# CHAPTER II
LITERATURE REVIEW

1.   Microemulsion

A microemulsion is a thermodynamically stable surfactant-oil-water system, which has important properties that correspond to the detergency such as the very high oil solubilization and the very low oil-water interfacial tension that is close to zero (Bourrel *et al.*, 1998). microemulsions can be characterized it four types of Winsor (Schulman *et al.*, 1940). Winsor Type I to Winsor Type IV. The system depends on solubilization of the surfactant systems in the aqueous phase.
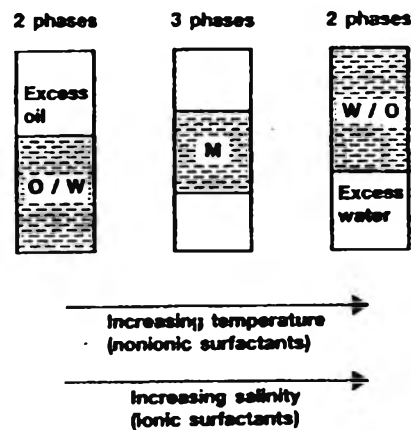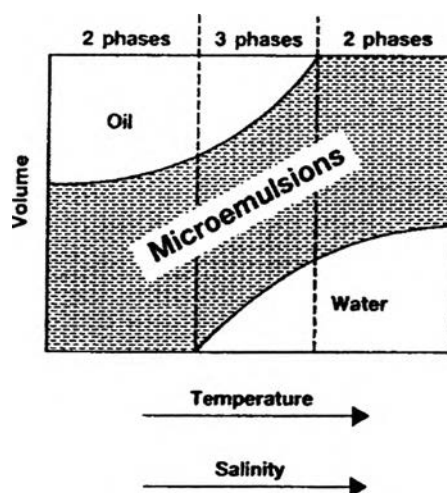

Figure 2.1 Type of microemulsion phase behavior showing the transition from oil in water (Type I) to bicontinuous structure (Type III) and water in oil structure (Type II).

The typical transition occurs from a Winsor type I to type III and to type II microemulsions, in order to. For **Winsor type I**, there are two fluid phases to consider in this system (water and oil). The surfactant is dominated in only one of the phases (the water). It forms oil-in-water (O/W) microemulsion where the surfactant is present as monomers at a small concentration. For **Winsor type III**, the bicontinuous phase, the formation is associated with achieving ultra-low interfacial tensions. The system separates into three phases, this middle phase contains oil,

water and the majority of the surfactant aggregate now exist in either the aqueous or oil phase. For **Winsor type II** or water-in-oil (W/O) microemulsion, the system becomes two phases again, but the surfactant is mainly in the oil. The surfactant is present as monomers at a small concentration. And for **Winsor type IV**, the single phase (isotropic), micellar solutions that form depend on the addition of a sufficient quantity of amphiphile (surfactant plus alcohol).

In the case of ionic surfactants, the phase changes are brought about by increasing the electrolytes concentration. Whereas for non-ionic surfactants, the same sequence of phases is produced by raising the temperature. Addition of electrolyte to ionic surfactants decrease the repulsive interaction between adjacent charged head groups, allow them to pack more closely together in oil-water interface and thus reducing the effective head group area. Similarly for non-ionic surfactant, increasing the temperature decreased the degree of hydration of the head group, thereby also decreasing its effective area at the interface. Illustrated relationship of temperature of the system and the salinity in figure 2.2

Figure 2.2 Phase behavior showing the relationship of temperature of the system and the salinity.

Not only a function of the concentration of surfactant added to the system to archive a middle-phase microemulsion, but also the hydrophile-lipophile balance (HLB), the salinity and temperature of the system.

The hydrophile-lipophile balance (HLB) is the value that can characterize water solubility; a higher HLB indicates higher water solubility HLB numbers are

useful because they provide a correlation between the materials to be emulsified and agents well suited to emulsify them. When the HLB of the substance to be emulsified is known, a surfactant or surfactant blend is chosen which gives the same number (Michael F. Cox).

The number of a surfactant can be obtained from literature sources. McCutcheon (1993) determined experimentally or estimated by empirically derived relationships that correlate surfactant structure to HLB behavior. The HLB of alcohol ethoxylate by dividing the weight percent ethylene oxide (EO) by 5 as equation shown below

$$\text{HLB (ethoxylates)} \approx \frac{\%EO}{5} \,. \qquad \text{(Eq.2.1)}$$
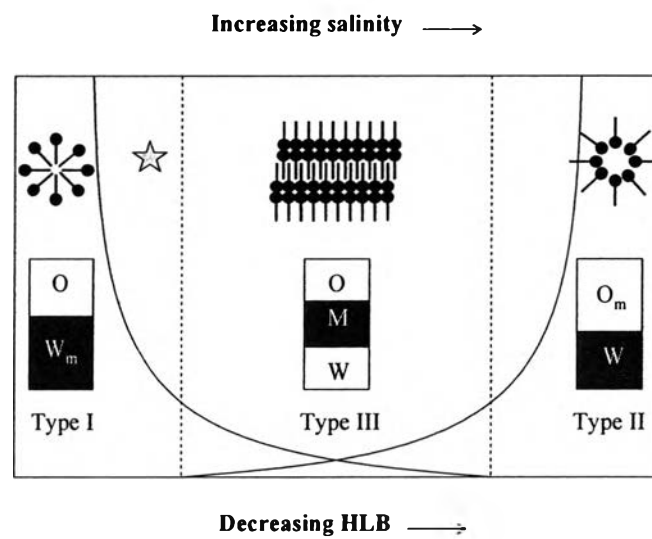
Figure 2.3 Phase behavior showing interfacial tension (IFT) as a function of the hydrophile-lipophile balance (HLB) and the salinity.

Figure 2.3 illustrate the phase diagrams of a surfactant-oil-water system of Winsor in terms of microstructure change in the relative volume of the phase as salinity and hydrophile-lipophile balance (HLB). A high salinity, low the hydrophile-lipophile balance (HLB) drive surfactant monomers into the oil phase, promoting the formation of a Winsor Type II system, while a low salinity, high hydrophile-lipophile balance (HLB) drive surfactant monomers into the oil phase, promoting the formation of a Winsor Type I system. The addition of salt can drive a

surfactant into the oil phase. The salinity at which a third-phase microemulsion forms is often referred to as the **optimum salinity**.

In addition, the supersolubilization region was found to give oil removal almost as high as that in the middle phase region. Besides, she found that her microemulsion formation required fairly high salinity (16 wt %) to achieve the supersolubilization condition or optimum conditions that it is not practical for real application Wu et al. (2000).

The effect of ethoxylation numbers in a nonionic surfactant on soil removal has also been studied by Wormuth *et al.* (1991). They determined that the oily soil removal decreased as the solubilization power of the surfactant decreased, which results from increasing ethoxylation numbers of the C12-14 alkylpolyglycol ether.

The region of Winsor type I that is close to the transition zone from Winsor type I to Winsor type III is known as the supersolubilization (SPS) region, where both high solubilization capacity and low IFT are obtained from the system (Wu *et al.*, 2000). In this region, the micelles are swollen, so the solubilization capacity increased up to one order of magnitude (Wu *et al.*, 2000). For some systems, a hazy or milky but translucent solution can appear. The microemulsion transition is governed by the hydrophilicity and lipophilicity of the system, as described by the Winsor R ratio of interactions, which is a semi-quantitative method of measuring the balance between the hydrophilic and lipophilic characters of the surfactant. The Winsor R ratio of interactions calculated from the following equation (Eq.2.2) (Rosen, 2004):

$$R = \frac{A_{CO} - A_{OO} - A_{LL}}{A_{CW} - A_{WW} - A_{HH}},$$ (Eq.2.2)

where A_{CO} is the interaction (per unit interfacial area) between the surfactant and the oil, A_{CW} is the interaction between the surfactant and the aqueous phase, L and H refer to lipophilic and hydrophilic, and A_{LL} and A_{HH} are self-interaction of the lipophilic and the hydrophilic portions of the surfactant, respectively. The parameters A_{WW} and A_{OO} are self-interaction in the water phase and oil phase, respectively. The numerator of the equation represents the net interaction of the lipophilic portion of the surfactant at the interface, and the

denominator represents the hydrophilic part of the interface. When R<1, the interface becomes more hydrophilic, and an O/W microemulsion exists (Winsor type I). For R>1, inverse micelles form and the solution becomes a W/O microemulsion (Winsor type II). For R=1, the interactions of the lipophilic and hydrophilic regions are in balance. So the optimal formation appears (Winsor type III) (Bourrel *et al.*, 1998). Besides type III, a single-phase (isotropic) microemulsion that forms upon the addition of a sufficient quantity of an amphiphile (surfactant plus alcohol) can appear, also. Because, when R=1, the larger the value of the numerator (or denominator) of the expression for R is, the greater the solubilization capacity for water (or oil) is and consequently the greater the tendency to form an isotropic system is that is called a Winsor type IV system. On the other hand, when R=1 and the A_{LL} and the A_{HH} interactions are large, liquid crystals or gels may form (Rosen, 2004).

2. Detergency

Detergency is the removal process of unwanted substances, which is called soils, from a solid surface or textile surface (fabric) by contact with a surfactant solution or bath (Kiss, 1987). Germain (2002), using a tergotometer, concluded that several factors, such as agitation speed, temperature, and amount of detergent should be taken into consideration, which supported the detergency experiment of Linfiled *et al.* (1962) which found that agitation speed, washing time, and detergent concentration affected the detergency performance. Their paper noted that with the conditions of washing at 48.9°C, 0.2% detergent, and 135 ppm water hardness, maximum detergency was obtained at around 150-170 rpm and around 15-20 min washing cycle. Webb *et al.* (1988) suggested soil removal from fibrous substrate depended on the nature of the soil, the order of application, temperature and type of detergent formulation. Ratchatawetchakul *et al.* (2005) found that, in considering the total oil removal with two rinse steps at different amounts of rinsing water, an amount of rinsing water did not affect significantly the total oil removal. From these results, two rinsing steps with the lowest volume of rinsing water were recommended for operating any washing machine units.

3. Oily Soils

The soil present may be classified as, particulate soils (organic and inorganic), and stains oily soils. Oily soils or water-soluble liquid soils mainly compose of nonpolar hydrocarbon saturate and unsaturated fatty acids which highly hydrophobic (it's means that they do not mix with water). It cannot be satisfactorily removed with pure water. Surfactant needs to be added to the water to reduce the interfacial tension.

In this research work oily soils is motor oil. motor oil commercially avaiable for use in gasoline engines, Castrol GTX type SAE 10w-30. The oil was kept in refrigerator at 4 degree celsius under close system.

4. Mechanism of oily soil removal

There are three primary mechanisms of oily soil removal that are well accept such as roll-up or roll-back, emulsification or snap-off or necking, and solubilization (Broze, 1994; Dillan *et al.,* 1979; Verma *et al.,* 1998).

4.1 Roll-up

The Roll-up or roll-back mechanism can be defined as oil detachment from the substrate. The oil is dropped on a fabric, and oil removal is done by increase the contact angle between the oil and the substrate, reducing the interfacial tension (IFT) between oil (soil) and water (bath), (γ_{OB}), and between the substrate (solid) and water (bath), (γ_{SB}), increasing in the contact angle of the attached oil droplet (Verma *et al.,* 1998). The Young's equation indicates the relationship between contact angle and interfacial tensions.
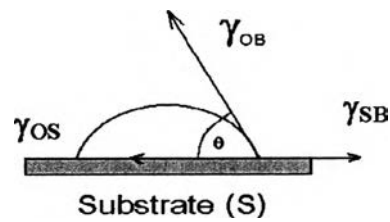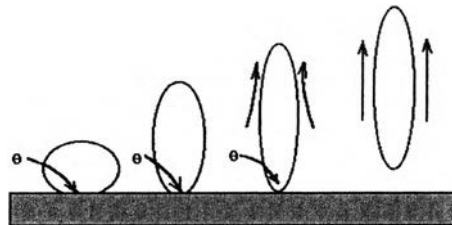
Figure 2.4 Contact angle between an oil droplet and substrate in bath.

Young's equation is as follow:

$$\cos\theta = \frac{\gamma_{SB} - \gamma_{SO}}{\gamma_{OB}} . \qquad \text{(Eq. 2.3)}$$

If the contact angle is 180° ($\cos\theta = 1$), the bath was spontaneouscompletely displace the oily soil from the substrate; if the contact angle is less than 180° but more than 90°, the oily soil will not be displaced spontaneously but can be removed by hydraulic currents in the bath (Rosen, 2004).


Figure 2.5 Roll-up mechanism shows the complete removal of oil droplets from the substrate by hydraulic currents when $\theta > 90°$ (Rosen, 2004).

4.2 Emulsification

      Emulsification, or snap-off, occurs when the contact angle between the oily soil droplets from the substrate is less than 90°. Emulsion is the dispersing of a liquid in another liquid in which it is not soluble. The oil droplet was coated by the surfactant molecule adsorbs at the surface to reduce the interfacial tension but incomplete detachment of the oily soil droplet occurs because a small residual drop remains on the substrate. Of course, a high surfactant concentration may at first appear to be beneficial, since micelles act as surfactant reservoirs. However, at

surfactant concentration above 5-10 times the CMC, the micelles can induce flocculation of the oil droplet. And a contact angle that is less than 90° causes the redeposion of the oil on the substrate.
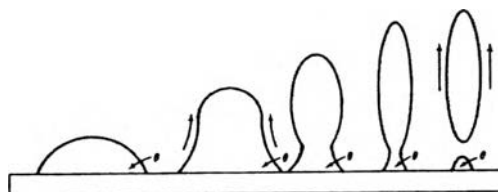
Figure 2.6 Emulsification mechanism shows partial removal of oil droplets from substrate $\theta < 90°$ (Rosen, 2004).

The ability of the bath to emulsify the oil soil is, however, in itself insufficient to keep all the soil from redepositing on the substrate. When the emulsified oil droplets impinge on the substrate, some of them may adhere to it in part, with the adhering portion tending to assume the equilibrium contact angle, unless the latter is 180° (i.e., unless complete oily soil removal by roll-up has been attained). This is in contrast to solubilization, which can result in complete removal of the oily soil from the substrate.
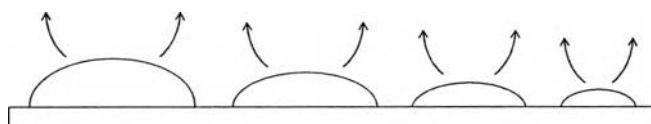
4.3 Solubilization

Solublilization occurrs when oil is adsorbed inside the core of the surfactant micelles, to a significant extent only in some cases and always above the CMC of the surfactant system for nonionics and even for some anionics having low CMCs, and reaches its maximum only at several times the CMC. This mechanism is to remove small amounts of oil, which cannot be removed either by roll-up or emulsification. 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 (Schwartz, 1971).

The solubilization depends on the shape of the micelles, the chemical structure of the surfactant, its concentration in the bath, and the temperature. The oil uptake capacity of globular micelles is limited because the addition of oil necessarily results in an increase of the micelle surface exposed to water. Rod-like micelles are

much better adapted to a higher oil uptake (Rosen, 2004). A surfactant forming rod-like micelles induces a lower oil-water interfacial tension and accordingly facilitates the transfer of oil from the substrate to the core of the micelles

Figure 2.7 The solubilization mechanism of removal of oily soil from a solid surface.

When insufficient surfactant is present to solubilize all the oily soil, the remainder was probably suspended in the bath by emulsification. In practice, this happens for a given surfactant system at a temperature referred to as the phase inversion temperature (PIT).

5. Surfactant

Surfactant Classification by charge

- Anionic surfactant: surfactant that have a negative charge when dissociated in water
- Nonionic surfactant: surfactants that do not ionize in solution
- Cationic surfactant: surfactants that have a positive charge when dissociated in water
- Amphoteric surfactant: surfactant that can carry both a positive and a negative charge when dissociated in water

Mixed surfactant contains surfactant to enhance detergency. It's substantially different from that in solution having only the pure surfactant. The mixed surfactant was speculated that the tendency of aggregated structure to form in solution. In this research work Anionic and nonionic surfactant used to study (A mixed surfactant system of branched alcohol propoxylate sulfate sodium salt with 14-15 carbon and 3 propylene oxides (Alflotera 145-3PO), an ionic surfactant and secondary alcohol exthoxylate nonionic surfactant (Tergital 15S5) used to form microemulsion) because they were commercial surfactant used in laundry

application and friendly to the environment and essential for many industry uses of surfactant.

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 was conducted by Goel also gave similar results. Goel (1998) 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 was 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 the maxima in detergency.

In 2003, Tongcumpou et al. found that the formulation of microemulsion by mixed surfactant system of sodium dioctyl sulfosuccinate (AOT, a surfactant of intermediate HLB), alkyldiphenyloxide disulfonate (ADPODS, very hydrophilic surfactant), and sorbitan monooleate (Span 80, very hydrophobic surfactant) with motor oil and hexadecane was considered as temperature- insensitive supposed by the results of Salager et al. (1979) and Anton et al. (1992). And she found that interfacial tension (IFT) values under supersolubilization (SPS) conditions were not substantially worse than under optimal conditions in a Winsor type III system (middle phase). In other words, quite low IFT was 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. Besides, she found that her microemulsion formation required fairly high salinity (16 wt%) to achieve the supersolubilization condition or optimum conditions that it was not practical for real application.

In 2005, Tongcumpou et al. found that, for her microemulsion formulation, 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. Because during the wash step, the spreading effect was occur supposed by other results (Thompson, 1994; Healy et al., 1976)

In addition, Korphol et al. (2004) found out 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%. With this selected formulation, detergency performance increased with increasing active surfactant concentration.

6. Factor Affecting Detergency Performance

6.1 Nature of oil

The soils that are present on a solid surface or fabric, from a detergency perspective, can be categorized into the following: particulates, which are solid phases such as carbon nanotube and iron dust or rust (usually inorganic); oils, which are liquid phases such as motor oil and palm oil (usually organic); waxy solids or greasy soil, which are the semi-solid phases such as butter, margarine, and grease (usually organic); and, stains (unwanted dyestuffs) (Carroll, 1996). Kissa (1987) claimed that oil viscosity affected oil removal; oil with a lower viscosity was usually removed more rapidly from the substrate than one with a higher viscosity. Chi et al. (1999) found that highly unsaturated oily soil was easily oxidation upon aging resulting in increasing removal, whereas saturated oils are relatively stable. In additional, they reported that aging made oils penetrate deeper into the fabric and fiber structures, resulting in removal being more difficult.

6.2 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. There was little or no difference between two detergents in total oil removal from the polyester/cotton fabric.

6.3 Salinity

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 toward a lower temperature as the electrolyte concentration increased (effect of salinity out).

6.4 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.