CHAPTER II
LITERATURE REVIEW

2.1 Surfactant Structure

Surfactant or the term "surface-active agent" can be defined as a heterogeneous and long-chain molecule containing both hydrophilic head and hydrophobic tail parts. When it presents at a low concentration in solution, it adsorbs preferentially onto the interphase and modifies the free energy (Rosen, 2004). Surfactants also show the unique property in an aqueous medium—when the concentration of surfactants exceeds a certain critical level, leading to the surfactant molecules forming organized aggregates of a large amount of molecules called "micelles". This certain critical value of surfactant concentration, which surfactant forms micelles, is called critical micelle concentration (CMC) (Paria, 2007).

Surfactants consist of a non–polar hydrophobic (lypophilic) portion which is attached to a polar hydrophilic (lypophobic) portion, called the amphipathic structure. Usually, the non–polar hydrophobic portion may have a strength or branched chain of hydrocarbon, fluorocarbon or siloxane and the chain has 8–18 carbon atoms. The polar or hydrophilic portion can be nonionic ionic or zwitterionic. In the last two cases, the hydrophilic part may be accompanied with counter ions.

When the surfactant molecules are soluble in a solvent, the hydrophobic portion may interfere the solvent structure, which enhances the increasing system free energy. To minimize the interaction between the hydrophobic and the solvent, the system replies in some fashion. In the case of aqueous medium, when surfactants molecules are dissolved in water, the hydrophobic part interacts weakly with water environment, whereas the hydrophilic part interacts strongly with water environment via electrical force (dipole or ion–dipole). Moreover, the hydrophobic portion can distort grouping of water molecule by breaking hydrogen bond between water molecules. As a consequence of this phenomenon, some certain amounts of surfactant are pushed to the interface of system with the hydrophobic portion oriented toward the air in order to minimize the free energy of the system. According to the accumulation of surfactants at the air/water interface, the water surface becomes covered with a layer of surfactants. As the hydrophobic group, air is contacted hydrophobic portion of surfactant with high degree of similarity. Consequently, the decrease in the dissimilarity of two phases contacted each other at interface results in decreasing water surface tension. With the amphipathic structure and the strong interaction between the hydrophilic portion/water molecules, surfactant molecules are not completely expelled from the aqueous medium as a separate phase. Accordingly, the amphipathic structure of surfactant causes not only the accumulation of surfactants at interface, leading to decreasing water surface tension with the configuration of surfactant molecules at the interface of water/air by having the hydrophobic portion oriented toward the air and hydrophilic portion oriented in the aqueous phase.

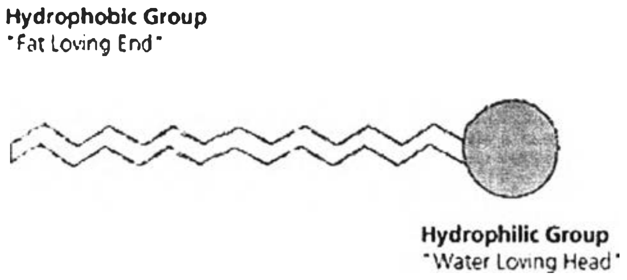


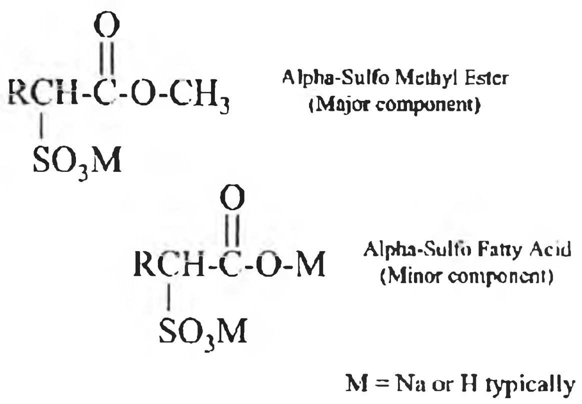
Figure 2.1 Surfactant structure.

A simple classification of surfactants based on the charge present in the hydrophilic portion of the molecule after dissociation in aqueous solution. Surfactants are classified as:

1. Anionic. The surface-active portion of the molecule bears a negative charge, for example, $RCOO^- Na^+$, $RC_6H_4SO_3^-Na^+$
2. Cationic. The surface-active portion of the molecule bears a positive charge, for example, $RNH_3^+Cl^-$, $RN(CH_3)_3^+Cl^-$.
3. Zwitterionic. Both positive and negative charge may be present in the surface-active portion, for example, RN+H2CH2COO-
4. Nonionic. The surface-active portion bears no apparent ionic charge, for example, $RCOOCH_2CHOHCH_2OH$, $RC_6H_4(OC_2H_4)_xOH$

2.1.1 Anionic Surfactants

Methylester sulfonates (MES or SME): The investigation of methylester sulfonates for laundry and personal care products has been increased rapidly in the last several years. The excellent MES properties, most notably the unsurpassed hard and cold water performance, allow a variety of applications. In markets where soap-based products are widely used, MES blends with soaps offer large performance improvements with very low cost. The environmental and health properties are also outstanding, generally comparable to alcohol ethoxysulfates. Figure 2.2 shows the chemical structure of MES (SME).



$$\underset{SO_3M}{RCH}-\overset{O}{\overset{\|}{C}}-O-CH_3$$

$$\underset{SO_3M}{RCH}-\overset{O}{\overset{\|}{C}}-O-M$$

Figure 2.2 SME and sulfonated fatty acid structure.

In 2002, Wen Huei Lim *et al.* studied the detergency profiles of sodium salt α-sulfonated methyl esters derived from palm stearin (α-SMEPS) and polyoxyethylene (20) sorbitan monoesters (POESE) in mixed micelle systems as a function of the weight ratios of α-SMEPS/POESE [polyoxyethylene (20) sorbitan monolaurate (12), polyoxyethylene (20) sorbitan monostearate (18:0), and polyoxyethylene (20) sorbitan monooleate (18:1)] at different water hardness values (5.12, 51.2, and 512.0 ppm CaCO3) and temperatures (20, 30, 45, and 65°C). All the mixtures of α-SMEPS/POESE (12, 18:0, and 18:1) systems exhibited a synergistic effect at 65°C in the absence of water hardness. This was evaluated by measuring the percentage of soil removed. The systems showed an increase in detergency with both the temperature and water hardness. Maximal detergency was observed with 5.12 ppm $CaCO_3$ in the mixed surfactant solution.

In 2004, Wen Huei Lim *et al.* reported the dishwashing performance of sodium salts of α-sulfonated methyl esters derived from palm stearin (α-SMEPS) and nonylphenol ethoxylate alcohol (NPEO) in mixed micelle systems as a function of weight ratio at different water hardness values (5.12, 51.2, and 512.0 ppm $CaCO_3$) and different temperatures (20, 30, and 45°C). the enhancement of detergency performance was achieved by manipulating several parameters, such as weight ratios in α-SMEPS and NPEO mixtures, washing temperature, and water hardness. In comparisons, the detergency efficiency were as follows: α-SMEPS/NPEO 400 < α-SMEPS/NPEO 120 < α-SMEPS/NPEO 95.

In 2002, Teruhisa Satsuki *et al.* investigated the detergency properties of a-sulfonated fatty acid methyl esters (a-SFMe) and compared to those of conventional anionic surfactants by using a model heavy, Jury detergent formuiation. Several physicochemical properties of surfactants were measured to investigate the effective factors on detergency. α–SFMe showed good detergency performance under various washing conditions. These results were considered to correlate well with the good adsorption behavior on oils and dispersing capabilities for particles, as well as with the good solubilization capacity. Solubilization behavior of α–SFMe was discussed in relation to micelle properties. It was suggested that α–SFMe can form suitable micelles for solubillzing polar oils advantageously, due to its bulky hydrophilic group.

In 2006, Zulina Abd Maurad *et al.* reported that the performance of powder detergents formulated with SME was excellent. At a total concentration of 0.8 g/L, good detergency of power detergent was obtained when only using 12% to 18% SME, compared to the commercial detergent with 27% surface- active agent. The foaming power and wetting characteristics of powder detergent were also comparable to the values of the commercial detergent. The study showed that PPD were able to be biodegraded faster than the commercial detergent, where the maximum time period to reach the pass level (60%) was within 14 days. The toxicity of the PPD, which ranged from 5.66 to 8.0 mg/L, was similar to the toxicity of the commercial detergent.

2.1.2 Nonionic Surfactants

Alcohol ethoxylates: Alcohol ethoxylates (AE) are a very widely used class of nonionic surfactants. Significant quantities of AE are converted to alcohol ethoxysulphates (AES) with the remaining AE used primarily in household laundry detergents. AEs have many desirable characteristics such as rapid biodegradation, low to moderate foaming ability, superior cleaning of man-made fibers and tolerance to water hardness. AEs are also used in lesser quantities in household cleaners, institutional and industrial cleaners, cosmetics, agriculture, textile, paper, oil and other process industries.

In 1997, Hama *et al.* found that Ethoxylated methyl laurate with about 60 to 70% EO content was the most suitable as a base surfactant for household detergents. Later, Goel (2000) studied phase behavior and detergency of lauryl alcohol ethoxylates with a high ethylene oxide content ($C_{12}EO_{14}$). The adsorption of broad-range ethoxylates, a sizable fraction of which is always removed from the cloud point at any operating temperature, was found to exhibit a rather flat curve and it increased with increasing surfactant concentration and reached a plateau at high surfactant concentrations. The only effect that took place with increasing temperature was the thermal softening of the fabric weave, facilitating dislodgment of particles and increasing convective currents helping suspend the particles. Both of these led to increasing particulate soil detergency.

2.2 Surfactant Adsorption

The adsorption of surfactant can be defined as the delivery of surfactant molucules from the surfactant bulk phase to the interface. The surfactant adsorption at an interfaces can be applied in many areas such as detergency, mineral flotation, oil recovery and so on. With their tendency to adsorb at the interface mostly in an oriented fashion, the presence of surfactants can alter significantly interfacial the properties. The adsorption phenomenons of surfactants have been studying in order to determine: (1) the concentration of surfactants at interface, sine this is a measure of coverage of interface by surfactants, which, in turn, affects the performance of surfactants in several interfacial processes (such as foaming, detergency and, emulsification), depending on their concentrations at interface; (2) the orientation and packing of the surfactant molucules at the interface, which, in turn, indicates how the interface will be affected by the adsorption, that is, whether it will become more hydrophilic or more hydrophobic. These properties provide the information on the type and the mechanism of any interactions involving, the surfactant at the interface and the efficiency and effectiveness of its operation as a surface-active material.

2.2.1 Adsorption of Ionic Surfactants

2.2.1.1 Surface Charge and Electrical Double Layer

At the interface, there is always a distribution of electrical charges in each phase which shows an unequal distribution. As a consequence of unequal distribution of electrical charges, it causes one surface of the interface to acquire charge of particular sign and the other side to acquire charge of opposite sign. It results 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.

Consider a surface charge with a surface charge density of $\sigma_0 Cm^{-2}$ and adjacent to this a layer of counter–ions. 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 is just the work done in bringing a point charge from infinity to this plane. This potential is known as z-potential and is the potential where the centre of the first layer of solvated ions that are moving relative to the surface. Now, unfortunately this is a difficult quantity to measure on a routine basis but the eletrokinetic measurement of the motion between the fluid and the interface is relatively easily to be measured. This is termed the 'shear plane', but it is not at a well defined distance from the surface and for a possible in the measurement a potential, the position is a little uncertain at ~ 0.5nm 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 2.3.

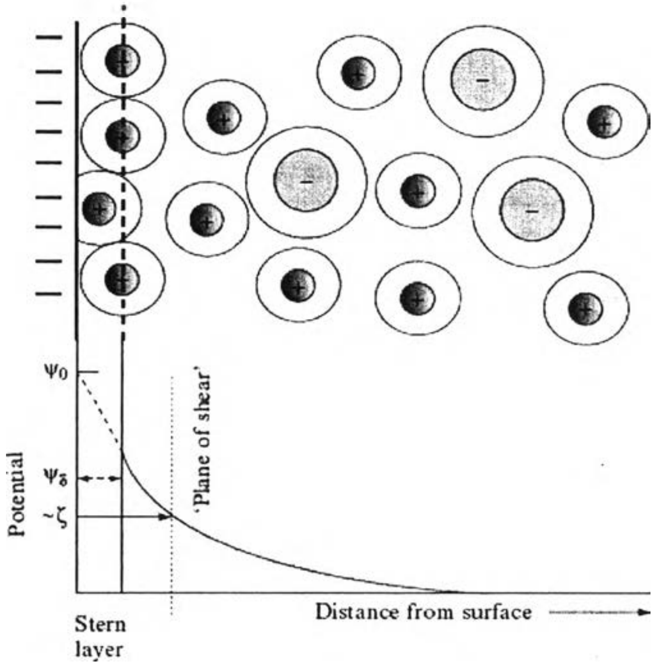


Figure 2.3 Schematic presentation of electrical double layer.

Point of Zero Charge (PZC) is a pH of zero zeta potential and it is also called the isoelectric point (IEP). At a lower pH than PZC, the surface has positive charge, resulting in the preferable adsorption of anionic surfactants while the adsorption of cationic surfactants occurs above the PZC.

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 anionic surfactants produce negative zeta potentials. The cationic and nonionic surfactants produce 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 with surfactants showed similar trends; however, the absolute magnitude of the zeta potential of quartz powder is higher than that of kaolinite.

2.2.1.2 Adsorption Isotherm

In 1982, Scamehorn showed that, a typical isotherm could be subdivided into four regions (attributed to three different mechanisms dominant in each region) when plotted on a log – log scale. Figure 2.4 presents the typical isotherm of adsorption of surfactants on the solid–liquid interface in a rather wide range of concentration of surfactants going beyond the CMC. In region I, the adsorption obeys Henry's law, adsorption increases linearly with increasing surfactant concentration and the slope of the curve is approximately one (Somasundaran *et. al.*, 1987) under condition with constant ionic strength. The adsorption occurs through the electrostatic interaction between the oppositely charge between solid surface and surfactants. At low concentrations, surfactants adsorb at the interface as individual ions and adsorption occurs by ions exchange of counter ions. Region II is marked by the onset of surfactant aggregation at the interface through lateral interaction between hydrocarbon chains (Somasundaran *et. al*, 1966). These surfactants aggregates were later termed as solloid or surface colloid (Somasundaran *et. al.*, 1989) and include aggregate such as hemimicelles, admicelles and self–assemblies (Harwell *et. al.*, 1987). In this region, the surface is not completely covered and enough sites on the surface are available for further adsorption. The slope of the isotherm decreases in region III because of the increasing electrostatic hindrance to surfactant adsorption. This is due to the surface charge reversal caused by surfactant adsorption on solid surface. The adsorption in region III occurs through the growth of the existing aggregates rather than the new aggregates formation of surfactants due to lack of adsorption sites. At the end of region III, the adsorption isotherm reaches a plateau region (region IV), corresponding to maximum surface coverage, at higher level of surfactant concentrations due to the formation of micelles in bulk or monolayer coverage, whichever is attained at the lowest surfactant concentration (Somasundaran *et. al.*, 1966). However, depending upon several factors the region IV may show a maximum. A schematic representation of the microstructure of adsorbed layer, deduced from fluorescence and ESR spectroscopic studies, for a similar anionic surfactant, sodiumdodecyl sulfate (SDS) at the alumina–water interface is shown in Figure 2.5 to explain the adsorption mechanism.

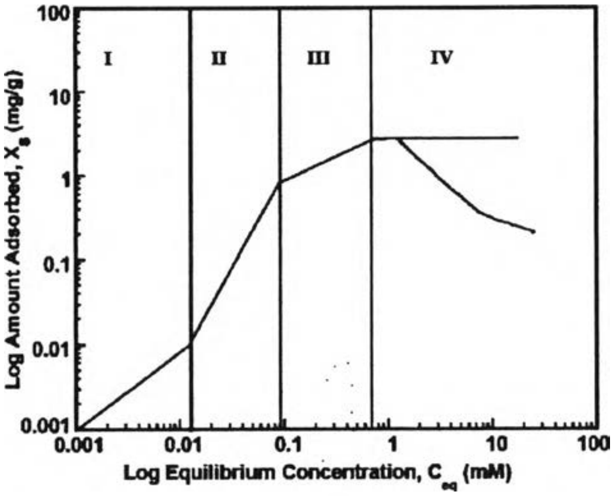


Figure 2.4 Schematic presentation of typical four-regime adsorption isotherm (Paria, *et al.*, 2004).

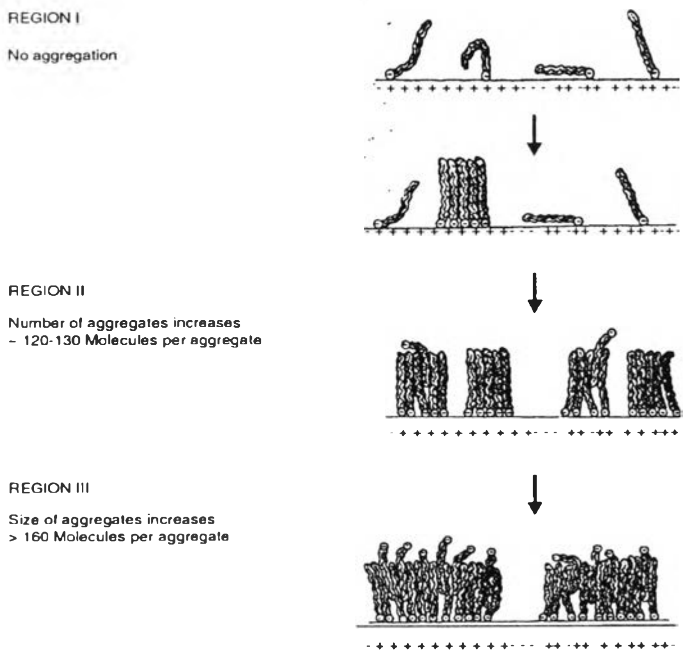


Figure 2.5 Schematic representation of the growth of aggregates of sodium dodecyl sulfate at the alumina–water interface (Somasundaran, *et al.*, 1999).

2.2.2 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 adsorbing from the dilute solution. Nonionic surfactants are physically adsorbed rather than electrostatically or chemisorbed. 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 adsorbate–adsorbate and adsorbate–solvent interactions, which causes surfactant aggregation in bulk solution and which leads to change in orientation and packing of surfactant at the surface. Fig. 2.6a shows a general scheme of the most likely orientation changes undergo in the adsorption of non-ionic surfactants from solution onto solid surface and Fig. 2.6b shows three adsorption isotherms corresponding to the different adsorption sequences shown in Fig. 2.6a (Clunie *et. al.*, 1983).

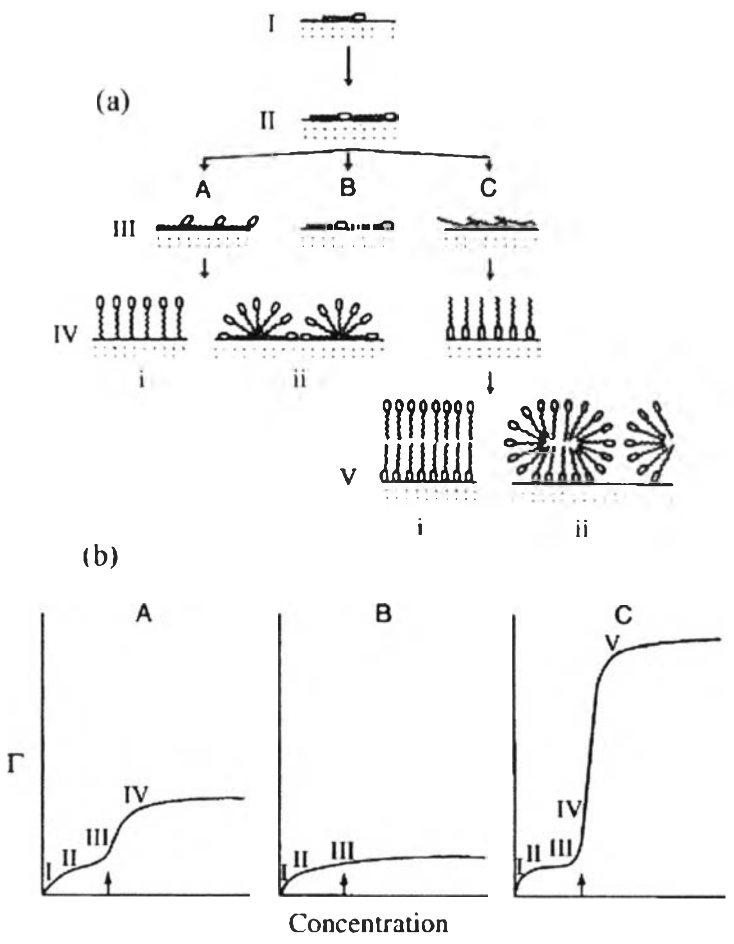


Figure 2.6 (a) Adsorption of nonionic surfactant I–V are the successive stages of adsorption. (b) Adsorption isotherms corresponding to the three adsorption sequences (Clunie *et al.*, 1983).

Adsorption in the first step (Fig. 2.6a I), 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 governed by the hydrophobic moiety of the surfactant. In the next stage of adsorption (Fig. 2.6a II), this region is accompanied by gradual decrease in the slope of the adsorption isotherm due to saturation of monolayer. The consequent region of adsorption are rapidly increasing amount of adsorbed dominated by 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 (Fig. 2.6a 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 (Fig. 2.6a IIIC). The intermediate situation when neither type of displacement is favored and the surfactant then remain flat on the surface (Fig. 2.6a 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. Fig. 2.6a IVC shows the case of adsorption of nonionic surfactants on hydrophilic solid surface.

2.2.3 Desorption of Mixed Anionic–Nonionic Surfactants Mixture

For more than one surfactant adsorbed, it significantly enhances the efficiency in interfacial properties, compared to the single surfactant adsorption. There have been only a few studies of mixed surfactant systems, although the adsorption of single surfactants at solid–liquid interface has been investigated intensively. The solution properties of mixed surfactant system always influence the adsorption of surfactants. Many researchers studied the solution properties of mixed surfactant systems and the resulting adsorption (Somasundaran *et al.*, 2000; Xia *et al.*, 1992; Somasundaran *et al.*, 1997; Scamehorn *et al.*, 1987; and Gao *et al.*, 1984). Adsorption of nonionic surfactant is enhanced where the nonionic alone shows trace adsorption and the adsorption of anionic surfactant slightly decreases. Another feather of mixed surfactant adsorption is that with increasing molar ratio of nonionic surfactant, the continuous shift of the plateau of the isotherm of anionic surfactant towards lower concentration and the hemimicelle concentration of anionic surfactant also shifts towards a lower concentration. In 1984, Gao *et al.* found that the adsorption of nonionic surfactant (TX-100) from the mixture of anionic and nonionic surfactants on the negatively charged silica gel showed the decreasing amount of adsorbed TX-100 above the CMC with increasing concentration of anionic surfactant and there was no change in the isotherm below the CMC between the mixed system and the pure TX-100 system. The decrease in limiting adsorption was greater at the same concentration of anionic surfactant with longer alkyl chain length. In 2000, Somasundaran and Huang found that when the hydrocarbon chain length of nonionic surfactant was equal or longer than that of anionic surfactant, the isotherms of anionic surfactant did not change with changing chain length of nonionic surfactant (in the case of adsorption of anionic/nonionic surfactant on kaolin). If the chain length of nonionic surfactant was shorter than that of anionic surfactant, different isotherms of anionic surfactant were obtained due to less shielding of anionic surfactant. Figure 2.7 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; (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 non-ionic surfactant.

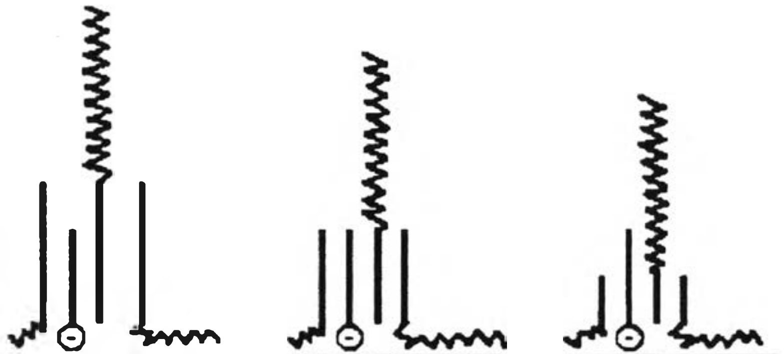


Figure 2.7 Schematic presentation of the effect of nonionic surfactant hydrocarbon chain length on the adsorption of the anionic sodium dodecyl sulfate(SDS) (Gao *et al.*, 1984).

2.2.4 Adsorption on Hydrophilic Surface

Obviously the nature of solid surface plays a crucial role in the adsorption of surfactants at solid-liquid interface. Broadly, adsorbents can be divided into two classes, hydrophilic (or polar) and hydrophobic (or nonpolar). Silicates, inorganic oxides and hydroxides, natural fibers and pertinacious materials have hydrophilic surfaces, whereas the surfaces of a number of carbonaceous materials and polymers are hydrophobic. This section reviews the research work on adsorption onto hydrophilic surface, especially ferric oxide.

In 1998, Dao, Bee, and Treiner studied the adsorption isotherm of sodium octylbenzenesulfonate on iron oxide particles in aqueous solutions. The results showed that maximum adsorption was found in the region of the surfactant concentration greater than the CMC. The maximum adsorption, in the case of ferric oxide, particle is due to the presence of very small concentrations of ferric oxide ions in the aqueous solution. These ions were found to form surface active complexs with sodium octylbenzenesulfonate. These complexes are adsolubilized in the surfactant layers on the particles below the critical micelle concentration. They are desorbed from the surface and transferred into free micelles above the CMC. The presence of ferric ions was found to decrease the surface tension minimum of the anionic surfactant at the air /water interface.

Rao and He (2005) studied the adsorption behavior of anionic surfactant (sodium dodecylbenzenesulfonate, SDBS) and nonionic surfactant (an alcohol ethoxylates with 12 carbons and 9 oxyethyl groups $A_{12}E_9$) mixtures from synthetic detergents. The results showed that the saturated adsorption amounts of SDBS and $A_{12}E_9$ on soils decrease respectively when $A_{12}E_9$ was added into soil firstly compared with that secondly, 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, adsorption amount of SDBS and $A_{12}E_9$ on soils decreased, respectively. The reduction of ion strength in soils resulted in the decrease in adsorption amount of SDBS and $A_{12}E_9$ on soils, respectively.

2.3 Wetting Phenomena

The wetting of a surface by a liquid and the ultimate extent of spreading of that liquid are very important aspects of practical surface chemistry. The term wetting is applied to the displacement from a surface of one fluid by another, usually of air from a solid surface by water or an aqueous solution. On the other hand, wetting means that the contact angle between a liquid and solid is zero, or so close to zero that the liquid spread easily over the solid surface while non-wetting means that the angle is greater than 90°, so that the liquid tends to ball-up and run off the surface easily (Garbassi *et al.*, 1994). Mostly, the addition of surfactants to water can enhance the ability of aqueous solution to wet and spread over a solid surface. However, the presence of surfactant does not always enhance wettability; it depends on several parameters, including molecular structure of the surfactant, and the nature of solid surface (Rosen, 1988).

In 2001, Kim and Hsieh studied the effect of changing aqueous solution properties by adding different nonionic surfactants (sorbitan monolaurate (Span 20) and polyoxyethylene(20) sorbitan monolaurate (Tween 20)) on wetting and absorbency in cotton fabrics. Span 20 has lower surface tension at the critical micelle concentration (CMC) and small molecular area, indicating it is more efficient in lowering the surface tension and effective in adsorption than Tween 20. The wetting properties of hydrophilic cotton fabrics are greatly improved by addition of nonionic surfactants in the aqueous systems.

2.3.1 Contact Angle

Contact angle is the angle formed between a solid surface and the tangent to a liquid drop on that surface at the line of contact between the liquid, the solid, and the surrounding phase (usually vapor or air), measured through the liquid drop.

The contact angle is a quantitative measure of the wetting of a solid by a liquid. Unless it is very volatile, any liquid (including liquid metals such as mercury) having a low viscosity can be used as a drop. A low value of contact angle indicates a strong liquid–solid interaction such that the liquid tends to spread on the solid, or wets well, while high contact angle values indicate weak interaction and poor wetting. If contact angle is less than 90°, then the liquid is said to wet (or sometimes partially wet) the solid. A zero contact angle represents complete wetting. If q is greater than 90°, then it is said to be non-wetting. 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 field 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 interphase region between two immiscible liquids). In 1805 T. Young was the first to describe contact angle equilibrium, as shown in Figure 2.8. The vectorial summation of forces at the three-phase intersection point (the so-called three-phase contact point) gives:

$$\gamma_{SV}=\gamma_{SL}+\gamma_{LV}\cos\theta \quad , \qquad (1)$$

where γ is the surface tension (or surface free energy) term. 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.

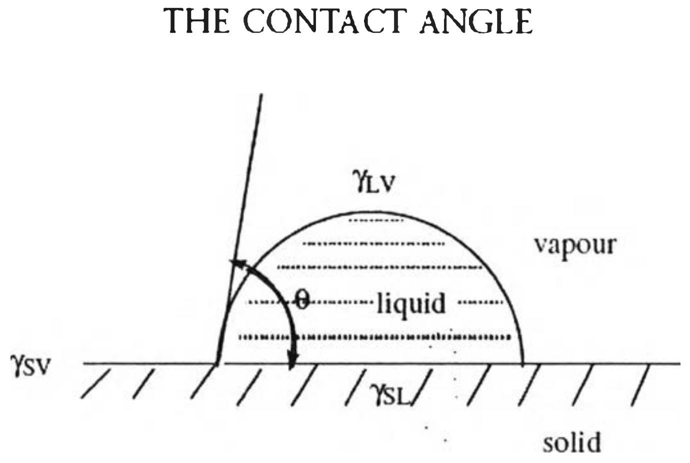


Figure 2.8 Contact angle.

2.4 Types of soils

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

2.4.1 Oily and greasy Soils

Oily soils mean soil is 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, and fatty acid. They are more polar oily materials but not polar enough to be dissolved by water.

2.4.2 Proteins and starchy soils

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

2.4.3 Particulate soils

Solid particle such as clay, alumina, silica, iron oxide, and other metal oxides are present in particulate soils, come mostly from air suspensions (dust). 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/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 (Lang, 1994).

Ferric oxide

Ferric oxide is a reddish-brown to black powder that occurs naturally as the mineral hematite. It can be produced synthetically by igniting virtually any ferrous compound in air. Ferric oxide is the basis of a series of pigments ranging from yellow to a red, known as Venetian red. The finely powdered red form, often called jewelers' rouge, is used for polishing precious metals and diamonds, as well as in cosmetics. Ferric oxide forms a number of hydrates with variable structures and compositions. A common form is iron rust, produced by the combined action of moisture, carbon dioxide, and oxygen in the air on metallic iron.

In 1970, Nakamura and Wakamatu carried out experiments with various fabrics (cotton, poester and polypropylene) to study detergency and redeposition of dirts using ferric oxide mixed in water as model soils. They found that the examined fabrics dipped in water with ferric oxide were easily soiled in the following order: polypropylene > polyester > cotton. They also found that cotton and polypropylene were good efficiency in detergency, while polyester was inefficient.

In 2002, Ken'IChi used ferric oxide as a model soil to study on particulate soil detergency. He found that the particles of Fe_2O_3 adhered to fabrics were detached much more effectively with aqueous solutions of anionic surfactants, especially sodium oleate, than with aqueous solution of nonionic $C_{17}P_{10}$. Alkaline builders enhanced the detachment of the particles. He concluded that the shift in the point of zero charge of the Fe_2O_3 particles to lower pHs by the adsorption of anionic surfactants, promoted the detachment of the particles from the substrate and prevented the re-adhension of detached particles on fiber.

2.5 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 particle 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 particle 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.

In 2001, Paria and coworkers, showed that the critical hydrodynamic force is defined as the minimum force required to detach the particle from the fiber under a given condition. The magnitude of critical hydrodynamic force is dependent on the particle size where the smaller the particle size, the larger the requirement of critical hydrodynamic force.

2.6 Soil Redeposition

Almost cleaning and washing processes are non–continuous processes. In cleaning and washing processes, process is ran with batch type, there will always has the probability that soils removed from surface of substrate will redeposit onto the substrate again as a consequence of a lack of stability of colloid in dispersion soils. For oily soils removed by solubilization, the process is thermodynamically driven so that it is essentially a one-way street and redeposition will be minimal. Solid soils, on the other hand, cannot be solubilized and redeposition must be retarded 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 redeposition. Nonionic surfactants perform the same manner by the formation of a steric or entropic barrier to approach, although the efficacy of such a mechanism is probably less than the electrostatic repulsions in most aqueous systems.