



CHAPTER II

BACKGROUND AND LITERATURE SURVEY

2.1 Surfactant Characteristics

Surfactant or surface-active agent is a substance that at low concentration adsorbs at the surface or interface and alters (reduces) the surface or interfacial free energies (Rosen, 1988). At sufficiently high concentration, surfactant can form colloid-sized aggregates in solution, called micelle. The lowest total surfactant concentration at which the first micelle is formed is critical micelle concentration (CMC).

Surfactants have a characteristic molecule structure consisting of a structural group that has very little attraction for the solvent, called lyophobic group, and a group that has strong interaction for solvent, known as lyophilic group. In the aqueous system, the lyophobic and lyophilic group is called hydrophobic and hydrophilic group respectively. The hydrophobic group is usually long-chain hydrocarbon while the hydrophilic group is an ionic or high polar group. Based on the nature of the hydrophilic group (head group) (Rosen, 1988), surfactant can be classified into four main groups: anionic, cationic, nonionic, and zwitterionic.

2.2 Adsorption of Surfactant at the Solid/Liquid Interface

The tendency to adsorb at the surface is one of the characteristic features of surfactants. Their adsorption at solid surfaces is in practice used to facilitate detergency, control wetting and penetration of solutions, stabilize foams and emulsions, and collect minerals in flotation operations (Tiberg *et al.*, 2000). For wetting of hydrophobic surfaces, surfactant adsorption makes the surface becomes more hydrophilic and consequently enhance the spreading of aqueous solution on surface.

The following factors influence the adsorption at the solid/liquid interface (Rosen, 1988).

1. The nature of the structural groups on the solid surface.

2. The molecular structure of the surfactant being adsorbed.
3. The environment of the aqueous phase such as pH, electrolyte, additive.

These factors altogether determine the adsorption mechanism and the efficiency and effectiveness of adsorption.

2.2.1 Adsorption Isotherm

An adsorption isotherm is a mathematical expression that relates the concentration of the adsorbate at the interface to its equilibrium concentration in the liquid phase. Since most of the information regarding adsorption onto solid/liquid interface can be deduced from the adsorption isotherm, the isotherm is the usual method of describing adsorption at the solid/liquid interface (Rosen, 1988). The nature of the true adsorption mechanism may also be obtained from the adsorption isotherm (Rybinski and Schwuger, 1987).

2.2.2 Adsorption on Hydrophobic Surface

Greenwood *et al.* (1968) studied the adsorption of an anionic surfactant, SDS, at carbon/aqueous interface. For carbon black, Spheron 6, the adsorption was of the Langmuir type and showed the surface saturation (plateau) near CMC. At low coverage, the adsorbate may adsorb parallel to the surface or slightly tilted because of hydrophobic chain-surface interactions (dispersion force). As coverage increases, the adsorbed molecules may become oriented more and more perpendicular to the surface with hydrophilic moiety pointed toward aqueous phase.

Adsorption isotherm for well-purified monofunctional anionic and cationic surfactant also exhibits the same trend on the surface of hydrophobic adsorbent such as carbon, polyethylene, and polypropylene (Rosen, 1988). Adsorption onto these surfaces is mainly by dispersion. However, in case of adsorption onto Graphon, isotherm showed an inflection point. Rosen (1988) explained this phenomena as a result of changing in orientation of surfactant from parallel to perpendicular.

Ali *et al.* (1987), Gwin (1988), and Hoeft and Zollars (1996) investigated the adsorption of a series of linear alkyl sulfonates and linear alkyl sulfates on sulfonated polystyrene latex of various charge densities. Ali *et al.* (1987)

found that the amount adsorbed appeared to increase as the surface initially obtained the anionic charge. This may correspond to the electrostatic repulsion between the charged surface and the anionic head groups, causing the surfactant molecules to adsorb in a more extended conformation. Works by Hoeft and Zollars (1990) further suggested that this effect extend to the charge density of $-7 \mu\text{C}/\text{cm}^2$. Beyond a surface charge density of $-7 \mu\text{C}/\text{cm}^2$, the growing repulsive forces dominated and the adsorbed amount gradually decrease as reported by Gwin (1988) and Brouwer and Zsom (1987).

However, when the cationic surfactant, a series of trimethylammonium bromides) adsorbed onto a negatively charged polystyrene surface, a well-defined knee was observed on the isotherm, as investigated by Ingram and Ottewill (1990) as shown in Figure 2.1. 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.

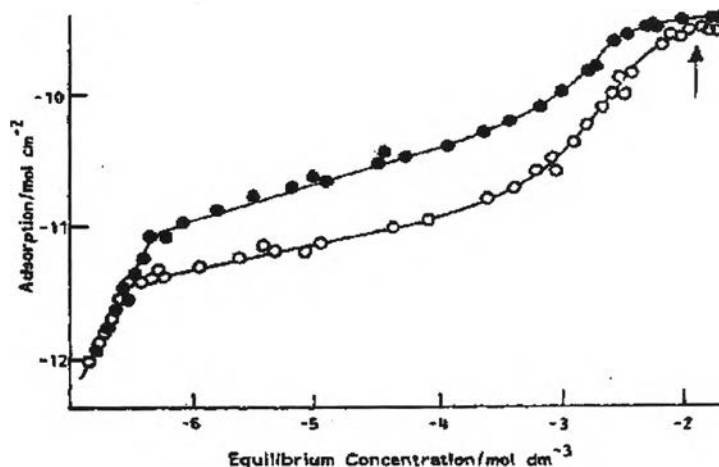


Figure 2.1 Adsorption isotherms for dodecyltrimethylammonium ions on polystyrene latex particles (carboxyl) in $10^{-3} \text{ mol}/\text{dm}^3$ potassium bromide solution at pH values of 0 , 4.6 ; \bullet , 8.0 , \uparrow CMC. (Ingram and Ottewill, 1990)

An increase in the length of the hydrophobic group increases the adsorption affinity (Rosen, 1988; Ihara, 1992). The addition of neutral electrolyte also increases the amount of adsorption of ionic surfactant. This is due to the shielding of the electric field around the adsorbates, which results in increasing the electrical repulsion between the similarly charged adsorbed surfactant and oncoming molecules (Rosen, 1988; Ihara, 1992).

POE nonionic surfactant appears to adsorb more onto hydrophobic surfaces than onto hydrophilic ones (Aston, 1982). They have larger tendency, compared to cationic surfactant, to preferentially adsorb onto hydrophobic surfaces. They are also less salt sensitive than anionic surfactant (Tiberg *et al.*, 2000). The longer the length of hydrophobic group results in the higher efficiency of adsorption (Rosen, 1988; Clint, 1992).

2.2.3 Structure of Adsorbed Layer

The structure of surfactant layer at the solid/liquid interface has been studied by the use of various surface specific techniques such as ellipsometry, neutron reflectivity, fluorescence spectroscopy, and atomic force microscopy (AFM). It has been found that surfactant often form monolayer or hemi-micellar aggregates at hydrophobic surface.

Several studies show that nonionic surfactant tend to form ordinary monolayer at hydrophobic non-crystalline surfaces (Bolze *et al.*, 1996; Fragneto *et al.*, 1996; Tiberg, 1996; Grant and Ducker, 1997; Grant *et al.*, 1998, 2000). However, in some cases for polyethylene oxide and zwitterionic surfactant, surfactant molecules with sufficiently long hydrophobic tail exhibit epitaxial adsorption, forming ordered hemicylinders, on hydrophobic crystalline graphite as illustrated in Figure 2.2 (Tiberg *et al.*, 2000)

Ionic surfactant also exhibit the same behavior, they tend to form monolayer type structures on amorphous hydrophobic surfaces at all concentrations, while form hemicylinders on crystalline graphite. The only exception as claimed by Tiberg *et al.* (2000) is the study of Wanless *et al.* (1997), in which the SDS-dodecanol system form a featureless monolayer on graphite below CMC.

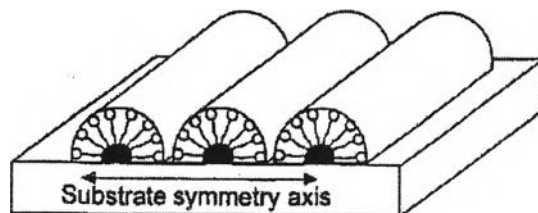


Figure 2.2 Hemi-micellar aggregates at the hydrophobic surfaces.

2.3 Wetting Phenomena

Wetting of solids by surfactant solution is important for many applications, for example, oil recovery, coating, printing, and detergency. In general, wetting is defined as the displacement of air from a liquid or solid surface by water or an aqueous solution. The addition of surfactant to water is a well-established means of enhancing the ability of aqueous solutions to wet and spread over solid surfaces (Pyter *et al.*, 1982). The ability to wet is a function of several parameters including molecular structure of the surfactant, its concentration, its environment, and the composition of the substrate to be wet (Luangpirom, 1999).

2.3.1 Contact Angle

The measurement of contact angle is the most rapid and convenient way of characterizing surface properties such as wetting, hydrophobicity and surface energies (solid/vapor and solid/liquid surface tension). Contact angle is the angle between the substrate surface and the liquid droplet. The closer the contact angle is to zero, the better the wetting is. There are three different types of contact angle which can be measured: advancing, receding, and static contact angle. An advancing contact angle is an angle obtained when the liquid is being added to the droplet and then comes to rest on the initially dry and clean surface. A receding contact angle is the angle obtained when the liquid is retreating from the surface, which is previously occupied by liquid. A static contact angle is the equilibrium contact angle.

The understanding of wettability was initiated by Young in 1805 , where the static contact angle was related to the free energies of the liquid/vapor (γ_{LV}), solid/liquid (γ_{SL}) and solid/vapor (γ_{SV}) interfaces through Young's equation.

$$\cos \theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} \quad (2.1)$$

This equation can be derived using the principle of energy minimization, as well as a force balance along the solid surface at the contact line, as shown in Figure 2.3. When using this approach, unfortunately, some difficulties arise in measuring γ_{SL} and γ_{SV} . These quantities are not experimentally and directly accessible (Lange, 1994).

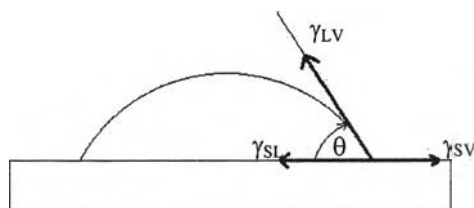


Figure 2.3 Contact angle and surface tension at three interfaces.

2.3.2 Measurement of Contact Angle

Several contact angle measurement techniques have been described in the literature such as the sessile drop, and Wilhelmy plate. For sessile drop method, a drop of liquid or solution is placed on a horizontal solid surface and the contact angle can be measured by a goniometer or computer program. This method is rapid and convenient; nevertheless, the error can be made by an operator.

2.3.3 Wetting by Aqueous Surfactant Solution

Water has a considerably high surface tension; hence, it does not readily spread over solids that have surface free energy of less than 72 erg/cm^2 . The addition of surfactant is, therefore, often necessary to enable water to wet on solid surface. Surfactant can improve wetting through altering the surface properties of the liquid phase by its presence at the interface. An equilibrium wetting can be related to adsorption, as developed by Lucassen-Reynders, by combining the Gibbs adsorption equation with Young's equation:

$$\frac{\partial(\gamma_{LV} \cos \theta)}{\partial \gamma_{LV}} = \frac{\Gamma_{SV} - \Gamma_{SL}}{\Gamma_{LV}} \quad (2.2)$$

Γ_{ij} represents the surface excess concentration of the surfactant at the ij interface. The slope of a plot of $\gamma_{LA} \cos \theta$ versus γ_{LA} consequently provides information at the three interfaces (Pyter *et al.*, 1982).

Pyter *et al.* (1982) measured contact angles of hydrocarbon (AOT) and fluorocarbon (perfluoro octanoic acid, PFO). Surfactants solutions on the low energy semi-polar solid, polymethylmethacrylate (PMMA), and the non-polar solid, paraffin. They found that surfactant solution did not produce the same contact angle compared with the pure liquids that have the same surface tension. For the hydrocarbon surfactant, this effect was much more significant for the PMMA than for the non-polar paraffin. For the PFO, this effect was found to be important for both solids. It was also revealed that the fluorocarbon surfactant was a much poorer wetting agent. These effects have been explained by invoking a lower adsorption of surfactant onto the solid-liquid interface in comparison to the vapor-liquid interface.

Less adsorption of surfactant at solid-liquid interface as the solid becomes more polar was also observed by Gau and Zografí (1990). In their works, advancing contact angle for aqueous solutions of the nonionic surfactant, penta(oxyethylene) dodecyl monoether, and penta(oxyethylene) decyl monoether were measured on surfaces prepared from polystyrene (PS), PMMA, latex particles, as well as paraffin. They discovered that wetting of surfactant solutions is less efficient relative to pure liquid for PS and PMMA due to less adsorption at

solid/liquid interface compared with adsorption at liquid/air interface. Γ_{SL} and Γ_{LV} were determined directly from adsorption experiments. If Γ_{SV} is assumed to be zero and the adhesion tension for pure water is known, the adhesion tension for aqueous surfactant solutions can then be predicted from the equation:

$$\begin{aligned}\gamma_{LV}(c)\cos\theta(c) &= \gamma_{LV}(w)\cos\theta(w) + \gamma_{SL}(w) - \gamma_{SL}(c) \\ &= \gamma_{LV}(w)\cos\theta(w) + \pi_{SL}\end{aligned}\quad (2.3)$$

$$\text{where } \pi_{SL} = \int_0^c \Gamma_{SL} d \ln c$$

This calculated adhesion tension appeared to show excellent agreement with the experimental values at the region of low surfactant concentration, up to concentration of surfactant corresponding to surface tension of about 40 mN/m. It was explained by the possible changes in the structure of the adsorbed monolayer at the solid-liquid interface at higher surfactant concentration.

In a study by Balasuwatthi and coworkers in 2002, the contact angle of a saturated aqueous surfactant solution onto the precipitate of that surfactant was measured by using the sessile drop method. The sodium and calcium salts of alkyl sulfates (C_{12} , C_{14} and C_{18}) have advancing contact angles higher than those of alkyl trimethylammonium bromides due to the larger hydrophilic group of the trimethylammonium group compared to the sulfate group. The contact angles of saturated calcium dodecanoate solutions containing a subsaturated sodium dodecyl sulfate (NaDS) decreases with increasing NaDS concentrations until reaching the CMC of surfactant mixture. Their results illustrates that the second surfactant can act as a wetting agent in this saturated surfactant system. Furthermore, application of Young's equation to contact angles showed that the solid/liquid surface tension is as important as the liquid/vapor surface tension in reducing contact angles.