



CHAPTER II

LITERATURE REVIEW

2.1 Hard Disk Drive

Hard disk drives (HDD) are a device which is used to store large amounts of data in computer system. Hard disk drives are also used for a great many applications such as MP3 players, digital cameras, portable gaming devices, personal digital assistants, digital video recorders and players, and mobile phones.

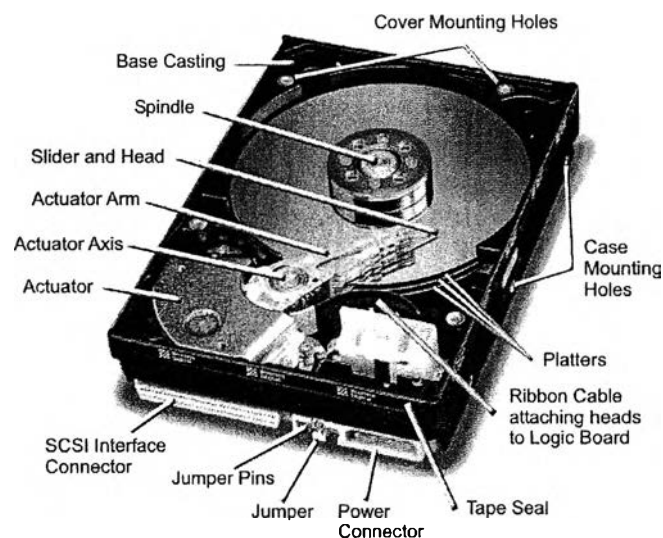


Figure 2.1 The structure and components within a hard disk drive. (Mustakallio, 2010).

The major components of a hard disk drive are platter, drive case, spindle, actuator, actuator arm, and head and slider, as shown in Figure 2.1. Hard disk platters or magnetic hard disks are accessed for read and write operations using the read/write heads mounted on the top and bottom surfaces of each platter. The read/write heads must be held in an exact position relative to the surfaces (Mustakallio, 2010).

The manufacturing of Hard Disk Drive consists of hundreds of process steps, many of which can be sensitive to particle contamination. Particulate contamination becomes an important issue in the performance and durability of hard disk drives because particles trapped between the head and disk can cause irrecoverable data losses in several ways such as head crash, circumferential scratching, embedding on the disk, and thermal asperities, which result in low efficiency of hard disk drive (Awad and Nagarajan, 2010). There are many sources of contamination such as personnel, process equipment, and chemicals. The personnel source of contamination was usually found in cosmetic such as powder, brush, eye shadow, and mascara.

2.2 Talcum Powder

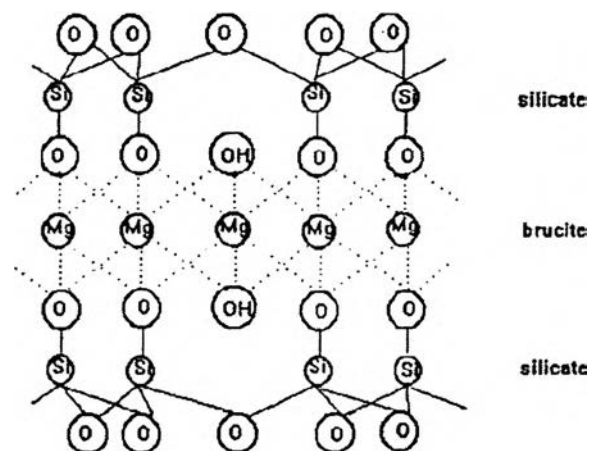


Figure 2.2 Structure of talcum (Linland Peck, 1994).

Talcum, having a chemical formula $Mg_3(Si_4O_{10})(OH)_2$, is composed from three layers: silicate-brucite-silicate, as shown in Figure 2.2. The upper and lower layers are both sheets of silicate tetrahedral. The middle layer is a brucite layer consisting of magnesium hydroxide to form the covalent bond with the oxygen atoms of upper and lower silicate layer (Linl and Peck, 1994). Each layer is electrically neutral and the adjacent layers are held together by Van der Waals force so that the

layers are capable of slipping easily over one another which accounts for the soft character of the talcum mineral. The basal surface does not contain hydroxyl groups or active site, which provides the basal surface of talcum with a natural hydrophobicity and floccatability. However, the edges of the talcum particles are created by the breakage of the Si-O or Mg-O bonds and consequently the edges are expected to be hydrophilic (Nalaskawski *et al.*, 2007 and Wallqvist *et al.*, 2006).

Talcum is one of the most important industrial minerals because of its lamellar habit softness, whiteness, fragrance retention, luster and chemical purity. Other commercially important properties of talcum are its chemical inertness, low abrasion, high thermal conductivity and stability, low electrical conductivity, and high oil and grease adsorption. The chemical properties of talcum's surface control many industrial processes that utilize this mineral are largely derived from its crystal structure and chemical composition (Castro, 2004). Talcum is used in many industries mainly in paints, plastics, rubber, soap and detergents, cosmetics, ceramic, textiles, and pharmaceuticals.

2.2.1 Use of Talcum in Cosmetic

Talcum is the most common mineral for daily use as a body and face powder. There are many grades of talcum each grade is categorized according to levels of purity. At the top of this purity scale is cosmetic grade talcum. Talcum is good at absorbing moisture, soft to the touch, and inert. Nowadays, it also play an important role in many cosmetic products, including products for feminine hygiene and baby powders and provides the silkiness in blushes, powder compacts and eye shadows, the transparency of foundations and the sheen of beauty creams (CTPA, 2011).

Kangwen and Garnet (1994) studied characterization of talc samples from different sources. For the nine different kinds of U.S.P. grade talc samples, which were examined for variations in density, particle size, surface area, tendency of preferred orientation, and maximum ejection force, it was found that U.S.P. grade talcs varied in physical properties. The relationships between various physical properties of talc were analyzed using the Pearson's correlation of coefficient. The results suggested that the talc sample with a higher tendency of preferred orientation

has closer bulk packing and talc with lower bulk density and higher surface area requires less peak force to break the tablet/die-wall adhesion.

2.3 Surfactant

2.3.1 General Principle

A surfactant or surface active agent is a substance that, when presents at low concentrations in the solution, 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 interface (Rosen,1989). Surfactants are amphipathic molecules that consist of a non-polar hydrophobic portion (lipophilic), usually a straight or branched hydrocarbon or fluorocarbon chain, which is attached to a polar or ionic portion (hydrophilic or lipophobic), as shown in Figure 2.3.

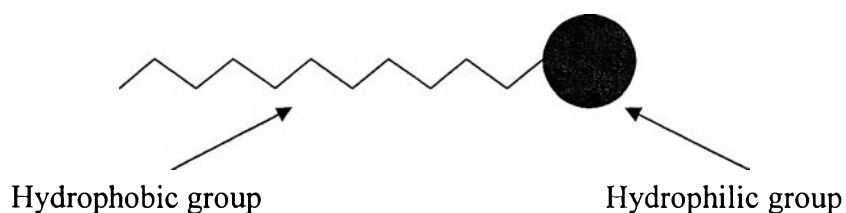


Figure 2.3 Surfactant structure.

The hydrocarbon chain interacts weakly with the water molecules in an aqueous environment, whereas the polar or ionic head group interacts strongly with water molecules via dipole or ion-dipole interactions. It is this strong interaction with the water molecules that renders the surfactant soluble in water. When surfactant dissolved in aqueous medium the hydrophobic group distorts the structure of the water. As a result of this distortion, some of the surfactant molecules are expelled to the interfaces of the system, with their hydrophobic groups oriented so as to minimize contact with the water molecules. The surface of the water becomes covered with a single layer of surfactant molecules with their hydrophobic groups oriented predominantly toward the air. Since air molecules are essentially non-polar in nature, as are the hydrophobic groups, this decrease in the dissimilarity of the two

phases contacting each other at the surface result in a decrease in the surface tension of the water (Tadros, 2005).

The Figure 2.4 shows the adsorption of surfactants which relate to surfactant concentration. At low concentrations the surfactant molecules remain as individual molecules in solution or they adsorb as isolated molecules on surfaces. As surfactant concentration increases, the surfactant's tendency to adsorb and/or form aggregate structures increases. However, at high concentrations they adsorb in layers or adsorbed aggregates or remain in solution primarily in aggregate structures. The concentration at which the transition from individual molecule adsorption and the adsorption of aggregates or layers occurs is known as the surface aggregation concentration or sac. The concentration at which the transition from individual molecules to solution aggregates occurs is known as the critical micelle concentration or cmc. The cmc and sac are usually very similar except that the sac tends to be slightly lower than the cmc (Free, 2007).

The micelles in aqueous solution, the surfactant hydrophobic groups are directed towards the interior of the aggregate and the surfactant hydrophilic groups are directed towards the solvent. In non-polar solution, the structure of the micelle is similar but reversed, the surfactant hydrophilic groups are directed towards the interior of the aggregate and the surfactant hydrophobic groups are directed towards the non-polar solvent (Tadros, 2005).

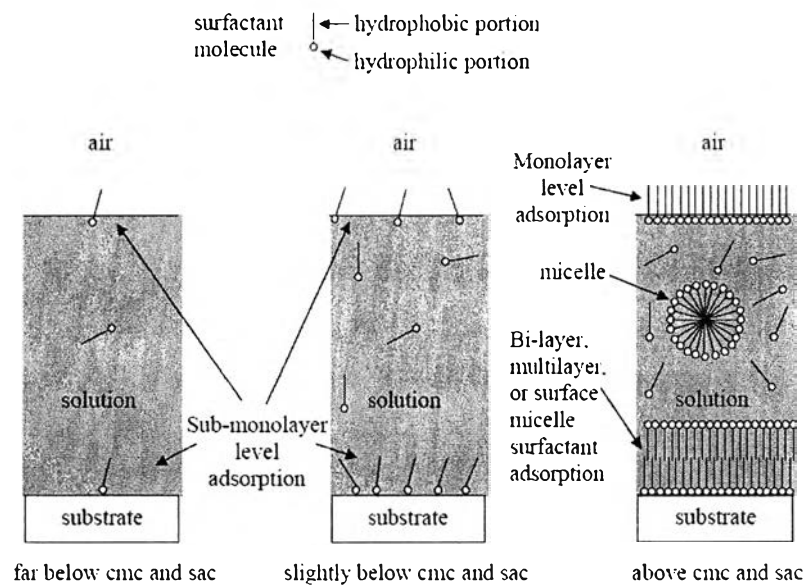


Figure 2.4 Surfactant aggregation and adsorption as a function of relative surfactant concentration (Free, 2008).

2.3.2 Basic Surfactant Classifications

A simple classification of surfactants based on the nature of the hydrophilic group is commonly used. The four basic classes of surfactants are defined as follows:

2.3.2.1 Anionic surfactants

The hydrophilic portion of molecule is a negatively charged group such as carboxyl ($\text{RCOO}^- \text{X}^+$), sulfonate ($\text{RSO}_3^- \text{X}^+$), sulfate ($\text{ROSO}_3^- \text{X}^+$), or phosphate ($\text{ROPO}_3^- \text{M}^+$).

2.3.2.2 Cationic Surfactants

The hydrophilic portion of molecule is a positively charged group. The most common cationic surfactants are the quaternary ammonium compound.

2.3.2.3 Nonionic Surfactants

The hydrophilic portion of molecule has no charge, but derives its water solubility from highly polar groups, for example organic compounds with oxygen containing groups such as alcohols, esters and ethers.

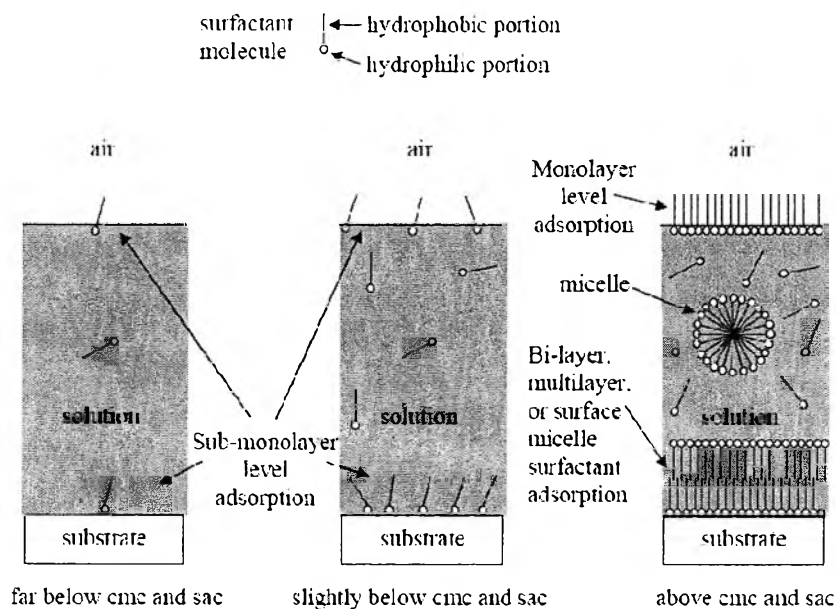


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2.3.2.4 *Amphoteric or Zwitterionic Surfactants*

The molecule contains both a negative charge and a positive charge. The charge depends on pH solution. At low pH (acidic solution), they form cation while at high pH (alkaline solution), they form anions. For example, polyoxyethylenatedalkylphenol, and laruramidopropylbetanie.

2.4 Adsorption of Surfactant

Surfactant adsorption is a process of transfer of surfactant molecules from bulk solution phase to the surface/interface. Surfactant adsorption at the solid/liquid interface is especially interesting because adsorbed surfactants from aggregates on the surface of solids can dramatically change the properties of the surfaces. 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 process, such as detergency or in environmental application 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: (1) the nature of structural groups on the solid surface (2) the molecular structure of the surfactant being adsorbed (the adsorbate) (3) the environmental of the aqueous phase such as pH, electrolyte, additive and temperature. (Rosen, 1989)

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

2.4.1 Mechanism of Adsorption

There are several different adsorption mechanisms, which influence the aggregation of surfactants at the solid/liquid interface. It classified the adsorption mechanism of surfactant as follows (Rosen, 1989):

2.4.1.1 Ion Exchange

Involve the replacement of counterions adsorbed onto the substrate from solution by similarly charged surfactant ion.

2.4.1.2 Ion Pairing

This mechanism involves adsorption of surfactant ions from solution onto oppositely charged sites unoccupied by counterions.

2.4.1.3 Acid-Base Interactions

Adsorption takes place by hydrogen bonding between substrate and adsorbate.

2.4.1.4 Adsorption by Polarization of π Electrons

Adsorption results from attraction between electron-rich aromatic nuclei of the adsorbate and positive sites on the substrate.

2.4.1.5 Adsorption by Dispersion Forces

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 adsorbate.

2.4.1.6 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.

2.4.2 Adsorption of Ion Surfactants

The adsorption isotherm of ionic surfactants onto an oppositely charged surface is typically an elongated S-shaped curve when one plots the log of the adsorbed surfactant density versus the log of the equilibrium concentration of surfactant (Scamehorn *et al.*, 1982). In general, a typical adsorption isotherm can be subdivided into four regions, as shown in Figure 2.5.

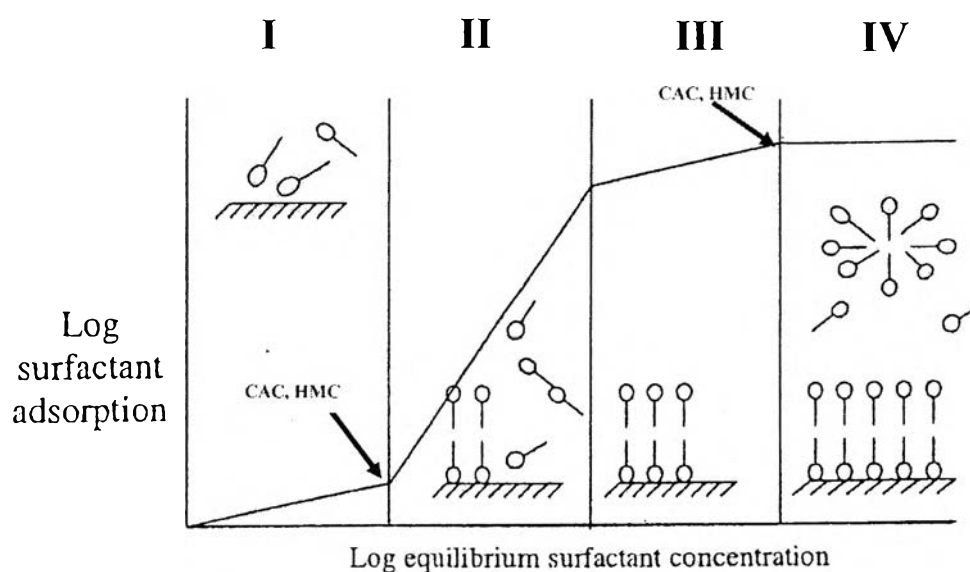


Figure 2.5 Adsorption isotherm of surfactant on an oppositely charged substrate (Pengjun, 2008).

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 this region, surfactant adsorption is the result of monomer interaction 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 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.

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 shown in the schematic, or it may be gradual. An explanation for this change in the slope is that with increasing adsorption of surfactants, 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 surfactant, and reflects the effect of micelle formation on the chemical potential of surfactant monomer, just as the formation of micelle 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 (Rosen, 1989).

2.4.3 Adsorption of Nonionic Surfactants

Nonionic surfactants are physically adsorbed rather than electrostatically or chemisorbed. However, they differ from many other surfactants in that, quite small changes in concentration, temperature, or molecular structure of the adsorbent can have a large effect on the adsorption. This is due to adsorbate-adsorbate and adsorbate-solvent interactions, which causes surfactant aggregation in bulk solution and which leads to change in orientation and packing of surfactant at the surface. The adsorption isotherms of nonionic surfactants from aqueous solutions on polar substrates are also sigmoidal in shape (S-shaped), indicative of a cooperative adsorption mechanism (Livitz and Damme, 1986). Figure 2.6 shows a scheme of the most likely orientation changes undergoes in the adsorption of

nonionic surfactants from solution onto solid surface. In the first stage of adsorption, the surfactant adsorbs on solid surface where there are very few molecules adsorbed. The surfactant-surfactant interaction is negligible and adsorption occurs mainly by Van der Waals interaction. In the next stage, the adsorption are rapidly increasing amount of adsorbed surfactant dominated by the surfactant-surfactant interactions. The subsequent stages of adsorption in region II and IV are determined by surfactant-surfactant interaction, although surfactant-surfactant interaction initially determines adsorption beyond stage II. This interaction depends on the nature of the surface and the hydrophilic-lipophilic balance of the surfactant molecule (HLB). When the hydrophilic group of surfactant is short, it will displace from the surface by the alkyl chains of the adjacent molecules, as show in Figure 2.6IIIA. However, when the hydrophilic group is strongly adsorbed (strong attraction between the hydrophilic group and the surface with hydrophilic adsorbent like silica or oxides), the alkyl chain is displaced as show in Figure 2.6IIIC. The intermediate situation when neither type of displacement is favored nor the surfactant then remains flat on the surface, as show in Figure 2.6IIIB. In the last stage of adsorption, the adsorption approaches a plateau above the CMC. There will be a tendency for the alkyl chains of the adsorbed molecules to aggregate (hemimicelle). This will cause the molecules to become vertically oriented and there will be a large increase in adsorption (Clunie *et al.*, 1983 and Tadros, 2005).

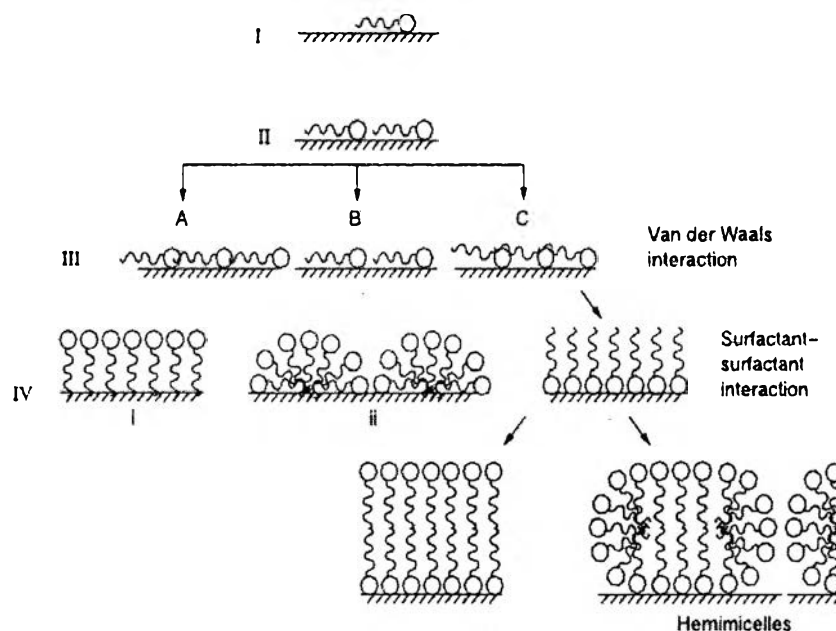


Figure 2.6 Adsorption of nonionic surfactants (Tadros, 2005).

2.5 Wetting Phenomena

Wetting in its most general sense is the displacement from a surface of one fluid by another. Generally, the term of 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° , 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 solutions, 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, the presence of surfactant does not always enhance wettability; it depends on several parameters including molecular structure of the surfactant, and the nature of solid surface (Rosen, 1989).

2.6 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/interface tension. The contact angle θ that the liquid makes when it is at equilibrium with the other phases in the contact with it is related to the interfacial free energies per unit area of those phases. When the liquid is at equilibrium with the other phases, gas and solid substrate, the diagram of the contact angle as shown in Figure 2.7 (Rosen, 1989). 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.

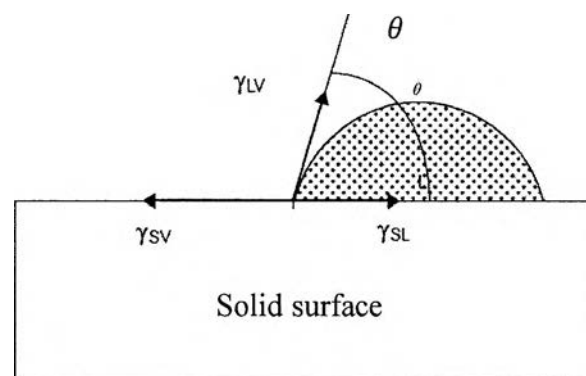


Figure 2.7 Contact angle (Birch *et al.*, 2008).

The contact angle value depends on the liquid surface tension, the surface free energy of the solid, and the interactions between the two materials. The equilibrium value of the contact angle, also known as the wetting angle, satisfies Young's equation, as shown in Equation 2.1 (Birch *et al.*, 2008).

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

Where γ_{SV} is the surface free energy of the solid, γ_{SL} is the interfacial free energy between the liquid and the solid, and γ_{LV} is the liquid surface tension, as shown in Figure 2.7.

2.6.1 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.

2.7 **Electrical Double Layer**

At any interface, there is always an unequal distribution of electrical charges between two phases. This unequal distribution causes one side of the interface to acquire a net charge of a particular sign and the other side to acquire a net charge of the opposite sign, giving rise to a potential across the interface and the so-called electrical double layer. A major problem for investigation has been the determination of the exact distribution of the neutralizing charges (counterions) in the solution surrounding a charged surface, since this distribution determines the rate at which the electrical potential will change with distance from the charged surface. Stern suggested the model, which divided the solution side of the double layer into two part: (1) a layer of strongly held counterions, adsorbed close to the charged surface on fixed sites, and (2) a diffuse layer of counterions similar to that of their model (Figure 2.8) (Rosen, 1989).

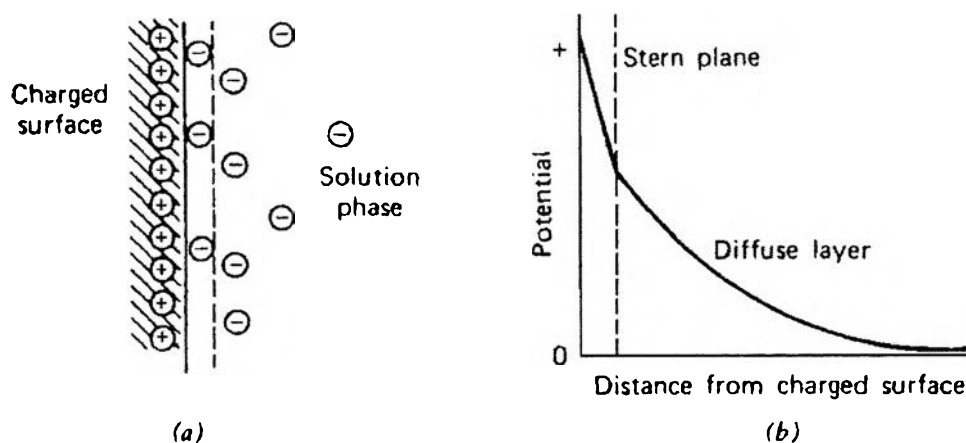


Figure 2.8 Stern model of electrical double layer. (a) Distribution of counterion in the charged surface. (b) Variation of electrical potential with distance from the charged surface.

2.7.1 Zeta Potential

A term often associated with the electrical double layer is the zeta potential, or electrokinetic potential. This is the potential of a charged particle as calculated from electrokinetic phenomena. It is the potential of the charged surface at the plane of shear between the particle and the surrounding solution as the particle and the solution move with respect to each other.

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

Gallardo-Moreno *et al.*, (2004) carried out zeta potential measurements carbonaceous materials; carbon blacks and activated carbons in a SDS solution. Although both studied solids had different zeta potential when they were suspended in pure water, the relative change of zeta potential at the maximum surfactant adsorption for each solid was found to be proportional to the area amount adsorbed. These results indicated that the adsorption of anionic surfactant on the surface with the ionic head to be exposed to the solution.

Kaya and Yukselen (2005) determined the zeta potential of kaolinite, montmorillnite, and quartz powder in the presence of alkali, alkaline earth, hydrolysable metal ions with anionic, cationic and nonionic surfactant in a systematic manner. The results indicated that the anionic surfactant was found to produce negative zeta potentials. The cationic and nonionic surfactants produce both positive and negative zeta potential depending on soli type and ion present in the system. The zeta potential of kaolinite and quartz powder with surfactants showed similar trends; however, the absolute magnitude of the zeta potential of quartz powder is higher than that of kaolinite.

2.8 Dispersion of Solids in Liquid Media

Dispersion is a process whereby aggregates and agglomerates of powder are dispersed into individual units and stabilization of the resulting dispersion against aggregation and sedimentation. Surfactants are used as dispersants in solid/liquid dispersion. For that reason, surfactants find application in almost every industrial preparation such as paints, dyestuffs, paper coatings, printing inks, agrochemicals, pharmaceuticals, cosmetics, food products, detergents, and ceramics (Tadros, 2005). Each of these applications, and many more, would be difficult if not impossible in the absence of the effects of adsorbed surfactants and stabilizers at the soild-liquid interface (Myers, 2006).

The role of surfactants in the dispersion can be by considering the stages involved. Three stages have been considered: wetting of the powder by the liquid, breaking of the aggregates and agglomerates, and comminution of the resulting particles into smaller units (Tadros, 2005).

Yao *et al.*, (2005) studied dispersion of talc particles in a silica sol by investigating zeta potential and sedimentation. Zeta potential of talc in silica sol changes significantly in comparison with that of talc in deionized water. This is attributed to the adsorption of silica colloidal particles with negative charge on the surface of talc particles. The lowest sedimentation for the suspension of talc at pH 10.5 is the best dispersion of talc in silica sol.

Bacchin *et al.*, (2006) studied carboxyl methyl cellulose (CMC) adsorption on talc particles to disperse talc particles. Because of hydrophobic properties of talc (low surface energy), it is difficult to disperse talc in water and without formation of foam or aggregate. They found that the adsorption of CMC onto talc was quantified at around 0.4 mg of CMC per m² of talc. They characterized surface properties of talc, it was found that CMC adsorption leads to increase of the wettability. Because of CMC adsorption on talc particles, the talc surface becomes hydrophilic in the presence of CMC. The CMC improves the dispersion of talc particles in solution which induced by electrosteric repulsion between talc surfaces where CMC is adsorbed, so it increases their stabilization. This is confirmed by measurement of zeta potentials of talc where adsorption leads to a higher negative zeta potential. This positive effect of CMC is also observed when CMC pre-coated talc particles are dispersed in water.

Zhang *et al.*, (2010) studied the dispersion of kaolin powder in silica. They found silica sol improved the dispersion of kaolin particle. The electrophoretic mobility and viscosity of kaolinite particles in the silica sol differed significantly from the dispersion in deionized water. This is attributed to the adsorption of negatively charged colloidal silica particles on the kaolinite particles, which increases the negative surface charges and the electrostatic repulsion between the silica covered kaolinite particles.

Ersoy (2011) observed the influence of pH on coagulation/dispersion behavior of talc suspension. The coagulation of talc suspension is reduced depending on the pH accompanying with increase in the absolute zeta potential (ZP), which enhances the electrostatic repulsive forces between the talc particles. The isoelectric point (iep) of the talc sample was determined at around pH 1.9. Even though the talc suspension used in this work has a sufficient ZP at neutral pHs to provide a better dispersion in suspension, the sedimentation tests and also the viscosity measurements showed that the powdered talc coagulated easily. This was attributed to the hydrophobic attraction between the basal surfaces of talc particles.

Zaman *et al.*, (2002) investigated the impact of self-assembled surfactant structures on rheology of concentrated nanoparticle dispersions. They used a cationic surfactant (C₁₂TAB) as the dispersing agent. Stability analysis through turbidity

measurements indicated that there is a sharp increase in the stability of the dispersion when the surfactant concentration is in the range of 8 to 10 mM in the system. They proposed that at low surfactant concentration (<8 mM), no repulsive forces are observed and the silica suspension is unstable. However, at high concentrations (>10 mM) of surfactant, a large repulsive barrier is observed via surface force measurement, and, correspondingly, the surfactant produces a stable suspension.

Kim *et al.*, (2002) studied the stability of dispersions of graphite in aqueous solution with ABDM (alkyl benzyl dimethyl ammonium chloride) as a surfactant. They found that the adsorbed amount of ABDM onto graphite particles was strongly dependent on its surface charge. The surface potential of graphite particles increased from negative to positive. They concluded that the highly dispersion stability of graphite was obtained at higher concentration correlated to zeta potential.