CHAPTER II
THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Gemini Surfactant

Gemini surfactants, sometimes also called dimeric surfactants, contain two hydrophobic groups (sometimes three) and two hydrophilic groups in the molecule, connected by a linkage close to the hydrophilic groups. They therefore have three structural elements, a hydrophilic group, a hydrophobic group, and their linkage that may be varied to change the properties of the surfactant. There has been considerable interest in these compounds, both academic and industrial, since it exhibits greater the C_{20} values, a measure of the efficiency of adsorption of the surfactant at the interface, lower critical micelle concentration (CMC), more effective in reducing the oil/water interfacial tension (IFT), being better wetting and more strongly adsorption to from closely packed monolayers at hydrophobic surfaces than those of comparable conventional surfactants (i.e., surfactants with single but similar hydrophilic and hydrophobic groups) (Menger *et al.*, 1993, Menger *et al.*, 2000, Chen *et al.*, 2007, Lin *et al.*, 2011, Xu *et al.*, 2011, Lu *et al.*, 2012, Rosen, 2012, Su *et al.*, 2012).
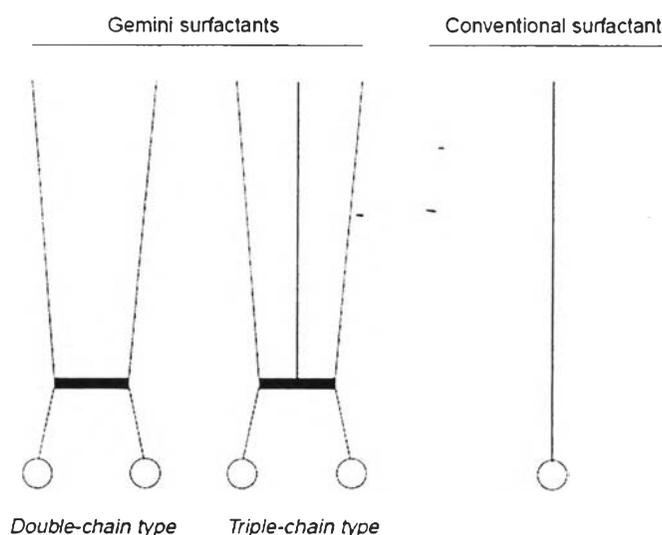

Figure 2.1 Conventional and gemini surfactants. ————, hydrophobic group , connecting group , hydrophilic group (Rosen, 2012).

2.1.1 Surface Activity (Menger *et al.*, 2000, Rosen, 2012)

Table 2.1 Critical micellization Concentrations (CMC) of representative gemini surfactants[a] (Menger *et al.*, 2000)

Entry	Surfactant	CMC [mм]
1	$C_{12}H_{25}N^+(CH_3)_3$ Br⁻	16
2	$C_{12}H_{25}N^+(CH_3)_3$ Cl⁻	22
3	$C_{16}H_{33}N^+(CH_3)_3$ Br⁻	1
4	$C_{12}H_{25}OSO_3$ Na⁺	8
5[b]	$C_{12}H_{25}N^+(CH_3)_2-(CH_2)_2-N^+(CH_3)_2C_{12}H_{25}$ 2 Br⁻	1
6	$C_{12}H_{25}N^+(CH_3)_2-(CH_2)_{16}-N^+(CH_3)_2C_{12}H_{25}$ 2 Br⁻	0.12
7	$C_{16}H_{33}N^+(CH_3)_2-(CH_2)_2-N^+(CH_3)_2C_{16}H_{33}$ 2 Br⁻	0.003
8	$C_8H_{17}N^+(CH_3)_2-(CH_2)_2-N^+(CH_3)_2C_8H_{17}$ 2 Br⁻	55
9	$C_{12}H_{25}N^+(CH_3)_2-(CH_2)_2-O-(CH_2)_2-N^+(CH_3)_2C_{12}H_{25}$ 2 Cl⁻	0.5
10	$C_{14}H_{29}N^+(CH_3)_2-(CH_2)_6-N^+(CH_3)_2C_{16}H_{33}$ 2 Br⁻	0.009
11	$C_{16}H_{33}N^+(CH_3)_2-(CH_2)_2-O-(CH_2)_2-N^+(CH_3)_2C_{16}H_{33}$ 2 Br⁻	0.004
12	$C_{16}H_{33}N^+(CH_3)_2-CH_2-(CH_2-O-CH_2)_3-CH_2-N^+(CH_3)_2C_{16}H_{33}$ 2 Br⁻	0.02
13	$C_{12}H_{25}N^+(CH_3)_2-CH_2-CH(OH)-CH_2-N^+(CH_3)_2C_{12}H_{25}$ 2 Br⁻	0.8
14[c]	$C_{12}H_{25}N^+(CH_3)_2-CH_2-C_6H_4-CH_2-N^+(CH_3)_2C_{12}H_{25}$	0.03
15	$C_{12}H_{25}N^+(CH_3)_2-CH_2-CH(OH)-CH(OH)-CH_2-N^+(CH_3)_2C_{12}H_{25}$ 2 Br⁻	0.7
16	$C_{12}H_{25}N^+(CH_3)_2-CH_2-CH(OH)-CH_2-N^+(CH_3)_2-CH_2-CH(OH)-CH_2-N^+(CH_3)_2C_{12}H_{25}$ 3 Cl⁻	0.5
17	$C_{12}H_{25}OPO_2^--O-(CH_2)_6-O-PO_2^-OC_{12}H_{25}$ 2 Na⁺	0.4
18	$C_{10}H_{21}O-CH_2-CH(OSO_3^-)-CH_2-O-(CH_2)_6-O-CH_2-CH(OSO_3^-)-CH_2-OC_{10}H_{21}$ 2 Na⁺	0.01

[a] Entries 1 – 4 list conventional surfactants for comparison purposes. [b] $n = 3 – 8$. [c] In 0.1 м NaCl.

Some examples of geminis (preceded by four conventional surfactants for comparison purposes) are shown in Table 2.1. As can be seen from the data in Table 2.1,

> Geminis have remarkably low CMC values compared with corresponding surfactants of equivalent chain length. (The comparison is, justifiably, made on a "per ionic headgroup" basis while neglecting the spacer.) For example, the CMC in entry 5 is 16 times smaller than in entry 1, and the CMC in entry 18 is 800 times smaller than in entry 4.

> Geminis are more responsive to tail length than conventional surfactants. Thus, increasing the tail length by four carbon atoms in a conventional cationic surfactant lowers the CMC 16-fold (entries 1 and 3). A corresponding tail lengthening in the gemini series lowers the CMC by two orders of magnitude (compare entries 5, 7, and 10).

Some examples of geminis, their C_{20} and CMC values, and those of comparable conventional surfactants, are shown in Table 2.2. As can be seen from the data in Table 2.2,

➤   The C_{20} values, a measure of the efficiency of adsorption of the surfactant at the interface, can be two to three orders of magnitude smaller than the C_{20} values of comparable conventional surfactants.

➤   Their CMCs can be one to two orders of magnitude smaller than those of comparable conventional surfactants.

The reason for this greater surface activity of geminis, compared to comparable conventional surfactants, is the larger total number of carbon atoms in the hydrophobic chains of the geminis. The larger total number of carbon atoms in the surfactant molecule, the greater the distortion of the water structure of the aqueous phase and the greater the tendency to adsorb at the interfaces surrounding the aqueous phase or to form micelles in the aqueous phase, i.e., greater surface activity. This results in smaller C20 values and smaller CMC values.

On the other hand, increase in the total number of carbon atoms in the hydrophobic chain(s) of the surfactant molecule decreases the solubility of the surfactant in water and limits its surface activity. When the surfactant contains two hydrophilic groups, however, its solubility in water increases and the molecule can accommodate more carbon atoms in the hydrophobic groups without becoming water-insoluble. Consequently, gemini surfactants are much more surface-active than their comparable conventional surfactants, which have only half the number of carbon atoms in the molecule. In addition, geminis are more water-soluble than comparable conventional surfactants and have much lower Krafft points.

2.1.2 Solubilization

It has been shown that the solubilization increases with the alkyl chain length, which is most likely due to the larger size of the micelle (Tehrani-Bagha *et al.*, 2012).

Table 2.2 C_{20} and CMC Values of Gemini and Comparable Conventional Surfactants at 25 ^{O}C (Rosen, 2012)

Compound	Medium	C_{20} (10^{-6}) M	CMC $(10^{-6}M)$
$[C_{10}H_{21}OCH_2CH(OCH_2COO^-Na^+)CH_2]_2O$	H_2O	4	84
$C_{11}H_{23}COO^-Na^+)$	H_2O	5,000	20,000
$[C_{10}H_{21}OCH_2CH(OCH_2CH_2CH_2SO_3^-Na^+]_2O$	H_2O	8	33
$C_{12}H_{25}SO_3^-Na^+$	H_2O	4,400	9,800
$[C_{10}H_{21}OCH_2CH(SO_4^-Na^+)CH_2OCH_2]_2$	H_2O	1	13
$C_{12}H_{25}SO_4^-Na^+$	H_2O	3,100	8,200
$[C_{12}H_{25}N^+(CH_3)_2CH_2]_2 \cdot 2Br^-$	H_2O	—	840
$[C_{12}H_{25}N^+(CH_3)_2CH_2CHOH]_2 \cdot 2Br^-$	H_2O	129	700
$C_{12}H_{25}N^+(CH_3)_3 \cdot Br$	H_2O	8,000	16,000
$[C_{12}H_{25}N^+(CH_3)_2CH_2]_2CHOH \cdot 2Cl^-$	0.1 M NaCl	0.9	9.6
$[C_{12}H_{25}N^+(CH_3)_2CH_2CHOH]_2 \cdot 2Br^-$	0.1 M NaCl	0.9	21
$C_{12}H_{25}N^+(CH_3)_3 \cdot Cl^-$	0.1 M NaCl	1,950	5,760
$(C_{11}H_{23}CONHCH[(CH_2)_3NHC(NH_2)_2^+]CONHCH_2)_2 \cdot 2Cl^-$	H_2O	1.9	9.5
$C_{11}H_{23}CONHCH[(CH_2)_3NHC(NH_2)_2^+]COOCH_3 \cdot Cl^-$	H_2O	630	6,000
$\{C_{11}H_{23}CONHCH[(CH_2)_3NHC(NH_2)_2^+]CONHCH_2\}_2 \cdot 2Cl^-$	0.01 M NaCl	1	9.2
$C_{11}H_{23}CONHCH[(CH_2)_3NHC(NH_2)_2^+]COOCH_3 \cdot Cl^-$	0.01 M NaCl	50	270

2.2 Methyl Ester Sulfonate (MES)

Alphasulfonated methyl ester (SME) is more commonly known to the industry as methyl ester sulfonate (MES). MES is new type of anionic surfactant which is derived from biorenewable resources. It is the derivative of Methyl Ester (ME) which 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. Since1980s, MES has been developed its properties and performance to be better than former due to an increase of petroleum and petrochemical price.

In the future, MES is expected to replace linear alkylbenzene sulfonate (LAS), which is the main component in commercial detergents. The reasons are

➢   The low cost of producing MES and its environmentally friendly properties have been the driving force behind the industry's interest in producing it commercially.

➢   MES has the potential to biodegrade faster than LAS.

➢   The cost to manufacture MES is lower than the cost to manufacture LAS due to the high cost of linear alkyl benzene which is produced from petroleum feed stocks.

➢   MES also has received worldwide recognition because of its excellent detergency and resistance to water hardness.

(Cohen *et al.*, 1999, Johansson *et al.*, 2001, Maurad *et al.*, 2006, Cohen *et al.*, 2008, Lim *et al.*, 2009)

2.2.1 Method of MES Preparation (Preechasil, 2009)

MES production, is a complex process that consists of several processes. Figure 2.2 is a schematic diagram illustrating all processes of MES production. First, natural fat & oil are used to produce methyl ester known as biodiesel by esterification process. Second, sulfur trioxide (SO_3) is added to the alpha carbon of a methyl ester in sulfonation process. Third, neutralization process is used to neutralise methyl ester sulfonic acid, received product from sulfonation process. Finally, MES is powdered by powderization process to be easy to handle.
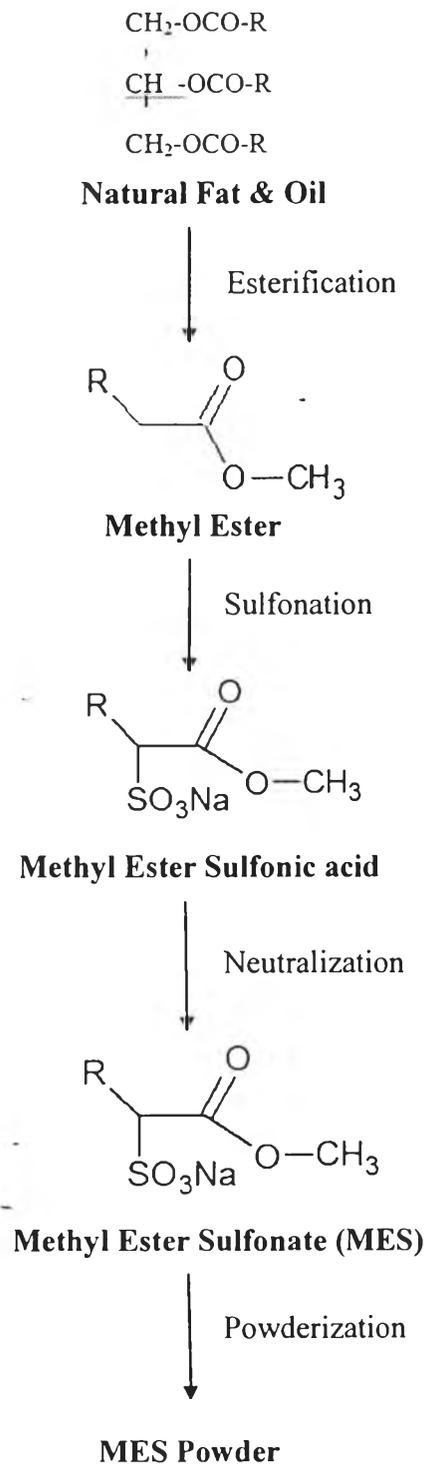
CH₂-OCO-R

CH -OCO-R

CH₂-OCO-R

Natural Fat & Oil

↓ Esterification

Methyl Ester

↓ Sulfonation

Methyl Ester Sulfonic acid

↓ Neutralization

Methyl Ester Sulfonate (MES)

↓ Powderization

MES Powder

Figure 2.2 MES Production Process. (Preechasil, 2009)

2.3 Methyl Ester Ethoxylate (MEE) (Cox *et al.*, 1997, Cox, 1998)

During the past decade or so, MEE gained increasing attention. The driving force for this attention is twofold:

➢ Methyl esters are major items of commerce available from triglyceride oils and from the esterification of fatty acids.

➢ MEE also gives detergent manufacturers another choice from the ethoxylate menu.

In the future, MEE is expected to replace alcohol ethoxylates (EO), which are the main components in commercial detergents and is produced from petroleum feed stocks. The reasons are

➢ MEE cost in comparison to other detergent from petroleum feed stocks due to an increase of petroleum and petrochemical price.

➢ MEE is a friendly environmental surfactant as it is produced from renewable resource.

➢ The organization for Economic Cooperation and Development would define methyl ester ethoxylates as being "inherently biodegradable"

➢ The better properties of MEE compared to alcohol ethoxylates (EO).

2.4 Palm Oil

Palm oil is the most popular vegetable oil worldwide. Recently palm oil became number one as the most widely produced and consumed oil in the world as shown in table 2.3. Production of palm oil is more sustainable than crop based vegetable oils such as soybean and rapeseed. It consumes considerably less energy in production, uses less land and generates more oil per hectare. Only 0.26 hectares of land are required to produce one ton of oil from oil palm, while soybean, sunflower and rapeseed require 2.2, 2 and 1.5 hectares respectively to produce one ton of oil (Products, 2012).

Palm oil is healthy and versatile, and it does not require hydrogenation for most of its use like all other vegetable oils. Palm oil has been designated as cholesterol-free and does not contain trans fatty acids. The oil is widely used as a cooking oil, as an ingredient in margarine, and is a component of many processed foods. It is also used as a feedstock for producing soaps, washing powders, personal care products, and biofuel (Products, 2012).

Palm oil has a balanced ratio of unsaturated and saturated fatty acids. It contains 40% oleic acid, 10% linoleic acid, 45% palmitic acid and 5% stearic acid (Products, 2012).

Table 2.3 World production and consumption of the main vegetable oils (millions of tonnes) (agritrade, 2012)

	2009/10	2010/11	2011/12'
Production	138.75	143.94	149.59
Palm oil	46.06	49.12	51.49
Soybean oil	38.89	41.38	41.72
Sunflower oil	12.62	12.45	14.63
Rapeseed oil	23.75	23.62	23.64
Consumption	138.11	143.87	149.67
Palm oil	46.45	48.25	51.43
Soybean oil	38.03	41.68	42.28
Sunflower oil	12.94	12.59	14.27
Rapeseed oil	23.23	24.04	23.7

2.4.1 Oleic Acid

Oleic acid is a fatty acid that occurs naturally in various animal and vegetable fats and oils. It is an odorless, colourless oil, although commercial samples may be yellowish. In chemical terms, oleic acid is classified as a monounsaturated omega-9 fatty acid, abbreviated with a lipid number of 18:1 cis-9. It has the formula $CH_3(CH_2)_7CH=CH(CH_2)_7COOH$. The term "oleic" means related to, or derived from, oil or olive, the oil that is predominantly composed of oleic acid (wikipedia, 2013).
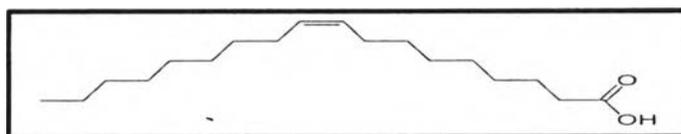
Figure 2.3 Structure of oleic acid. (wikipedia, 2013)

Table 2.4 Properties of oleic acid (wikipedia, 2013)

Properties	
Molecular formula	$C_{18}H_{34}O_2$
Molar mass	$282.46 \text{ g mol}^{-1}$
Density	0.895 g/mL
Melting point	13-14 °C, 286-287 K, 55-57 °F
Boiling point	360 °C, 633 K, 680 °F
Solubility in water	Insoluble
Solubility methanol	Soluble

2.4.2 Linoleic Acid

Linoleic acid (LA) is an unsaturated omega-6 fatty acid. It is a colorless liquid at room temperature. In physiological literature, it has a lipid number of 18:2 cis,cis-9,12. Chemically, linoleic acid is a carboxylic acid with an 18-carbon chain and two *cis* double bonds; the first double bond is located at the sixth carbon from the methyl end. Linoleic acid belongs to one of the two families of essential fatty acids. The body cannot synthesize linoleic acid from other food components .
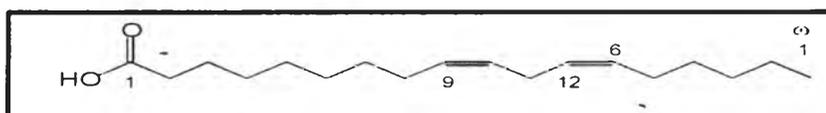
Figure 2.4 Structure of linoleic acid. (wikipedia, 2013)

Table 2.5 Properties of linoleic acid (wikipedia, 2013)

	Properties
Molecular formula	$C_{18}H_{32}O_2$
Molar mass	280.45 g mol^{-1}
Appearance	Colorless oil
Density	0.9 g/cm^3
Melting point	-5 °C (23 °F) -12 °C (10 °F)
Boiling point	230 °C (446 °F) at 21 mbar 230 °C (446 °F) at 16 mmHg
Solubility in water	0.139 mg/L
Vapor pressure	16 Torr at 229 °C

2.4.3 Palmitic Acid

Palmitic acid, or hexadecanoic acid in IUPAC nomenclature, is the most common fatty acid (saturated) found in animals, plants and microorganisms.[4] Its molecular formula is $CH_3(CH_2)_{14}CO_2H$. As its name indicates, it is a major component of the oil from palm trees (palm oil, palm kernel, and palm kernel oil), but can also be found in meats, cheeses, butter, and dairy products. Palmitate is a term for the salts and esters of palmitic acid. The palmitate anion is the observed form of palmitic acid at basic pH (wikipedia, 2013).
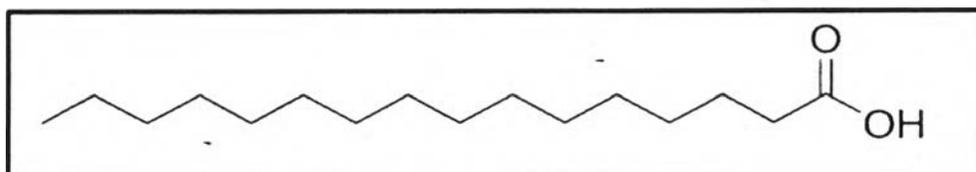

Figure 2.5 Structure of palmitic acid. (wikipedia, 2013)

Table 2.6 Properties of palmitic acid (wikipedia, 2013)

Properties	
Molecular formula	$C_{16}H_{32}O_2$
Molar mass	256.42 g/mol
Appearance	White crystals
Density	0.853 g/cm^3 at 62 °C
Melting point	62.9 °C
Boiling point	351-352 °C, 215 °C at 15 mmHg
Solubility in water	Insoluble
Acidity (pK_a)	4.78

2.4.4 Stearic Acid

Stearic acid is the saturated fatty acid with an 18 carbon chain and has the IUPAC name octadecanoic acid. It is a waxy solid, and its chemical formula is $CH_3(CH_2)_{16}CO_2H$. Its name comes from the Greek word στέαρ "stéar", which means tallow. The salts and esters of stearic acid are called stearates. Stearic acid is one of the most common saturated fatty acids found in nature following palmitic acid (wikipedia, 2013).
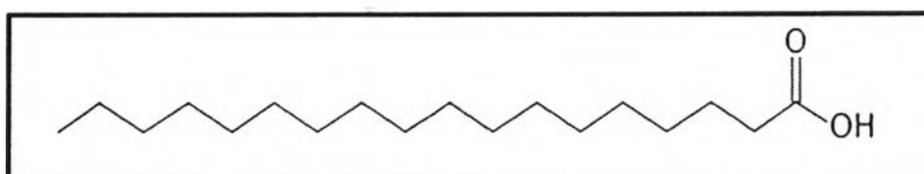

Figure 2.6 Structure of stearic acid. (wikipedia, 2013)

Table 2.7 Properties of stearic acid (wikipedia, 2013)

Properties	
Molecular formula	$C_{18}H_{36}O_2$
Molar mass	284.48 g mol^{-1}
Appearance	white solid
Density	0.847 g/cm^3 at 70 °C
Melting point	69.6 °C, 343 K, 157 °F
Boiling point	383 °C, 656 K, 721 °F
Solubility in water	3 mg/L (20 °C)
Refractive index (n_D)	1.4299

These fatty acids are bonded in groups of three linked by a glycerine molecule to form a triglyceride as shown below:
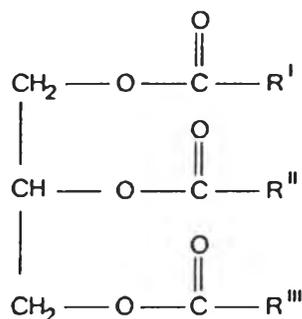
$$CH_2 - O - \overset{\overset{\displaystyle O}{\|}}{C} - R^I$$
$$CH - O - \overset{\overset{\displaystyle O}{\|}}{C} - R^{II}$$
$$CH_2 - O - \overset{\overset{\displaystyle O}{\|}}{C} - R^{III}$$

Figure 2.7 Structure of triglyceride.

Where R^I, R^{II}, R^{III} represent fatty acids which may or may not be the same (Plc, 2013)

2.5 Removal of Oily Soil from Fabrics

Removal of oily soil from fabrics is a complicated process that has been studied for many years (Hillyer, 1903). Several mechanisms can cause oily soil removal, including roll-up or roll-back, emulsification and solubilization (Tanthakit *et al.*, 2008).

2.5.1 Roll-up or Roll-back Mechanism (Rosen, 2012)

Oily soil is generally removed by the roll-back mechanism in which the contact angle that the liquid soil makes with the substrate is increased by adsorption of surfactant from the cleaning bath.
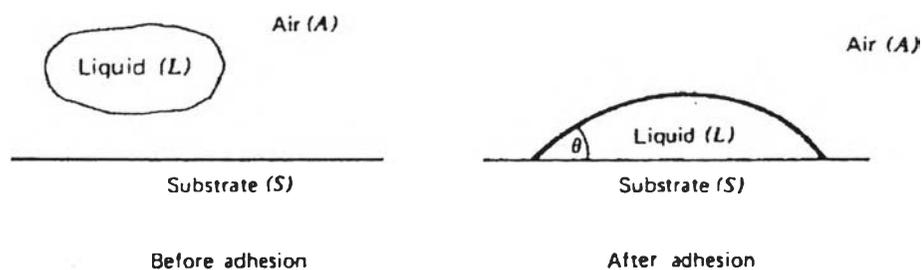

Figure 2.8 Adhesional wetting. (Rosen, 2012)

Figure 2.8 shows the situation of a liquid soil adhering to a substrate in the presence of air. The reversible work to remove the liquid oily soil (O) from the substrate is given by the expressions

$$W_{O/S(A)} = \gamma_{SA} + \gamma_{OA} - \gamma_{SO} \tag{2.1}$$

$$W_{O/S(A)} = \gamma_{OA}(\cos\theta + 1) \tag{2.2}$$

Where θ is the contact angle.

On the other hand, if the air is replaced by cleaning bath as shown in Figure 2.8, the work of adhesion of the liquid soil for the substrate will be now given by the expression

$$W_{O/S(B)} = \gamma_{SB} + \gamma_{OB} - \gamma_{SO} \tag{2.3}$$

$$W_{O/S(B)} = \gamma_{OB}(\cos\theta + 1) \tag{2.4}$$

and the contact angle by the expression

$$\cos\theta = \frac{\gamma_{SB} - \gamma_{SO}}{\gamma_{OB}} \tag{2.5}$$
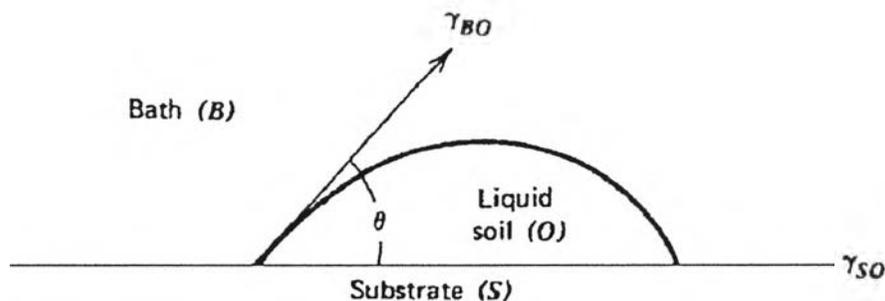

Figure 2.9 Contact angle at the bath–liquid soil–substrate junction. (Rosen, 2012)

At a cleaning bath, surfactants will adsorb at the substrate–bath (SB) and liquid soil–bath (OB) interfaces as to reduce γ_{SB} and γ_{OB}. Reduction in γ_{SB} will also cause a decrease in $\cos\theta$ and an increase in θ, resulting in the observed roll-back of the liquid soil.

➤ If the contact angle is 180°, the bath will spontaneously completely displace the liquid soil from the substrate.

> ➢ If the contact angle is less than 180° but more than 90° as shown in Figure 2.10, the soil will not be displaced spontaneously but can be removed by hydraulic currents in the bath.
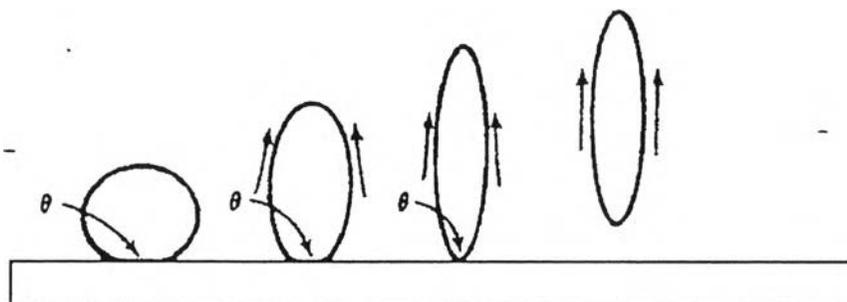

Figure 2.10 Complete removal of oil droplets from substrate by hydraulic currents (arrows) when $90^0 < \theta < 180^0$. (Rosen, 2012)

> ➢ If the contact angle is less than 90° as shown in Figure 2.11, at least part of the oily soil will remain attached to the substrate, even when it is subjected to the hydraulic currents of the bath, and mechanical work or some other mechanism (e.g., solubilization) is required to remove the residual soil from the substrate.
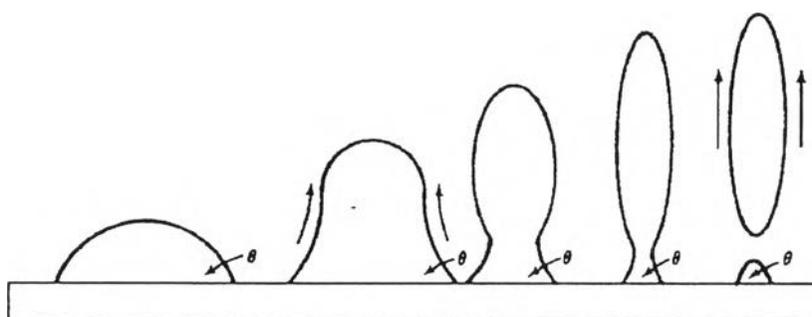

Figure 2.11 Rupture and incomplete removal of large oil droplets by hydraulic currents (arrows) when $\theta < 90°$. A small droplet remains attached to the substrate. (Rosen, 2012)

2.5.2 Solubilization (Tanthakit, 2009)

Solubilization is one of the important properties of surfactants that is directly related to micelle formation. Solubilization may be defined as the spontaneous dissolving of a substance (solid, liquid, or gas) by reversible interaction with the micelles of a surfactant in a solvent to form a thermodynamically stable isotropic solution with reduced thermodynamic activity of the solubilized material.

Solubilization is distinguished from emulsification by the fact that in solubilization, the solubilized material (the 'solubilizate') is in the same phase as the solubilizing solution and the system is consequently thermodynamically stable.

In detergency, where solubilization is believed to be one of the major mechanisms involved in the removal of oily soil. This is based on the observation that oily soil removal from both hard and textile surfaces becomes significant only above the CMC for nonionics and even for some anionics having low CMCs. A considerable amount of research has been devoted to the removal of oily soil by nonionic surfactants and found that optimal oily soil detergency has been correlated with the PIT, both for POE nonionic surfactants and for POE nonionic–anionic mixtures, because Y_{OW} reaches its minimum value at the PIT. Moreover, the solubilization of nonpolar material increases markedly with separation of the surfactant-rich middle phase. Thus, conditions are optimum at the PIT for the removal of oily soil by the roll-back mechanism.

The extent of solubilization of the oily soil depends on the chemical structure of the surfactant, its concentration in the bath, and the temperature. At low bath concentrations only a relatively small amount of oily soil can be solubilized, whereas at high surfactant concentrations (10–100 times the CMC), solubilization is more similar to microemulsion formation and the high concentration of surfactant can accommodate a much larger amount of oily matter.

2.5.3 Emulsification (Tanthakit, 2009, Rosen, 2012)

An emulsion is a significantly stable suspension of particles of liquid of a certain size within a second, immiscible liquid. The term significantly stable means relative to the intended use and may range from a few minutes to a few years.

Investigators in this field distinguish between three different types of emulsions, based upon the size of the dispersed particles:

(1) macroemulsions, the most well-known type, opaque emulsions with particles >400 nm (0.4 mm), easily visible under a microscope.

(2) microemulsions, transparent dispersions with particles <100 nm (0.1 mm) in size.

(3) nanoemulsions (miniemulsions), a type that is blue-white, with particle sizes between those of the first two types (100–400 nm [0.1–0.4 mm]).

2.6 Microemulsion

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

Several special characteristics are present in microemulsion:

(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 (the numbers of oil can be hold in micelle, 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 micro-emulsion have been increased for supplying of the world. The application of microemulsion is not only in detergency aspect but also in several aspects such as enhanced oil recovery, coatings and textile finishing, cosmetics, food, pharmaceuticals, etc (Tongcumpou *et al.*, 2003, Chen *et al.*, 2007, Rosen, 2012).

2.6.1 Type of Microemulsions

Microemulsions can be classified into four types which base on phase equilibrium (Rosen, 2012);

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

2. Winsor Type II: Two phases are present in this type. Water in oil (w/o), water droplets (discontinuous or inner phase) disperse in the oil phase (continuous or outer phase), can be 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 surfactant) can be in equilibrium with both excess of water and oil phases.

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

2.7 Phase Behavior and Microemulsion Formation (Tongcumpou *et al.*, 2003, Preechasil, 2009, Rosen, 2012)

In the phase transition behavior and microemulsion formation are controlled by the hydrophile-lipophile balance (HLB) of the system. It means that to achieve a microemulsion, the HLB of the system must be changed to be suitable for forming that 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) type of surfactant and that of oily soil (each surfactant and oily soil have an individual HLB).

(2) Electrolyte concentration or Salinity (This factor is always used for ionic surfactant system. When the salinity is increased, the HLB decrease because 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 increase).

(3). Temperature (Temperature can often affect nonionic surfactant system. If the temperature is raised, the HLB decrease due to the increased dyhydration of POE chains which increases the lipophilic. In contrast, the temperature is lowered, the HLB increase).

(4). Present of cosurfactants (If a system has two or more two surfactants (which have the different HLB), the HLB number of the mixture is the weighted average of the individual HLB numbers.

For example, if a mixture of 20% paraffin wax (HLB = 10) and 80% aromatic mineral oil (HLB = 13) is to be emulsified then the HLB number of the emulsifying agent combination should be $(10 \times 0.20) + (13 \times 0.80) = 12.4$. For this purpose a mixture of 60% of POE lauryl alcohol made from 23 mol of ethylene oxide (HLB = 16.9) and 40% POE of cetyl alcohol made from 2 mol of ethylene oxide (HLB = 5.3) could be tried:

$$HLB = (16.9 \times 0.60) + (5.3 \times 0.40) = 12.2$$

To determine the optimum emulsifier combination, however, various mixtures of other types of emulsifying agents with the same weighted average HLB number must then be tried to determine which structural types of emulsifying agents give the best results with this particular combination of emulsion ingredients, since the HLB number is indicative only of the type of emulsion to be expected, not the efficiency or effectiveness with which it will be accomplished.

As known the HLB can control the phase transition behavior and micro-emulsion formation. At high HLB values, or low salinity or low temperature, (Fig 2.12 and 2.13 left side) the surfactant is hydrophilic and is preferably in the water phase, which is in equilibrium with an excess oil phase having a very low surfactant concentration. This is known as a winsor type I microemulsion or Wm or an O/W (oil-in-water) microemulsion. With further decrease in HLB or further increase in temperature and salinity, the POE chain nonionic surfactant become more and more dehydrate or head group of ionic surfactant become more and more repulse, the surfactant become more lipophilic causing the volume of the aqueous phase Wm

increase and that of the oil phase decrease and a decrease in IFT between oil and water interface (IFT $_{O/Wm}$). (Figure 2.12 left side)

If the HLB is still decreasing or temperature 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 winsor type III microemulsion. (Figure 2.12 middle) 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 nonionic 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 or salinity continues to increase. The surfactant becomes more and more lipophilic and it is preferably in the oil phase. At this point the micelles start to invert and dissolve in the excess oil causing the volume of the oil phase (Om) increase and that of aqueous phase (W) decrease, the middle phase disappears, and a increase in IFT between oil and water interface.(Figure 2.12 and 2.13 right side)
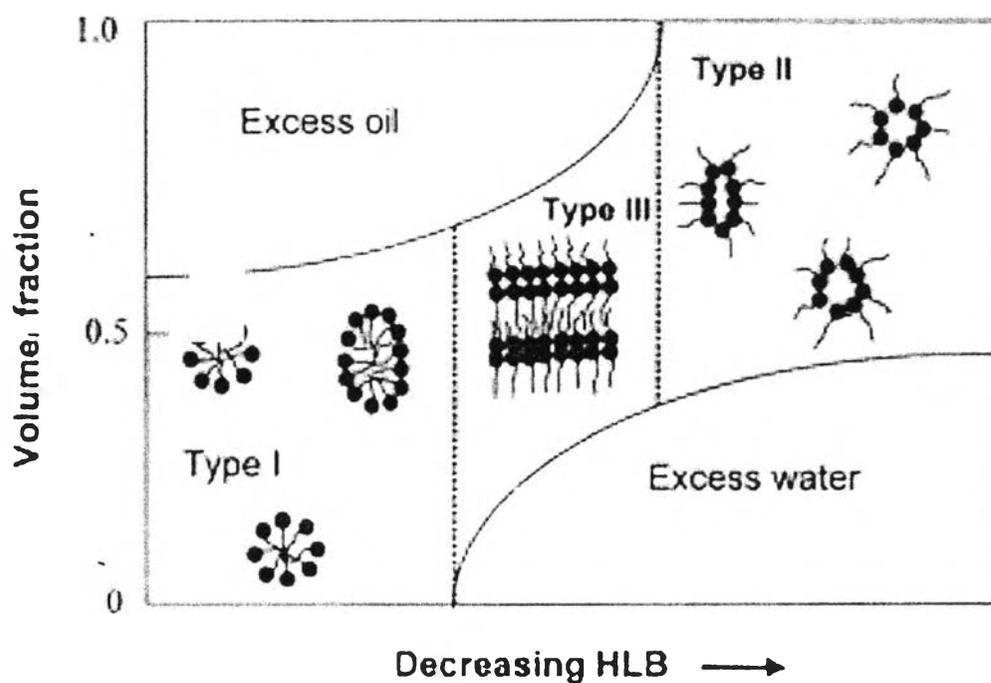
Figure 2.12 Correlation between Typical phase behavior of microemulsion and HLB. (Tongcumpou *et al.*, 2003)
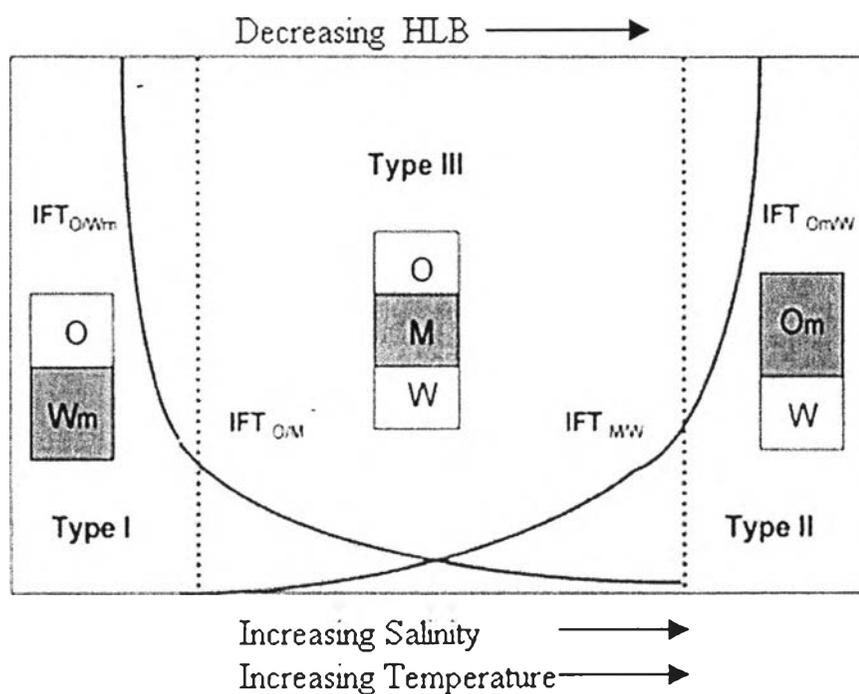

Figure 2.13 Correlation between interfacial tension (IFT) and HLB, salinity, temperature. (Tongcumpou *et al.*, 2003)

The HLB value for some types of nonionic surface-active agents can be calculated from their structural groupings. Thus, for fatty acid esters of many polyhydric alcohols,

$$HLB = 20 \times \left(1 - \frac{S}{A}\right) \tag{2.6}$$

where S is the saponification number of the ester and A is the acid number of the fatty acid used in the ester. For example, glyceryl monostearate has S = 161, A = 198, and hence HLB = 3.8.

For esters for which good saponification data are not readily obtainable, the following formula can be used:

$$HLB = \frac{E + P}{5} \tag{2.7}$$

where E is the weight percentage of oxyethylene content and P is the weight percentage of polyol content.

For materials where a POE chain is the only hydrophilic group, this reduces to

$$HLB = \frac{E}{5} \tag{2.8}$$

Thus, a POE cetyl alcohol made from 20 mol of ethylene oxide (77% oxyethylene) would have a calculated HLB of 15.4.

A commonly used general formula for nonionics is

$$HLB = 20 \times \frac{M_H}{M_H + M_L} \tag{2.9}$$

Where M_H is the formula weight of the hydrophilic portion of the molecule and M_L is the formula weight of the lipophilic (hydrophobic) portion of the molecule.

2.8 Application of Microemulsion for Detergency

Due to the characteristic properties of microemulsion namely, ultralow in terfacial tension, high ability for solibilizing a compounds and etc, microemulsion can help to support the detergency power for removal unwanted material.

There are several reports that encourage a use of microemulsion for detergency;

Preechasil (2009) reported that high efficiency of soil removal from textile fabrics was found when the surfactant formed the microemulsion which it was compared with a use of a commercial liquid detergent for soil removal.

Tanthakit *et al.* (2010) have studied fabric detergent using palm oil. She found that the winsor type III, middle phase, microemulsion is a better for detergency.

The maximum detergency performance corresponds to the winsor type III, middle phase, microemulsion, which it is formed by using sodium dioctyl sulfosuccinate(AOT), alkyl diphenyl oxide disulfonate(ADPODS), and sorbitan monooleate(span 80),when it was compared with a commercial liquid detergent product (Tongcumpou *et al.*, 2003).