming power.

In 2006, Maurad and coworker investigated the performance of PPD (palm-based powder detergent) or MES in terms of their detergency, foaming power, stability, and wetting characteristics. They found that foaming power and wetting characteristics of MES could compare to those of commercial LAS – based detergents. Moreover, the detergency results showed that MES provided better soil removal. In addition, the biodegradability of MES and commercial detergent was determined. The study found that the biodegradability of MES was faster than that of commercial detergent.