CHAPTER II
LITERATURE SURVEY

2.1 Surfactant Characteristics

A surfactant, surface-active agent, is a substance that at low concentration adsorbs at some or all of the interfaces in the system and alters the surface or interfacial free energies of those interfaces to a marked degree (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 an amphiphilic molecular structure. That is, a structure that is polar (hydrophilic) at one end and non-polar (lyophilic/hydrophobic) at the other.

Hydrophilic is a characteristic of materials exhibiting an affinity for water. Hydrophilic literally means "water-loving" and such materials readily adsorb water. The surface chemistry allows these materials to be wetted forming a water film or coating on their surface. Hydrophilic materials also possess a high surface tension value and have the ability to form "hydrogen-bonds" with water.

Surfactants are classified into four main groups due to their hydrophilic groups:

- Cationic: The hydrophilic portion of the molecule bears a positive charge, for example, organic amines — especially with three hydrocarbon chains attached to the nitrogen atom.
- Anionic: The hydrophilic portion of the molecule holds a negative charge, for example, fatty acids or sulfates with hydrocarbon chains.
- Nonionic: The surface-active portion bears no apparent ionic charge, for example, organic compounds with oxygen containing groups such as alcohols, esters and ethers.
- Zwitterionic: Both positive and negative charges are present in the surface-active portion, for example, long chain amino acid.

Hydrophobic or lyophilic groups have the opposite response to water interaction compared to hydrophilic materials. Hydrophobic materials possess low surface tension values and lack active groups in their surface chemistry for formation of "hydrogen-bonds" with water. Hydrophobic groups may be large, straight or branched chain hydrocarbons, cyclic hydrocarbons, aromatic hydrocarbons and/or combinations of them.

2.2 Adsorption of Surfactant at the Solid/Liquid Interface

A molecule is adsorbed when it accumulates at a surface or an interface. Surfactants-being surface active-adsorb on almost every surface and at almost every interface. Surfactants adsorb at the interface between oil and water. Surfactants adsorb at the interface between liquids and gases (the water and air interface, for example). Still, their behavior at a solid-liquid interface is unique. Surfactant adsorption at the solid-liquid interface is especially interesting because adsorbed surfactants form aggregates on the surface of solids that can dramatically change the properties of the interface. This is an important factor in solid-liquid dispersions, in wetting of surfaces, and in cleaning.

Adsorption of a surfactant at a solid-liquid interface can be good or bad. In order to modify the properties of the interface, as wetting applications, the surfactant need to adsorb. In dispersions surfactant adsorption is used to control the interaction between solid particles. But in cleaning operations, such as detergency or in environmental applications of surfactants, most of the time surfactant adsorption represents a loss or even degradation in the cleaning efficiency. It is very important, therefore, to be able to choose a surfactant system so that the surfactant adsorption is low when adsorption represents a loss, and is high when it is needed to control the properties of the surface or interface.

Adsorption of a surfactant at a solid-liquid interface is strongly influenced by a number of factors (Rosen, 1988):

- The nature of the structural groups on the solid surface.
- The molecular structure of the surfactant being adsorbed (the adsorbate).

- The environment of the aqueous phase such as pH, electrolyte, additive and temperature.

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

2.2.1 Mechanism of Adsorption

There are several different adsorption mechanisms, which influence the aggregation of surfactants at the solid/liquid interface. Rosen (1988) classified the adsorption mechanism of surfactant as follows:

- Ion exchange. Involves the replacement of counterions adsorbed onto the substrate from solution by similarly charged surfactant ion.
- Ion pairing. This mechanism involves adsorption of surfactant ions from solution onto oppositely charged sites unoccupied by counterions.
- Acid-Base interactions. Adsorption takes place by hydrogen bonding between substrate and adsorbate.
- Adsorption by polarization of π electrons. Adsorption results from attraction between electron-rich aromatic nuclei of the adsorbate and positive sites on the substrate.
- Adsorption by dispersion force. Occur via London-Van der Waals dispersion forces acting between adsorbent and adsorbate molecules. Adsorption by this mechanism generally increases with increase in the molecular weight of the adsorbate.
- Hydrophobic bonding. This mechanism takes place when the mutual attraction forces between hydrophobic groups of the surfactants and their tendency to escape from an aqueous environment become large enough to permit them to adsorb onto the solid surface by chain aggregation. By this mechanism, adsorption of the surfactant molecules onto or adjacent to other surfactant molecules already adsorbed on the solid surface may take place.

2.2.2 Adsorption Isotherm

An adsorption isotherm is an 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 Sohwuger, 1987). Different assumptions about the adsorption process lead to quite different variations of the adsorbed amount (surface excess). Some simple models include the Gibbs adsorption equation for solutions and the Langmuir isotherm for adsorption to solid substrates.

2.2.3 Adsorption on Hydrophobic Surface

The adsorption of molecular chains such as surfactants onto solid/liquid interfaces especially hydrophobic surface is of a great interest because of its role in nature and industrial applications. Each improvement in the knowledge of this phenomenon has important consequences for different fields including industry, medicine, and biology (Dobias, 1999)

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, in the region of low surface charge density, the amount of adsorbed surfactant appeared to increase with the increase in magnitude of the negative charge on the surface. 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

However, when the cationic surfactants, 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). 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.

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 surfactants. 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 surfactants and oncoming molecules (Rosen, 1988; Ihara, 1992).

Singh (1998) studied the adsorption kinetics of DAB (cationic surfactant) and SDS (anionic surfactant) on fine clean coal at their natural pH (5.2). The equilibrium adsorption for DAB was much higher than SDS. This difference is attributed to the highly electronegative surface of coal at the system pH. Increasing the temperature decreased the amount of DAB and SDS adsorption, the temperature dependence of DAB adsorption was very low compared with SDS adsorption. This difference in adsorption pattern at different temperatures suggests that the two surfactants may be adsorbed by different mechanisms. The low temperature dependence for DAB is possibly due to chemisorption, whereas the higher temperature dependence of SDS is typical of physisorption.

Examining the adsorption isotherms of all the amphiphilic molecules studied on the different latices (Reyes *et al.*, 2005). It can conclude that the hydrophobic attraction between the nonpolar part of the molecule (tail) and the apolar regions of the surface is the main mechanism involved in the adsorption. In fact, higher adsorption is achieved by increasing the hydrophobic character of the surface and is hindered when a hydrophilic polymer (HDMA) is used as a copolymer in the synthesis.

2.2.4 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, fluolescence spectroscopy, and atomic force microscopy (AFM). It has been found that surfactants often form monolayer or hemi-micellar aggregates at hydrophobic surface.

Wanless *et al.* (1997) observed the surfactant surface aggregation, by using AFM, is shown in Figure 2 for the cationic surfactant cetylpyridinium chloride (CPC) adsorbed to graphite. Instead of a monolayer of surfactant as previously imagined, the adsorbed layer consists of parallel hemicylindrical surfactant aggregates as shown schematically in cross-section. The surfactant hydrophobic tails are attracted strongly to the hydrophobic substrate, which induces surface aggregation at a concentration significantly below the CMC in the bulk solution.

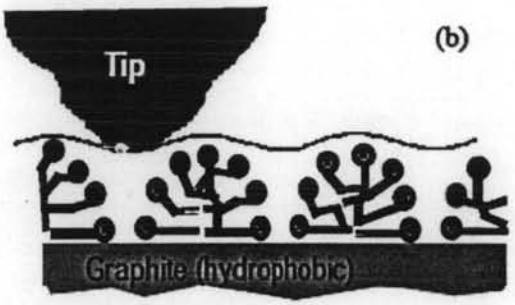

Figure 2.1 Schematic cross-section of the hemicylindrical surface aggregates being imaged nondestructively by the AFM tip as it traverses the surface.

Several studies show that nonionic surfactants 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 surfactants, surfactant molecules with sufficiently long hydrophobic tail exhibit epitaxial adsorption, forming ordered hemicylinders, on hydrophobic crystalline (Tiberg *et al.*, 2000).

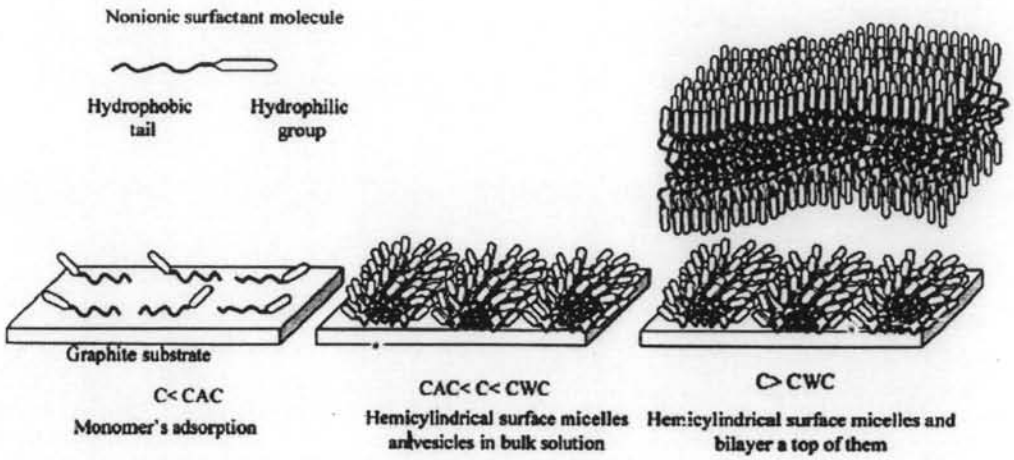

Figure 2.2 Schematic of non-ionic surfactant adsorption layers on graphite at different concentrations (Svitova, 2001).

2.3 Wetting Phenomena

Wetting of solids by surfactants is important for many applications, for examples, 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 surfactants 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).

Wettability is a surface property characteristic for all materials which yields a unique value for each compound. The surface tension value of a material can be utilized to determine wettability of a material by specific liquids. Through the measurement of the contact angle between a solid surface and a droplet of liquid on the surface, the surface tension for the solid material can be calculated.

2.3.1 Contact Angle

The Contact Angle is a quantitative measure of the wetting of a solid by a liquid. It is defined geometrically as the angle formed by a liquid at the three-phase boundary where a liquid, gas and solid intersect.

Figure 2.3 Liquid droplet in equilibrium: definition of the contact angle.

The low values of contact angle indicate that the liquid spreads well, while high values indicate less complete wetting. If the angle is less than 90 degrees the liquid is said to wet the solid. If it is greater than 90 degrees it is said to be non-wetting. A zero contact angle represents "complete wetting".

The contact angle is a function of the liquid's surface tension and the surface 'free' energy of the substrate. At the heart of theory of Contact Angles, lies the Young equation :

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

Where, γ represents the surface tension values between the corresponding interfaces. However, this equation is only valid for finite contact angles in case of mechanical equilibrium, so it does not apply when spreading takes place. Thus to encourage wetting, γ_{SL} , γ_{LV} should be made as small as possible. This is done in practice by adding a surfactant to the liquid phase. The surfactant adsorbs to both the liquid-solid and liquid-vapor interfaces, lowering those interfacial tensions.

For systems, which fail to attain equilibrium, instead of Contact Angle, we define another characteristic parameter known as Spreading Coefficient (S), which is the free energy change per unit area of the spreading of liquid film on the solid and is defined as:

$$S_{L/S} = \gamma_{SA} - (\gamma_{SL} + \gamma_{LA}) \quad (2)$$

Depending on different values of Spreading Tension coefficient, two different situations may arise. It can be seen from Equation 1, above that S=0 corresponds to cos θ attaining its maximum value of unity ($\theta = 0$) and corresponds to the onset of complete wetting. For different values of spreading coefficient ($S \neq 0$) partial wetting occurs resulting in a finite value of θ

2.3.2 Measurement of Contact Angle

Sessile drop method is the most commonly used technique. 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.

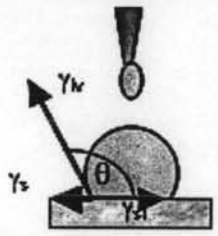

Figure 2.4 Sessile or Static drop.

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 72 erg/cm^2 or lower. 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.

Zisman and co-workers (1964) characterized the wetting of solids by measuring contact angle for different pure liquids and ploting cos θ vs γ_{LV}. They observed that cos θ is usually a monotonic function of γ_{LV} for a homologous series of liquids. Extrapolation of such plots to zero θ allows estimation of γ_C, the liquid surface tension required to give a contact angle of zero degrees, which Zisman has called the critical surface tension. The more nonpolar the solid surface, the lower the value of γ_C obtained. Bernett and Zisman (1959a, 1959b) expanded these studies to

the use of surfactant solutions. They found that, for polyethylene, the hydrocarbon surfactants gave γ_C values that were identical with those obtained using pure liquids, but the fluorocarbon surfactants gave a lower γ_C value

An equilibrium wetting can be related to adsorption, as developed by Lucassen-Reynders, by combining the Gibbs adsorption equation with Young's equation:

$$\frac{\partial(\gamma_{LV}\cos\theta)}{\partial\gamma_{LV}} = \frac{\Gamma_{SV} - \Gamma_{SL}}{\Gamma_{LV}} \tag{3}$$

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.

That the surfactants increasingly less adsorb at solid-liquid interface as the solid becomes more polar was also observed by Gau and Zografi (1990). In their works, advancing contact angle for aqueous solutions of the nonionic surfactants, 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:

$$\gamma_{LV}(c)\cos\theta(c) = \gamma_{LV}(w)\cos\theta(w) + \gamma_{SL}(w) - \gamma_{SL}(c) \quad (4)$$
$$= \gamma_{LV}(w)\cos\theta(w) + \pi_{SL}$$

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

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.

2.3.4 Critical Surface Tension

The critical surface tension of a solid surface is an indication of its relative water-hating or water-loving character. A low critical surface tension means that the surface has a low energy per unit area. The quantity is based on experiments with a series of pure liquids. These experiments have to be conducted on a flat, non-porous sample of that solid. A small droplet of each liquid is placed onto the surface. One measures the angle of contact at the solid-liquid-air contact line. The angle is drawn through the liquid phase. One plots the cosine of the angles of contact versus the surface tension of each liquid. For example, the surface tension of water, in equilibrium with its vapor at room temperature, is 72 mNm-1. Surface tensions of other liquids are widely available. The critical surface tension equals the surface tension at which the plotted line intersects 1.0.

2.3.5 Zisman Theory

The Zisman theory is a formalism widely used to describe the wetting of surfaces by molecular liquids. In this theory, the wetting behaviour of a surface is described by a single parameter, γ_c, sometimes known as the surface energy or the critical surface tension. Substrates can be divided arbitrarily into those of high surface energy and those of low surface energy.

Experimentally, the γ_c is obtained from the Zisman plot, in which the cosine $\cos\theta$ of the wetting angle for a series of liquids is plotted against the surface tension γ of the liquid. The resulting points often lie to a good approximation on a straight line. γ_c is the value at which the line extrapolates to 1 (perfect wetting).

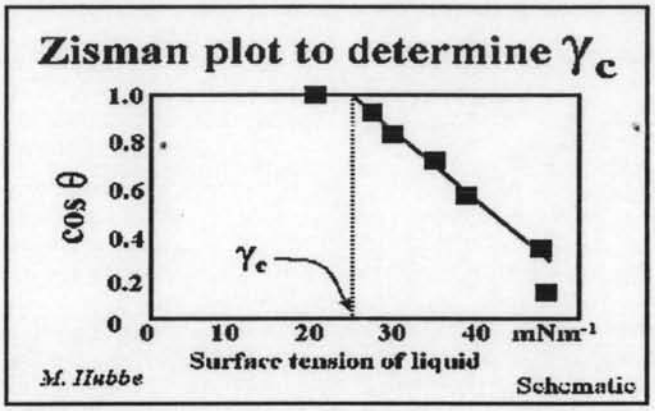

Figure 2.5 Zisman plot.