CHAPTER II
THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Microemulsion

Microemulsion are isotropic, low viscosity and thermodynamically stable solutions in which two immiscible liquids (for example, water and oil) are brought into a single phase by adding a surfactant or mixture of surfactants and/or co-surfactant (Solan *et al.*, 1997; Evans and Wennerstrom, 1994).

Microemulsions contain oil (or water) droplets with radii of <100 nm, surrounded by surfactant layer, dispersed in a water (O/W) and water in oil (W/O) microemulsions can often occur with the same surfactant but with different temperature ranges (Rosano, 1974; Prince, 1997; Overbeek *et al.*, 1984; Friberg, 1985; Langevin, 1986; Shinoda and Lindman, 1987; Aveyard, 1987).

Microemulsions containing aliphatic or aromatic hydrocarbons with low molecular weights have been extensively studied and much data on their compositions, properties and structures reported (Shinoda and Friberg, 1986; Aveyard *et al.*, 1987; 1990). There are numerous applications for these, for example in detergents (Azemar, 1997; Salager, 1999). Under washing conditions, liquid crystalline phases and, recently, microemulsions play a predominant role in the mechanisms of soil removal (Azemar, 1997). The most significant properties of microemulsions for detergency are improved solubilization for both polar and non-polar soil compounds, very low interfacial tension between the aqueous and oily phases are brought together.

A well-known classification of microemulsions is that of Winsor who identified four general types of phase equilibrium:

• Type I: the surfactant is preferentially soluble in water and oil-in-water (o/w) microemulsions form (Winsor I). The surfactant-rich water phase coexists with the oil phase where surfactant is only present as monomers at small concentration.

• Type II: the surfactant is mainly in the oil phase and water-in-oil (w/o) microemulsions form. The surfactant-rich oil phase coexists with the surfactant-poor aqueous phase (Winsor II).

• Type III: a three-phase system where a surfactant-rich middle-phase coexists with both excess water and oil surfactant-poor phases (Winsor III or middle-phase microemulsion).

• Type IV: a single-phase (isotropic) micellar solution, that forms upon addition of a sufficient quantity of amphiphile (surfactant plus alcohol).
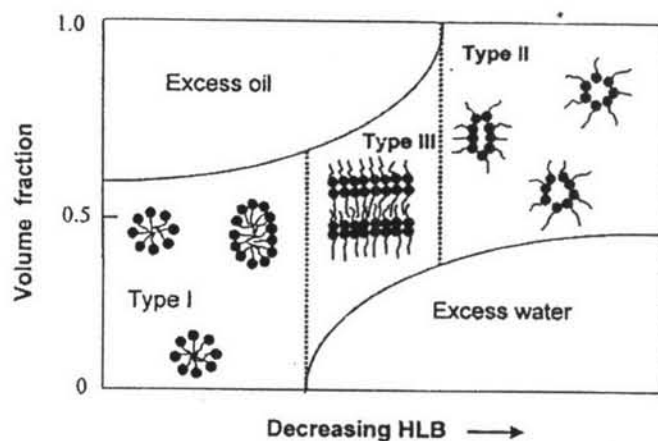

Figure 2.1 Typical phase behavior showing the transition from oil in water (Type I) to bicontinuous structure (TypeIII) and water in oil structure(Type II); initial ratio of oil to water = 1:1. HLB, hydrophile-lipophile balance.

Typical phase diagrams of a surfactant/water/oil system are illustrated in Figures 2.1 and 2.2 in terms of microstructure and IFT of the system, respectively. Microemulsion properties are change by varying a single parameter such as electrolyte concentration when ionic surfactants are present, while temperature is used for nonionic surfactant systems

The microemulsion phase contains most of the surfactant. At high HLB values (Figure 2.1, left side) the surfactant is predominantly in the water phase, which is in equilibrium with excess oil phase having a very low surfactant concentration. This is known as Winsor type I microemulsion. In this region, the IFT between excess oil and the O/W microemulsion of the system decrease as the HLB at the interfacial of the system decreases. At an appropriate HLB, the system splits into three phases, the new third phase is called Winsor type III microemulsion system. The IFT in the region of the middle phase is often as low as 10^{-3} mN/m,

called ultralow IFT. The lowest value of IFT, called the optimum IFT, is at the intersection point between the IFT of excess oil and middle phase and the IFT of middle phase and excess water. The HLB is further decreased from a Winsor type III to type II, the W/O microemulsion is presented.
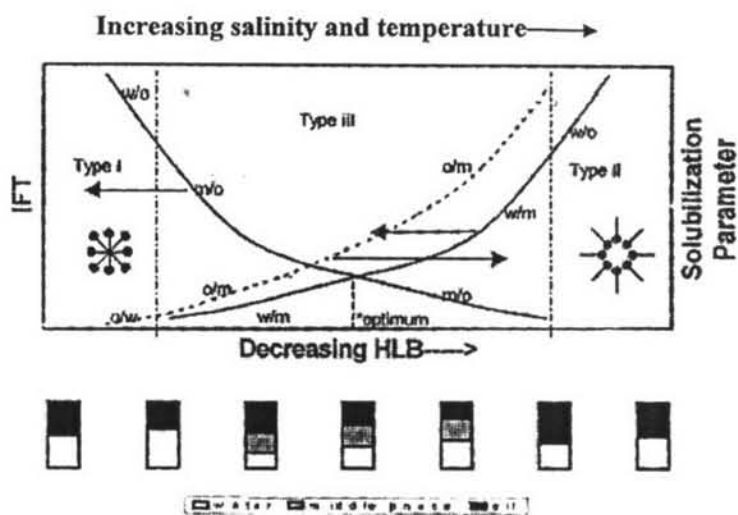

Figure 2.2 Phase behavior showing interfacial tension (IFT) as a function of scaning variable.where o is oil; w is water; m is middle phase.

2.2 Mechanism of Oily Soil Removal

It is useful to examine the three oily soil removal mechanisms in more detail to understand the basis for the choice of an appropriate physical property to correlate with detergency. In 1993, Carroll compiles a good review of the soil removal process from fabric.

2.2.1 Roll-up

A schematic for the definition of contact angle is shown in Fig 2.3 by an oil drop on a fabric surface. Roll-up may be defined as the detachment of an oil droplet from a substrate due to the increase in contact angle between the liquid soil and the substrate.

The contact angle θ is related to various interfacial tensions by Young's equation.
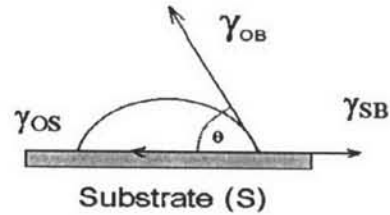
Figure 2.3 The contact angle between an oil droplet and substrate in bath.

Young's equation $$\cos\theta = \frac{\gamma_{SB} - \gamma_{SO}}{\gamma_{OB}}$$ (2.1)

Many researchers have found reduction of interfacial tension at the soil-bath (γ_{OB}) and/or increase in θ, measured in the oily soil phase.

It is evident that equilibrium contact angle, the more easily the soil is removed. If the reduction of interfacial is so strong that the sum of oil-water interfacial tension reached the oil-substrate interfacial tension, the contact angle is 180° ($\cos\theta = 1$), which means that no oil is left on the substrate (spontaneous perfect cleaning), (K.R> Lange, 1994), as it is shown in the Figure 2.4
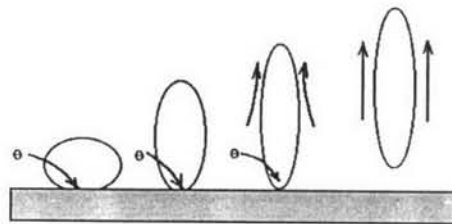

Figure 2.4 Roll-up mechanism shows complete removal of oil droplets from substrate by hydraulic currents when $\theta > 90°$ (Rosen, 1988).

As the result, if the contact angle in the detergent solution is more than 90°, complete detachment may be achieved. On the other hand, when the contact angle θ in detergent solution remained less than 90°, a small residual drop remains

on the substrate which undergoes a similar removal by a much slower repeat of the process.

2.2.2 Emulsification

Emulsification is probably one of the most important mechanisms contributing to oily-greasy soil removal. An emulsion is a dispersion of a liquid in another liquid which is not soluble. Mechanical agitation is able to generate an emulsion, but, to remain dispersed, the oil droplet need to be coated with a layer of surfactant molecules to reduce the interfacial tension with the continuous phase.

When surfactant is added to pure water, the interfacial tension between oil and water is dropped. This reduction occurs because the surfactant molecules adsorb at the surface of oil and reduce the number of contacts between oil and water. Since a surfactants contains a part that is completely water soluble (its polar head group), the interfacial tension could go to very low values and even completely vanish.

Of course, a high surfactant concentration may at first appear to be beneficial, since micelles act as surfactant reservoirs. This is only partly true, however. At surfactant concentration above 5-10 times the cmc, the micelles can induce flocculation of the oil droplet, which has an adverse effect on the physical stability of the emulsion.

However, emulsification occurs when the contact angle is less than 90°. A schematic for this mechanism is shown in the Figure 2.5.
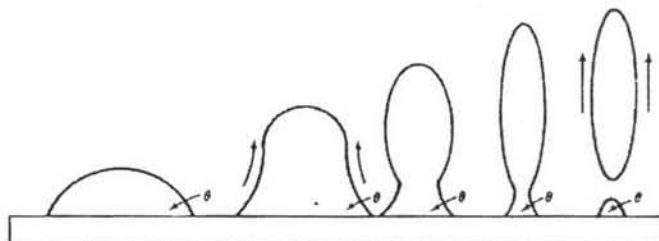

Figure 2.5 Emulsification or Necking mechanism shows partial removal of oil droplets from substrate by hydraulic currents when $\theta < 90°$ (Rosen, 1988).

2.2.3 Solubilization

In particular, solubilization is useful mechanism for removing small amount of oil, which cannot be removed either by roll-up or emulsification. Solubilization occurs to a significant extent only in some cases and always above the cmc of the surfactant system. Solubilization is not really the appropriate term, in as much as oil is not molecularly dissolved in the water phase but is absorbed inside the core of the surfactant micelles.

The solubilization, or oil uptake capacity, of a surfactant system depends on the shape of the micelles. Nonionic surfactants such as polyethoxylate fatty alcohols exhibit a much higher potencial for solubilization.

Solubilization has long been known to be a major factor in the removal of oily soil and its retention by the bath. This is based upon the observation (Ginn, 1961; Mankowich, 1961) 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, and reaches it maximum only at several times the CMC. In recent years, a considerable amount of research has been devoted to the removal of oily soil by POE nonionic ' surfactants, particularly from polyester or polyester/cotton (Pierce, 1980; Benson, 1982,1985,1986; Dillan, 1979, 1984). The data indicate that maximum soil removal occurs at temperatures 15-30° C above the cloud point of the POE nonionic, where a surfactant-rich phase separa0tes. Benson (1986) showed that suggests that maximum detergency occurs at, or close to the phase immersion temperature, PIT. Moreover, the solubilization of nonpolar material increases markedly with separation of thesurfactant-rich phase. Thus, conditions are optimum at the PIT for the removal of oily soil by the roll-back mechanism and its retention in the bath via solubilization.

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 (Schwartz, 1972). With ionic surfactants, the use concentration is generally not much above the CMC;

consequently, solubilization is almost always insufficient to suspend all the oily soil. When insufficient surfactant is present to solubilize all the oily soil, the remainder is probably suspended in the bath by emulsification.

Besides, the maximum solubilization capacity of a given surfactant is also mentioned by Bronze (1994). It occurs when the surfactant divides equally well between the water and the oily phase. In practice, this happens for a given surfactant system at a temperature referred to as the phaseinversion temperature (PIT). The phase inversion temperature depends on the surfactant structure, on the oil, and on 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.

2.3 Factors of 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.

2.3.1 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, G, E., 1967; Powe, W, C., 1972; Morris, M, A. 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.

2.3.2 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 there two detergents in total oil removal from the polyester/cotton fabric.

Webb et al. (1983) studied the detergent performance for triolein removal by mixed surfactant. They found that a mixed surfactant 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 detergent 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 has also studied by Wormuth *et al,* (1991). They conducted that the oily soil removal decreased as the solubilization power of surfactant decreased which is resulting from increasing ethoxylation numbers of the C_{12-14} 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/$C_{12}EO_3$ and NaLAS/$C_{12}EO_7$) 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 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 related to corresponding 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 tend to perform best on polar and nonpolar soils,

respectively. In addition, it is easier to clean fibers soiled with polar oil than fibers soiled with nonpolar oil.

2.3.3 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 (LAS surfactant). 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.

2.3.4 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. Squaiene, 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.

2.3.5 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 that mechanical action and detergent concentration affected 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 optimum detergency. The maximum detergent action 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 interesting factor for enhancing the cleaning efficiency. Webb *et al.* (1988) also found the largest difference in soil removal and appearance amoung the formulations of detergents was based on the presence or absence of builder. Builder enhances the cleaning efficiency of the surfactant.

2.4 Motor Oil

Motor oil is complex in composition and has high hydrophobicity. It generally consists of at least five main components: (a) n-parafins, (b) isoparafins, (c) cycloparafins, (d) aromatic hydrocarbons, and (e) mixed aliphatic and aromatic compounds. In addition to these components, several additives are commomly 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 14 hydrophobicity of the mixed oil is. Wu et al. (2000) studied and reported the EACN value of the motor oil to be 23.5.