CHAPTER II

THEORETICAL BACKGROUND AND LITERATURE REVIEWS

2.1 Surfactant Structures

The word *surfactant* is short for “surface-active agent”. The term is literally descriptive because a surfactant does in fact concentrate at the boundaries between two immiscible phases: air-water interfaces, soil-solvent interfaces and fabric-water interfaces. Basically, the molecular structure of surfactants consists of two parts: a water-soluble part (called the hydrophilic, “Head group”) and an oil-soluble part (called the hydrophobic or lipophilic, “Tail group”), as shown in Figure 2.1. Accordingly, the surfactant molecules orient themselves in such a way that the hydrophilic portion of the molecule is associated with the more hydrophilic phase of the interface while the hydrophobic portion of the molecule associates with the hydrophobic phase of the interface (Rosen, 1989 and Lance, 1994). Surfactants also have the property of forming colloid-sized aggregates in a solution called micelles at sufficient high concentrations. The lowest total surfactant concentration at which micelles are present is called critical micelle concentration (CMC).

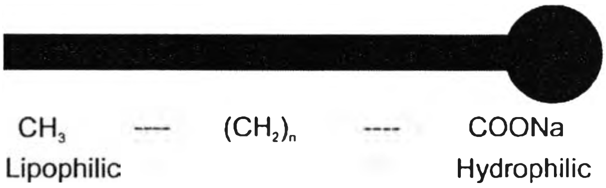

Figure 2.1 surfactant structures (Ellis *et al.*, 2005).

Generally, the hydrophobic part is a long-chain hydrocarbon but it may contain aromatic. For the hydrophilic part carries a positive or negative charge, giving rise to cationic or anionic surfactants, respectively otherwise it contains ethylene oxide chains, sugar or saccharine group, as in the case of nonionic surfactants (Goddard and Ananth, 1993). Based on the charge present in the hydrophilic group, surfactants can be categorized in to 4 types.

1. *Anionic surfactant.* The hydrophilic portion has a negative charge, for example, $RCOO^-Na^+$ (soap), and $RC_6H_4SO_3^-Na^+$ (alkyl benzene sulfonate).

2. *Cationic surfactant.* The hydrophilic portion has a positive charge, for example, $RNH_3^+Cl^-$ (salt of a long-chain amine), and $RN\ (CH_3)_3^+Cl^-$(quaternary ammonium chloride).

3. *Nonionic surfactant.* No charge presents in the hydrophilic portion, for example, $RCOOCH_2CHOHCH_2OH$ (monoglyceride of long chain fatty acid), and $RC_6H_4\ (OC_2H_4)_xOH$ (polyoxyethylenated alkylphenol).

4. *Zwitterionic surfactant.* Both positive and negative charge may be present in the hydrophilic portion which leads to the head group hydrophilicity being an intermediate between the ionic and conventional nonionic classes. The charge depends on pH of solution. At low pH (acidic solution), they form cations, and at high pH (alkaline solutions), they form anions. For example, $RN^+H_2CH_2COO^-$ (long chain amino acid), and $RN^+(CH_3)_2CH_2CH_2SO_3$ (sulfobetaine).

2.1.1 Anionic Surfactants

2.1.1.1 Sodium Dodecyl Sulphate

Sodium dodecyl sulphate (SDS) is one of the most well-known anionic surfactants used in many cleaning products. The structure of SDS consists of a 12-carbon tail attached to a sulfate head group, as shown in Figure 2.2

Figure 2.2 Sodium dodecyl sulphate (SDS) structure.
(http://en.wikipedia.org/wiki/Sodium_dodecyl_sulfate)

2.1.1.2 Linear Alkyl Benzene Sulphonate

Nowadays, linear alkyl benzene sulphonate (LAS) is a widely used surfactant in all cleaning and detergent products. It is not only the most efficient (cost-performance ratio) and versatile, but also the safest from both environmental and human health points of view. LAS is derived from petroleum-based stocks. The structure of LAS is shown in Figure 2.3.

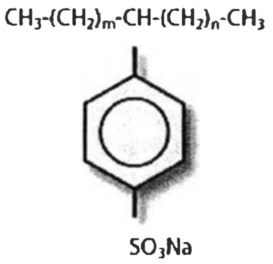

Figure 2.3 Linear alkyl benzene sulphonate (LAS) structure (http://www.lasinfo.org/w_las_nut.html).

2.1.1.3 Methyl Ester Sulfonate

Methyl ester sulfonate (MES), a new type of anionic surfactant, is an attractive one because it is synthesized from oleo chemical feedstocks (natural fats and oils) and their hydrophobic part is a long alkyl chain (C14-C18) of methyl ester fatty acid, as shown in Figure. 2.4. Major sources for the MES production are palm kernel oil and coconut oil. Many researchers reported that MES based-surfactant systems have numerous outstanding properties for detergent and personal care applications such as good solubility, excellent biodegradability, high compatibility with enzymes and high tolerance to water hardness than high-molecular-weight LAS or alcohol sulfates. (Cohen *et al.*, 2001)

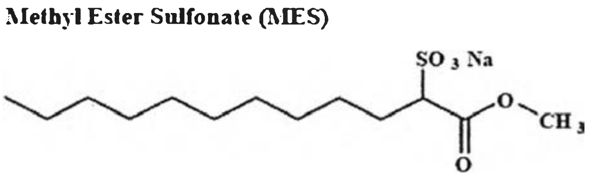

Figure 2.4 Methyl ester sulfonate (MES) structures (Okumura, *et al.*, 1976).

Okumura *et al.* (1976) studied the mechanism of the sulfonation of fatty acid esters with sulfur trioxide and the properties of alpha-sulfo fatty acid esters. They found that MES had an excellent resistance to water hardness. Moreover, MES with carbon chains C14 to C18 showed good detergency.

Satsuki *et al.* (1992) studied the detergency performance of α-sulfo fatty acid methyl esters (α-SFME) compared to a conventional anionic surfactant under various washing conditions by using a model heavy duty detergent formulation. Several physicochemical properties of α-SFME surfactants were investigated in order to correlate to the effective factors on detergency. The results showed that α-SFME exhibited good detergency performance under various washing conditions due to the higher adsorption, the better dispersing and solubilization ability as well as the better emulsification of oil. All of these were considered as an important factor in washing performance. The solubilization ability was found to depend on the molecular structure and micelles properties of surfactants. α-SFME could form suitable micelles which are effective in solubilizing polar oils due to its bulky hydrophilic groups.

Cohen *et al.* (2001) studied the use of MES for hand dishwashing formulations by mixing MES with others types of surfactants such as linear alkylbenzene sulfonate (LAS), alkyl ether sulfate (AES), and alcohol ethoxylate (AE). The results showed that the hand dishwashing formulation containing MES exhibited the best performance even in high water hardness. Moreover, it showed good properties including solubility, foam stability, and skin compatibility.

Lim *et al.* (2002) studied the dishwashing performance in mixed surfactant systems of α-sulfonated methyl esters derived from palm stearin (α-SMEPS) and three types of polyoxyethylene sorbitan esters (POESE) with different hydrophobic chain lengths [polyoxyethylene (20) sorbitan monolaurate (12:1), polyoxyethylene (20) sorbitan monostearate (18:0), polyoxyethylene (20) sorbitan monooleate (18:1)] at different α-SMEPS/POESE ratios, water hardness values (5.12, 51.2, and 512.0 ppm $CaCO_3$) and temperatures (20, 30, 45, and 65°C). They obtained that the mixed surfactant systems could enhance the cleaning performance caused by the energetically favored as compared to the individual surfactants. The detergency performance increased in the following order: α-SMEPS/POESE (12:1) < α-SMEPS/POESE (18:1) < α-SMEPS/POESE (18:0). Because of the α-SMEPS/POESE (18:0) systems had a high affinity to dissolve oily components caused by the hydrophobic portion of POESE (18:0). For a mixed surfactant system with a ratio of 80:20, increasing temperature improved the cleaning efficiency and a temperature of 65°C showed the best synergistic effect. This is mainly because, at that temperature, all the oily soil was fully liquidized. The cleaning efficiency is governed by the roll-up, emulsification, and solubilization. In the presence of water hardness, an addition of electrolyte in the surfactant solution also enhanced the surfactant adsorption at the interface and modified the surfactant species solubility due to the inverse in ionic strength. The experimental results clearly showed that a small amount of water hardness (5.12 ppm $CaCO_3$) was necessary for detergency improvement but a further increase of water hardness (51.2 and 512.0 ppm $CaCO_3$) decreased the detergency performance severely because the hardness ions diminish the solubility of α-SMEPS.

Lim *et al.* (2004) further studied the dishwashing performance in mixed surfactant systems of sulfonated methyl esters derived from palm stearin and three types of nonylphenol ethoxylate alcohol (NPEO) with different ethoxylate hydrophilic lengths—9.5 (NPEO 95), 12 (NPEO 120), and 40 (NPEO 400)— along with several parameters, such as the weight ratio of α-SMEPS-to-NPEO, washing temperature, and water hardness. The results show that the presence of NPEO (95, 120, and 400) in α-SMEPS solution reduced the Kraft temperature and produced lower foaming as compared to α-SMEPS alone. Nevertheless the dishwashing performance of almost all mixed surfactant systems of α-SMEPS and NPEO (95, 120, and 400) was lower than the α-SMEPS system as a result of the steric hindrance among the long hydrophilic chains of the NPEO surfactant adsorbing on the soil surface, further reducing the competition among the surfactants (especially α-SMEPS) to adsorb onto the soil. However, the detergency performance of α-SMEPS/NPEO mixtures can be enhanced by increasing washing temperature. On the other hand, the cleaning efficiency can be diminishing by increasing water hardness. Among the three mixed systems, detergency efficiency increased as follows: α-SMEPS/NPEO 400 < α-SMEPS/NPEO 120 < α-SMEPS/NPEO 95, indicating that the mixtures of α-SMEPS with short oxyethylene chains (EO) of NPEO have better washing power.

Maurad *et al.* (2006) studied the performance of powder detergents (PPD) formulated with sulfonated methyl ester (SME). The results showed that a total concentration of 0.8 g/L which contained 12 to 18% SME exhibited excellent detergency compared to commercial detergency with 27% surface-active agent. In addition, the foaming power and wetting characteristics of PPD were also comparable. Moreover, PPD was found to be able to biodegraded faster than the commercial detergent.

2.1.2 Nonionic Surfactants

2.1.2.1 Octylphenol Ethoxylate (Trade name; Triton X-100)

Octylphenol ethoxylate (TritonX-100) consists of a hydrophilic polyethylene oxide group (an average 10 ethylene oxide groups per molecule) and a hydrocarbon lipophilic or hydrophobic group. The hydrocarbon group is a 4-(1, 1, 3, 3-tetramethylbutyl)-phenyl group. Triton X-100 is a commonly used detergent in laboratories. But it can be found in several types of cleaning compounds ranging from heavy-duty industrial products to gentle detergents. It is also a popular ingredient in homemade vinyl record cleaning fluids together with distilled water and isopropyl alcohol. The structure of Triton X-100 is shown in Figure 2.5

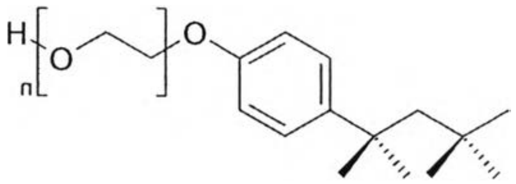

Figure 2.5 Octylphenol ethoxylate (Triton X-100) structures (http://en.wikipedia.org/wiki/Triton_X-100).

2.1.2.2 Alcohol Ethoxylates

Alcohol ethoxylates (AE) are an important class of nonionic surfactants which are widely used in detergent applications because of low price, low to moderate foaming ability, low critical micelle concentrations, high water hardness tolerance, and high solubilization capacity for oily soils, mildness, and good biodegradability. AEs are also used in lesser quantities in household cleaners, institutional and industrial cleaners, cosmetics, agriculture, and in textile, paper, oil and other process industries. The structure of AE is shown in Figure 2.6.

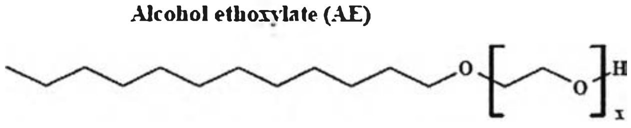

Figure 2.6 Alcohol ethoxylate (AE) structure (http://discovery.kcpc.usyd.edu.au/9.5.5/9.5.5_nonionic.html).

Hama *et al.* (1997) concluded that ethoxylated methyl laurate with 60 to 70% EO content was found to be the most suitable candidate for household detergents.

Goel (2000) studied the phase structure and clouding behavior of tetradecyl ethylene-oxide mono dodecyl alcohol ($C_{12}EO_{14}$), a broad-range ethoxylate, as a function of the concentration of various electrolytes. The results showed that beyond a certain critical concentration, the cloud point decreased monotonically with increasing salt concentration. For sodium salts of various anions, the cloud point depression was inversely proportional to the lyotropic number of the anion. Similarly, for chloride salts of various cations, the cloud point depression was inversely proportional to the lyotropic number of the cation. However, the effect of changing anion was stronger than that of changing cation. The micrograph results of water penetration scans at room temperature indicated the presence of isotropic L1; hexagonal, isotropic L2; and solid phases with increasing surfactant concentration. In the case of low-EO nonionic surfactant, a maximum detergency of model oily soil removal was found to correlate well with the minimum in oil/water interfacial tension when plotted vs. temperature. In addition, Ross Miles foam height increased with increasing concentration of salt.

2.1.3 Cationic Surfactant

2.1.3.1 Cetyl Trimethyl Ammonium Bromide (CTAB)

Cetyl trimethyl ammonium bromide (CTAB) is a common cationic surfactant consists of quaternary ammonium ions which have four carbons bond to a positive nitrogen atom which displays *sp*^{3} bonding. From acid-base perspective, this cationic molecule lacks of both acidic protons and non-bonding electron pairs; therefore, it is neutral in water. If the anionic partner in such a salt is also neither acidic nor basic, as the true of bromide, the molecular structure of this salt is independent of pH (Rubingh and Holland, 1990), as shown in Figure 2.7. Generally, cationic surfactants are often used as fabric softeners because they are attracted to negatively-charged sites that occur naturally on most fabrics which can bind to these sites and provide the fabric with a soft feel.

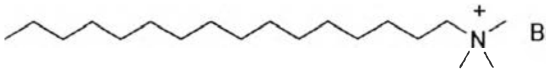

Figure 2.7 Cetyltrimethylammonium bromide (CTAB structure) (http://en.wikipedia.org/wiki/Cetyl_trimethylammonium_bromide).

2.2 Surfactant Adsorption

Surfactant adsorption is a process of surfactant molecules to transfer from the bulk solution phase to the interface. The adsorption of surfactant at the solid-liquid interface plays an important role in many processes such as detergency, wetting, mineral flotation, corrosion inhibition, dispersion of solid, oil recovery and etc. The adsorption of surfactant at solid-liquid interface is strongly influenced by a number of factors; (1) the nature of the structural groups on the solid surface, (2) the molecular structure of the surfactant being adsorbed (the adsorbate), and (3) the environment of the aqueous phase such as pH and electrolyte content (Rosen, 1989).

The adsorption of surfactants at solid/liquid interfaces can be calculated in the terms of "adsorption density", Γ_i, (mol/m^2) as show in the following equation:

$$\Gamma_i = \frac{\Delta c \times V}{m \times a}$$

Where

- Δc (mol/l) is the concentration difference between initial and equilibrium concentrations.
- V (l) is the volume of the liquid phase.
- m (g) is the weight of the adsorbent.
- a (m^2/g) is the specific surface area of adsorbent.

The adsorption isotherm for monoisomeric surfactant was first appeared in the work of Somasundaran and Fuerstenau in 1966. The schematic diagram of a typical adsorption isotherm for monoisomeric surfactant is illustrated in Figure 2.8. The adsorption isotherm can be divided into four distinct regions when plotted on a log - log scale as follows; as shown in Figures 2.8 and 2.9.

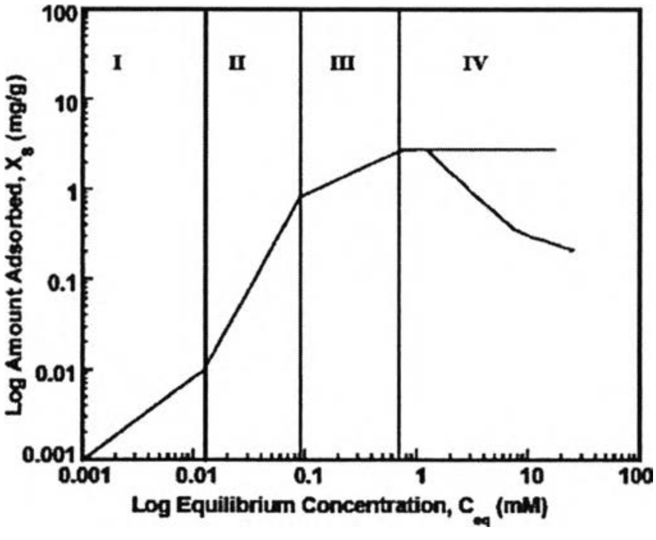

Figure 2.8 Typical four-regime adsorption isotherms (Paria, *et al.*, 2004).

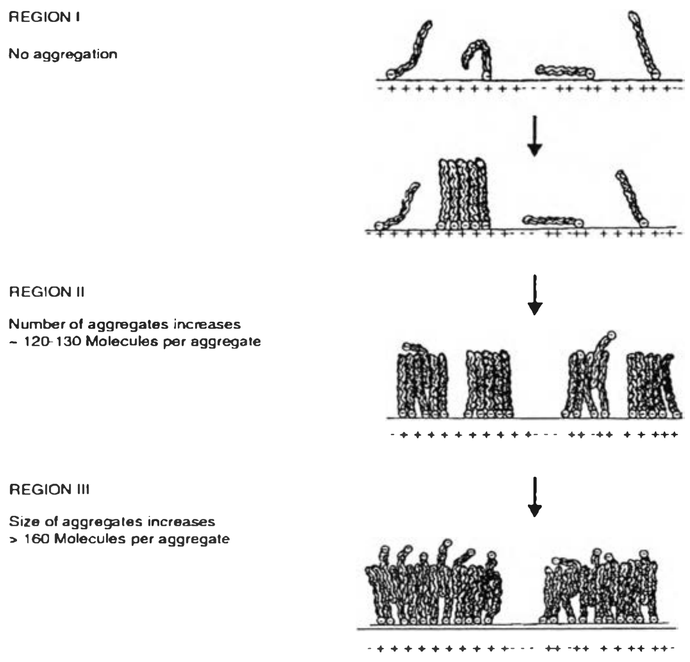

Figure 2.9 Schematic representation of the growth of aggregates of sodium dodecyl sulfate (SDS) at the alumina–water interface. (Somasundaran, *et al.*, 1999).

Region I: The adsorption occurs at a very low surfactant concentration and it is commonly referred as the Henry's Law region due to the mono isomeric surfactant isotherms are linear and have a slope of unity (Somasundaran *et al.*, 1987). In this region, surfactants adsorb at the interface as individual ions and the adsorption occurs by ions exchange of counter ions. Under constant ionic strength, the adsorption occurs through the electrostatic interaction between the oppositely charge between solid surface and surfactants (Scamehorn *et al.*, 1982).

Region II: The adsorption in this region is characterized by a sharply increased isotherm slope relative to the slope in the Henry's Law region. This is a general indication of the onset of cooperative effect between adsorbed molecules. It is widely accepted that this cooperative consists of the formation of micelle-like aggregates of adsorbed surfactants. These aggregates are frequently called admicelles or hemimicelles and self-assemblies (Harwell *et al.*, 1987), depending on whether their morphology is viewed as local bilayers or local monolayer, and the transition point from Region I to Region II is called the critical admicelle concentration (CAC) or hemimicelle concentration (HMC). As the driving force for micelle formation is the tail-tail interactions in the micelles, so for admicelles and hemimicelles their formation is driven by hydrophobic interactions between tail groups. In this region, the surface is not completely covered and enough sites on the surface are available for further adsorption.

Region III: In this region, the adsorption is characterized by a decrease in the isotherm slope relative to the slope in Region II because of the increasing in electrostatic hindrance to surfactant adsorption causing the surface becomes like-charged to the surfactant and the surface beings to repel the surfactant ions. In addition, the adsorption in this region occurs through the growth of exiting aggregates rather than the new aggregates formation of surfactants due to lack of adsorption sites.

Region IV: In this final region, the adsorption isotherm reaches a plateau region corresponding to the maximum surface coverage. Generally, the region III/region IV transition occurs approximately at the CMC of surfactant, and reflects the effect of micelle formation on the chemical potential of surfactant monomer, just as the formation of micelle affects the variation of surface tension with surfactant concentration. In some systems, however, the Region III/ Region IV transition can be reached when the surface becomes saturated with adsorbed surfactant. For the adsorption of surfactants from aqueous solutions, this will correspond to bilayer completion for ionic surfactants adsorbed on oppositely charged surfaces, or to monolayer completion for adsorption on hydrophobic surfaces. However, several factors can affect the maximum adsorption as shown in Figure 2.9; a schematic representation of the microstructure of adsorbed layer, deduced from fluorescence and ESR spectroscopic.

The nature of solid surface plays an important role in the adsorption of surfactants at solid-liquid interface. Generally, adsorbents can be divided into two types: hydrophilic (or polar) and hydrophobic (or nonpolar). Silicates, inorganic oxides and hydroxides, natural fibers and protinacious materials can be classified as hydrophilic surfaces, whereas the surfaces of carbonaceous materials and polymers are hydrophobic. In the next section, the related research work on surfactant adsorption onto hydrophobic and hydrophilic surface will be reviewed.

2.2.1 Surfactant Adsorption on Hydrophobic Surface

A hydrophobic surface has a unique characteristic to repel from water and it is unable to form hydrogen bonds with water environment. Many substrates are grouped in this hydrophobic class such as Teflon, polystyrene, polyethylene, polypropylene, polymethylmethacrylate, and carbon. On these substrates, the dispersion force (hydrophobic bonding) plays an important role in adsorption of surfactants. Moreover, the adsorption isotherms for well-purified monofunctional anionic and cationic surfactants are similar (Rosen, 1988). Many researches working on the adsorption of surfactants on hydrophobic surfaces, especially carbon black is summarized as follows.

Day *et al.* (1967) and Greenwood *et al.* (1968) studied the adsorption of an anionic surfactant, sodium dodecyl sulfate (SDS) onto carbon/aqueous solution interface, focusing on three types of carbon; carbon black, spheron 6 and graphon. Their results show that the adsorption isotherms of carbon black and spheron 6 were Langmurian shape and the plateau adsorption occurred at the CMC but different results for graphon. There was a marked inflection in the isotherm, which started to rise double from an area per SDS ion of about 0.72 nm^2 to about 0.43 nm^2 at the plateau region. At a very low SDS concentration, was assumed to adsorb parallel to the surface as a result of hydrophobic chain-surface interaction, and at a high surfactant concentration (high coverage), it was expected to adsorb vertically to the surface, resulting from chain-chain interactions. The hydrophilic heads oriented toward the water and hydrophobic tails oriented toward the solid surface (Rosen, 1988; Zettlmoyer, 1968). Moreover, they also investigated the system of Graphon at a 0.1 M NaCl and found that the inflection point disappeared. The plateau adsorption was achieved at a lower SDS concentration and the area per molecule in plateau region was reduced in the presence of salt.

Ali *et al.* (1987) studied the adsorption of anionic surfactant, sodium dodecyl sulfate (SDS) and nonionic surfactants on sulfonated polystyrene latex of various charge densities. For nonionic surfactants, the adsorption area per molecule increased with surface polarity increased. The packing of the nonionic surfactant became less dense as the hydrophilic character of the surface increased (Romero-caro *et al.*, 1998). Similarly, the area per molecule of sodium lauryl sulfate (or SLS) at various polymer-water interfaces increased with increasing polarity of polymer (Vijayendran, 1979).

Dixit and Vanjara (1999) studied the effect of adding electrolyte on the adsorption of DTAB on latex surface. The addition of NaBr effectively screened the electrostatic repulsion between head groups of DTAB and latex surface, therefore, the adsorbed amounts increased. The addition of neutral electrolyte increased both the efficiency and the effectiveness of adsorption of ionic surfactants by decreasing electrical repulsion between adsorbed molecules (Rosen, 1988).

Mishra *et al.* (2003) studied the adsorption isotherms of sodium dodecyl benzene sulfonate (NaDBS) on coal. The adsorption isotherms exhibited two stages of saturation with non-Langmuirian behavior. The adsorption was not proportional to the concentration with the slope less than 1, suggesting the multilayer adsorption.

Gurses *et al.* (2003) studied the adsorption of CTAB on active carbon-water interface. They reported that the adsorption mainly took place through the ion exchange, the ion pairing and hydrophobic bonding. The predominant mechanisms at lower CTAB concentrations were probably ion exchange and ion pairing, but at high CTAB concentrations, the predominant mechanism was the hydrophobic bonding.

2.2.2 Surfactant Adsorption on Hydrophilic Surfaces

A Hydrophilic surface has a characteristic to exhibit an affinity to water. In this case, the surface functional groups have ability to form the hydrogen bond with water such as mineral oxides and silica surfaces.

Scamehorn *et al.* (1981) studied the adsorption of surfactant on mineral oxide surfaces in aqueous solutions with three isomerically pure anionic surfactants which are sodiumnonylbenzene sulfonate (3-ø-C_9ABS), sodiumdecyl benzene sulfonate (3-ø-C_{10}ABS) and sodiumdodecylbenzene sulfonate (4-ø-C_{12}ABS). The results of adsorption isotherms for three ABS isomers on alumina and kaolinite were in good agreement with the theory. The schematic of adsorption model below the CMC was found to compose of bilayer adsorption, lateral interactions, and two-dimensional phase transitions. At a low concentration (Henry's

Law Region), surfactant molecules were found to adsorb on the surface through alkyl chain strongly interacting with the surface and charged head-surface electrostatic attraction. With further increasing surfactant concentration, the adsorption increased rapidly due to the formation of hemimicelles, resulting from increasing lateral interaction between adsorbed surfactants. Finally, above the CMC, the adsorption was independent on surfactant concentration.

Dao *et al.* (1998) studied the adsorption isotherm of sodium octylbenzenesulfonate (NaOBS) on iron oxide particles in aqueous solutions. The results showed that the maximum adsorption was found in the region of surfactant concentration greater than the critical micelle concentration. In the case of ferric oxide particles, these ions were found to complex with sodium octylbenzenesulfonate. These complexes were adsolubilized in the surfactant layer on the particles below the critical micelle concentration. They desorbed from the surface and transferred into free micelles above the critical micelle concentration. These two phenomena were believed to be responsible for the maximum adsorption. The presence of ferric ions was found to induce a reduction of surface tension at the air /water interface of the anionic surfactant.

Rao and He (2005) studied the adsorption behavior of anionic surfactant (sodium dodecylbenzene sulfonate, SDBS) and nonionic surfactant (an alcohol ethoxylates with 12 carbons and 9 oxyethyl groups $A_{12}E_9$) mixtures from syntertic detergents on soils. The results showed that the saturated adsorption amounts of SDBS and $A_{12}E_9$ on the studied soils decreased, possibly resulting from the screening of $A_{12}E_9$ to part adsorption sites on soils and the hydrocarbon chain-chain interactions between SDBS and $A_{12}E_9$. With the increase of pH in mixed surfactant solutions, the adsorption amounts of SDBS and $A_{12}E_9$ on the soils decreased. The reduction of ion strength in soils resulted in the decrease in the adsorption amounts of SDBS and $A_{12}E_9$ on the soils.

2.2.3 Adsorption of Nonionic Surfactants

The adsorption of nonionic surfactants on the solid–liquid interface has not been studied as extensively as ionic surfactants (Douillard *et al.*, 1992). The adsorption isotherms of nonionic surfactants are generally Langmurian (Clunie *et. al.*,

1983) like those of most other highly surface-active solutes in a dilute solution system. Nonionic surfactants physically adsorb rather than electrostatically or chemically. However, they differ from many other surfactants in that; quite small changes in concentration, temperature, or molecular structure of the adsorbent can have a large effect on the adsorption. This is due to strong adsorbate–adsorbate and adsorbate–solvent interactions, causing surfactant aggregation in bulk solution and changing change in orientation and packing of surfactant at the surface. Figure 2.10a shows a general scheme of the most likely orientation changes undergo in the adsorption of nonionic surfactants from solution onto solid surface and Figure 2.10b shows three adsorption isotherms corresponding to the different adsorption sequences (Clunie *et al.*, 1983).

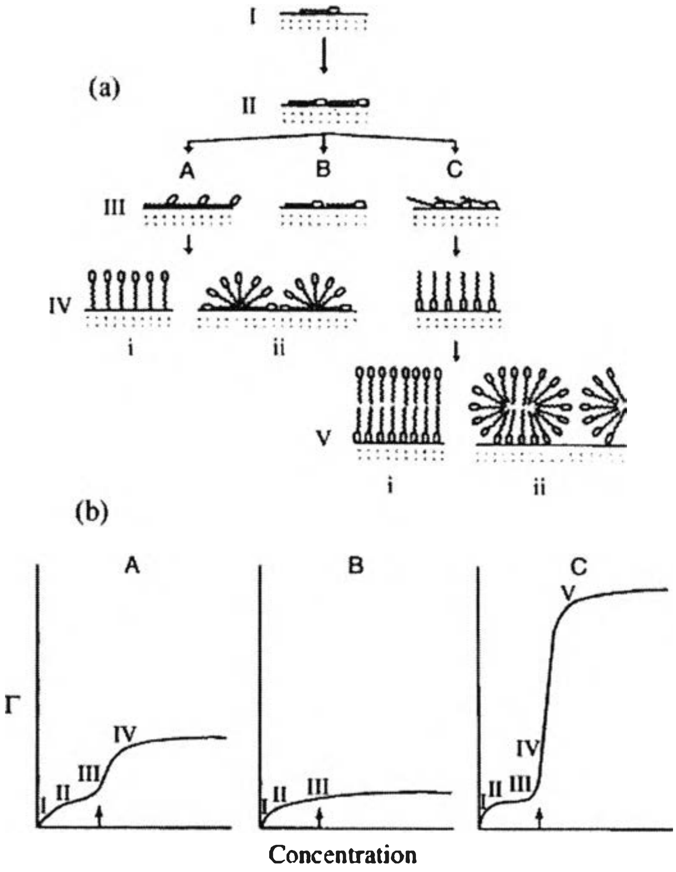

Figure 2.10 (a) Adsorption of nonionic surfactant in I–V successive stages of adsorption. (b) Adsorption isotherms corresponding to the three adsorption sequences (Clunie *et al.*, 1983).

Adsorption in the first step, the surfactant adsorbs on a solid surface where there are very few molecules adsorbed, obeying Henry's law. The molecules are far away from each other, so that the adsorbate–adsorbate interactions are negligible. The adsorption of this region occurs because of Van der Waals force interaction, and, therefore, it is mainly determined by the hydrophobic moiety of the surfactant. In the next stage of adsorption, this region is accompanied by gradual decrease in the slope of the adsorption isotherm due to the saturation of monolayer adsorption. The consequent region of adsorption are rapidly increasing amount of adsorbed surfactant dominated by the adsorbate–adsorbate interactions. This shows how the adsorption progresses when stage II is complete. The adsorbate–adsorbate interaction depends on the hydrophilic–lipophilic balance (HLB) in the surfactant and on the nature of adsorbents. When the hydrophilic group is weekly adsorbed or when the adsorbent is hydrophobic and hydrophilic group of surfactant is short, it will be displaced from the surface by the alkyl chains of the adjacent molecules (Figure 2.10a IIIA). However, when the hydrophilic group is strongly adsorbed (strong attraction between the hydrophilic group and the surface with hydrophilic adsorbent like silica or oxides), the alkyl chain is displaced (Figure 2.10a IIIC). The intermediate situation when neither type of displacement is favored nor the surfactant then remains flat on the surface (Figure 2.10a IIIB). In the last stage of adsorption (region IV), the adsorption approaches a plateau above the CMC. There will be a tendency for the alkyl chains of the adsorbed molecules to aggregate (hemimicelle). This will cause the molecules to become vertically oriented and there will be a large increase in adsorption. This occurs for the hydrophobic adsorbent. Figure 2.10b IVC shows the case of adsorption of nonionic surfactants on hydrophilic solid surface.

Gao *et al.* (1984) found that for the mixture of anionic and nonionic surfactants, the adsorption of TX-100 onto negatively charged silica gel decreased with increasing concentration of the anionic surfactant (sodium n-alkyl sulfates) at total surfactant concentrations above the CMC. Below the CMC, there is insignificantly difference in the adsorption isotherm for either the mixed surfactant systems or the pure TX-100 systems. In 2000, Somasundaran and Huang found that when the hydrocarbon chain length of nonionic surfactants was equal or longer than that of an anionic surfactant, the adsorption isotherms of the anionic surfactant did not change with changing the chain length of nonionic surfactant (in the case of adsorption of anionic/nonionic surfactant on kaolin). When the chain length of the nonionic surfactant was shorter than that of the anionic surfactant, different isotherms of the anionic surfactant were obtained due to less shielding of anionic surfactant. Figure 2.11 shows the effect of nonionic surfactant hydrocarbon chain length on the adsorption of the anionic sodium dodecyl sulfate (SDS): (a) nonionic surfactant hydrocarbon chains longer than that of SDS; (b) nonionic surfactant hydrocarbon chain length equal to that of SDS; and (c) nonionic surfactant hydrocarbon chain length shorter than that of SDS, partially exposing SDS hydrocarbon chains to the aqueous solution or the hydrophilic ethoxyl chains of the nonionic surfactant.

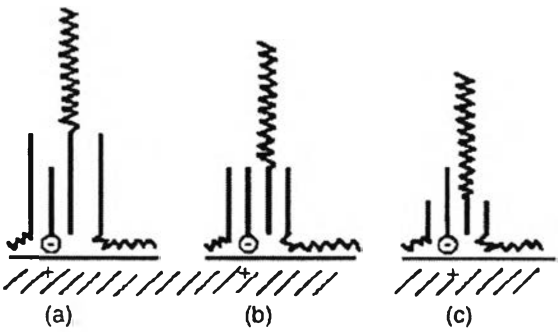

Figure 2.11 Schematic presentation of the effect of nonionic surfactant hydrocarbon chain length on the adsorption of the anionic sodium dodecyl sulfate (SDS) (Gao *et al.*, 1984).

Gonzalez-Garcia *et al.* (2002) studied the free energy of the adsorption process of anionic surfactant (SDS) from aqueous solutions onto a set of carbon black in the range of low concentrations. From the results obtained in this study, it was concluded that the free energy of interaction between adsorbent and adsorbate through water resulted mainly from the Lifshitz-van der Waals and electrostatic interactions, and its value showed a good correspondence with a combination of the model proposed by van Oss and co-workers and the double-Langmuir equation.

2.3 Zeta Potential (ζ)

At the interface, there is always a distribution of electrical charges between each phase with an unequal distribution. As a consequence, it causes one surface of the interface to acquire charge of particular sign and the other side to acquire charge of opposite sign, resulting in giving rise to a potential between the interface, known as "electrical double layer". Since the neutrality of overall electrical charges must be preserved, the net charge on one side of interface must be balanced by an opposite sign charge on the other side of interface with an exactly equal amount. At the plane (the outer edge of the counter–ions layer), the adsorbed ions have changed the charge to σ_δ and the potential relative to ground is ψ_δ. This is just the work done in bringing a point charge from infinity to this plane. This potential is known as the z-potential and is the potential where the centre of the first layer of solvated ions that are moving relative to the surface is located. Now, unfortunately this is a difficult quantity to measure on a routine basis but we can relatively easily estimate a potential from electrokinetic measurements where we have a motion between the fluid and the interface. This is termed the 'shear plane', but it is not at a well-defined distance from the surface and so we have the situation where we can determine a potential but where the position is a little uncertain at ~ 0.5 nm or so from the surface. This distance would be about three times the radius of a solvated ion, but the utility of the z-potential is that it reflects the value of ψ_δ which can differ in sign as well as markedly in magnitude from the potential at the surface, ψ_0. An illustration of the electrical double layer is given in Figure 2.12.

The zeta potential can be related to the stability of colloidal dispersions, which indicates the degree of repulsion between the similarly charged particles in dispersion. For a low zeta potential, the attraction force can overcome the repulsion force, which can cause coagulation. Hence, colloids with high zeta potentials (negative or positive) are electrically stabilized while colloids with low zeta potentials tend to coagulate or flocculate, as shown in the Table 2.1.

Table 2.1 The relation between zeta potential and the stability behavior of the colloid (http://en.wikipedia.org/wiki/Zeta_potential)

Zeta potential [mV]	Stability behavior of the colloid
From 0 to ±5	Rapid coagulation or flocculation
From ±10 to ±30	Incipient instability
From ±30 to ±40	Moderate stability
From ±40 to ±60	Good stability
More than ±61	Excellent stability

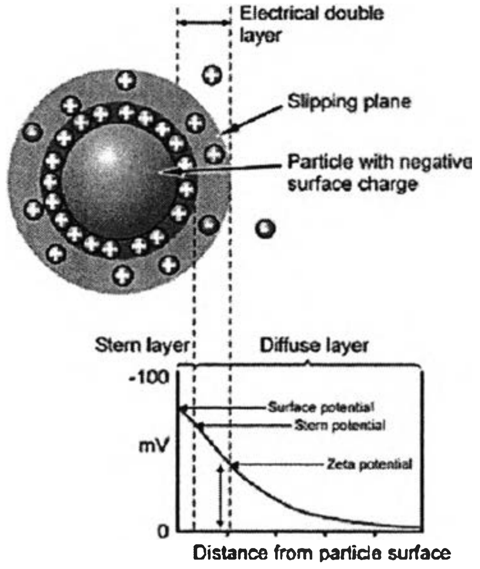

Figure 2.12 Schematic presentation of electrical double layer (http://www.malvern.de/LabGer/technology/zeta_potential/zeta_potential_LDE.htm)

2.3.1 Point of Zero Charge (PZC)

Point of Zero Charge (PZC) is a pH which makes the charge at the shear plane of solid particle becomes zero and it is also called the isoelectric point (IEP). Figure 2.13 shows the typical plots the zeta potential (mV) as a function of pH levels for determination the PZC. At a solution pH lower than the PZC, the surface has positive charge resulting in the preferable adsorption of anionic surfactants while at a solution pH higher than the PZC, the surface has negative charge, resulting in the adsorption of cationic surfactants.

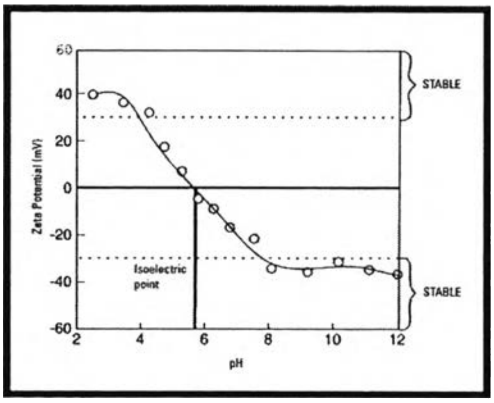

Figure 2.13 Typical plots the zeta potential measured as a function of pH determination the PZC (http://www.silvercolloids.com/Tutorials/Intro/pcs18A.html).

Kaya and Yukselen (2005) determined the zeta potential of kaolinite, montmorillonite, and quartz powder in the presence of alkali, alkaline earth, hydrolysable metal ions with anionic, cationic and nonionic surfactants in a systematic manner. The results indicated that the anionic surfactants produced negative zeta potentials. The cationic and nonionic surfactants produced both positive and negative zeta potentials, depending on soil type and ion present in the system. The results also indicated that the zeta potential of kaolinite and quartz powder in surfactant solutions showed the similar trends; however, the absolute magnitude of the zeta potential of quartz powder is higher than that of kaolinite.

Tschapek *et al.* (1974) studied the PZC of H^+-kaolins by titration method. They found that the PZC was affected by the composition of kaolinite, corresponding to the amount of SiO_2 and Al_2O_3. Moreover, they obtained the PZC of 3 for H^+-kaolins.

2.4 Wetting Phenomena

Wetting is defined as the displacement of air from a solid or a liquid by an aqueous solution. In more basic terms, wetting refers to the ability of a liquid to spread over a given surface. It is important in detergency process because it helps bring solvent and soil together. Mostly, the addition of surfactants to water can enhance the ability of an aqueous solution to wet or spread over the solid surface because it can lower the energy barrier between the solvent and the substrate. However, the presence of surfactant does not always enhance the wetting ability (or wettability); it depends on several parameters including molecular structure of the surfactant, surfactant concentration, environmental conditions and the nature of solid surface (Rosen, 1988 and Lance, 1994)

Wettability can be examined by measuring the "contact angle" of a liquid drop on a test substrate surface. Complete wetting means the contact angle between a liquid and solid is zero, or so close to zero, in which the liquid easily spread over the solid surface. While non-wetting means the contact angle is greater than 90°, so the liquid tends to ball-up and easily run off the surface (Garbassi *et al.*, 1994) as shown in Figure 2.14.

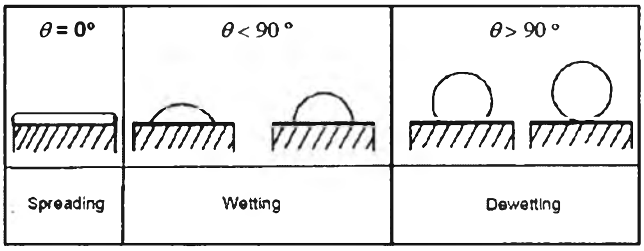

Figure 2.14 Wetting performance correlated to the Contact angle (http://www.adhesives.org/trainingeducation/studentresources/wetting.aspx).

2.4.1 Contact Angle

The Contact angle is a quantitative measure of the wetting of a solid by a liquid. It is the angle between the substrate surface and the liquid droplet (Figure 2.15). Low values of contact angle indicate a strong liquid–solid interaction such that the liquid tends to spread on the solid, or wets well, while high contact angle values indicate a weak interaction between liquid and solid surfaces, resulting in poor wetting. If contact angle is lower than 90°, then the liquid is said to wet (or sometimes partially wet) the solid. A zero contact angle represents complete wetting. If contact angle is greater than 90°, then it is said to be non-wetting (Figure 2.14). From a microscopic point of view, if the solid has a low-energy surface, it attracts the molecules of the liquid with less force than the liquid molecules attract one another. Therefore, the molecules in the liquid next to the surface have a weaker force than in the liquid surface, so that the liquid molecules at the interface are pulled more strongly into the bulk of the liquid than they are by the solid. There is a tension in the layer adjacent to the solid, and the liquid molecules are somewhat separated, owing to the one-sided force field. The situation is analogous to the behavior of a drop of one liquid on another immiscible liquid, the drop liquid having a higher surface tension than that of the lower liquid (but not equivalent because of the mobility of surface molecules at the interface region between two immiscible liquids).

Regarding to the basis of the measurement of solid surface tension by contact angle, there is the equilibrium at the three-phase boundary. The drop of liquid that put on a solid surface will modify its shape under the pressure of the different surface or interfacial tensions, until reaching equilibrium (Garbassi *et al.*, 1994). The three-phase equilibrium is described in terms of the vectorial sum as shown in Figure 2.15 resulting in the following equation of interfacial equilibrium;

$$\gamma_{LV} \cos\theta = \gamma_{SV} - \gamma_{SL} \qquad (1)$$

The equation 1 is generally called Young's equation which the static contact angle (θ) is related to the interfacial free energies per unit area of the liquid-vapor (γ_{LV}), solid-vapor (γ_{SV}), and solid-liquid (γ_{SL}) interfaces.

If [$\gamma_{SV} > (\gamma_{SL} + \gamma_{LV})$] which shows the presence of a high surface energy solid, then Young's equation indicates ($\cos\theta = 1$), corresponding to ($\theta = 0$), which means the complete spreading of the liquid on this solid.

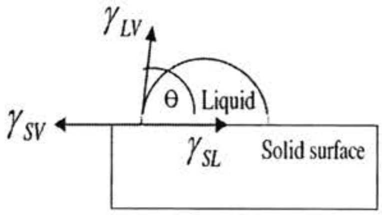

Figure 2.15 Three-phase intersection point of Contact angle measurements.

[www. adhesives.org/…/wetting.aspx].

2.4.2 Surface Pressure (Spreading Pressure)

Surface pressure (spreading pressure) at the solid/liquid interface (π_{SL}) is the different between interfacial tensions at solid/liquid interface for the solvent (γ_{SL}^{o}) and surfactant solution (γ_{SL}), which indicates the effect of surfactant on the reduction of interfacial tension (IFT). It can be calculated by subtracting Young's equation (Rosen, 2004) for surfactant solution from that for the surfactant-free solution as shown in the Equation 2. A higher surface pressure means a higher ability of surfactant in lowering IFT.

$$\pi_{SL} = \gamma_{SL}^{o} - \gamma_{SL} = [\gamma_{LV}\cos\theta] - [\gamma_{LV}\cos\theta]^{o} \qquad (2)$$

where;

π_{SL} = surface pressure at solid/liquid interface

γ_{SL} = interfacial tension at solid/liquid interface

γ_{LV} = interfacial tension at liquid/vapor interface

superscript "o" refers to surfactant-free solution

2.5 Types of Soils

Soils can be defined as unwanted substances that make a garment or fabric unclean. In general, it is either colorless or colored and also soluble or insoluble in water. Soils can be divided into three categories: oily and greasy soils, proteins and starchy soils and particulate soils

2.5.1 Oily and Greasy Soils

Oily soils mean soil only composed of nonpolar hydrocarbons such as diesel and motor oils, usually liquid and highly hydrophobic, which means that they do not mix with water. Greasy soils mainly refer to triglycerides and their derivatives: mono- and triglycerides, fatty acid. They are more polar but not polar enough to be dissolved by water.

2.5.2 Proteins and Starchy Soils

Protein and starch are polymeric materials that can resist conventional cleaning. They act as glue, making cleaning more difficult. A typical example is cheese. These soils are best removed by enzymatic cleaning. Proteolytic and amylolytic enzymes are currently used for this purpose in modern automatic laundry detergents.

2.5.3 Particulate Soils

Solid particles such as clay, alumina, silica, iron oxide, and other metal oxides are present in particulate soils, deposited mostly from air suspensions (dust). They are soluble neither in water nor in organic 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/crosslinking of unsaturated triglycerides. Since they are not water soluble, the particulate soils can be redeposited on surfaces that have been cleaned. It is accordingly important to keep such soils effectively dispersed in the washing liquid (Lance, 1994).

2.5.3.1 Carbon Black

Carbon black is a material produced by the partial combustion of heavy petroleum products. Carbon black is a form of amorphous carbon that has a high surface area to volume ratio usually used as a pigment and reinforcing agents in automobile tires, rubber and plastic products. Carbon black is extremely black pigments of high hiding power in printing ink, paint, and carbon paper. The arrangement of carbon atoms in carbon black has been well established by x-ray diffraction method. Carbon black can have a degenerated graphitic crystalline structure. Figure 2.16 shows the three dimensional order of graphite as compared to the two dimensional order of carbon black. From the x-ray data, carbon black consists of well-developed graphite structure platelet roughly parallel to one another but random in orientation with respect to adjacent layers.

Rao and Stenius (1998) studied the mechanisms of ink (carbon black) removal from cellophane, a polyamide sheet and photocopy paper by several types of nonionic surfactants. They found that the addition of surfactant can soften the carbon black and affect the carbon black/fiber interactions. Moreover, they reported that the structural difference of surfactants affect the kinetics of carbon black removal rather than the actual detachment mechanism.

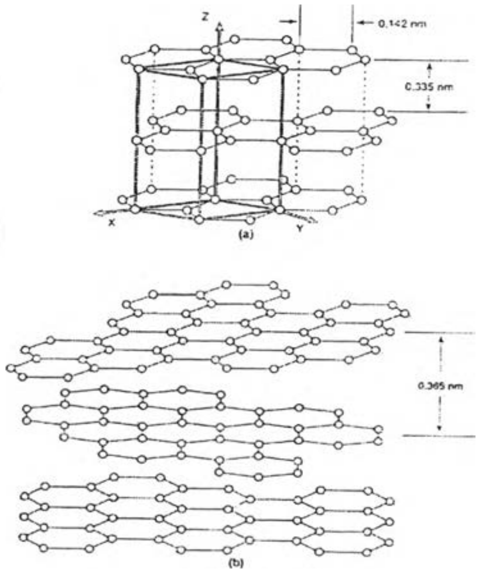

Figure 2.16 Atomic structural models of (a), graphite, and (b) carbon black (Baker *et al.*, 1992).

2.5.3.2 Ferric Oxide

Ferric oxide is an inorganic compound that occurs naturally as the mineral hematite which is the main source of iron for the steel industry. It is a reddish-brown to black powder. Ferric oxide forms a number of hydrates with various structures and compositions. A common form is iron rust, produced by the combined action of moisture, carbon dioxide, and oxygen in the air with metallic iron.

Reich *et al.*, (1959) found that the controlling factor in preventing deposition of carbon black or ferric oxide on a fabric surface was the reduction of agglomerate particle sizes. The agglomeration of small particles is an irreversible process. But for larger particles, agglomeration and dispersion occur simultaneously.

Schott *et al.*, (1967) concluded that the discoloration of fabrics in laundry detergency by colloidal dispersion occurred in the rinse step rather than wash step. Yoshikawa (2002) found that particles of Fe_2O_3 adhered to fabrics were detached much more effectively with aqueous solutions of anionic surfactants, especially sodium oleate, than a nonionic surfactant (polyoxyethylene olein ether (C17P10)). It was concluded that the shift in the point of zero charge of the Fe_2O_3 particles to a lower pH by the adsorption of anionic surfactant promoted the detachment of the particles from the fabric surface and prevented the re-adhesion of detached particles onto the fabric. The statistical analysis of washing efficiency of solid particulate soil (ferric oxide) was studied by Ishikawa *et al.* (2007).

2.5.3.3 Kaolinite

Kaolinite is an aluminosilicate material, mostly found on fabrics as a result from a wide variety of products using kaolinite as a raw material, such as ceramics, medicine, coated paper, food additive, and toothpaste. Kaolinite is white, soft, and mainly composed of fine-grained plate-like particles. Kaolinite is composed of a two-layer sheet of silica tetrahedral and aluminum hydroxide octahedral, which held together by hydrogen bonds and van der Waals interactions, as shown in Figure 2.17 (Legaly, 1993). The basal planes are negatively charged and independent of pH, while the edge charge created by the dissociation of silanol and aluminol groups changes from positive at a low pH to negative at a higher pH (Miller et al., 2007). Powe (1959) suggested that the presence of clay particles on washed fabric contributed to the unremovable portion of soil material. Tuzson and Short (1962) studied the similarity between the agglomeration–dispersion process and the deposition–removal process of clay particles during washing. They found that the same types of forces are responsible for the agglomeration-dispersion process as for the deposition-removal process. Moreover, the agglomeration properties can be related to the soil characteristics. For example, the interaction of anionic detergents (sodium decyl sulfonate and sodium dodecyl sulfate) with montmorillonite clays was discussed by Schott (1967). He concluded that the sorption of anionic detergents onto the montmorillonite clays occurred in two steps. First, alkyl sulfonate and sulfate anions were bound through the counterions of the montmorillonite clays followed by the sorption of sodium alkyl sulfonate and sulfate by association between their hydrocarbon tail and those of previously sorbed detergent anions through van der Waals forces.

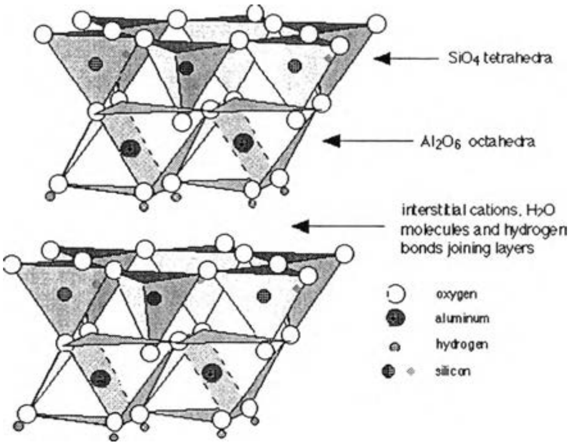

Figure 2.17 Structural models of kaolinite
(http://www.chem1.com/acad/webtext/geochem/04txt.html)

2.6 Mechanisms of Particulate Soils Removal

Particulate soils almost always occur with other soils such as oily and greasy soils. The particulate soils contribute to the toughness of the soil deposit, and the grease acts as cement, binding the particles together. The first step, just after wetting, is to attack the oily-greasy component. The particulate soils are then made available. The best way to clean particulate soils is to use a surfactant that adsorb efficiently at the water-solid particle interface, to reduce the interfacial tension and, accordingly, to reduce the adhesion forces binding the particles together. This can be achieved with an anionic surfactant, in which case the surface of solid particles is made more negative and electrostatic repulsion can occur between adjacent particles. Since particulate soils are not water soluble, they have a tendency to redeposit in the later stages of the washing operation.

Paria *et al.*, (2001) showed that the magnitude of critical hydrodynamic force, which defined as the minimum force required for detaching the particle from the fiber surface under a given condition, is dependent on the particle size. The smaller the particle size is the larger the requirement of critical hydrodynamic force.

2.7 Soil Redeposition

In cleaning and washing processes, the redeposition of detached soil generally occurred as a result of the lack of colloid stability in the dispersion medium. In general, the oily soils are removed by the solubilization process, which is the thermodynamically driven, so the redeposition will be minimal. Solid soils, on the other hand, cannot be solubilized, thus the redeposition must be retarded by other kinetically controlled. As showed out earlier, one main role of surfactants at the interfaces of solid is to tell the degree of colloidal stability of the 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 the redeposition. Nonionic surfactants perform the same manner by the formation of a steric or entropic barrier, although the efficiency of such a mechanism is probably less than the electrostatic repulsions in most of aqueous systems.