CHARPER II
THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Microemulsion

Microemulsion is one type of emulsion, miscibility or suspension a liquid in a second immiscible liquid with a role of emulsifying agent, which it is classified by depending on the size of the dispersed particles (the particles that are dispersed in another liquid). Microemulson has the size of dispersed particles < 100 nm (0.1 μm). At this research work, two immiscible liquid are oil and water, the emulsifying is surfactant.

Several special characteristics are present in microemulsion:

(1) Ultralow interfacial tension (water-oil interfacial tension ≈ 10^{-3} mN/m which is lower than ordinary water-oil interfacial tension)

(2) High Solubilization (the numbers of oil can be hold in micelle, clusters of surfactant, to prevent oil redeposition)

(3) Spontaneous Formation (requiring little or no input of mechanical energy for microemulsion formation)

(4) Thermodynamic Stability

(5) Optically Clear Appearance

(6) Low Viscosity

As a result of these special characteristics, uses and applications of microemulsion have been increased for supplying of the world. The application of microemulsion is not only in detergency aspect but also in several aspects such as enhanced oil recovery, coatings and textile finishing, cosmetics, food, pharmaceuticals, etc.(Kumar et al.)

2.1.1 Type of microemulsions

Microemulsions can be classified into four types which base on phase equilibrium (Winsor, 1954);

1. Winsor Type I: There are two phases in this type which consists of oil in water (o/w), oil droplets (discontinuous or inner phase) disperse in the water phase (continuous or outer phase), can be in equilibrium with an excess oil phase. Surfactant is preferentially soluble in water.

2. Winsor Type II: Two phases are present in this type. Water in oil (w/o), water droplets (discontinuous or inner phase) disperse in the oil phase (continuous or outer phase), can be in equilibrium with an excess water phase. Surfactant is preferentially soluble in oil.

3. Winsor Type III: This type consists of three phases. The middle phase (oil, water, and surfactant) can be in equilibrium with both excess of water and oil phases.

4. Winsor Type IV: This type has only one phase (single phase). Oil, water, and surfactant are homogeneously mixed.

2.2 Phase Behavior and Microemulsion Formation

In the phase transition behavior and mocroemulsion formation are controlled by the hydrophile-lipophile balance (HLB) of the system. It means that to achieve a microemulsion, the HLB of the system must be changed to be suitable for forming that microemulsion. The HLB is the balance between the hydrophilic and lipophilic (hydrophobic) portions of surfactant. There are several factors that influence the HLB alteration; (1) type of surfactant and that of oily soil (each surfactant and oily soil have an individual HLB). (2) Electrolyte concentration or Salinity (This factor is always used for ionic surfactant system. When the salinity is increased, the HLB decrease because reduction of the electrical interaction of the ionic head group can cause the surfactant to change from hydrophilic to lipophilic. On the other hand, if the salinity is decreased, the HLB increase). (3). Temperature (Temperature can often affect nonionic surfactant system. If the temperature is raised, the HLB decrease due to the increased dyhydration of POE chains which increases the lipophilic. In contrast, the temperature is lowered, the HLB increase). (4). Present of cosurfactants (If a system has two or more two surfactants (which have the different HLB), the HLB of cosurfactants system will be different from the HLB of single surfactant).

As known the HLB can control the phase transition behavior and micriemulsion formation. At high HLB values, or low salinity or low temperature, (Fig 2.1 and 2.2 left side) the surfactant is hydrophilic and is preferably 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 or Wm or an O/W (oil-in-water) microemulsion. With further decrease in LB or further increase in temperature and salinity, the POE chain nonionic surfactant become more and more dehydrate or head group of ionic surfactant become more and more repulse, the surfactant become more lipophilic causing the volume of the aqueous phase Wm increase and that of the oil phase decrease and a decrease in IFT between oil and water interface (IFT $_{O/Wm}$). (Figure 2.2 left side)

If the HLB is still decreasing or temperature or salinity is still increasing, the system will separate into three phase: an excess water phase (W) with low surfactant concentration, a middle phase (M) or microemulsion phase, and excess oil phase (O) with low surfactant concentration. This system is known as winsor type III microemulsion. (Figure 2.1 middle) The IFT in the region of the middle phase or winsor type III is often as low as 10^{-3} mN/m, so- -called ultralow IFT. The lowest value of IFT where the IFT between the excess oil phase and the middle phase (IFT $_{O/M}$) equals the IFT between the middle phase and the excess water phase (IFT $_{M/W}$) (Figure 2.2 middle), is known as the optimum interfacial tension. In a nonionic surfactant system, the temperature that can product the optimum interfacial tension knowing as the phase inversion temperature (PIT). For the anionic surfactant system, the salinity that can make the optimum interfacial tension knowing as optimum salinity.

If the HLB continues to decrease or temperature or salinity continues to increase. The surfactant becomes more and more lipophilic and it is preferably in the oil phase. At this point the micelles start to invert and dissolve in the excess oil causing the volume of the oil phase (Om) increase and that of aqueous phase (W) decrease, the middle phase disappears, and a increase in IFT between oil and water interface.(Figure 2.1 and 2.2 right side)

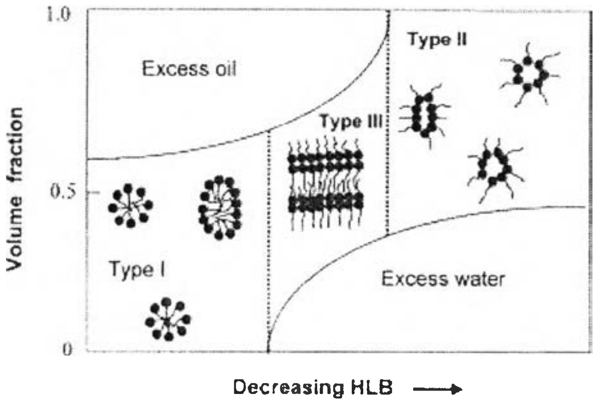

Figure 2.1 Correlation between Typical phase behavior of microemulsion and HLB.

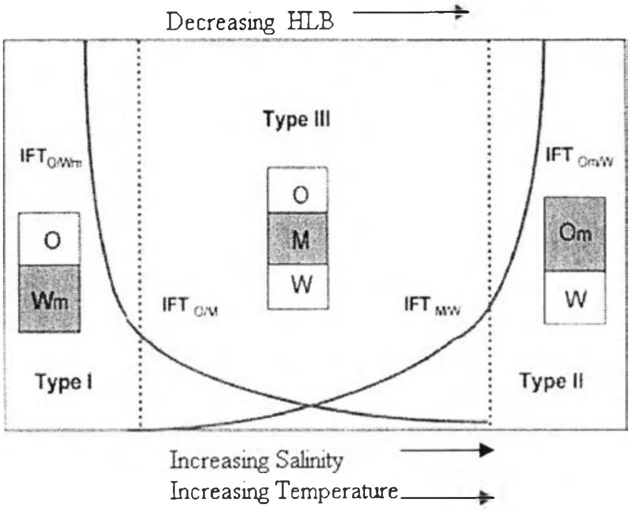

Figure 2.2 Correlation between interfacial tension (IFT) and HLB, Salinity, Temperature.

2.3 Mechanism of Oily Soil Removal

There are several mechanisms in oily soil removal. However, the three primary mechanisms—roll-up, emulsification, and solubilization—were well accepted (Verma et al., 1998; Rosen, 2004)

1. Roll-up Mechanism

Roll-up or roll-back mechanism is 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.

1.1 The increased contact angle process

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

$$\cos\theta = \frac{\gamma_{SB} - \gamma_{SO}}{\gamma_{OB}}$$

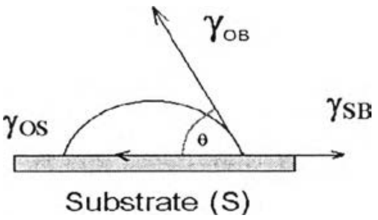

Figure 2.3 The contact angle between an oil droplet and substrate in bath (surfactant Solution).

When surfactants are present 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 θ 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 θ =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 3.2). 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.

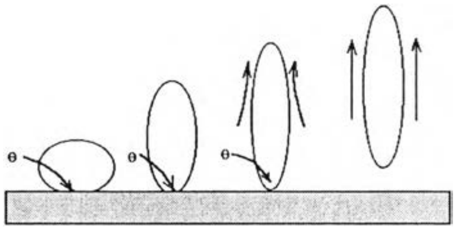

Figure 2.4 Roll-up mechanism shows the complete removal of oil droplets from the substrate by hydraulic currents when θ > 90° (Rosen, 2004).

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 3.3)

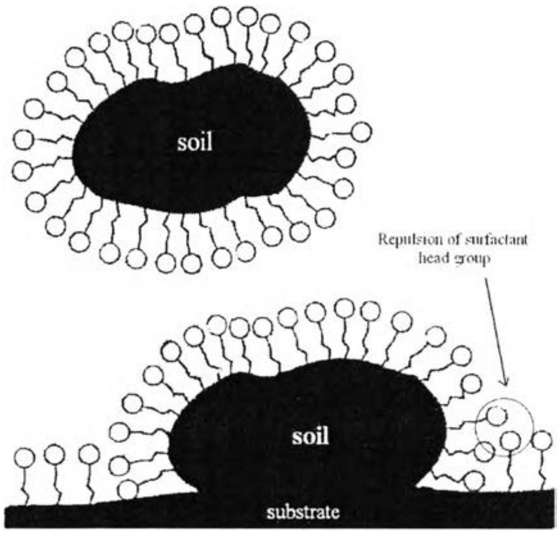

Figure 2.5 Repulsion force of surfactant head group.

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 a 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 some residual soil remaining on the substrate since the soil/bath interfacial tension is decreased, but the substrate/bath interfacial tension is not change substantially (Figure 3.4).

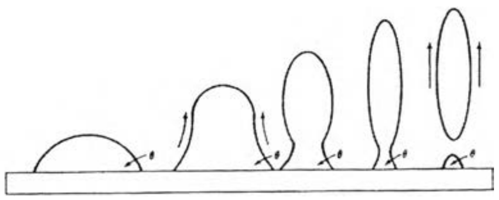

Figure 2.6 Emulsification mechanism shows partial removal of oil droplets from substrate $\theta < 90°$ (Rosen, 2004).

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) removal small amount of residual oil which cannot be removed by roll-up or emulsification and (2) prevention 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 occur when the concentration of surfactant solution are 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.

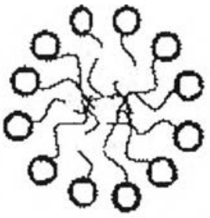

Figure 2.7 Solubilization.

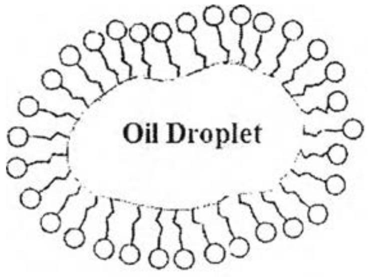

Figure 2.8 Emulsification.

2.4 Application of Microemulsion for Detergency

Due to the characteristic properties of microemulsion namely, ultralow interfacial tension, high ability for solibilizing 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;

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 is a better for detergency.

The lowest oil/water IFT and highest oil solubilization correspond to microemulsion formation which Bourrel et al., (1998) used Aerosol OT (di-octyl sulfosuccinate) at 20°C in 100 ml of 25% (wt/vol) solution of Aerosol OT in carbon tetrachroride/paraffin mixture.

The maximum detergency performance corresponds to the winsor type III, middle phase, microemulsion, which it is 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.(Tongcumpou, 2002; Korphol, 2003; and Pantipa, 2004)

2.5 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.

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. (1988) 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 C_{12-14} 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 corresponding the maxima in detergency.

In 2003, Tongcumpou et al. found that the formulation of microemulsion by mixed surfactant system of sodium dioctyl sulfosuccinate (AOT, a surfactant of intermediate HLB), alkyldiphenyloxide disulfonate (ADPODS, very hydrophilic surfactant), and sorbitan monooleate (Span 80, very hydrophobic surfactant) with motor oil and hexadecane 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. 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 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 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.

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

4. Substrate

The performance relating to soil removal is influenced markedly by the nature of the substrate (Christ *et al.*, 1994). Recently, Chi (2001) investigated the effect of the substrate on the removal of unaged oily soil and found it was higher for nylon than cotton or polyester. Squalene, a nonpolar hydrocarbon, was difficult to remove from polyester, a nonpolar substrate. On the other hand, cotton, a very polar substrate from polyester, a nonpolar substrate, might be expected to release oily soil fairly well in an aqueous detergent system, but this was not the case. 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.

5. Water Hardness

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

The presence of polyvalent cations, notably Ca2+ and Mg2+, in the bath water is invariably detrimental to the cleaning process for a number of reasons (Rosen, 2004):

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 (Porter, 1967; Schwuger, 1971).

5.2 Polyvalent cations can act as linkages negatively charge substrate and negatively charged soil, thus promoting soil redeposition (deJong, 1966). 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.

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.

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; Brysson, 1971).

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.