



CHAPTER II

THEORETICAL BACKGROUND AND LITERATURE REVIEW REFERENCES

2.1 Surfactants

Nowadays surfactants play an important role in which they are generally added to the process in order to produce various kinds of products that can be used in every human daily's life. They are used in many applications ranging from the mining industry to the nutrition industry. The largest market for surfactants is the household and personal-care product. The personal-care sector comprises of toilet soaps, hair-care products, skin-care products and oral care products (Behler *et al.*, 2000).

The term “surfactant” is shortened from “SURFace ACTive AgeNT”. By definition, surfactants are compounds that reduce the surface tension of a liquid, the interfacial tension between two liquids, or that of between a liquid and a solid due to their preference to adsorb or accumulate at surfaces and interfaces or form structures to create new molecular surfaces. Surfactants may also function as detergents (for cleansing), wetting agents (in perms), emulsifiers (in creams and lotions), foaming agents (for shampoos), and dispersants (for perfumes and flavors) (Brannon, 2011).

Surfactants are amphipathic molecules which consist of a non-polar hydrophobic portion; usually a straight or branched hydrocarbon or fluorocarbon chain containing 8–18 carbon atoms, which is attached to a polar or ionic portion (hydrophilic). The hydrophilic portion can; therefore, be nonionic, ionic or zwitterionic. Figure 2.1 shows a typical structure of a surfactant. The hydrocarbon chain interacts weakly with the water molecules in an aqueous environment, whereas the polar or ionic head group interacts strongly with water molecules (Tadros, 2005).

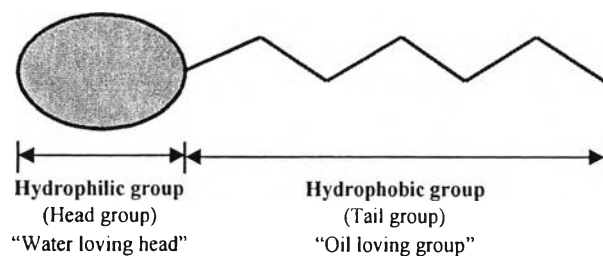


Figure 2.1 A typical structure of a surfactant.

According to the type of the charge of the hydrophilic head group, surfactants can be classified into four types as follow.

2.1.1 Anionic Surfactants

The hydrophilic head group is negatively charged. It is effectively for particulate soil removal. For example, RCOO^-Na^+ (soap), $\text{RC}_6\text{H}_4\text{SO}_3^-\text{Na}^+$ (alkylbenzene sulfonate).

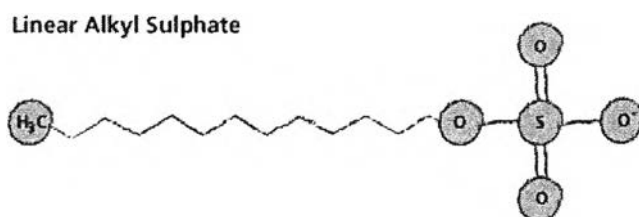


Figure 2.2 An example of anionic surfactant.

2.1.2 Cationic Surfactants

The hydrophilic head group is positively charged. It is effectively for oily soil removal. For example, $\text{RNH}_3^+\text{Cl}^-$ (salt of a long-chain amine), $\text{RN}(\text{CH}_3)_3^+\text{Cl}^-$ (quaternary ammonium chloride).

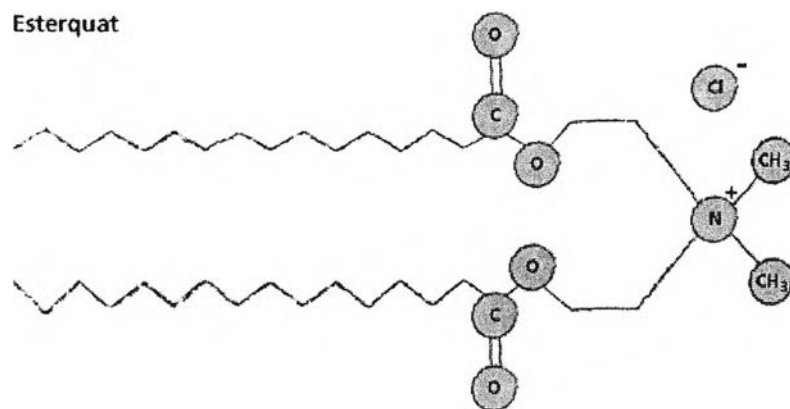


Figure 2.3 An example of cationic surfactant.

2.1.3 Nonionic Surfactants

There is no apparent of any electrical charge in the hydrophilic head group which makes them resistant to water hardness deactivation. It is effectively for grease removal. For example, $\text{RCOOCH}_2\text{CHOHCH}_2\text{OH}$ (monoglyceride of long-chain fatty acid), $\text{RC}_6\text{H}_4(\text{OC}_2\text{H}_4)_x\text{OH}$ (polyoxyethylenated alkylphenol).

Non Ionic Surfactants

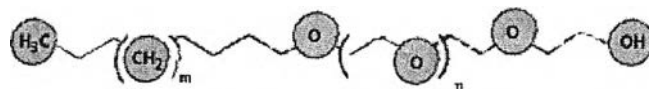


Figure 2.4 An example of nonionic surfactant.

2.1.4 Amphoteric/zwitterionic Surfactants

These surfactants may contain two charged groups of different sign and also have excellent dermatological properties. They are very mild which making them particularly suited for using in personal care and household cleaning products. They can be anionic (negatively charged), cationic (positively charged) or nonionic (no charge) in solution, depending on the acidity or pH of the water (Procter&Gamble, 2011). It is effectively for high concentration of electrolytes, acids, and alkalis.

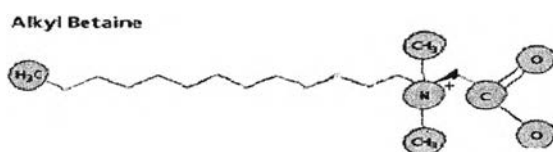


Figure 2.5 An example of amphoteric/zwitterionic surfactant.

Anionic surfactants are the most important class of surfactants regarding volume followed by the nonionic surfactants. Cationic and amphoteric surfactants are less important. Surfactants are generally available from two different sources which are petrochemicals and oleochemicals. The feedstocks for petrochemicals are crude oil and natural gas and that of for oleochemicals are the fats and oils.

The source of oils and fats are various vegetable and animal raw materials. The vegetable oils; soybean, palm, rape seed, and sunflower, are the most important ones regarding volume. Fats and oils are triglycerides; for example, esters of fatty acids and glycerol. The composition of the fatty acid is different in the various fats and oils and is decisive for further usage. Generally, there are two different types of fatty acids. First, the lauric oil that contains high amounts of lauric and medium chain fatty acids like myristic acid, e.g. coconut oil and palm kernel oil. Second, the long chain fatty acids, e.g. steric acid, that are incorporated in e.g. tallow and palm oil.

Based on fats and oils the three types of oleochemical raw materials are available which are fatty acids, fatty acid methyl ester and fatty alcohol. The latter one plays the most important role as a raw material for manufacturing of surfactants (Behler *et al.*, 2000).

2.2 Extended Surfactants

Extended surfactants are the ones that have a dual anionic and nonionic character, and are expected to exhibit an intermediate change in hydrophilicity with temperature. They contain intermediate polarity groups; such as short-chain polypropylene oxide (POs) or polypropylene-polyethylene oxide (POs-Eos) groups, which located between the conventional hydrophile and lipophile groups.

Due to the presence of intermediate-polarity groups, the extended surfactants do not only increase the tail length but also propose a smoother interfacial transition from a polar aqueous to a nonpolar oil region which resulted in forming middle-phase microemulsions with a superior solubilization and low interfacial tension (Miñana-Perez *et al.*, 1995 and Witthayapanyanon *et al.*, 2009).

Miñana-Perez *et al.* (1995) studied the solubilization of polar oils with extended surfactants. The extended surfactants; alkyl polypropylene oxide ether sulfates, were first used and investigated which were found to exhibit the intermediate behavior between anionic and nonionic surfactants. They shown three-phase behavior at optimum formulation with a variety of long chain oils, in particular mono-, and triglyceride esters.

Witthayapanyanon *et al.* (2009) studied the interfacial properties of extended-surfactant-based microemulsions and related macroemulsions. The equilibrium and kinetic aspects of extended-surfactant-based micro- and macroemulsions were studied in this research. In addition, the interfacial morphology of the extended surfactant membrane; such as characteristic length (ξ) and interfacial rigidity (E_r) at optimum middle-phase microemulsion conditions, was also characterized. The resulted showed that the extended surfactants had relatively rigid interfacial membrane compared with conventional surfactants having similar hydrocarbon chain length. Furthermore, both characteristic length (ξ) and interfacial rigidity (E_r) parameters increased with the length of polypropylene oxide groups. Although increasing in the interfacial rigidity (E_r) values related with the slow coalescence rates of the extended surfactant emulsified systems, two alternative ways; such as the addition of combined linkers and co-surfactant, were found to overcome the slow kinetics of coalescence while maintaining desirable high solubilization and low interfacial tension.

In this research, the extended surfactant named is “Alfoterra[®] C145-4PO” was used to study the detergency performance under various conditions.

Alfoterra[®] C145-4PO, beta-Branched, alcohol polypropoxy sulfate, or Branched alcohol propoxylate sulfate, sodium salt is the anionic surfactant which having four groups of propylene oxide as an intermediate-polarity group. It is used in

soil remediation and enhanced recovery techniques. The information and properties of Alfoterra[®] C145-4PO are shown in the Table 2.1.

Table 2.1 The information and properties of Alfoterra[®] C145-4PO (Sasol, 2011)

Information and properties of Alfoterra [®] C145-4PO	
1. Synonyms	Alcohol propoxysulfate, sodium salt (aqueous solution)
2. Color	Light yellow to brown
3. Odor	Slight hydrocarbon-like
4. Form	Liquid, slurry
5. Water solubility	Completely miscible
6. pH	7-10
7. % Active	29.5

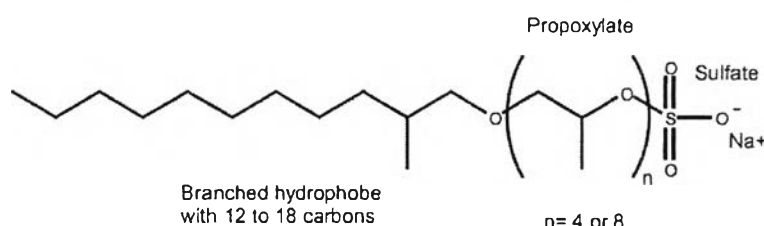


Figure 2.6 The molecular structure of Alfoterra[®].

2.3 Types of Soils

Soils can be defined as the contaminant on substrate. In general, it is either colorless or colored and also soluble or insoluble in water. There are three types of soils which are oily and greasy soils, particulate soils or solid soils, and stains.

2.3.1 Oily Soils

Oily soils are mostly composed of nonpolar hydrocarbons. They are usually liquid and highly hydrophobic. So, they do not dissolve with water. For instance, hydrocarbons, saturated or unsaturated fatty acids, and ester of fatty acids and alcohols.

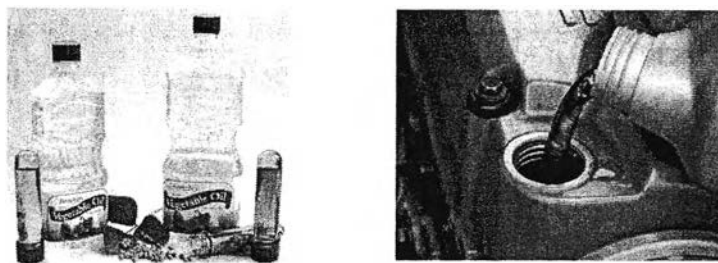


Figure 2.7 Oily soils.

2.3.2 Particulate Soils or Solid Soils

The examples of particulate soils are dust, clay, iron, dust, metal oxide, and carbon black. There are several properties that affect the detergency such as size, shape, and surface geometry of soil. They are soluble neither in water nor in inorganic solvents. They usually exhibit a large surface area, on which the oils and greases adsorb very strongly. Particulate soils contribute significantly to the difficulty of removing oily and greasy soils because they contribute to their rigidification and, sometimes, they act as catalyst in the oxidation/cross-linking of unsaturated triglycerides. Since they are not water soluble, the particulate soils can be re-deposited on surfaces that have been cleaned. It is accordingly important to keep such soils effectively dispersed in the washing liquid (Lance, 1994).



Figure 2.8 Particulate soils.

2.3.3 Stains

Coffee, tea, blood, ink, and fruit juices stains are the example of stains. They can form physical or chemical bond with the substrate and bring about

the difficulty in soils removal. Therefore, the substrate can be destroyed by this type of soils.

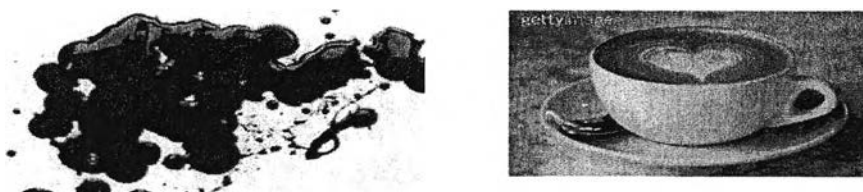


Figure 2.9 Stains.

2.4 Semi-solid Soils

Semi-solid soil is a substance that has an intermediate in properties; especially in viscosity and rigidity, between a solid and a liquid; for example, a stiff dough, firm gelatin, butter, margarine, and etc. For example, margarine has a melting point between 34 °C to 37 °C. If it is heated or put in the hotter surroundings, it gradually melts and finally becomes liquid. On the other hand, if it is put at the temperature lower than its melting point, it becomes solid.

In this research, methyl palmitate; one kind of semi-solid soil, was used to study the formation of middle-phase microemulsions with the extended surfactants in various temperatures and also to study the detergency efficiency from the fabric under various conditions.

Methyl palmitate or palmitic acid methyl ester is a colorless liquid with a boiling point of 185 °C and a melting point of 29 to 35 °C. It is soluble in alcohol and ether and is used in the manufacture of detergents, resins, plasticizers, lubricants, and animal feed. The information and properties of methyl palmitate are shown in the Table 2.2.

Table 2.2 The information and properties of methyl palmitate (Cayman, 2011 and Sigma-Aldrich 2011).

Information and properties of Methyl Palmitate	
1. Synonyms	Methyl hexadecanoate, Palmitic acid methyl ester.
2. CAS number	112-39-0
3. Linear formula	$\text{CH}_3(\text{CH}_2)_{14}\text{CO}_2\text{CH}_3$
4. Molecular weight	270.45
5. Refractive index	$n_{20/D}$ 1.4512 (lit.)
6. Boiling point	185 °C/10 mmHg (lit.)
7. Melting point	29-35 °C (lit.)
8. Density	0.852 g/mL at 25 °C (lit.)
9. Allergen	no known allergens
10. Flash point	235.4 °F (113 °C)
11. Personal Protective Equipment	Eyeshields, Gloves, type N95 (US), type P1 (EN143) respirator filter.

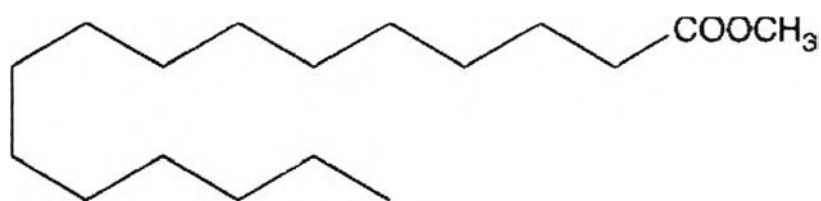


Figure 2.10 The molecular structure of methyl palmitate.

2.5 Microemulsions

Microemulsions are emulsions which are generally transparent, clear and isotropic liquid mixtures of oil, water and surfactant or mixtures of surfactant. The water (aqueous) phase may contain salt or other ingredients, and the oil phase may actually be a complex mixture of different hydrocarbons and olefins. In addition,

the surfactant molecules may form a monolayer at the interface between the oil and water, with the hydrophobic tails groups of the surfactant molecules dissolved in the oil phase and the hydrophilic head groups in the aqueous phase. The important thing is that microemulsions should be in thermodynamically equilibrium. The reason why microemulsions are thermodynamically stabilized is that the oil-in-water dispersion is stabilized by the presence of surfactant and their formation involves the elastic properties of the surfactant film at the oil/water interface which involves parameters such as the curvature and the rigidity of the film. These parameters may depend on pressure, temperature, and/or the salinity of the aqueous phase which may be used to infer the region of stability of the microemulsions, or to describe the region where three coexisting phases occur. The differences between emulsions and microemulsions are particle sizes and stability; i.e., kinetically stable and thermodynamically stable. Microemulsions can be classified into two types which are microemulsions and macroemulsions. The difference between microemulsions and macroemulsions is size of droplet which the former is in the droplet less than 100 nm in diameter but the latter is more than 400 nm in diameter. Moreover, the microemulsions must be thermodynamically stable but the macroemulsion is not (only kinetically stable).

Microemulsions, like micelles, are considered to be lyophilic, stable, colloidal dispersions (Holmberg *et al.*, 2002). Some systems add a fourth component called co-surfactant to an oil/water/surfactant system that can cause the interfacial tension to drop to near-zero values, easily on the order of $10^{-3} - 10^{-4}$ mN/m, allowing spontaneous or nearly spontaneous emulsification to very small drop sizes, typically about 10–100 nm, or smaller. The droplets can be so small that they scatter little light, so the emulsions appear to be transparent. Unlike coarse emulsions, microemulsions are thought to be thermodynamically stable: they do not break on standing or centrifuging. The thermodynamic stability is frequently attributed to a combination of ultra-low interfacial tensions, interfacial turbulence, and possibly transient negative interfacial tensions (Schramm, 2005).

The systems of microemulsions may be water continuous (O/W) or oil continuous (W/O) as shown in Figure 2.7. In the Oil-in-Water (O/W) microemulsions, there is a continuous phase of water containing unconnected

droplets of the oil phase. The O/W microemulsions will exhibit the ability to wet hydrophilic surfaces on contact and will exhibit electrical conductivities characteristic of an aqueous phase. On the other hand, The W/O microemulsions will exhibit the ability to wet hydrophobic surfaces on contact and will exhibit electrical conductivities characteristic of the oil phase. When the volume of oil and water in the microemulsions are approximately equal, the microemulsions may have a bicontinuous structure (Holmberg *et al.*, 2002).

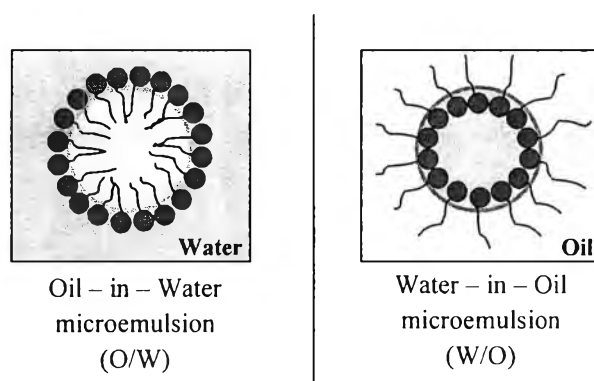


Figure 2.11 Illustration of the Oil in Water (O/W) and the Water in Oil (W/O) microemulsions.

There are four types of the Winsor-Type microemulsions which are the most studied phase equilibria of microemulsions as shown in Figure 2.12.

2.5.1 Winsor's Type I

This type is an Oil-in-Water microemulsions in equilibrium with excess oil.

2.5.2 Winsor's Type II

It shows Water-in-Oil microemulsions in equilibrium with excess water.

2.5.3 Winsor's Type III

This type shows middle phase microemulsions in equilibrium with an excess of both water and oil.

2.5.4 Winsor's Type IV

It is a single phase microemulsions.

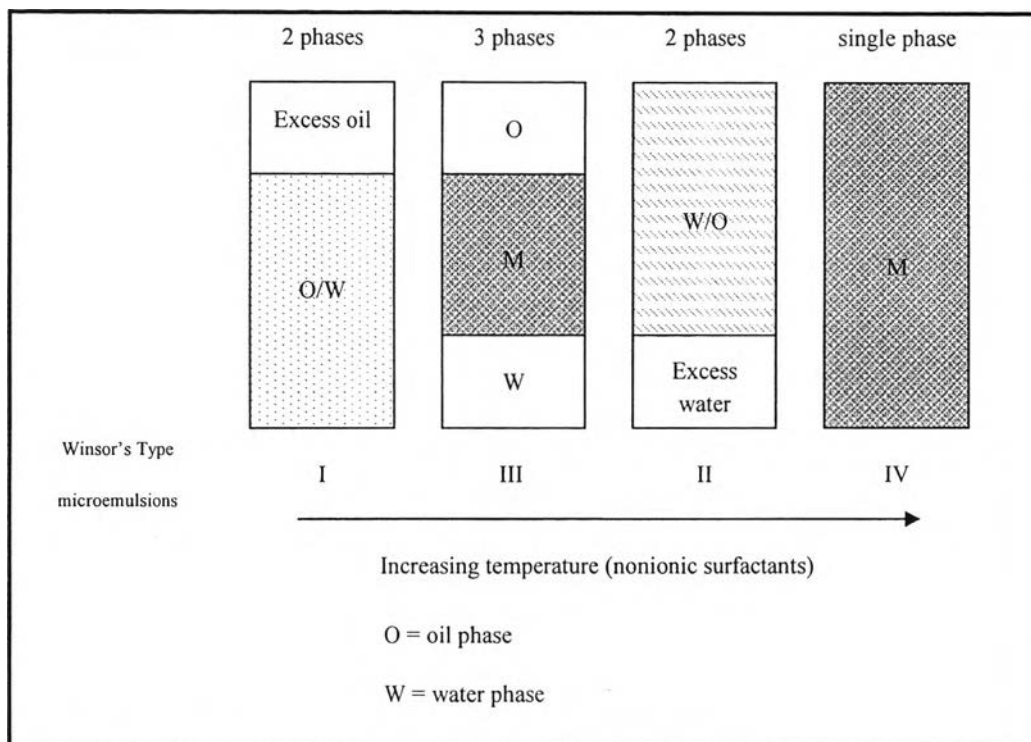


Figure 2.12 Winsor classification and phase sequence of microemulsions encountered as temperature for nonionic surfactant.

For nonionic surfactant, a transformation in the system from Winsor's Type I to Type III to Type II can be achieved by progressively changing temperature, the molecular structure of the surfactant and cosurfactant, the oil-to-water ratio, or the structure of oil in a homologous series.

For a given chemical system, phase-type diagrams can be constructed that show the regimes in which each type of microemulsions will exist. These can be used to understand and predict the effects of, for example, increasing salinity or temperature, which tend to shift the microemulsions type directionally from Type I to Type III to Type II. Type III microemulsions can be thought of as bi-continuous in which the aqueous and oil phases are mutually intertwined.

The transition of Winsor's Type I-III-II influences the two interesting properties of microemulsions which are solubilization and interfacial tension (IFT), due to the changing of the microstructure. Figure 2.13 shows the relationship between the type of microemulsions and the interfacial tension.

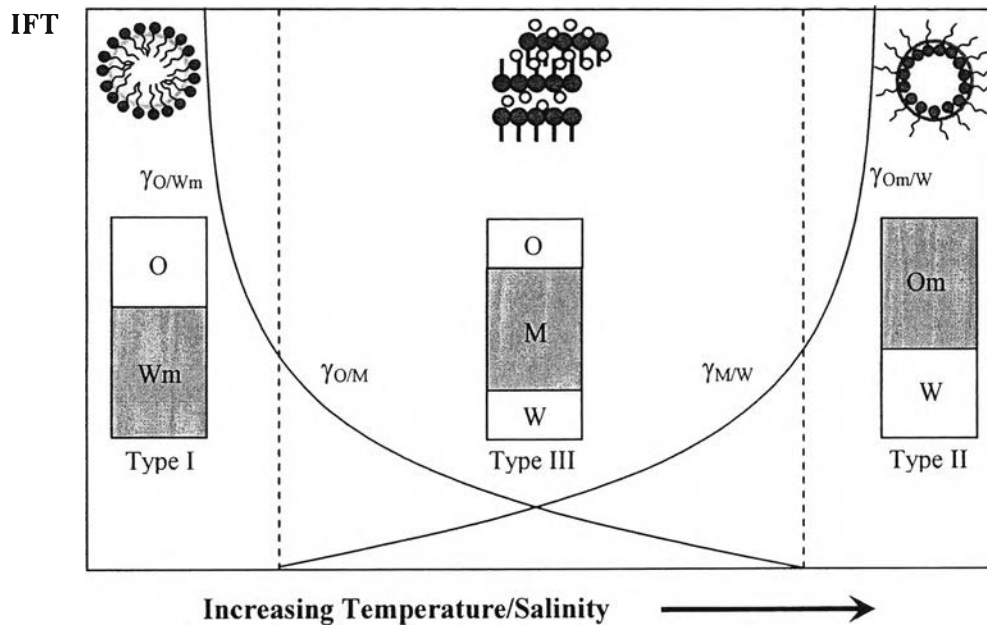


Figure 2.13 Phase behavior showing interfacial tension (IFT) as a function of scanning variables. Where O is oil; W is water; M is middle phase; Wm is Oil-in-Water (O/W) microemulsions; Om is Water-in-Oil (W/O) microemulsions.

The region on the left hand side of Figure 2.13 is Winsor's Type I where Oil-in-Water (O/W) microemulsions exist along with an excess oil phase. IFT between the excess oil phase and the micellar solution ($\gamma_{o/m}$) decreases with increasing temperature or salinity. When the middle phase is formed, the microemulsions become a bicontinuous structure in equilibrium with excess of both oil and water phases. IFT between the excess oil and the middle phase ($\gamma_{o/m}$) further decreases with increasing temperature of salinity while IFT between the excess water and the middle phases ($\gamma_{w/m}$) is increased. The point in the Type III region where $\gamma_{o/m}$ equals to $\gamma_{w/m}$ is known as the minimum IFT or optimum state.

Microemulsion applications span many areas including enhanced oil recovery, soil and aquifer decontamination and remediation, foods, pharmaceuticals

(drug delivery systems), cosmetics, and pesticides. The widespread interest in microemulsions and use in these different industrial applications are based mainly on their high solubilization capacity for hydrophilic and lipophilic compounds, their large interfacial areas, the ultra-low interfacial tensions achieved when they coexist with excess aqueous and oil phases, and their long-term stability.

2.6 Zeta Potential

Zeta Potential (ζ) is the value of electrical potential difference between the surrounding solution and the layer of solution which attached to the dispersed particle. It can be used to indicate the charge stability of colloidal dispersions by applying an electric field across the liquid suspension and measuring their average velocity via the mobility of particles. For high value (positive or negative) of zeta potential, it means that the colloidal dispersion system is quite stable or disperses well while low value (positive or negative) of zeta potential or approach zero means that the colloidal dispersion system tends to aggregate as in Figure 2.14.

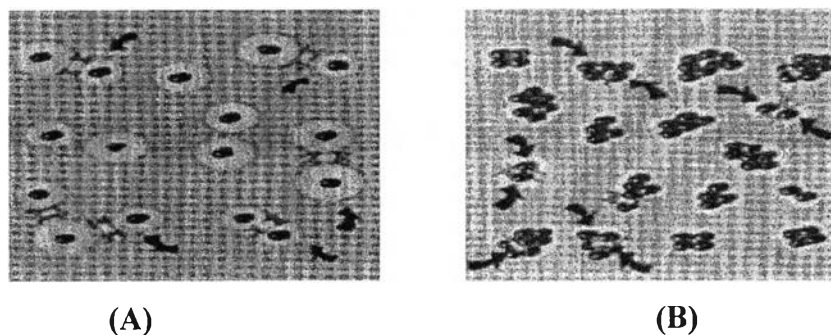


Figure 2.14 A) Particle disperses well and B) Particle aggregation.

The factors affect the zeta are the changing in the pH of solution, the conductivity of the medium, and the concentration of a particular additive in contact with the molecules. At low pH, the solution consists of positive charge from H^+ . Therefore, the zeta potential tends to be positive value. At the isoelectric point which has balancing in positive and negative charge, so the zeta potential tends to be zero.

In case of high pH, the zeta potential tends to be negative value as show in Figure 2.15.

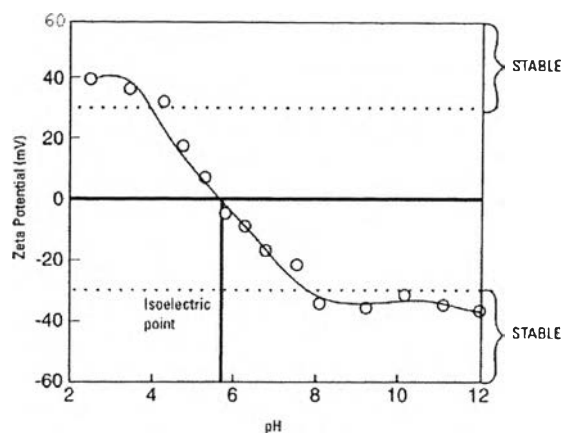


Figure 2.15 A plot of the zeta potential measured as a function of pH.

2.7 Mechanism of Oily Soil Removal

There are several mechanisms in oily soil removal. However, the three primary mechanisms with the used of surfactants are roll-up mechanism, emulsification (or snap-off mechanism), and solubilization.

2.7.1 Roll-up Mechanism

Roll-up or roll-back mechanism is a complete detachment of oily soil from substrate. The mechanism can remove oil droplet with two processes. First, an increase in the contact angle between the oil droplet and the substrate due to reduce in interfacial tension (IFT) between oil and water. Second, the occurrence of the repulsion force between head group of surfactant.

2.7.1.1 *The Increased Contact Angle Process*

This process can be explained by Young's equation which is as follow:

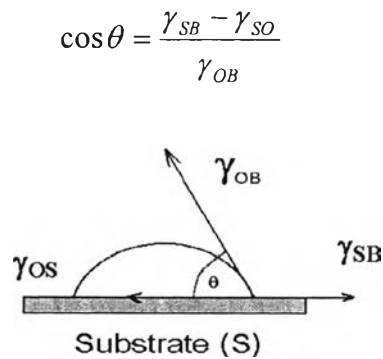


Figure 2.16 The contact angle between an oil droplet and substrate in bath (surfactant solution).

When surfactants are presented in the bath (B) or surfactant solution, they will adsorb at two interfaces. First interface is interface between substrate and bath (SB). Another is interface between oily soil and bath (OB). As the result, the interfacial tension (IFT) between the substrate and the bath (γ_{SB}) and that between oily soil and bath (γ_{OB}) are reduced causing the decrease in $\cos \theta$ and the increase in θ , resulting oily soil detachment from substrate. However, this mechanism will be accomplished when the contact angle is more than 90° . The higher contact angle, the soil is more easily removed (Broze, 1994). If the contact angle is 180° ($\cos \theta = 1$), which means that the soil will be spontaneously completely removed. If the contact angle is between 90° and 180° , the soil must be removed by hydraulic currents in the bath (Figure 2.17). In contrast, if the contact angle is less than 90° , the soil will not be completely removed which there is some part of the soil remaining in the substrate. To remove the residual soil, mechanical work or some mechanical (e.g. solubilization) will be used.

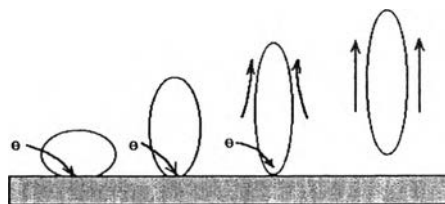


Figure 2.17 Roll-up mechanism shows the complete removal of oil droplets from the substrate by hydraulic currents when $\theta > 90^\circ$ (Rosen, 2004).

2.7.1.2 Surfactant Head Group Repulsion Process

After the surfactants adsorb at substrate-bath interface (SB) and oily soil-bath interface (OB), the head group of surfactants which adsorb at substrate-bath interface repulsing with the head group of surfactants which adsorb at oily soil-bath interface. From this repulsion, the oil droplet can be raised from the substrate. (Figure 2.18)

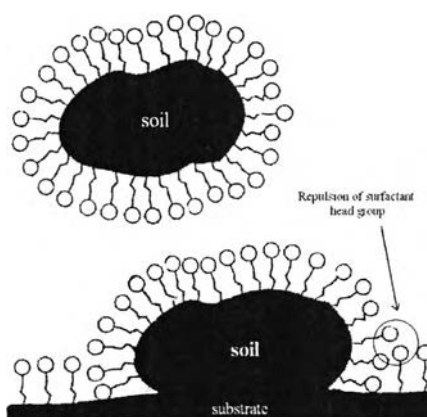


Figure 2.18 Repulsion force of surfactant head group.

2.7.2 Emulsification Mechanism

Emulsification, or snap-off, or necking mechanism, will take place when the contact angle between the oily soil droplet and the substrate is less than 90° . The principle of this mechanism is same as roll-up mechanism but the difference is the contact angle between the oil soil droplet and the substrate. Nevertheless, the disadvantage of this mechanism is that some residual soil remaining on the substrate since the soil/bath interfacial tension is decreased, but the substrate/bath interfacial tension is not changed substantially (Figure 2.19).

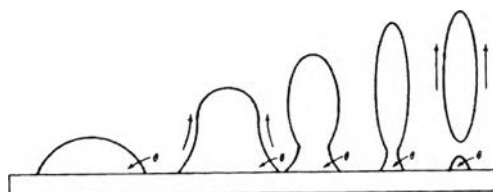


Figure 2.19 Emulsification mechanism shows partial removal of oil droplets from substrate $\theta < 90^\circ$ (Rosen, 2004).

2.7.3 Solubilization Mechanism

Solubilization, or oil uptake capacity, is oil adsorption inside the core of the surfactant micelles. The roles of this mechanism are; (1) remove small amount of residual oil which cannot be removed by roll-up or emulsification and (2) prevent the oily soil from redeposition on the substrate. The solubilization depends on several factors, such as nature of oil and surfactant, surfactant concentration, electrolyte concentration, and temperature. The solubilization will substantially be occurred when the concentration of surfactant solution is above the critical micelle concentration (CMC) where surfactant will form micelles. The capacity of solubilized oil in the micelle core depends on the chemical structure of the surfactant, surfactant concentration, shape of the micelles and temperature. When the surfactant concentration is low, the small amount of oily soil can be solubilized. On the other hand, at high surfactant concentrations (10-100 time the CMC), large amount of oily soil can adsorb in the micelle core which is similar to microemulsion formation (Schwartz, 1972). The difference between solubilization and emulsification is the thermodynamic stability of keeping all the oily soil from redepositing on the substrate which the emulsification cannot prevent all the redeposition of the oily soil on the substrate. An important of solubilization is not only in detergency aspect but also in polymerization, waste water treatment, separation of materials, etc.



Figure 2.20 A) solubilization and B) emulsification.

2.8 Detergency

Detergency is the removal of unwanted substances which called as “soils” from a solid surface by using detergent (surfactant) solution via several mechanisms

of surfactants which adsorb onto the surface. The surfactant has been displayed to enhance the detergency by lowering the interfacial tension (IFT) between the fabric and the wash solution and the oil and the wash solution, emulsification, solubilization, and charge modification in cleaning process in order to remove the soil from the substrate and prevent the removed soil to re-deposit (Tongcumpou *et al.*, 2003 and Phan *et al.*, 2010).

2.9 Soil Re-deposition

As a result of non-continuous processes of almost all cleaning and washing processes, the re-deposition of the removed soils has been occurred several times because the cleaning and washing processes are performed with batch type. So, they always have the probability that the removed soils from the surface of the substrate will re-deposit onto the substrate again due to a lack of stability of colloid in soils dispersion. For oily soils removed by solubilization, the process is thermodynamically driven so that it is essentially a one-way street and re-deposition will be minimal. On the other hand, solid soils cannot be solubilized and re-deposition must be slow down by other kinetically controlled means. Emulsified oily soils, where they occur, must be handled similarly. As showed out earlier, one main role of surfactants at interfaces of solid is to tell a degree of colloidal stability to deeply divided particles in aqueous solutions. The adsorption of ionic surfactants at the solid interfaces produces an electrical double layer that retards the approach of the interfaces and prevents or at least hinders re-deposition.

2.10 Application of Microemulsion for Detergency

Due to the characteristic properties of microemulsion; namely ultralow interfacial tension, high ability for solubilizing 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 as follow.

Solan et al. (1985) reported that high efficiency of soil removal from textile fabrics was found when the surfactant formed the microemulsion which it was compared with a used of a commercial liquid detergent for soil removal.

Azemar et al. (1993) have studied fabric detergent using pure triolein as a triglyceride oil representative. He found that the Winsor type III, middle phase, microemulsion was better for detergency.

Bourrel et al. (1998) reported that the lowest oil/water IFT and highest oil solubilization corresponded to microemulsion formation by using Aerosol OT (dioctyl sulfosuccinate) at 20 °C in 100 ml of 25% (w/v) solution of Aerosol OT in carbon tetrachloride/paraffin mixture.

From Tongcumpou (2002), Korphol (2003), and Pantipa (2004) found that the maximum detergency performance corresponded to the Winsor type III; middle-phase microemulsion, which it was 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.

2.11 Factors Affecting Oily Soil Detergency

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.*, (1998) suggested soil removal from fibrous substrate 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.

2.11.1 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. However, there was little or no difference between two detergents in total oil removal from the polyester/cotton fabric.

The effects of nonionic surfactant and temperature on detergency efficiency were studied by Solan *et al.* (1985) for nonpolar soils (hexadecane, squalene, mineral oil) on polyester/cotton fabric. It was found that the maximum detergency efficiency corresponded with the phase inversion temperature (PIT). Moreover, they reported that the optimum temperature was increased when the degree of ethoxylation of the surfactant increased.

The effect of ethoxylation numbers in nonionic surfactant to soil removal was also studied by Wormuth *et al.* (1991). They found that the oily soil removal was influenced by the ethoxylation numbers in nonionic surfactant because when the ethoxylation numbers of the C₁₂₋₁₄ alkylpolyglycol ether was increased, the solubilization power of surfactant decreased which resulting the decrease in oily soil removal.

The advantages of using surfactant mixtures were reported by Ogino *et al.* (1992). They found that mixed surfactant systems generally exert greater than single surfactant systems for enhancing of solubilization. However, this enhancement does not apply to all mixed system.

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 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 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 correspond the maximum 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 can be 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 can be 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 is 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 can 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.

2.11.2 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, 1963; Morris *et al.*, 1982). They conducted that residual oily soil contains 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 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.* (1999) found that highly unsaturated oily soil was easily oxidize 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.

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

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

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).

2.11.4 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 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. 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 soil.

2.11.5 Water Hardness

Hard water affects detergency in several ways. Incomplete soil removal normally occurs when hard water is used in detergency (laundry) (Tanthakit, 2009).

The presence of polyvalent cations, notably Ca^{2+} and Mg^{2+} , in the bath water is invariably detrimental to the cleaning process for a number of reasons (Rosen, 2004):

2.11.5.1 Adsorption of polyvalent cations onto the negatively charged substrate and soil reduces their electrical potentials, thus impeding soil removal and facilitating its redeposition. The detrimental effect attributed to this has been noted also in the detergency studied involving only nonionic surfactants.

2.11.5.2 Polyvalent cations can act as linkages negatively charge substrate and negatively charged soil, thus promoting soil redeposition. They can also act as linkages between the negatively charged hydrophilic groups of anionic surfactants and the negatively charged soil or substrate, causing adsorption of the former with their hydrophilic groups oriented toward the latter and their hydrophobic groups toward the bath. Adsorption with this orientation results in increases in the interfacial tensions at the substrate-bath and soil-bath interfaces, increasing in work of adhesion and impeding wetting and oily soil roll back.

2.11.5.3 Adsorption of polyvalent cations onto solid soil particles dispersed in the bath can reduce their (negative) electrical potentials and cause them to flocculate and redeposit onto the substrate.

2.11.5.4 At high polyvalent cation concentrations, the corresponding metal salts of anionic surfactants and other anions (e.g., phosphates, silicates) in the bath may precipitate onto the substrate. (Rutkowski, 1971) or produce other deleterious effects (Vance, 1969).

Prevention of soil re-deposition can be done by adding of anti-soil re-deposition agent such as sodium carboxymethyl cellulose into the detergent. This agent can prevent the removed soil to redeposit back onto cleaned fabric by formation of barrier between suspended soil and cleaned fabric electrostatic repulsion for ionic surfactant and stearic hindrance for nonionic surfactants (Fong *et al.*, 1953).

2.11.6 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. They reported that 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, but its concentration in 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.

Webb *et al.* (1988) reported that builder is another influencing factor for enhancing the cleaning efficiency.