

CHAPTER II

THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Detergency

Detergency is a removal process of unwanted substances, which is called soils, from a solid surface or textile surface (fabric) by contact with a surfactant solution or bath (Kiss, 1987). Detergency is a complex dynamic process that depends on several factors, such as the nature and composition of the washing solution, salinity, temperature, surfactant concentration, washing time, agitation speed, water hardness and hydrodynamic conditions. This detergency or soil removal process involves interactions between surfactants, soil and solid surface (Azemar, 1996 and 1997; Verma *et al.*, 1998 and Whang *et al.*, 2001). Linfidd *et al.* (1962) conducted a detergency study using a Terg-O-Tometer and found that an increase in agitation speed, washing time or detergent concentration produced better fabric detergency performance. These results were supported by that of Germain (2002). Korphol *et al.* (2004) found that the detergency performance increased with increasing total surfactant concentration and the detergency improved with increasing hydrophilicity of the fabric with cotton that was easier than polyester to clean which agrees with the results of Chi *et al.* (1999) and Obendorf *et al.* (1982). Moreover, they found that increasing the amount of rinsing water did not significantly affect the detergency performance and a lower amount of rinse water could be used if a higher rinsing number with a lower volume rinse water was employed. These results were also supported by Ratchatawetchakul *et al.* (2005).

The soils that present on the solid surface or fabric in detergency perspective can be categorized into particulates which are solid particles such as soot, clay and iron dust or rust (usually inorganic), oils which are typically in a liquid form such as motor oil and palm oil (usually organic), waxy solids or greasy soil which are semi-solid such as butter, margarine and grease (usually organic) and stains (unwanted dyestuffs) (Carroll, 1996).

According to previous works the detergency performance has been found to correspond to the phase behavior or microemulsion formation. Both ultra-low

interfacial tension (IFT) and high solubilization are believed to be important parameters in promoting detergency efficiency. This correlation has been studied comprehensively for decades; several studies reported that the maximum detergency corresponds to the optimum condition in a Winsor type III system (Dillan *et al.*, 1979 and 1980; Dörfler *et al.*, 1996; Korphol *et al.*, 2004; Raney *et al.*, 1987; Robbins, 1976; Tongcumpou *et al.*, 2003 and 2005).

2.2 Microemulsion

A microemulsion is a solution in one liquid of micelles swollen by a solubilized second liquid or a dispersion of tiny droplets with diameters of 10-100 nm of one liquid in a second liquid that both liquids are immiscible (for example, oil and water) (Rosen, 2004). Microemulsion systems are isotropic, low-viscosity and thermodynamically stable surfactant-oil-water systems that have important properties relating to the detergency such as a very high oil solubilization and very low oil-water IFT that is close to zero (Bourrel *et al.*, 1998). The characteristics of microemulsions were first reported in the 1940s by Schulman (Schulman *et al.*, 1940). But a well known classification of microemulsions is that of Winsor.

Typical phase diagrams of a surfactant-oil-water system of Winsor are illustrated in Figures 2.1 and 2.2 in terms of microstructure and IFT of the system, respectively.

The typical transition occurs from Winsor type I to type III and to type II microemulsions when the hydrophile-lipophile balance (HLB) decreases. The HLB for ionic surfactant systems decreases as increasing salinity or electrolyte concentration (NaCl) and for nonionic surfactant systems as increasing temperature. The HLB is the value that can characterize water solubility; a higher HLB indicates a higher water solubility (Jacques, 1999).

For Winsor type I, its region is at high HLB values so the surfactant is predominantly in the water phase or it prefers to dissolve in the water and it forms oil-in-water (o/w) microemulsions. This region the surfactant-rich water phase is in equilibrium with excess oil phase having a very low monomer-surfactant concentration (2 phases; the surfactant-rich water phase and excess oil phase). The

value of IFT between excess oil and the o/w microemulsion of this region decrease as the value of HLB at the interfacial decreases.

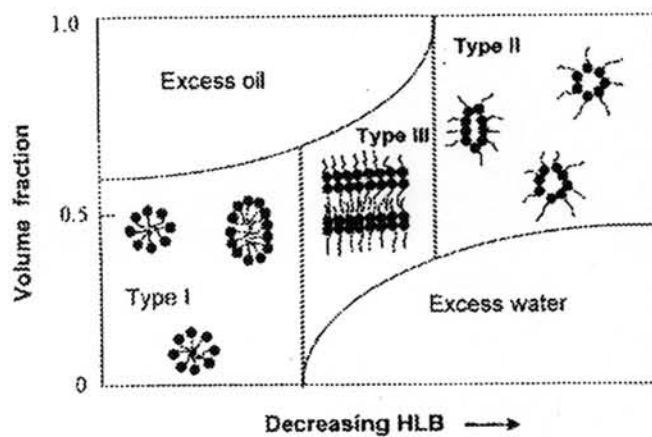


Figure 2.1 Typical phase behavior showing the transition from oil-in-water microemulsion (Type I) to bicontinuous structure (Type III) and water-in-oil microemulsion (Type II) at an initial ratio of oil to water = 1:1 when HLB increases.

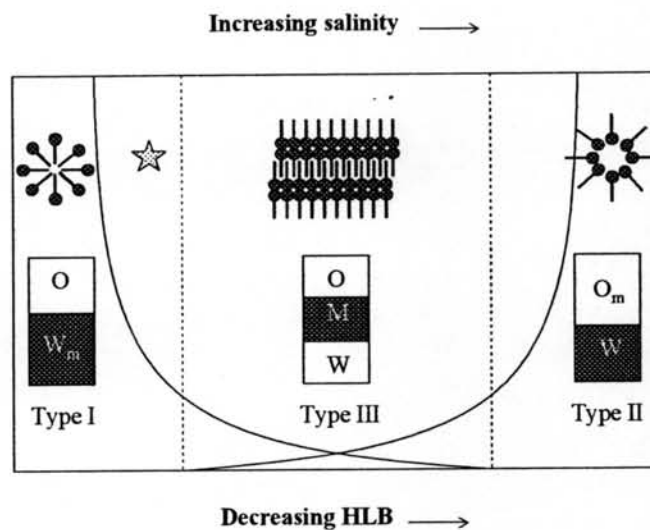


Figure 2.2 Phase behavior showing interfacial tension (IFT) as a function of scanning variable, where o is oil; w is water; m is middle phase, and the star show the supersolubilization (SPS) region.

For Winsor type III, its region is at appropriate HLB that the system splits into three phase (surfactant-rich middle-phase, excess water and oil surfactant-poor phase). The middle phase of a Winsor type III system has a bicontinuous structure (Cates *et al.*, 1988) in equilibrium with excess oil and excess water phases and the point in the middle phase where the IFT between the excess oil phase and the middle phase (IFT_{o/w}) equals the IFT between the middle phase and the excess water phase (IFT_{m/w}) is known as the optimum condition, because it has the lowest IFT that is as low as 10^{-3} mN/m, called ultra-low IFT or the optimum interfacial tension (IFT*) and highest solubilization (Bourrel *et al.*, 1998). In a nonionic surfactant system, temperature scans are commonly used to obtain the optimum condition in the Winsor type III region and the temperature at the optimum point is known as the phase inversion temperature (PIT). In an ionic surfactant system, salinity or salt concentration scans are commonly used to produce the optimum condition and the salinity at the optimum point is known as the optimum salinity (S*) (Broze *et al.*, 1994). This Winsor type III, the volumes of oil and of water solubilized in the middle phase are equal. The volumes of oil and water that are solubilized in the middle phase can be indicated as the solubilization parameter (SP) that is the volume of oil or of water per weight of surfactant in the microemulsion phase. At the optimum condition, SP is referred to as SP* (Healy *et al.*, 1976).

For Winsor type II, its region is at low HLB values. Hence, the surfactant is predominantly in oil phase or it prefers to dissolve water in oil to form water-in-oil (w/o) microemulsions. The surfactant-rich oil phase is in equilibrium with excess water phase having a very low monomer-surfactant concentration (2 phases; the surfactant-rich oil phase and excess water). The value of IFT between the excess water and w/o microemulsion increases as the value of HLB at the interface decreases.

The region of Winsor type I close to the transition zone from a Winsor type I to Winsor type III is known as the supersolubilization (SPS) region, where both high solubilization capacity and low IFT are obtained from the system (Wu *et al.*, 2000). In this region, the micelles are swollen so the solubilization capacity increases up to one order of magnitude (Wu *et al.*, 2000). For some systems, a hazy or milky but translucent solution can appear.

The microemulsion transition is governed by the hydrophilicity and lipophilicity of the system as described by the Winsor R ratio of interactions which is a semi-quantitative method of measuring the balance between the hydrophilic and lipophilic characters of the surfactant. The Winsor R ratio of interactions is calculated from the following equation (Eq.2.1) (Rosen, 2004).

$$R = \frac{A_{CO} - A_{OO} - A_{LL}}{A_{CW} - A_{WW} - A_{HH}} \quad \dots\dots\dots \text{(Eq.2.1)}$$

Where A_{CO} is the interaction (per unit interfacial area) between the surfactant and the oil, A_{CW} is the interaction between the surfactant and the aqueous phase, L and H refer to lipophilic and hydrophilic, and A_{LL} and A_{HH} are self-interaction of the lipophilic and the hydrophilic portions of the surfactant, respectively. The parameter A_{WW} and A_{OO} are self-interaction in the water phase and oil phase, respectively. The numerator of the equation represents the net interaction of the lipophilic portion of the surfactant at the interface, and the denominator represents the hydrophilic part of the interface. When $R < 1$, the interface becomes more hydrophilic, and an o/w microemulsion exists (Winsor type I). For $R > 1$, inverse micelles form and the solution becomes a w/o microemulsion (Winsor type II). For $R = 1$, the interactions of the lipophilic and hydrophilic regions are in balance. So the optimal formation appears (Winsor type III) (Bourrel *et al.*, 1998). Besides type III, a single-phase (isotropic) microemulsion that forms upon addition of a sufficient quantity of amphiphile (surfactant plus alcohol) can appear, also. Because, when $R = 1$, the larger the value of the numerator (or denominator) of the expression for R, the greater the solubilization capacity for water (or oil) and consequently the greater the tendency to form an isotropic system that is called Winsor type IV system. On the other hand, when $R = 1$ and the A_{LL} and the A_{HH} interactions are large, liquid crystals or gels may form (Rosen, 2004).

The value of A_{OO} or the self-interaction of the oil or the value of hydrophobicity can be indicated by the EACN values. The EACN is an equivalent number of carbons in complex mixed oil as compared to single component alkane oil. A high EACN signifies a high hydrophobicity or a high A_{OO} value of the mixed

oil. Wu and Sabatini (2000) used an alcohol partition method to determine EACN values of several oils including motor oil. Wu et al. (2000) further studied and reported the EACN value of their motor oil to be 23.5, hexadecane or cetane, whose EACN is 16. Salager *et al.* (1979) described the relationship of the Winsor R ratio of interactions to the SP that enhances the solubilization of both oil and water, the interactions of both the hydrophilic and the lipophilic parts of the interface must be increased. From previous studies (Tongcumpou *et al.*, 2003 and 2005), studies of detergency were carried out using motor oil and hexadecane which in high and low hydrophobicity (A_{OO}), respectively. For hexadecane with a low A_{OO} value, the value of the numerator will be lower than that of motor oil. To reach the optimal condition at $R=1$, the denominator has to increase as well. This can be achieved by reducing the salinity of the system, which will lead to an increase in A_{CW} . Consequently, the salinity of the hexadecane system is lower than that of the motor oil system and the SP^* value of the system with hexadecane was higher than for the system with motor oil; 2.69 and 1.98 mL/g, respectively. These results correspond to the other results (Bourrel *et al.*, 1982 and 1998; Salager, 1999).

2.3 Mechanism of oily soil removal

Mechanism of oily soil removal that is well accepted has three primary mechanisms: roll-up or roll-back, emulsification or snap-off or necking, and solubilization (Broze, 1994; Dillan *et al.*, 1979; Verma *et al.*, 1998.)

2.3.1 Roll-up

Roll-up or roll-back is a major mechanism of oily soil removal (Broze, 1994) or the major detachment of an oil droplet from a substrate by reducing the interfacial tension (IFT) between oil (soil) and water (bath), (γ_{OB}), and between the substrate (solid) and water (bath), (γ_{SB}), increase in the contact angle of the attached oil droplet (Verma *et al.*, 1998).

Removal of oily soil by roll-up or roll-back can be explained by the work of adhesion of the oily soil for the substrate in the presence of a cleaning bath

(Thompson, 1994) and the young's equation that indicates relationship between contact angle and interfacial tension, as shown in Figure 2.3.

The work of adhesion:

$$W_{O/S(B)} = \gamma_{SB} + \gamma_{OB} - \gamma_{SO} = \gamma_{OB}(\cos\theta + 1) \quad \text{..... (Eq.2.1)}$$

The young's equation:

$$\cos\theta = \frac{\gamma_{SB} - \gamma_{SO}}{\gamma_{OB}} \quad \text{..... (Eq.2.2)}$$

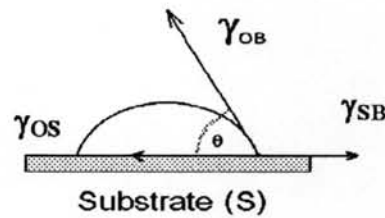


Figure 2.3 The contact angle between an oil droplet and substrate in bath.

When surfactant are added in the bath, they will adsorb at the substrate-bath (SB) and oily soil-bath (OB) interfaces as to reduce γ_{SB} and γ_{OB} , with consequent reduction in the work to remove the soil from the substrate or reduction in the work of adhesion. Reduction in γ_{SB} will also cause a decrease in $\cos\theta$ and an increase in θ to the value greater than 90° , resulting in the observed roll-up of the oily soil (Rosen, 2004), as shown in Figure 2.4.

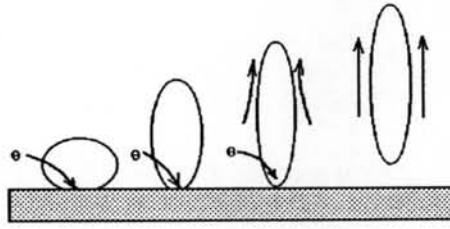


Figure 2.4 Roll-up mechanism shows complete removal of oil droplets from substrate by hydraulic currents when $\theta > 90^\circ$ (Rosen, 2004).

If the contact angle is 180° ($\cos\theta = 1$), the bath will spontaneously completely displace the oily soil from the substrate; if the contact angle is less than 180° but more than 90° , the oily soil will not be displaced spontaneously but can be removed by hydraulic currents in the bath (Rosen, 2004). On the other hand, when the contact angle is less than 90° , at least part of the oily soil will remain attached to the substrate which is called snap-off (Rosen, 2004).

2.3.2 Emulsification

Emulsification or snap-off or necking is a mechanism that a part of the oil droplet is drawn off into the wash liquor by hydrodynamic forces, and it occurs when the contact angle is less than 90° . In Emulsification mechanism, incomplete detachment of the oily soil droplet occurs because a small residual drop remains on the substrate, and the detached oil is then emulsified in water (bath) or it disperses in the water, as shown in Figure 2.5.

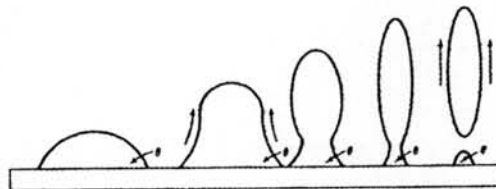


Figure 2.5 Emulsification or Necking mechanism shows partial removal of oil droplets from substrate by hydraulic currents when $\theta < 90^\circ$ (Rosen, 2004).

This phenomenon can be understood using the concepts of cohesion work (W_c) (Thompson, 1994).

$$W_c = 2\gamma_{o/w} \dots\dots\dots (\text{Eq.2.3})$$

Where $\gamma_{o/w}$ is the IFT between oil and the surfactant solution (bath). It is clear that a reduction in IFT reduces the work of cohesion, which, in turns, makes it easier to “break up” or “snap-off” oily aggregates deposited on the surface of the fabric.

Agitation is able to generate an emulsion, but, to remain dispersed, the oil droplet need to be coated with a large of surfactant molecules to reduce the interfacial tension with the continuous phase. Of course, a high surfactant concentration may at first appear to be beneficial, since micelles act as surfactant reservoirs. However, at surfactant concentration above 5-10 times the CMC, the micelles can induce flocculation of the oil droplet. But, the contact angle that is less than 90° causes the redeposition of the oil on the substrate.

The ability of the bath to emulsify the oily soil is, however, in itself insufficient to keep all the soil from redeposition on the substrate. When the emulsified oil droplets impinge on the substrate, some of them may be adhere to it in part, with the adhering portion tending to assume the equilibrium contact angle, unless the latter is 180° (i.e., unless complete oily soil removal by roll-up has been attained). This is in contrast to solubilization, which can result in complete removal of the oily soil from the substrate.

2.3.3 Solubilization

In particular, the solubilization or oil uptake capacity of a surfactant system is a major mechanism for removing small amount of oil, which cannot be removed either by roll-up or emulsification, as shown in Figure 2.6. The solubilization occurs to a significant extent only in some cases and always above the CMC of the surfactant system. This is based upon the observation (Ginn *et al.*, 1961; Mankowich, 1961) that oily soil removal from both hard and textile surfaces becomes significant only above the CMC for nonionics and even for some anionics

having low CMCs, and reaches its maximum only at several times the CMC. At low bath concentrations only a relatively small amount of oily soil can be solubilized, whereas at high surfactant concentrations (10-100 times the CMC), solubilization is more similar to microemulsion formation and the high concentration of surfactant can accommodate a much larger amount of oily matter (Schwartz, 1972). With ionic surfactants, an applied surfactant concentration is generally not much above the CMC; consequently, solubilization is almost always insufficient to suspend all the oily soil. When insufficient surfactant is present to solubilize all the oily soil, the remainder is probably suspended in the bath by emulsification. Besides, the maximum solubilization capacity of a given surfactant is also mentioned by Bronze (1994) that it occurs when the surfactant divides equally well between the water and the oily phase. In practice, this happens for a given surfactant system at a temperature referred to as the phase inversion temperature (PIT).

The solubilization depends on the shape of the micelles, the chemical structure of the surfactant, its concentration in the bath, and the temperature. The oil uptake capacity of globular micelles is limited because the addition of oil necessarily results in an increase of the micelle surface exposed to water. Rod-like micelles are much better adapted to a higher oil uptake (Rosen, 2004). A surfactant forming rod-like micelles induces a lower oil-water interfacial tension and accordingly facilitates the transfer of oil from the substrate to the core of the micelles. Nonionic surfactants such as polyethoxylate fatty alcohols exhibit a much higher potential for solubilization. Azemar *et al.* (1997) proposed that the solubilization can result in more complete removal of oily soil from substrate than emulsification.

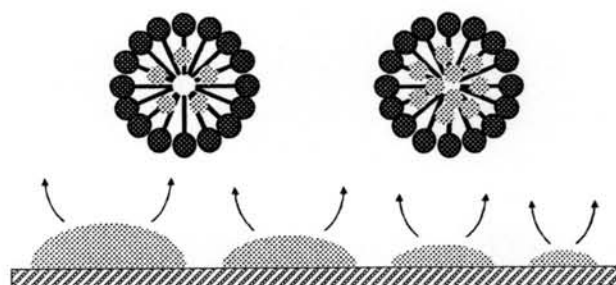


Figure 2.6 The solubilization mechanism of removing oily soil from a solid surface.

2.4 Maximum detergency (D_{max})

Several studies have concluded that the maximum detergency corresponds to the optimum condition in a Winsor type III microemulsion where the lowest oil/water IFT and the highest oil solubilization occur (Raney *et al.*, 1987; Robbins, 1976; Dillan *et al.*, 1979 and 1980; Azemar, 1997). In a nonionic surfactant system, the maximum detergency achieve at the phase inversion temperature (PIT) (Mori *et al.*, 1989; Azemar, 1996). In an anionic surfactant system, the maximum detergency achieve at the optimum salinity (S^*) (Broze, 1994; Salans *et al.*, 1992).

The relationship between microemulsion conditions and detergency was also demonstrated by Dörfler and coworkers (Dörfler *et al.*, 1996). They reported that the maximum detergency was found to correspond to the microemulsion region which exhibits ultra-low interfacial tension with maximum solubilization power.

However, Thompson argued that D_{max} was not always found at IFT_{min} or at optimum condition (Thompson, 1994). Because, at the same time, the separate microemulsion phase (middle-phase microemulsion) was trapped in fiber bundles, resulting in the vast majority of the surfactant is lost from the solution. The consequent redeposition of detached oil can take place because insufficient surfactant is present in solution to form stable emulsions of detached oil droplets. Redeposition is promoted when emulsified oil droplets contact fabric and tend to stick to it and wet the fabric surface (the oil become wetted) (Healy *et al.*, 1976; Tongcumpou *et al.*, 2005). That all is called Thompson effect or spreading effect (the surfactant lost into/onto the fabrics).

The fate of the oil film deposited on the surface of the fabric can be indicated by the spreading coefficient (S).

$$S = \gamma_{o/w}(\cos\theta - 1) \quad \dots\dots\dots (\text{Eq.2.4})$$

When S is zero, the oil film will spread and coat the surface. At optimal conditions the contact angle is still close to 90° , but since the interfacial tension is ultra-low, it

can produce a near zero spreading coefficient, which means that it is very likely to form a coating microemulsion film on the surface of the fabric.

The Thompson effect or the spreading effect or the coating microemulsion film is supported by measurements of pre and post-wash of surfactant concentration and IFT at the optimum condition. When it is obvious that the surfactant has been lost from solution, the explanation according to the coating microemulsion film hypothesis is that the surfactant will come out of solution to partition into this microemulsion film. Once the surfactant comes out of the solution, it is logical to expect that the post-wash oil-water IFT will be higher than that of pre-wash because of the reduced surfactant concentration. If the coating film hypothesis is true, rinsing under the same optimum condition (i.e., optimum salinity or optimum temperature in the case of anionic surfactant or nonionic surfactant, respectively), the microemulsion film would remain in equilibrium and little oil would be removed. On the other hand, if during the rinse step on electrolyte concentrations that correspond to a Winsor Type I system far from the optimum, where the oil is non wetting on the surface, and thus the roll-up mechanism can easily detach the microemulsion film from the surface. Consequently, the oil removal in the rinse step is almost as high as that in the wash step (Tongcumpou *et al.*, 2003). During the wash step, the contact angle of the oil on the fabric surface is progressively increased resulting in the detachment of the oil droplets. However, owing to the very low IFT, the spreading effect is dominant, thereby causing incomplete oil removal. During the subsequent rinse step, the IFT increases, passing through a composition at which the roll-up mechanism causes additional oil removal.

With the Thompson effect at the optimum condition, researchers started to try to find another condition that could achieve the maximum detergency. They found that the maximum detergency corresponded to formation of a Winsor type III microemulsion as well as to the SPS (West *et al.*, 1992; Wu *et al.*, 2000; Durbut, 1999; Tongcumpou *et al.*, 2003). The region of type I close to the transition region from type I to type III is known as the supersolubilization region (SPS). In this region, the micelles are swollen and that the solubilization capacity can be increased up to one order of magnitude. For some systems, a hazy or milky but translucent solution appears in the SPS zone. Even though the IFT in the SPS region is not as

low as at the optimal conditions in a type III system, SPS still provides considerably high solubilization and low IFT without formation of middle phase. SPS was first proposed with regard to surfactant enhanced remediation because it is believed to be able to avoid the problem of coating microemulsion film or the potential disadvantages of having a middle phase present when using Winsor type III system (Durbut, 1999; West *et al.*, 1992; Wu *et al.*, 2000).

Besides the argument of Thompson, he also proposed another mechanism which the maximum detergency might correlate with an increase in oil/substrate contact angle (Thompson, 1994).

2.5 Surfactant Adsorption

The adsorption of an ionic surfactant on oppositely charged surfaces involves many mechanisms. However, only a few parameters affect the adsorption including 1) the nature of the structural groups on solid surface 2) the molecular structure of the adsorbate (the surfactant being adsorbed) and 3) the environment of the aqueous phase such as pH (Rosen, 1989).

The adsorption isotherm for a 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 2.7. The adsorption isotherm is divided into three (or four) distinct regions as follows:

Region I is commonly referred to as the Henry's law region because in this region monoisomeric surfactant isotherms are linear and have a slope of unity. In the Henry's law region, surfactant adsorption is the result of monomer interactions with the surface. There is little or no interaction between individual adsorbed surface ions.

Region II 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 effects between adsorbed molecules. It is widely accepted that this cooperatively consists of formation of micelle-like aggregates of adsorbed surfactants. These aggregates are frequently called admicelles or hemimicelles, depending on whether their morphology is viewed as local bilayers or local monolayers, 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. Scamehorn *et al.*, (1982) demonstrated that hemimicelles first formed on the most energetic surface sites.

Region III is characterized by a decrease in the isotherm slope relative to the slope in Region II, the change in slope may be abrupt, as in the schematic, or it may be gradual. An explanation for this change in slope is that with increasing adsorption of surfactant, the surface becomes like-charged to the surfactant and the surface begins to repel the surfactant ions. However, this mechanism cannot be the explanation for the same isotherm shape for nonionic surfactant adsorption.

Region IV is the plateau adsorption region for surfactants. Generally, the Region III/Region IV transition occurs approximately at the CMC of the surfactant, and reflects the effect of micelle formation on the chemical potential of surfactant monomers, just as the formation of micelles 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.

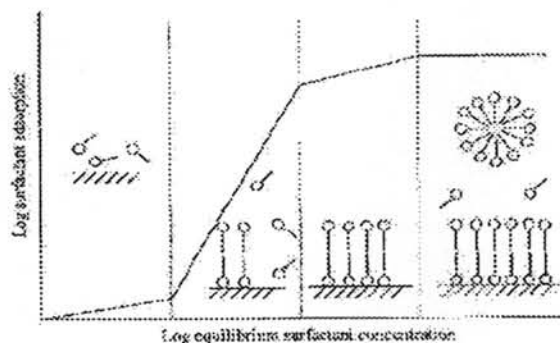


Figure 2.7 Adsorption isotherm of surfactant on an oppositely charged substrate (Rosen, 2004).

2.5.1 Adsorption Isotherm

An adsorption isotherm is a relation of the concentration at the interface and its equilibrium concentration in bulk or the liquid phase. The adsorption isotherm is the usual method of describing adsorption at the solid-liquid interface. Much valuable information is obtained from the adsorption isotherm as follows (Rosen, 1988):

1. The amount of surfactant adsorbed per unit area of the solid adsorbent.
2. The equilibrium concentration of surfactant in the liquid phase required to produce a given surface concentration of surfactant.
3. The concentration of surfactant on the adsorbent at surface saturation.
4. The orientation of the adsorbed surfactant.
5. The effect of adsorption on other properties of adsorbent.

2.5.2 Adsorption on Hydrophobic Surface

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

Greenwood *et al.* (1968) studied the adsorption of an anionic surfactant, sodium dodecyl sulfate (SDS) at carbon/aqueous solution interface. They found that the results for carbon black, Spheron 6, were Langmuirian shape, and the plateau adsorption occurred at the CMC. However, the results for Graphon, were different. There was a marked inflection in the isotherm, which started to rise a second time at area per SDS ion of about 0.72 nm^2 and the area at the plateau level being about 0.43 nm^2 . At low coverage, SDS was assumed to adsorb parallel to the surface as a result of hydrophobic chain-surface interaction, and at high coverage it was expected to adsorb vertically to the surface, a result from chain-chain interactions. Moreover, they also investigated the system of Graphon with 0.1 M .

NaCl interface, and found that the inflection point appeared to be absent, the plateau adsorption was achieved at a lower SDS concentration, and the area per molecule in plateau region was reduced by the presence of salt.

Many substrates are grouped in this hydrophobic class such as Teflon, polystyrene, polyethylene, polypropylene, polymethylmethacrylate, and carbon. On these adsorbents, the adsorption isotherms for well-purified monofunctional anionic and cationic surfactants are similar (Rosen, 1988). Dispersion force (hydrophobic bonding) plays an important role in adsorption of surfactants on these substrates.

The adsorption of CTAB onto active carbon-water interface mainly takes place through ion exchange, the ion pairing and hydrophobic bonding. The predominant mechanisms in the lower CTAB concentrations are probably ion exchange and ion pairing. The hydrophobic bonding mechanism predominates with increasing CTAB concentration (Gurses *et al.*, 2003).

The orientation of the surfactants initially might be parallel to the surface of the solid or slightly tilted. As adsorption continues, the adsorbed molecules might be oriented more perpendicular to the surface. In case of sodium dodecyl sulfate, SDS, adsorption onto Graphon, the adsorption isotherm shows an inflection point with hydrophilic heads oriented toward the water and hydrophobic tails oriented toward the solid surface (Rosen, 1988; Zettlmoyer, 1968).

Likewise, the adsorption isotherms of sodium dodecyl benzene sulfonate, NaDBS, on coal also exhibited two stages of saturation (Mishra *et al.*, 2003). These plots showed the non-Langmuirian behavior, i.e., adsorption was not proportional to concentration (slope < 1). They suggested that multilayer adsorption was a possible reason.

Furthermore, a well-defined knee on the adsorption isotherm of the cationic surfactant, a series of trimethylammonium bromides, which adsorbed onto a negatively charged polystyrene surface, was observed by Ingram and Ottewill (1990). The knee occurred at the point where the surface charge of the particles reversed (Zollar, 2001). They concluded that the adsorption process up the knee of the isotherm occurred via ionic interaction between the cationic head group and the negatively charged surface. The adsorption isotherm above the knee closely resembled that observed onto an uncharged polystyrene surface.

The effect of polymer polarity on surfactant adsorption was also studied by many researchers. The adsorption of sodium dodecyl sulfate, SDS, and nonionic surfactants on sulfonated polystyrene latex of various charge densities was investigated by Ali *et al.* (1987). For nonionic surfactants, the adsorption area per molecule increased with increasing the surface polarity. 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 SDS) at various polymer-water interfaces increased with the polarity of polymer (Vijayendran, 1979).

However, Ali *et al.*, (1996) reported the opposite trend for SDS. They explained that it might be due to the surfactant molecules were likely to adsorb in more tightly packed configuration. This effect of surface charge density on adsorption extended to the region from -3 to $-7 \mu\text{C}/\text{cm}^2$ (Hoeft and Zollars, 1996).

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

2.5.3 Structure of Adsorbed Layer

The structure of an adsorbed surfactant layer at the solid-liquid interface has been evaluated by using many techniques such as ellipsometer, neutron reflectivity, fluorescence spectroscopy, and atomic force microscopy (AFM). AFM can be used to image directly the structure of surfactant aggregated at the solid-liquid interface (Garbassi *et al.*, 1994).

Atkin *et al.* (2003) studied the image of interfacial aggregation for CTAB on graphite by using AFM. They indicated that the most likely surface conformation of surfactant was a hemicylindrical arrangement. The adsorbed structure of C_{12}TAB on graphite showed a flat monolayer at low concentrations, followed by the formation of hemicylindrical interfacial aggregates (Kiraly and Findenegg, 1998).

Nonionic surfactants appear to form laterally homogenous monolayers on amorphous hydrophobic surface. On graphite, the same surfactants organised parallel to the surface at low concentrations. Templating self-assembly leads to the formation of hemicylindrical structures (loser to the CMC). Ionic surfactants are also found to exhibit the same behavior (Tiberg *et al.*, 2000).

Most surfactants form hemicylindrical structures on graphite. The nonionic C₁₀ surfactant does not. They form a homogeneous layer on graphite. It is suggested that there is probable a specific attractive interaction between graphite and alkyl chains that increases in magnitude with the number of methylene units (Grant and Ducker, 1997; Grant *et al.*, 1998). Atkin *et al.* (2003) proposed that this was likely due to the tail length failing to reach a critical length to successfully adsorb epitaxially and act as a template for hemicylindrical aggregation as shown in Figure 2.8.

Furthermore, Grosse and Estel (2000) explained that hemicylinders dominated on hydrophobic materials because a large contact area between the hydrophobic chains of the surfactant and the solid surface was thermodynamically favorable.

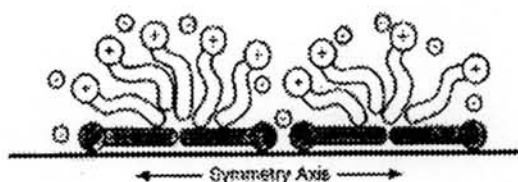


Figure 2.8 Hemicylinders aggregate at the hydrophobic surface (Atkin *et al.*, 2003).

2.6 Water Hardness

Water hardness or the presence of polyvalent cations, notably Ca²⁺ and Mg²⁺, in the bath water is invariably detrimental to the cleaning process because polyvalent cations can precipitate anionic surfactant as shown in Figure 2.9 (Scamehorn *et al.*, 1993; Rosen, 2004). In addition, they can adsorb onto the negatively charged substrate and soil, leading to lowering their electrical potentials, thus impeding soil removal and facilitating its redeposition. They can also act as

linkages between negatively charged substrate and negatively charged soil, thus promoting soil redeposition. And they can also act as linkages between the negatively charged hydrophilic groups of anionic surfactant 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 γ_{SB} and γ_{OB} , the interfacial tensions at the substrate-bath and soil-bath interfaces, respectively, increasing the work of adhesion and impeding wetting an oily soil roll-up. In addition, at high polyvalent anion concentrations, the corresponding metal salts of anionic surfactants and other anions (e.g. phosphates, silicates) in the bath may precipitate onto the substrate. In some cases, this may mask the presence of soil on the substrate or produce other deleterious effects (Rosen, 2004).

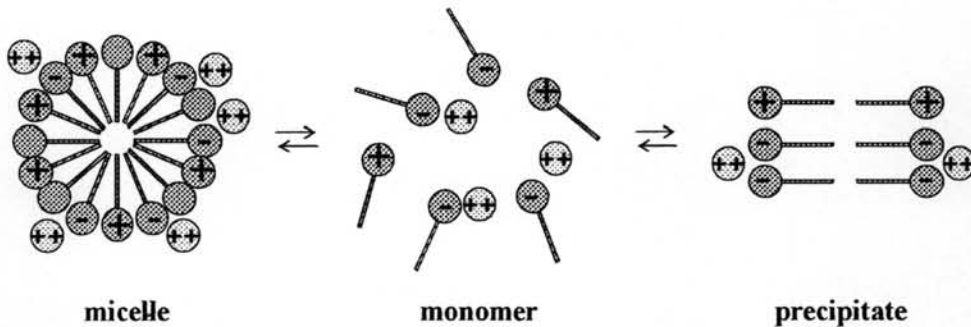


Figure 2.9 Precipitation of anionic surfactant by polyvalent cations.

2.7 Builders

Builders are considered to be of nearly equal importance to surfactants because they support and enhance overall wash performance of the bath by lowering water hardness, controlling alkalinity, buffering the pH, and acting as dispersants, antiredeposition agents, corrosion inhibitors, etc. The primary function of builders is to counter the detrimental effects of polyvalent cations such as calcium or magnesium on detergency by removing them from solution either as a soluble complex or as a precipitate. Polyvalent cations are introduced into the wash bath

mainly by water hardness but may also come from soil or substrate. Most builder salts provide alkalinity to neutralize acid soils, producing soaps which aid further in the detergency process and decrease soil redeposition by stabilization of the dispersed soil (Motoko *et al.*, 2002; Rosen, 2004).

However, few cleaning studies have focused on the detergency performance of the builder alone. This is especially true for polyelectrolyte builders, even though they have been designed to change the physical and chemical nature of the washing bath, sorb strongly onto fabric surface, and improve the detergency performance of surfactants (Motoko *et al.*, 2002; Webb *et al.*, 1987).

Tripolyphosphate (TPP) or sodium triphosphate (STPP), $\text{Na}_5\text{P}_3\text{O}_{10}$, is the most common historical builder in use because it is cheap and effective. But it has questions about its contribution to eutrophication. In quiet water, phosphate causes water pollution because it will act as a fertilizer that causes algae grow rapidly. When algae die, it will sink to bottom of the pool and use oxygen (O_2) for decomposition it. As a result, the oxygen in water decreases. Consequently, fish die by the insufficiency of oxygen to breathe and that further causes water pollution by producing hydrogen sulfide (H_2S). For turbulent water (such as river in Thailand) which has enough oxygen for decomposition of algae, phosphate will not cause water pollution. Phosphate is recognized to be highly effective in performance enhancement in cleaning. Figure 2.10 shows the molecular structure of sodium tripolyphosphate. Non-phosphate formulation tends to be less effective, even more so, on a cost basis.

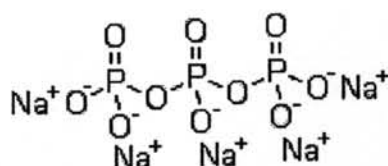


Figure 2.10 The molecular structure of sodium tripolyphosphate.

Ethylenediaminetetraacetic acid (EDTA), $\text{C}_{10}\text{H}_{16}\text{N}_2\text{O}_8$, is the one of builders which is highly effective. Figure 2.11 shows the chemical structure of EDTA. It is a

novel molecule for complexing metal ions. It is a polyprotic acid containing four carboxylic acid groups and two amine groups with lone pair electrons. The unusual property of EDTA is its ability to chelate or complex metal ions in 1:1 metal-to-EDTA complexes. The fully deprotonated form (all acidic hydrogens removed) of EDTA binds to the metal ion. The equilibrium or formation constants for most metals, especially the transition metals, are very large; hence, the reactions are shifted to the complex. Many of the reactions are pH dependent, especially the weaker forming complexes with Ca^{+2} or Mg^{+2} , as shown in Equation 2.5.

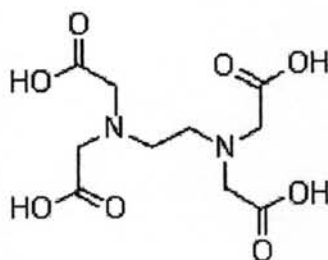


Figure 2.11 The molecular structure of ethylenediaminetetraacetic acid.