

CHAPTER II

BACKGROUND AND LITERATURE REVIEW

2.1 Microemulsions

Microemulsions are thermodynamically stable consisting of water, oil and surfactant. Microemulsions are known to have remarkable properties of ultralow interfacial tension between water and oil phases and high solubilities of both oil and water. Schulman and Cockbain first reported the characteristics of microemulsion in 1940. A middle phase microemulsion can be produced by altering the HLB of the surfactant system by varying several system parameters (e.g., electrolyte, temperature, surfactant, cosurfactant and oil). Adjusting the system's salinity while holding other variables constant is known as salinity scan (Bourrel *et al.*, 1988)

Microemulsions can be divided in two cases by Rosen (1988). For the first case, a first liquid is completely solubilized in a second liquid to have a single phase. There has no interface against either liquid as the micelles are capable of solubilizing more of the first liquid.

In the second case, a dispersion of the tiny droplets of a first liquid in a second liquid, the interfacial tension of the microemulsion against both these liquids must be close to zero. The interfacial area is so large that an exceedingly low interfacial tension must be present to permit formation at the microemulsion with so little work.

2.1.1 Types of Microemulsions

Most studies of phase equilibria of microemulsions are probably known as the Winsor Type microemulsions (Winsor, 1954). There are four types of microemulsions as following;

1. Winsor Type I : Oil in water microemulsion in equilibrium with an excess oil phase. Oil droplets disperse in the water phase.
2. Winsor Type II : Water in oil microemulsion in equilibrium with an excess water phase. Water droplets disperse in the oil phase.

3. Winsor Type III : Bicontinuous phase is shown in Winsor Type III microemulsion in equilibrium with both excess water and excess oil phases. It is known as middle phase microemulsion.

4. Winsor Type IV : The single phase of microemulsion appears for Winsor Type IV microemulsion.

The transformation from Winsor Type I to Winsor Type III to Winsor Type II can be achieved by progressively changing temperature, salinity, the molecular structure of surfactant and cosurfactant, an oil to water ratio, or the structure of oil in a homologous series. This studied phase diagram is carried out by increasing salinity which is known as salinity scan. Relationship between the type of microemulsion and the interfacial tension is shown in Figure 2.1. The region on the left hand side of this figure is Winsor Type I microemulsion or oil-in-water microemulsion (o/w) equilibrating with an excess oil phase. Interfacial tension between the excess oil phase and the micellar solution ($\gamma_{o/m}$) decreases with increasing salinity. When the middle phase is formed, microemulsion becomes bicontinuous structure in equilibrium with excess oil and excess water phases. Interfacial tension between excess oil and the middle phase ($\gamma_{o/m}$) and between the excess water and the middle phases ($\gamma_{w/m}$) further decreases. The point in the middle phase microemulsion region, where the interfacial tension between the excess water and the middle phase ($\gamma_{w/m}$) equal to the interfacial tension between the the excess oil and the middle phase ($\gamma_{o/m}$) is known as the minimum interfacial tension or the optimum point that is shown as the optimum salinity. If HLB is further decreased, Winsor Type II microemulsion transforms to Winsor Type III microemulsion as shown on the right hand side of this figure. Interfacial tension between the excess water and the micellar phase ($\gamma_{w/m}$) increases rapidly.

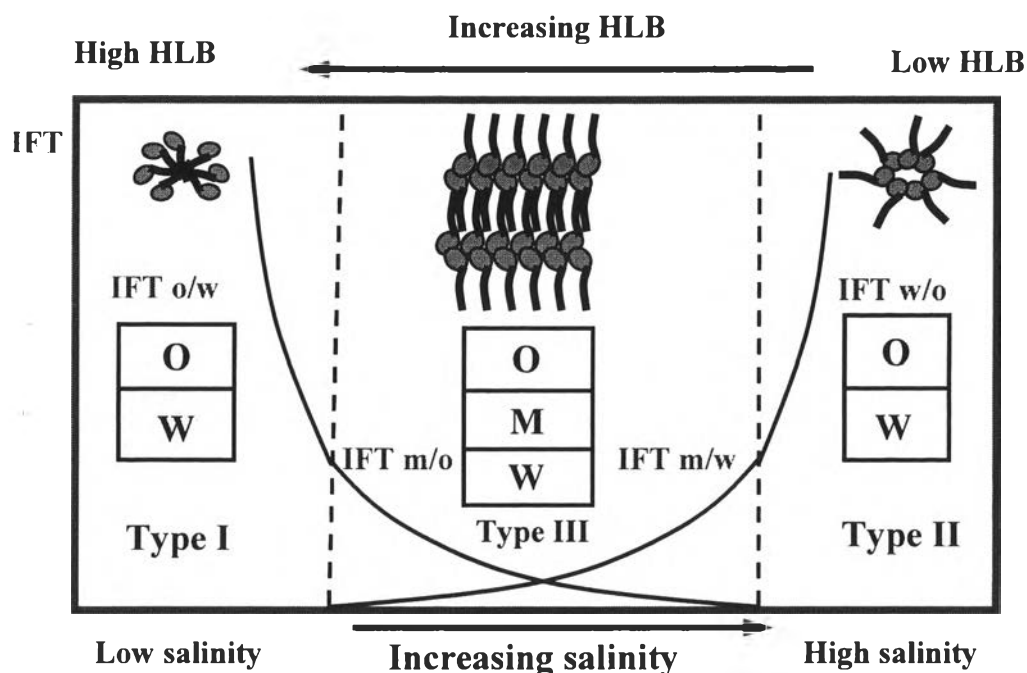


Figure 2.1 The relationship between microemulsion structure and interfacial tension of salinity scan and HLB value (Rosen, 1988).

2.2 Application of Microemulsion for Detergency

The washing efficiency with microemulsions was evaluated by Solans *et al.* (1985). High efficiency of soil removal from textile fabrics was found in the presence of the microemulsion of water/tetraethyleneglycol dodecyl ether/hexadecane even in conditions of minimum mechanical energy and at low temperatures. In addition, they found experimentally that a higher washing efficiency of the system with microemulsions was observed in comparison with 1% aqueous solution of a commercial liquid detergent. Furthermore, addition of a small amount of sodium tripolyphosphate or sodium citrate enhanced considerably the efficiency of soil removal.

Thompson (1994) reported a sharp detergency maxima which did not quite coincide with the minimum interfacial tension and therefore did not entirely confirm the correspondence of detergency maxima and interfacial tension minima. Its failure to match the position of γ_{\min} is attributable to the low contact angle below 80° , which allows the fabric yarn containing a continuous oil phase. Double detergency maxima

were also observed, one of them always corresponds to the minimum in γ_{ow} which promote the microemulsion of oil removal. Whereas a second detergency maximum is attributable to the roll-up mechanism.

Another study of application microemulsion for detergency and relationship between interfacial tension and detergency was also carried out by Dörfler et al., (1996). The optimum detergency of the microemulsion systems in this work condition was found to correspond to a minimum value of the interfacial tension about 10^{-3} mN/m between the microemulsion and the water or oil excess phases in the heterogeneous regions of phase diagram. In this work, comparison between the detergency of already formed microemulsions containing commercial grade components of water/n-decane/ C_{12-14} alkylpolyglycol ether/n-pentanol and a standard detergent solution was evaluated. The information shows that samples obtained from microemulsion region have a bicontinuous sponge-like structure and exhibit ultralow interfacial tension with maximum solubilizing power.

Furthermore, the influence of polyols and short-chain alcohols were studied to improve oil solubilization in oil/water food grade microemulsions (Garti *et al.*, 2001). It was concluded that the oil solubilization capacity was dramatically improved by using a suitable nonionic surfactant together with polyols and short-chain alcohols.

2.3 Principal Mechanisms of Oily Soil Removal

Removal of oily soil from fabrics is a complex phenomenon which takes place by a combination of mechanisms such as roll-up, emulsification, and solubilization.

2.3.1 Roll-up Mechanism

Roll-up mechanism was first implied by Raney and coworkers (1987), this mechanism depends on the wetting properties of aqueous surfactant solutions. Basically, thin layers of the oily attach soil on the surface of strongly wetting surfactant solutions. Furthermore, Rosen (1988) also described this mechanism in which the contact angle that the liquid soil makes with the substrate is

increased by adsorption of surfactant from the cleaning bath. Many researchers have found that reduction of interfacial tension at the soil-bath interface (γ_{OB}) and/or an increase in contact angle (θ), correlates well with increasing detergency.

The correlation between interfacial tension and contact angle is given by Equation 2.1, known as Young's equation (Rosen, 1988).

$$\gamma_{SB} = \gamma_{OB} \cos\theta + \gamma_{SO} \quad (2.1)$$

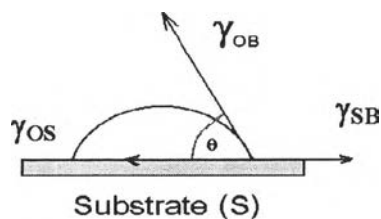


Figure 2.2 The contact angle between an oil droplet and substrate in bath.

Figure 2.2 illustrates the situation of a liquid soil adhering to substrate in the presence of a cleaning bath. In many cases, γ_{SB} is reduced to point where $\gamma_{SB} - \gamma_{OS}$ is negative, with resulting increase in 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 is so strong that the sum of soil-bath and substrate-bath interfacial tension reaches the soil-substrate interfacial tension, the contact angle is 180° ($\cos\theta = 1$), which means that no soil is left on the substrate (spontaneous perfect cleaning), as known is the roll-up mechanism that is illustrated in Figure 2.3. On the other hand, if the reduction of interfacial tension is so weak, the contact angle is so small, which means that only a small quantity of soil is removed. Such a situation is illustrated in Figure 2.4 as known is the snap-off mechanism.

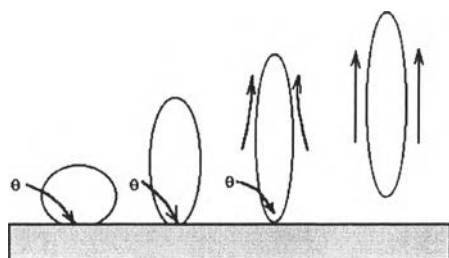


Figure 2.3 Roll-up mechanism shows complete removal of oil droplets from substrate by hydraulic currents when $\theta > 90^\circ$ (Rosen, 1988).

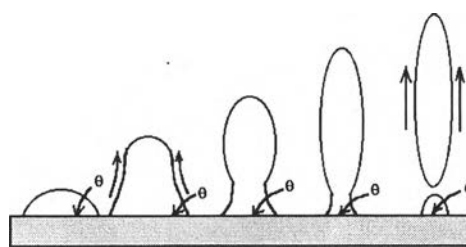


Figure 2.4 Snap-off mechanism shows incomplete removal of oil droplets from substrate by hydraulic currents when $\theta < 90^\circ$. A small droplet remains attached to the substrate (Rosen, 1988).

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 achieved 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.

2.3.3 Solubilization

The solubilization, or oil uptake capacity, of the surfactant system depends on the shape of the micelles. Rodlike micelles are much better adapted to higher oil uptake than globular micelles (Rosen, 1988). The oil uptake capacity of globular micelles is limited because the addition of the oil necessarily results in an increase in the micelle surface exposed to water. Even if the interfacial tension is

low, an increase of surface implies an increase in energy that can hardly be balanced by the entropy of dispersion of the oil in micelles. Moreover, the interfacial tension between a flat oil surface and the aqueous surfactant solution creates a kinetic barrier to spontaneous solubilization, as the adsorption efficiency is not maximum.

In contrast, 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 adsorption of oil allows micellar internal tensions to relax, and the volume increases to a significant extent without increasing surface exposed to the water phase. Rodlike micelles can be obtained with ethoxylated nonionic surfactants at temperatures just below their cloud points. Rodlike micelles can also be obtained with some anionic surfactants in the presence of magnesium or calcium counterions.

As shown, the maximum solubilization capacity of a given surfactant occurs when the surfactant divides equally well between the water and the oily phases (Broze, 1994). In practice, this happens for a given surfactant system at a temperature referred to as the phase inversion temperature (PIT). The phase inversion temperature depends on the surfactant structure, the oil structure, and the presence of ingredients dissolved in water. Another point, Azemar *et al.*, (1997) proposed that the solubilization can result in more complete removal of oily soil from substrate than emulsification.

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 and detergent concentration affected the detergency performance. Webb *et al.* (1988) suggested soil removal from fibrous substrate that was depended on the nature of the soil, the order of application, temperature and 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.

2.4.1 Nature of Oil

Scott (1963) found that the presence of polar oil enhanced 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 is reversed after aging.

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

Kissa (1987) claimed that the 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 was 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.

2.4.2 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 the cotton fabric more effectively than a nonionic detergent. As expected, anionic surfactants are effective on more polar fiber surfaces. There was little or no difference between these two detergents in total oil removal from the polyester/cotton fabric.

Webb *et al.* (1983) studied the detergency performance for triolein removal by mixed surfactants. They found that a mixed surfactant system of a poor surfactant and an efficient surfactant resulted in poor performance in oil removal even though the poor surfactant was only 10% of the total surfactant concentration.

The effects of nonionic surfactant and temperature on detergency efficiency were studied by Solans *et al.* (1988) for nonpolar soils (hexadecane, squalene, mineral oil) on polyester/cotton fabric. It was found that the optimum detergency efficiency was achieved at the phase inversion temperature. Furthermore, they reported that the optimum temperature became higher as the degree of ethoxylation of the surfactant increased. The results were in good agreement with the work done by Azemar *et al.* (1997).

The effect of ethoxylation numbers in nonionic surfactant to soil removal was also studied by Wormuth *et al.* (1991). They reported that the oily soil removal decreased as the solubilization power of surfactant decreased which is resulting from increasing ethoxylation numbers of the C₁₂₋₁₄ alkylpolyglycol ether.

Generally, a surfactant mixture that can exhibit a low oil-water interfacial tension was considered to provide superior oily soil detergency. Verma *et al.* (1998). measured the oil-water interfacial tension for 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 surfactants. It was proposed that the diffusivity of this hydrophobic fraction into the oil 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 (1998) investigated detergency performance at different ratios of nonionic to NaLAS concentrations. He found that the minimum

value of interfacial tension was a function of the EO moles in the nonionic surfactant. These minima was found to exhibit high solubilization of oily soil and which corresponded to maxima in detergency.

The effect of surfactant mixtures on the detergency of oil-soiled single fiber was also studied (Whang *et al.*, 2001). In terms of effective oily soil removal, anionic and nonionic surfactants tended to perform best on polar and nonpolar soils, respectively. It was also reported that it was easier to clean fibers soiled with polar oil than fibers soiled with nonpolar oil.

2.4.3 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 m NaCl was about half that of the nonionic alone. They also found that an addition of a surface active component having less active lead to a significant increase in the interfacial tension of the mixture and so adversely influenced the oil removal.

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

The effects of temperature and salt concentration to detergency efficiency were investigated by Azemar *et al.* (1993). They concluded that detergency efficiency with both 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). As known, the shift has attributed to the effect of salting-out electrolytes on the HLB-temperature of ternary water/nonionic surfactant/oil systems.

2.4.4 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 substrate on the removal of unaged oily soil and found 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, might be expected to release oily soil fairly easily in aqueous detergent systems, but this 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 be removed.

Soil removal from cotton fabrics that had been chemically modified by mercerization and carboxymethylation were studied by Obendorf (2001). It was proposed that the carboxymethylation changed the chemistry of the fiber by increasing the carboxyl group content, this structure changed was believed to reduce 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

In the study of detergency formulation and performance, Linfield *et al.* (1962) found that an increase in agitation speed, washing time or detergent concentration, resulted in increasing detergency performance to the maximum levels. Their paper noted that for the conditions of washing 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) 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 from inter fiber capillaries, but the concentration of triolein in the cotton fibers remained high.

In 1987, Raney *et al.* 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. The combination of solubilization and emulsification was also proposed as the predominant mechanisms for oily soil removal rather than the roll-up mechanism.

As known, builder is another influencing factor for enhancing the cleaning efficiency. Webb *et al.* (1988) also found the largest difference in soil removal and appearance among the formulations of detergents was based on the presence or absence of builder. Builder enhances the cleaning efficiency of the surfactant.

2.5 Motor Oil

Motor oil is complex in composition and has high hydrophobicity. It generally consists of at least five main components: n-paraffin, isoparaffin, cycloparaffin, aromatic hydrocarbon, and mixed aliphatic and aromatic ring (Tungsubutra *et al.*, 1992). In addition to these main 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. The EACN (equivalent alkane carbon number) is a parameter used to characterize the hydrophobicity of the 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 motor oil to be 23.5.