

CHAPTER II

LITERATURE SURVEY

2.1 Microemulsions

Microemulsions are the thermodynamically stable droplet-like or bicontinuous isotropic dispersion of oil-rich and aqueous domains without macroscopic order, which are stabilized by surfactants at a relatively low surfactant-to-oil ratio. Microemulsions exhibit an ultralow interfacial tension at their own oil-water interface as well as with other coexisting oil-rich and aqueous domains. As microemulsions are known to possess high limits for oil solubilization.

Microemulsions can be of the droplet type, either with spherical oil droplets dispersed in a continuous medium of water (oil-in-water microemulsions, O/W) or with spherical water droplets dispersed in a continuous medium of oil (water-in-oil microemulsion, W/O). The droplet type microemulsions can be either a single-phase system or part of a two-phase system wherein the microemulsion phase coexists with an excess dispersed phase. There are also non-droplet-type microemulsions, referred to as middle-phase microemulsions (Nagarajan and Ruckenstein, 2000). Winsor referred to this new phase as a Type III microemulsion, as opposed to Type I (micelles) and Type II (reverse micelles) microemulsions; these are now known as Winsor type I, II and III microemulsions, as illustrated in Figure 2.1.

2.1.1 Microemulsion Transformation Parameters

A middle-phase microemulsion can be produced by altering the HLB_d value of the surfactant system by varying several system variables e.g. electrolyte, temperature, surfactant, cosurfactant and oil.

2.1.1.1 Electrolyte Concentration

A typical phase diagram of a surfactant/water/oil system is illustrated in Figure 2.1 in terms of IFT of the system. When the microemulsion properties are changed by varying any single parameter, the resulting graph is known as a “scan”. Electrolyte concentration is commonly used as a scan variable for

microemulsion formation when ionic surfactants are present, whereas temperature is often used for nonionic surfactant systems.

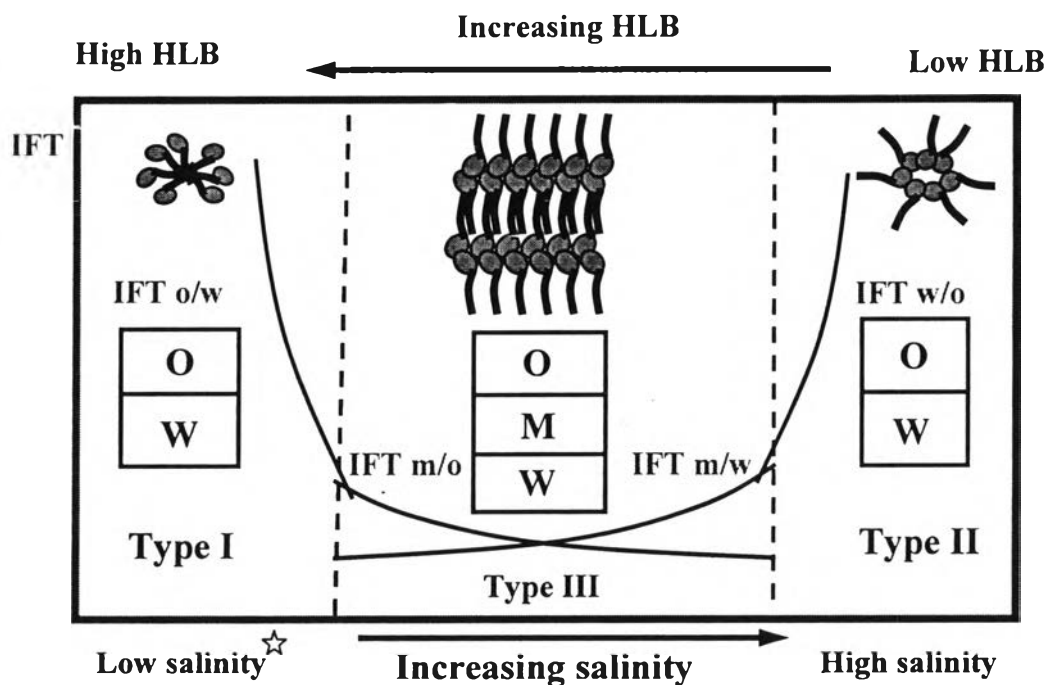


Figure 2.1 The relationship between microemulsion structure and interfacial tension with salinity scan and HLB value. (☆ Corresponds to the supersolubilization region)

2.1.1.2 The R Ratio

The Winsor ratio R is convenient for relating changes in the hydrophilic solvent W , the lipophilic solvent O , and the surfactant C to interfacial tensions and phase volumes by explaining them in terms of the molecular interactions involved (Bourrel, 1983, 1984). It is based upon the relative tendencies of the system to solubilize both W and O . The ratio is

$$R = \frac{A_{co} - A_{oo} - A_{ll}}{A_{cw} - A_{ww} - A_{hh}} \quad (2.1)$$

The ratio measures the solubilization capacity of the surfactant micelles for W relative to that for O . A_{co} and A_{cw} are the interaction strengths per unit area of interface of C with O and W , respectively, promoting solubilization of the other

liquid phase; A_{oo} and A_{ww} are respective self-interaction strengths of the solvent molecules in O and W, respectively, opposing solubilization into them; A_{ll} and A_{hh} are the strengths of the self-interactions between the lipophilic and hydrophilic portions, respectively, of the surfactant molecules, also opposing solubilization. When $R \ll 1$, the micelles solubilize O much more readily than W, and a Winsor type I microemulsion forms; when $R \gg 1$, they solubilize W much more readily than O, and a Winsor type II microemulsion forms. When $R \approx 1$, the type III or IV system forms, depending upon the magnitude of the numerator (or denominator). The type III is a three-phase system; type IV is a one-phase microemulsion.

2.1.1.3 Hydrophilic-Lipophilic Balance (HLB)

HLB is a number indicative of emulsification behavior and related to the balance between the hydrophilic and lipophilic (hydrophobic) portions. (Griffin, 1949) The microemulsion “phase” contains most of the surfactant. At high HLB values (Fig. 2.1, left side) the surfactant is predominantly present 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, which water is a continuous phase. In this region, the IFT between the excess oil phase and the O/W microemulsion decreases as the HLB of the system decreases. At an appropriate HLB, the system splits into three phases: an excess water phase with low surfactant concentration, a middle-phase or microemulsion phase, and an excess oil phase with low surfactant concentration. This new third phase is called a Winsor type III microemulsion system which contains most of surfactant leading to both high contents of oil and water. The IFT of a middle-phase system or Winsor type III is often as low as 10^{-3} mN/m, a so-called ultralow IFT. The lowest value of IFT, which is called the optimum interfacial tension (IFT*), is at the point where the IFT between the excess oil and the middle-phase ($IFT_{o/m}$) intersects with the IFT between the middle-phase and the excess water ($IFT_{w/m}$).

2.2 Supersolubilization

The region of Winsor type I close to the transition region from Winsor type I to Winsor type III is known as the supersolubilization region (see Figure 2.1). In

this region, micelles are swollen due to high solubilization of oil. The salinity scan is commonly used to identify the supersolubilization regime for each surfactant system. It has been demonstrated that Winsor type I solubilization is less efficient than the system exhibiting supersolubilization. Only a slight increase in removal efficiency can be achieved when the transition enters into the most efficient system that is Winsor type III.

In this study, supersolubilization system was exploited in detergency application because the low interfacial tension attained at this point is low enough to remove the oily soil from the fabric at room temperature. Another reason is the ultra-low interfacial tension from middle-phase microemulsion might cause soil redeposition onto the fabric.

2.3 Mechanisms for Removal of Oily Soil

Three principal mechanisms for removal of oily soils by surfactants are described by Rosen (1988).

2.3.1 Roll-up Mechanism

Removal of oily soil by aqueous baths is accomplished mainly by a “roll-up” mechanism in which the contact angle (θ) that the oily soil makes with the substrate is increased to more than 90° by adsorption of surfactant from the cleaning bath. Many researchers have found that reduction of interfacial tension at the liquid soil-bath (γ_{OB}) and/or increase in θ , measured in the oily soil phase, correlates well with an increase in detergency.

Figure 2.2 illustrates the correlation between interfacial tension and contact angle is given by equation 2.2, known as Young’s equation

$$\gamma_{SB} = \gamma_{OB} \cos\theta + \gamma_{SO} \quad (2.2)$$

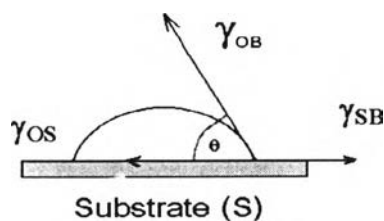


Figure 2.2 The contact angle between the droplet and substrate.

In many cases, γ_{SB} is reduced to point where $\gamma_{SB} - \gamma_{SO}$ is negative, resulting in increasing θ to a value greater than 90° . It is evident that the higher contact angle, the more easily the soil is removed (Broze, 1994). If the reduction of interfacial tension of γ_{SB} is so large that the sum of soil-bath and substrate-bath interfacial tension reaches the soil-substrate interfacial tension, the contact angle will approach 180° ($\cos\theta = 1$), which means that no soil is left on the substrate, as illustrated in Figure 2.3 (spontaneous perfect cleaning). On the other hand, if the reduction of interfacial tension is so low, the contact angle will be increased but not greater than 90° : leading to a partial oil removal known as snaff off as shown in Figure 2.3.

In 1997, another suggestion of roll-up mechanism (Azemar *et al.*, 1997), it has been accepted as the predominant mechanism in oily soil removal.

2.3.2 Emulsification

Raney *et al.*(1987) explained that the mechanism of direct emulsification of the thick layer of an oily liquid requires the formation of emulsion or agitation to deform the oil-water interface to the extent that individual drops break off.

According to Rosen (1988) and Azemar (1997), they noted that the interfacial tension between oily soil droplet and bath is low in this mechanism, so the emulsification is achieves with a minimum of mechanical work. However, emulsification occurs when the contact angle less than 90° , partial drop detachment that is illustrated in Figure 2.3. Therefore, the ability of emulsification for oily soil removal is insufficient to keep all the soil from redepositing on the substrate.

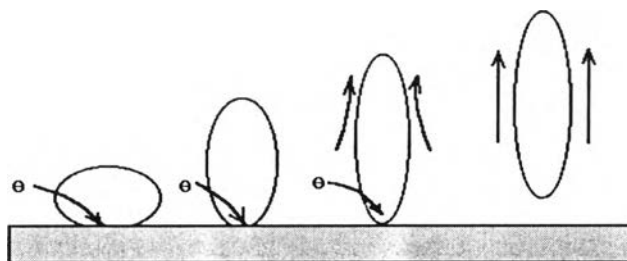


Figure 2.3 Complete removal of oil droplets from substrate when $\theta > 90^\circ$.

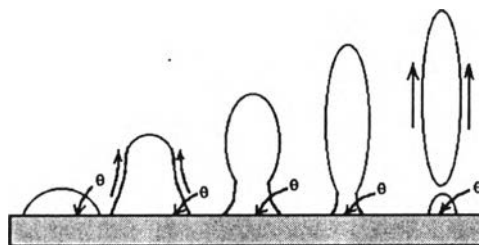


Figure 2.4 Incomplete removal of oil droplets from substrate known as snaff off when $\theta < 90^\circ$.

2.3.3 Solubilization

The third mechanism is solubilization. The solubilization, or oil uptake capacity, of a surfactant system depends on the shape of the micelles. 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. Rodlike micelles are much better adapted to a higher oil uptake (Rosen, 1988). A surfactant forming rodlike micelles induces a lower oil-water interfacial tension and accordingly facilitates the transfer of oil from the substrate to the core of the micelles. The solubilization capacity of a given surfactant is maximum if the surfactant divides equally well between the water and the oil phase.

2.4 Factors Affecting Oily Soil Removal

In the study of detergency formulation and performance, Linfield *et al.* (1962) found that agitation speed, washing time or detergent concentration affected the detergency performance. In addition, soil removal from fibrous substrates, depends on the nature of oily soil, the order of application, wash temperature and type of detergent formulation. (Webb *et al.*, 1988)

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

2.4.1 Nature of Oil

In 1963, Scott reported the presence of a 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. But upon aging, the effect of mixing on the removal of squalene was reversed.

After that, there are many research works relating to polar/nonpolar soils removal. Several studies of the selective removal of oily soil upon washing (Gordon, G. E., 1967; Powe, W. C., 1972; Morris, M. A. *et al.*, 1982) reported that after washing, the residual oily soil contained a greater percentage of nonpolar components than that in the fresh oily soil. They can conducted that polar soils tended to be more easily removed in aqueous detergent system.

Kissa (1987) claimed that an oil with lower viscosity was usually removed more rapidly from the substrate than ones with higher viscosity. He also reported that the viscosity of the emulsion of used motor oil with the aqueous detergent solution was 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 support the interfacial tension reduction at 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 at the washing temperature.

Chi *et al.* (1998) found that highly unsaturated oily soil was easily oxidized upon aging resulting in increasing removal of oil. While saturated oils are relatively stable to oxidation, thus aging may allow the oils to penetrate deeper into the fabric and fiber structures, making removal more difficult.

2.4.2 Surfactant System

Obendorf *et al.* (1982) found that the type of surfactant system affected detergency performance. The powdered, anionic detergent removed oil from the cotton fabric more effectively than the liquid, nonionic detergent. They expected this result since it is known that anionic surfactants are effective on more polar fiber surfaces. There was little or no difference of total oil removal on the polyester/cotton fabric between the anionic and the nonionic surfactants.

Webb *et al.* (1983) presented the detergent performance for triolein removal by mixed surfactants. It was reported that a combination of a poor surfactant with an efficient surfactant for oil removal resulted in poor detergency performance even though the poor surfactant comprised only 10% of the total surfactant concentration. This effect was found with both nonionic/ionic and nonionic/nonionic mixtures.

Solans *et al.* (1988) studied the effect of nonionic surfactant and temperature on detergent efficiency of nonpolar soils (hexadecane, squalene and mineral oil) on polyester/cotton fabrics. It was found that the maximum detergent efficiency was achieved at the phase inversion temperature. Furthermore, he found that the optimum temperature was higher as the degree of ethoxylation of the surfactant increased. Azemar (1997) also reported the similar results.

The effect of ethoxylation numbers in nonionic surfactants to soil removal was also reported by Wormuth *et al.*, (1991). They explained that the oily soil removal decreased could be due to a decrease of the solubilization power of surfactant with increasing ethoxylation numbers of the C₁₂₋₁₄ alkylpolyglycol ether.

Generally, a surfactant mixture that exhibits a low oil-water interfacial

tension is considered to provide superior oily soil detergency. Vermar *et al.* (1998) measured the oil-water interfacial tensions of $C_{12}EO_3/NaLAS$ and $C_{12}EO_7/NaLAS$ blends as a function of temperature and time. The oil-water interfacial tension was found to decrease as a function of time for both mixed surfactant systems. It was believed that the diffusivity of this hydrophobic fraction into the oil phase leads to a decline in oil-water interfacial tension.

According to the investigation by Goel (1998), the optimal EO moles (for maximal detergency) showed a monotonically increasing trend when plotted as a function of the ratio nonionic to anionic concentration 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 found to be much stronger than the effect of electrolytes on the optimal EO moles.

In the study of the correlation of detergency and a ratio of nonionic to NaLAS by Goel, he found that the minimum of interfacial tension as a function of the EO moles present in nonionic. These minima were found to represent the condition for high solubilization of oily soil corresponding to the maxima in detergency.

As described before, there are many studies on the effect of ethoxylation numbers in nonionic surfactant on soil removal. Interestingly, the effect of surfactant mixtures on the detergency of oil-soiled single fiber was investigated by Whang *et al.*, (2001). In terms of effective oily soil removal, anionic and nonionic surfactants were found to tend to perform best on polar and nonpolar soils, respectively. In addition, it was also reported that it was easier to clean fibers soiled with the polar oil than those soiled with the nonpolar oil.

2.4.3 Salinity

Oil removal performance in the presence of electrolytes was reported by Webb *et al.* (1983). They found that, for anionic surfactant system (LAS), an addition of 0.5 NaCl, reduced the mineral oil removal less than that without salt. They also found that addition of a less surface active component can lead to a significant increase the interfacial tension of the mixture and so adversely influence oil removal.

Furthermore, Solans *et al.* (1992) observed that detergent efficiency as a function of salt was temperature independent. The maximum detergency efficiency was obtained at 10%wt NaCl corresponding to the optimum salinity at which the conditions for microemulsion formation are favored.

Zemar *et al.* (1993) studied the effect of temperature and salt concentration on detergency performance. They concluded that for both systems with and without electrolyte the detergency efficiency increased with temperature in the same trend. However, the optimum temperature for the maximum detergency shifted toward a lower temperature with increasing electrolyte concentration. The shift has attributed to the effect of salting-out on the HLB-temperature of ternary water/nonionic surfactant/oil systems.

2.4.4 Substrate

Relative performance of oily soil removal has been influenced markedly by the nature of the substrate (Christ *et al.*, 1994). Recently, Chi (2001) investigated the effect of substrate on oily soil removal. The removal of unaged oily soil was found to be 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, was expected to release oily soil fairly easily in aqueous detergent systems, but it was not the case. Low removal of squalene from cotton was thought to be due to morphological characteristics of cotton that made oil difficult to remove.

Oily soil removal from cotton fabrics that had been chemically modified by mercerization and carboxymethylation was studied by Obendorf in 2001. It was proposed that the carboxymethylation changed the chemistry of the fiber by increasing the carboxyl group content, this structure changed reduces the amount of soil deposited in the lumen of fiber. In the mercerization was indicated that chemical accessibility and hydrophilicity of the fiber structure influence both soil deposition and soil removal of lipid soils.

2.4.5 Other Factors

Linfield *et al.* (1962) found that an increase in agitation speed, washing time or detergent concentration, resulted in increasing detergency performance. They noted that for the washing conditions at 48.9°C, 0.2% detergent and 135 ppm water hardness, the maximum detergency was obtained at around 150-170 rpm and around 15-20 min washing cycle.

Obendorf *et al.* (1982), pointed out that increasing mechanical action or detergent concentration resulted in increasing removal of triolein from inter fiber capillaries, but concentration of triolein in the lumen and crevices of the cotton fibers remained high.

In 1987, Raney *et al.* studied the correlation of PIT and optimum detergency. The optimum detergency was found at the temperature close to the PIT of the system composed of water, the surfactant and the hydrocarbon soil itself. The combination of solubilization and emulsification was also proposed as the predominant mechanisms for oily soil removal rather than the roll-up mechanism.

Another interesting factor to enhance the cleaning efficiency is a builder, Webb *et al.* (1988) found the largest difference in soil removal and appearance with different detergent formulations was based on the presence or absence of builder. The presence of builder was found to enhance the cleaning efficiency.

2.5 Motor oil

Motor oil is complex in composition and has high hydrophobicity. It generally consists of at least five main components: (a) n-paraffins, (b) isoparaffins, (c) cycloparaffins, (d) aromatic hydrocarbons, and (e) mixed aliphatic and aromatic compounds. In addition to these components, several additives are commonly added to the oil to act as rust inhibitor, oxidation inhibitor, detergent-dispersant, viscosity-index improver, pour-point dispersant, and antifoam (Furby, 1973). The EACN (equivalent alkane carbon number) is a parameter used to characterize the hydrophobicity of motor oil. It is an equivalent number of carbons in the complex mixed oil as compared to single component alkane oil. The higher EACN, the higher

hydrophobicity of the mixed oil is. Wu *et al.* (2000) studied and reported the EACN value of the motor oil to be 23.5.