

CHAPTER II

BACKGROUND AND LITERATURE SURVEY

2.1 Surfactant Characteristics

A surfactant or surface active agent is a substance that, when present at low concentration in a system, has the property of adsorbing onto the surfaces or interfaces of the system and modifying degree the surface or interfacial free energy of those surfaces or interfaces (Rosen, 1988). Surfactant also has the property of forming colloid-sized aggregates in solution called micelle at sufficient high concentration. The lowest total surfactant concentration at which micelles are present is called critical micelle concentration (CMC).

Surfactants have a characteristic molecular structure consisting of a structural group that has very little attraction for the solvent, called the lyophobic group (hydrophilic), together with a group that has strong attraction for the solvent, called the lyophilic group (hydrophobic).

The hydrophilic part may carry a positive or negative charge, giving rise to cationic or anionic surfactants, respectively, or may contain ethylene oxide chains or sugar or saccharine group, as in the case of nonionic surfactants. The hydrophobic part of the molecule is generally a hydrocarbon chain, but may contain aromatic groups (Goddard and Ananth, 1993).

The most useful chemical classification of surfactant is based on the nature of the hydrophlic group. The four basic classes of surfactants are defined as follows (Myers, 1992):

1. Anionic surfactant. The hydrophilic group carries a negative charge, for examples, RCOONa^+ (soap), and $\text{RC}_6\text{H}_4\text{SO}_3^-\text{Na}^+$ (alkylbenzene sulfonate).
2. Cationic surfactant. The hydrophilic group carries a positive charge, for examples, $\text{RNH}_3^+\text{Cl}^-$ (salt of long-chain amine), and $\text{RN}(\text{CH}_3)_3^+\text{Cl}^-$ (quaternary ammonium chloride).

3. Zwitterionic surfactant. Both positive and negative charges may be present in the surface-active portion, for examples, $\text{RN}^+\text{H}_2\text{CH}_2\text{COO}^-$ (long-chain amino acid), and $\text{RN}^+(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{SO}_3^-$ (sulfobetaine).
4. Nonionic surfactant. The surface-active portion bears no apparent ionic charge, for examples, $\text{RCOOCH}_2\text{CHOHCH}_2\text{OH}$ (monoglyceride of long-chain fatty acid), and $\text{RC}_6\text{H}_4(\text{OC}_2\text{H}_4)_x\text{OH}$ (polyoxyethylenated alkylphenol).

2.2 Adsorption at Solid-Liquid Interface

The tendency to adsorb at the surface is one of characteristic features of surfactants. The adsorption of surfactants at solid-liquid interfaces is important in many industrial applications, e.g. the dispersion of solids in aqueous solution, detergency, solubilization of chemicals, and etc. The adsorption of surfactants at the solid-liquid interface is strongly influenced by a number of factors: (1) the nature of the structural groups on the solid surface; (2) the molecular structure of the surfactant being adsorbed (the adsorbate); and (3) the environment of the aqueous phase such as its pH, its electrolyte content, and etc (Rosen, 1988).

The adsorption of surfactants at solid-liquid interface leads to a layer or film formation on the solid surface which affects its surface tension (Janczuk *et al.*, 1997). For wetting of hydrophobic surfaces, surfactant adsorption makes the surface becomes more hydrophilic and consequently enhance the spreading of aqueous solution on surface.

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. The adsorption isotherm is the usual method of describing adsorption at the solid-liquid interface and traditionally determined by solution depletion method.

Depletion experiment is accomplished by mixing a surfactant solution with adsorbate which known mass and surface area (Atkin *et al.*, 2003). After equilibration, the surface excess is determined by the change in the solution

surfactant concentration. A series of experiment conducted at appropriate surfactant concentrations allows the adsorption isotherm to be resolved. Generally, ionic surfactants exhibit four distinct adsorption regions over a full range of concentration up to the critical micelle concentration (Douglas and Jia, 2004).

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.

2.2.2 Adsorption on Hydrophobic Surface

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

The adsorption of cetyltrimethylammonium bromide (CTAB) onto active carbon-water interface mainly took place through ion exchange, the ion pairing and hydrophobic bonding. The predominant mechanisms in the low CTAB concentrations were probably ion exchange and ion pairing. The hydrophobic bonding mechanism predominated with increasing CTAB concentration (Gurses *et al.*, 2003).

The adsorption of AOT, short chain anionic surfactant, on graphite particles in aqueous solutions was driven by the interactions of the hydrophobic chains of the surfactant with predominantly hydrophobic graphite surface (Krishnakumar and Somasundaran, 1996).

Janczuk *et al.* (1997) suggested that, at high CTAB concentration in aqueous solution (γ_{LV} values from 38.1 to 69.2 mN/m), the adsorbed amount at the Teflon-water interface was close to that adsorbed at the water-air interface, whereas at low CTAB concentration (γ_{LV} values higher than 69.2 mN/m) the adsorbed amount at Teflon-water interface was several times higher than at water-air interface. This might be a result of the presence of a weak acid-base interaction across the Teflon-water interface which played an important role in the mechanism of adsorption at low CTAB concentration.

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).

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 variation of chain length is a factor that also affects the adsorption of surfactants. The adsorbed amount of cationic surfactants, alkyltrimethylammonium ions, and anionic surfactants, a series of linear alkyl sulfonates and linear alkyl sulfates, on polystyrene latexes increased with increasing the chain length of both surfactants (Hoeft and Zollars, 1996; Dixit and Vanjara, 1999). An increase in the length of the hydrophobic group increased efficiency and effectiveness of adsorption (Rosen, 1988; Clint, 1992).

The effect of polymer polarity on surfactant adsorption also was 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 surfactant, 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.* 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 increased 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 screened the electrostatic repulsion between head groups of DTAB and latex surface, therefore, the adsorbed amounts increased (Dixit and Vanjara, 1999).

In 2004, Supalaset studied the adsorption of surfactant on plastic surfaces and its relation to wetting phenomena. The results showed that the adsorption of surfactant at solid/liquid interface caused Zisman plot to deviate. The deviation of Zisman's plot appeared in the case of CPC on polystyrene and polyethylene terephthalate. It can be indicated that the polarity of plastics had an effect on wettability of CPC while had no effect on wettability of NaOBS. The possible reason is the difference in the length of hydrophobic tails of CPC and NaOBS.

2.2.3 Structure of Adsorbed Surfactant Layer

The structure of an adsorbed surfactant layer at the solid-liquid interface has been studied 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).

The image of interfacial aggregation for CTAB on graphite was obtained by using AFM. Atkin *et al.* (2003) indicated that the most likely surface conformation of surfactant was a hemicylindrical arrangement which is represented by Figure 2.1. The adsorbed structure of C₁₂TAB on graphite showed a flat monolayer at low concentration, followed by the formation of hemicylindrical interfacial aggregates (Kiraly and Findenegg, 1998).

Nonionic surfactants appeared to form homogenous monolayers on amorphous hydrophobic surface. On graphite, the same surfactants organized parallel to the surface at low concentration. Templating self-assembly led to the formation of hemicylindrical structures (lower to the CMC). Ionic surfactants also exhibited the same behavior (Tiberg *et al.*, 2000).

Most surfactants form hemicylindrical structures on graphite. However, the nonionic C₁₀ surfactants did not. They formed a homogeneous layer on graphite. This suggested that there was probably a specific attractive interaction between graphite and alkyl chains that increased 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.

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.

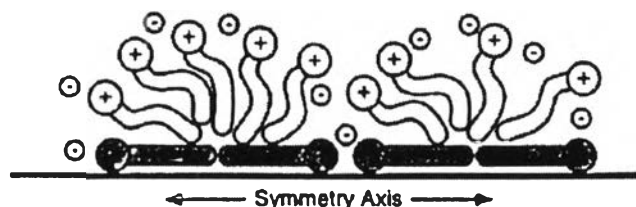


Figure 2.1 Hemicylinders aggregate at the hydrophobic surface.

2.3 Wetting Phenomena

Wetting in its most general sense is the displacement from a surface of one fluid by another. Commonly the term wetting is applied to the displacement of air from a liquid or solid surface by water or an aqueous solution.

Wetting can be examined by measuring the contact angle of a drop of surfactant solution sitting on the substrate. Wetting means that the contact angle between a liquid and a solid is zero, or so close to zero that the liquid spreads easily over the solid surface, while non-wetting means that the angle is greater than 90 degrees, so that the liquid tends to ball-up and run off the surface easily (Garbassi *et al.*, 1994).

Wetting, especially wetting of solids by surfactant, is a key phenomenon in many applications such as oil recovery, coating, painting, and detergency. Mostly, the addition of surfactants to water can enhance the ability of aqueous solution to wet and spread over solid surface. However, it does not always enhance wettability; it depends on several parameters including molecular structure of the surfactant, and the nature of solid surface (Rosen, 1988).

2.3.1 Contact Angle

Contact angle is the angle between the solid surface and the tangent of liquid droplet. The measurement of contact angle is the most rapid and convenient way of characterizing surface properties such as wetting, hydrophobicity, and surface/interfacial tension which cannot be measured directly.

At the basis of the measurement of solid surface tension by contact angle there is the equilibrium at the three-phase boundary. The drop of liquid that

put on a solid surface will modify its shape under the pressure of the different surface or interfacial tensions, until reaching equilibrium (Garbassi *et al.*, 1994).

The three-phase equilibrium is described in terms of the vectorial sum, shown in Figure 2, resulting in the following equation of interfacial equilibrium;

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

Equation 2.1 is generally called Young's equation which the static contact angle (θ) was related to the interfacial free energies per unit area of the liquid-vapor (γ_{LV}), solid-vapor (γ_{SV}), and solid-liquid (γ_{SL}) interfaces.

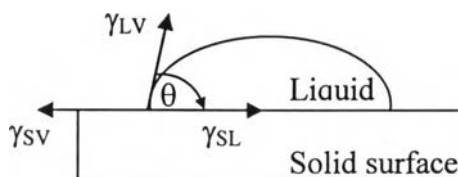


Figure 2.2 Schematic representation of the force balance affecting contact angle.

2.3.2 Measurement of Contact Angle

The three most commonly used method of contact angle measurement are the sessile drop, the captive bubble and the Wilhelmy plate technique.

In the sessile drop experiment, a droplet of properly purified liquid is put on the solid surface by means of a syringe or a micropipette. The droplet is generally observed by a low magnification microscope, and the resulting contact angle, according to Figure 2, is measured by a goniometer fitted in the eyepiece or computer program. The sessile drop is the most rapid and convenient method, whereas the Wilhelmy plate technique requires the two surfaces of the sample must be identical and its plots are difficult to interpret (Garbassi *et al.*, 1994).

2.3.3 Wetting by Aqueous Surfactant Solution

The addition of surfactant to water is often necessary to enable water to wet the solid or liquid surface because of water has high surface tension, 72 dyn/cm, and does not spontaneously spread over covalent solids that have surface free energies less than 72 erg/cm². The interfacial tensions of the system will be modified by the adsorption of surfactants to the interfaces; therefore, an equilibrium wetting can be related to adsorption of the surfactants.

Wetting and adsorption are intimately related phenomena of large importance to numerous applications including flotation, detergency, enhanced oil recovery, painting and printing. To predict the effect of added surfactants on wetting, one needs to know the adsorption isotherms for all three interfaces (Eriksson *et al.*, 2001).

A direct method to investigate in the relation of adsorption to equilibrium wetting has been developed by Lucassen-Reynders. By combining the Young and Gibbs equations yields

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

where Γ_{SV} , Γ_{SL} , and Γ_{LV} represent the surface excess of surfactants at solid-vapor, solid-liquid, and liquid-vapor interfaces respectively. If Γ_{SV} for a surfactant is assumed to be zero, a plot of $\gamma_{LV} \cos \theta$, the adhesion tension, versus γ_{LV} should have a slope of $-(\Gamma_{SL}/\Gamma_{LV})$. When the slope of the plot is negative, wetting is improved by the presence of the surfactant; when it is positive, wetting is impaired by its presence (Rosen, 1988).

For low surface energy, hydrophobic, solids such as paraffin and Teflon, the slope is usually close to -1. Janczuk *et al.* (1996) showed the linear relationship between $\gamma_{LV} \cos \theta$ and γ_{LV} for Teflon-CTAB aqueous solution drop-air system. The slope was equal to about -1 in the range of high CTAB concentration. It was indicated that CTAB adsorption at the Teflon-water interface was the same at the water-air interface. However, in the range of low CTAB concentration the slope was considerably lower than -1.

The relationship between adsorption and wetting of nonionic surfactant solutions, penta (oxyethylene) dodecyl monoether, $C_{12}E_5$, and penta(oxyethylene) decyl monoether, $C_{10}E_5$, on several polymer surfaces was studied by Gau and Zografi (1990). Only on paraffin, wetting of surfactant solutions was the same as with pure liquids at the same surface tension, whereas wetting was increasingly less efficient relative to pure liquids for PS and PMMA. The anionic surfactant solution, AOT, also exhibited the same behavior (Pyter *et al.*, 1982).

From their adhesion tension plots of paraffin, it appeared that Γ_{SL} was essentially equal to Γ_{LV} over the entire concentration range. On the other hand, for PS and PMMA the ratio of Γ_{SL} to Γ_{LV} became less than 1, indicative of increasingly less efficient wetting as the solid became more polarity.

Moreover, the adhesion tension plots for PS and PMMA by using determined contact angles and contact angles estimated from adsorption data were compared. The results showed that wetting behavior could be quantitatively predicted very well at higher surface tension, in more dilute surfactant solutions down to surface tension of about 40 mN/m, by the relative adsorption of surfactants to the solid-liquid and liquid-vapor interfaces without including the term Γ_{SV} .

In 2003, Dutshk *et al.* studied the dynamic wetting behavior of aqueous solutions of three surfactants, SDS, DTAB, and $C_{12}E_5$, for various polymer surfaces. They found that ionic surfactant solutions did not spread on low energy surfaces at any concentrations and spread over moderately hydrophobic surfaces (with surface energy about 36 mJ/m²). As to the nonionic $C_{12}E_5$, the wetting behavior was quite different. This surfactant was found to enhance spreading in aqueous solutions on both highly hydrophobic and moderately hydrophobic surfaces.

2.3.4 Critical Surface Tension

The plot of advancing contact angles ($\cos\theta$) as a function of the liquid surface tension (γ_{LV}) is usually called the Zisman plot. A typical Zisman plot on a hydrophobic polymer is shown in Figure 3.

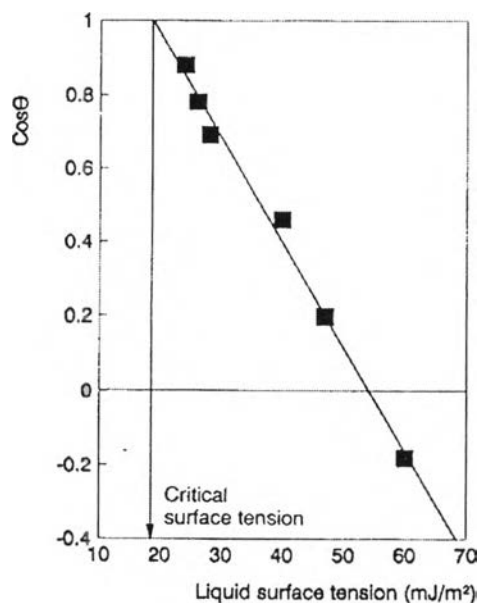


Figure 2.3 Typical Zisman's Plot (the substrate is PTFE).

The critical surface tension (γ_C), the value of liquid surface tension required to give a contact angle of zero degree, was defined by the extrapolation of the Zisman plot to $\cos\theta = 1, \theta = 0^\circ$, (Zisman, 1964). The more nonpolar the solid surface (low-energy solid surface), the lower the value of γ_C obtained (Goddard and Ananth, 1993). Furthermore, tension of the wetting liquid must not exceed a certain critical value that is characteristic of particular substrate (Rosen, 1988).