

CHAPTER II

BACKGROUND AND LITERATURE REVIEW

2.1 Surfactant Structures

A surfactant or surface active agent is a substance that, when presents at low concentrations in a 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 interfaces (Rosen, 1988). Surfactants also have the property of forming colloid-sized aggregates in solution called micelles at sufficient high concentrations. 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 organic solvent, called the lyophobic group (hydrophilic), together with a group that has strong attraction for the organic solvent, called the lyophilic group (hydrophobic). This is known as an amphipathic structure as shown in Figure 2.1

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 saccharide 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).

Surfactants are classified according to the charge present in the hydrophilic portion of the molecule (after dissociation in aqueous solution). They can be categorized into 4 types (Porter, 1994).

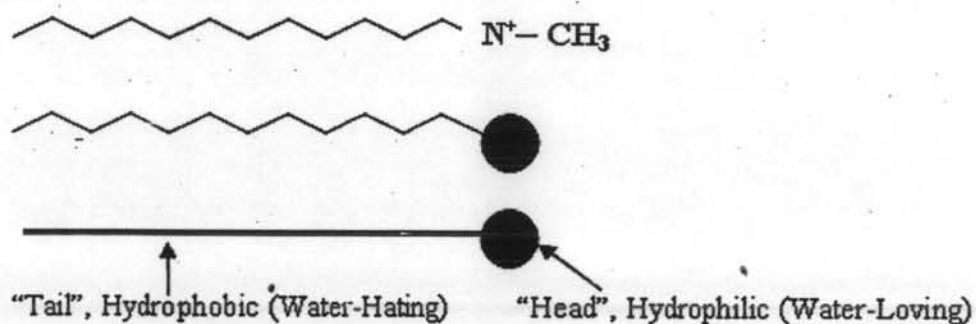


Figure 2.1 Surfactant structure.

Anionic surfactant: surfactant molecule, whose polar group is negatively charged; for example, alkylbenzene sulfonate, and sodium dodecylsulfate.

Nonionic surfactant: no ion charge appears on the hydrophilic portion; for example, polyoxyethylenated alkylphenol.

Cationic surfactant: positive charge of the surfactant molecules appears on the hydrophilic portion; for example, quaternary ammonium chloride, and laurylamine hydrochloride.

Ampholytic or zwitterionic surfactant: surfactant molecule, which has both positive and negative charged portions. The presence of both charged hydrophilic groups in the same molecule leads to the head group hydrophilicity being an intermediate between the ionic and conventional nonionic classes (Laughlin, 1991). The charge depends on pH of solution. At low pH (acidic solutions), they form cations, and at high pH (alkaline solutions), they form anions. For example, polyoxyethylenated alkylphenol, and lauramidopropylbetaine.

2.1.1 Anionic Surfactants

One of the most well-known anionic surfactant is sodium dodecylsulphate (SDS) that has a long chain alkylsulphate. The molecular shape of the bile salt exhibits a planar polarity due to spatial distribution of lateral groups in their steroid backbone. The bile salt structure result in smaller and more rigid aggregates than the micelles formed by conventional alkylsurfactants, providing highly non polar microenvironments with chiral properties. Indeed, the balance of

hydrophobic and electrostatic forces in the polymer-surfactant interaction in moderate ionic strength has been shown sensitive to different surfactant structures being the hydrophobic component more relevant to bile salt aggregation. Sodium Dodecyl Sulphate (SDS) is a familiar anionic surfactant as shown in Figure 2.2

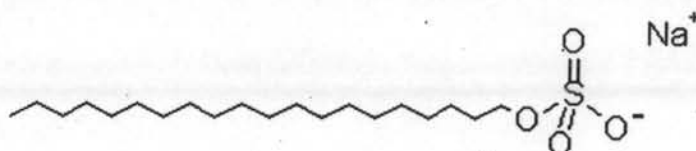


Figure 2.2 Structure of SDS.

Ionic surfactant 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 Tiger *et al.* (2000) is the study of Wanless *et al.* (1997), in which the SDS system forms a featureless monolayer on graphite below CMC.

2.1.2 Cationic Surfactants

The term “cationic surfactant” is used to denote an ionic compound in which the cation is amphiphatic and strongly surface active. Considering the effect of pH on molecular structure and physical chemistry, the cationic hydrophilic groups can be divided into two sub-groups; neutral and acidic.

Cetyltrimethylammoniumbromide (CTAB) is a familiar cationic surfactant in the neutral sub-group as shown in Figure 2.3.

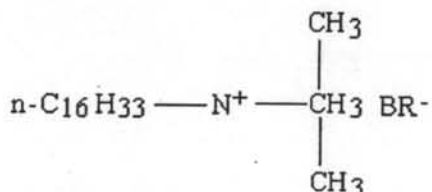


Figure 2.3 Structure of CTAB.

Quaternary ammonium ions have four carbons bond to a positive nitrogen atom. Quaternary ammonium surfactants have one or more of these substituents group as lypophillic (oil-loving). The cationic molecule exists paired with an anionic molecule in an electrically neutral salt. The quaternary ammonium nitrogen in CTAB displays sp^3 bonding. This cationic molecule lacks both acidic protons and non-bonding electron pairs; therefore, it is neutral in water from an acid-base perspective. If the anionic partner in such a salt is also neither acidic nor basic, as the true of bromide, the molecular structure of this salt is independent of pH (Rubingh and Holland, 1990).

Ismail *et al.* (1997) studied the effects of a cationic surfactant (fatty diamine), termed a multifunctional additive (MFA), and a commercial silane coupling agent on the properties of a silica filled natural rubber compound. These results not only contributes to a better silica-elastomer adherence but also improve dispersion leading to a lower hysteresis and enhancing the mechanical properties of natural rubber.

2.2 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 absorption 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 was illustrated in Figure 2.5. The adsorption isotherm was 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 cooperativity 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. Cases and vilieras, (1992) have represented evidence to indicate that the reason for the formation of these aggregates locally or patchwise at the interface is due to the heterogeneity of the surface.

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 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 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.

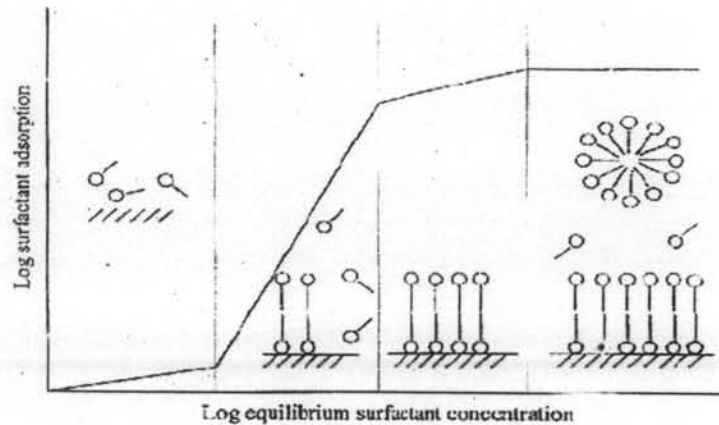


Figure 2.4 Adsorption isotherm of surfactant on an oppositely charged substrate.

2.2.1 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. Many valuable information are 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

Obviously the nature of solid surface plays a crucial role in the adsorption of surfactants at solid-liquid interface, although in many reports studied the nature of the surface is not defined. 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) and Day *et al.* (1967) 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 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).

2.2.3 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).

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. The adsorbed structure of C₁₂TAB on graphite showed a flat monolayer at low concentrations, followed by the formation of hemicylindrical interfacial aggregates (Kiraly and Findenegg, 1998).

Nonionic surfactants appeared 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 lead to the formation of hemicylindrical structures (loser to the CMC). Ionic surfactants were also found to exhibit the same behavior (Tiberg *et al.*, 2000).

Most surfactants form hemicylindrical structures on graphite. The nonionic C₁₀ surfactants 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.

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.

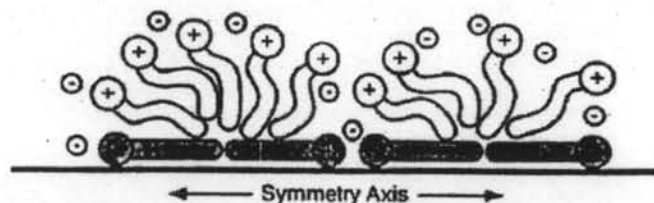


Figure 2.5 Hemicylinders aggregate at the hydrophobic surface (Atkin *et al.*, 2003).

2.3 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, 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. Contact angle data, especially in the case of polymeric materials, can be obtained with low price instruments and with simple techniques.

Regarding to 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 as shown in Figure 2.6 resulting in the following equation of interfacial equilibrium;

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

Equation 1 is generally called Young's equation which the static contact angle (θ) is 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.

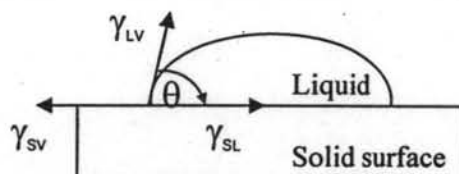


Figure 2.6 Schematic representation of the force balance affecting contact angle.

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 technique, 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 2.6, 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 a solid or liquid surface because of water has a high surface tension, 72 dyn/cm., and does not spontaneously spread over covalent solids which 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

$$\frac{\partial (\gamma_{LV} \cos\theta)}{\partial \gamma_{LV}} = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} \quad (2)$$

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.

2.4 Carbon Black

Carbon black is a generic term for an important family of products used principally for the reinforcement of rubber, as a black pigment, and for its electrically conductive properties. It is a fluffy powder of extreme fineness and high surface area, composed essentially of elemental carbon. Plants for the manufacture of carbon black are strategically located worldwide in order to supply the rubber tire industry consuming 70 % of production. About 20 % is used for other rubber products and 10 % is used for special non-rubber applications. Carbon black differ from other form of bulk carbon such as diamond, graphite, cokes, and charcoal in that they are particulate, composed of aggregates having complex configurations, quasi-graphite in structure, and of colloid in dimensions. They differ from other bulk carbons in having their origin in the vapor phase through the thermal decomposition and the partial combustion of hydrocarbons. Carbon black is a product of a process incorporating the latest engineering technology and process controls. Its purity differentiates it from soot that is impure by products from the combustion of coal and oils and from use of diesel fuels.

The arrangement of carbon atoms in carbon black has been well established by x-ray diffraction method. Carbon black can have a degenerated graphitic crystalline structure. Figure 2.7 show the three-dimensional order of graphite as compared to the two dimensional order of carbon black. From the x - ray data, carbon black consists of well-developed graphite structure platelet roughly parallel to one another but random in orientation with respect to adjacent layers.

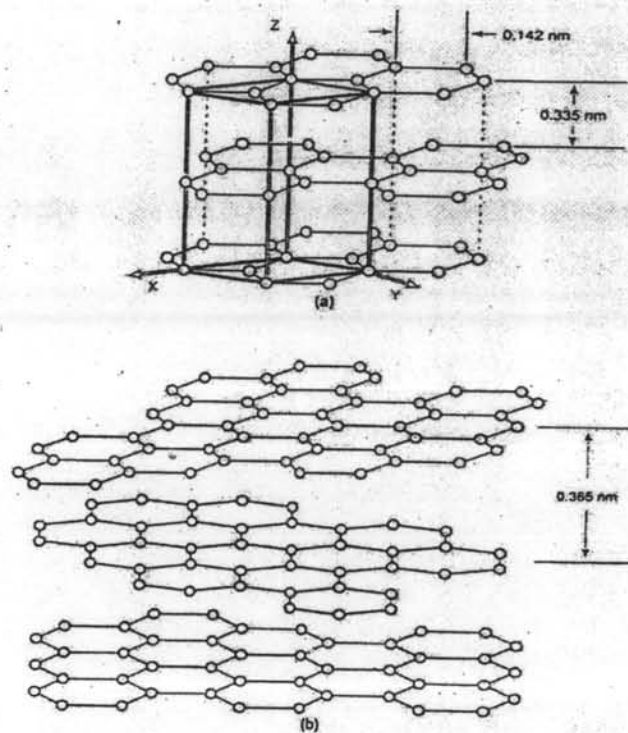


Figure 2.7 Atomic structural models of (a), graphite, and (b) carbon black (Baker *et al.*, 1992).

Larsson *et al.* (1984) studied the zeta potential and flotation efficiency as a function of the addition of calcium ion concentration to carbon black dispersions in the presence of sodium stearate. The investigators observed that absolute value of negative zeta potential of carbon black particles decreased with increasing calcium concentration while the flotation efficiency increased. Microscopic analysis of the carbon black particles revealed that precipitated calcium distearate adhered to the surface of the carbon black. They concluded that precipitation of calcium dicarboxylate created a micro-encapsulation carbon black particles causing aggregation, hydrophobicity and subsequent flotation.

Rao and Stenius (1998) studied the mechanisms of ink (carbon black) and the influence of several nonionic surfactants on release of carbon black from cellophane, a polyamide sheet and photocopy paper, were used as model substrates. A simple model of the structure of dry ink, which was assumed to consist of a

primary layer (directly bound to the substrate), a secondary layer, and tertiary layer, was used to elucidate how carbon black detachment takes place. They found that the addition of surfactant was crucial because it softens the carbon black and affects the carbon black/fiber interactions. For complete detachment of ink generally required mechanical force, however mechanical action alone could not successfully remove ink in direct contact with the fibers. Moreover, they indicated the structural difference in surfactants might affect kinetics rather than actual detachment mechanism.

2.4.1 The Adsorption of Non-Ionic Surfactant on Carbon Black

Gonzalez-Garcia et al.(2001) studied the adsorption of a nonionic surfactant (Triton X-100 (TX-100)) onto a set of carbon blacks and activated carbons to compare to the results of the calorimetric study. Different behaviours in the progress of the adsorption enthalpy as a function of surface coverage were obtained. However, irrespective of the nature of the carbon support, was related to the same types of interactions since the evolution of adsorption enthalpy in these systems depends mainly on the porosity of the samples but not on the chemistry surface composition. The results at low coverage, indicated two kinds, at least, of adsorption behaviour: the first related to the adsorption of TX-100 in the narrowest pores with a suitable width and the second on more open surfaces. In the narrowest micropores, the adsorption enthalpy can be twice that for a non-microporous surface as can be expected for slit-shaped micropores accommodating only one molecule. At higher coverage, the retention is due to interactions between surfactant molecules at the adsorbent-solution interface leading to the formation of interfacial aggregates.

2.4.2 The Adsorption of Cationic Surfactant on Carbon Black

Bele and Kodre (1998) studied the adsorption of cationic surfactant cetyltrimethylammonium bromide (CTAB) onto carbon black. Charge-compensating polyelectrolyte titration was used for quantitative determination of the surfactant content in solution. Sharp saturation was observed. The saturated surface concentration of the adsorbed CTAB was found to be the same in the dispersed and

air-dried product. Fourier transformed infrared spectroscopy and extended X-ray absorption fine structure (EXAFS) analyses suggested $-CTA^+$ and Br^- ion sites in the dried product.

- In 2002 Gurses and Yalcin studied the adsorption mechanism of cetyltrimethylammonium bromide (CTAB), a cationic surfactant, onto powdered active carbon (PAC) was investigated and also some thermodynamic quantities such as isosteric adsorption enthalpy and entropy of this system were determined. In addition, the mechanistic and thermodynamic results of the experiments were supported with the surface zeta potential measurements. It was found that 5 min is sufficient in order to reach adsorption equilibrium. The adsorption of CTAB onto active carbon/water interface mainly takes place through ion exchange, the ion pairing and hydrophobic bonding. The predominant mechanisms at a low CTAB concentration are probably the ion exchange and ion pairing. The hydrophobic bonding mechanism predominates at high CTAB concentrations. It was determined that the signs of isosteric adsorption enthalpy and isosteric adsorption entropy for adsorption of CTAB onto PAC are negative and positive, respectively. As temperature increases, the amount of CTAB adsorbed is decreased indicating the exothermic nature of adsorption process.

2.4.3 The Adsorption of Anionic Surfactant on Carbon Black

Garcia (2001) studied the free energy of the adsorption process of anionic surfactant from aqueous solutions onto a set of carbon blacks in the range of low concentrations using the model proposed by van Oss and co-workers. The obtained results indicated that the free energy of interaction between adsorbent and adsorbate through water results mainly from Lifshitz-van der Waals and electrostatic interactions, and its value showed a good correspondence with that previously found from a combination of the classical measurements of adsorption isotherms and the Langmuir model.

Moreno (2004) studied the measurements of the amount adsorbed of an anionic surfactant from aqueous solutions on activated carbons and carbon blacks, together with zeta potential determination of the suspended particles. Changes in adsorption isotherms and zeta potential curves with the equilibrium concentration in

solution exhibited a similar behavior. Although the solids had different zeta potential when they were suspended in pure water, it was found that the relative change of the zeta potential at the maximum adsorption for each solid was proportional to the area amount adsorbed, this proportion being similar for all the samples despite of their surface area or porosity. These results indicate that adsorption of the anionic surfactant has to take place on parts of the surface which allows the ionic head to be exposed to the solution, probably the more inner parts of the surface being not allowable to the adsorbate.

Garcia (2004) studied adsorption enthalpies of sodium dodecyl sulphate onto a set of carbon blacks in the low concentration range. The surfactant was found to adsorb on the carbon surface exothermally in the whole studied coverage. From the calorimetric results and the analysis of the adsorption isotherms by the double Langmuir equation, a model of the adsorption mechanism in these systems was proposed. The adsorption of the surfactant onto the carbon blacks can be explained by two energetically distinct steps corresponding to the adsorption of SDS in two different types of porosity. The first step corresponds to adsorption in pores where the surfactant molecule experiences some enhanced potential without a noticeable contribution from the surface chemical composition. The second step corresponds to adsorption in pores where this enhancement is no more efficient.

2.5 The Double Layer

The diffuse layer can be visualized as a charged atmosphere surrounding the colloid as in Figure 2.8. (Adamson, 1990) The double layer model is used to visualize the ionic environment in the vicinity of a charged colloid and explains how electrical repulsive forces occur. We first look at the effect of the colloid on the positive ions (often called counter-ions) in solution. Initially, attraction from the negative colloid causes some of the positive ions to form a firmly attached layer around the surface of the colloid; this layer of counter-ions is known as the stern layer. Additional positive ions are still attracted by the negative colloid, but now they are repelled by the stern layer as well as by other positive ions that are also trying to approach the colloid. This dynamic equilibrium results in the formation of a diffuse

layer of counter ions. They have a high concentration near the surface, which gradually decreases with distance, until it reaches equilibrium with the counter-ion concentration in the solution.

In a similar, but opposite fashion, there is a lack of negative ions in the neighborhood of the surface, because they are repelled by the negative colloid. Negative ions are called co-ions because they have the same charge as the colloid. Their concentration will gradually increase with distance, as the repulsive forces of the colloid are screened out by the positive ions, until equilibrium is again reached.

The charge density at any distance from the surface is equal to the difference in concentration of positive and negative ions at that point. Charge density is the greatest near the colloid and gradually diminishes toward zero as the concentration of positive and negative ions merge together. The attached counter-ions in the stern layer and the diffuse layer are what we refer to as the double layer. The thickness of this layer depends upon the type and concentration of ions in solution.

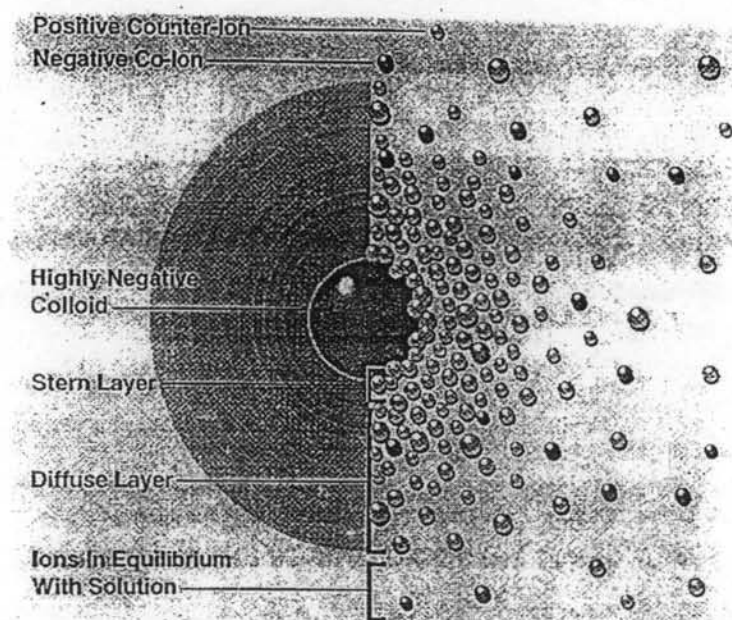


Figure 2.8 Visualization of the Double Layer.

2.6 Zeta Potential

The double layer is formed in order to neutralize the charged colloid and, in turn, causes an electrokinetic potential between the surface of the colloid and any point in the mass of the suspending liquid. This voltage difference is on the order of millivolts and is referred to as the surface potential. Figure 2.9 shows the magnitude of the surface potential through the distance from colloid. It is related to the surface charge and the thickness of the double layer. As we leave the surface, the potential drops off roughly linearly in the stern layer and then exponentially through the diffuse layer, approaching zero at the imaginary boundary of the double layer. The potential curve is useful because it indicates the strength of the electrical force between at which this force comes into play. A charged particle will move with a fixed velocity in a voltage field. This phenomenon is called electrophoresis. The particle's mobility is related to the dielectric constant and viscosity of the suspending liquid and to the electrical potential at the boundary between the moving particle and liquid. This boundary is called the slip plane and is usually defined as the point where the stern layer and the diffuse layer meet. The stern layer is considered to be rigidly attached to the colloid, while the diffuse layer is not. As a result, the electrical potential at this junction is related to the mobility of the particle and is called the zeta potential.

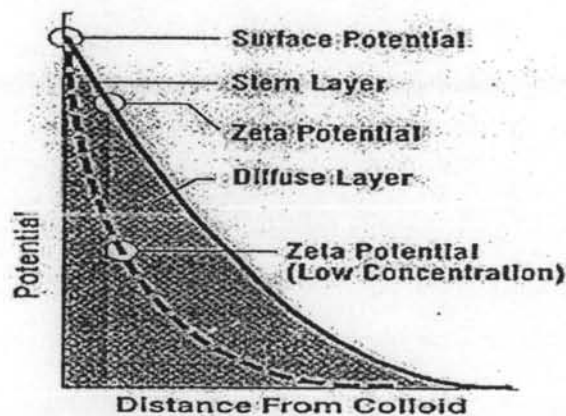


Figure 2.9 Relationship between zeta potential and surface potential.

2.7 Removal of Particulate Soil

In the study of detergency formulation and performance, Linfield *et al.* (1962) found that an increase in agitation speed, washing time or detergent concentration, resulted in increasing detergency performance to the maximum levels. Their paper noted that for the conditions of washing at 48.9°C, 0.2% detergent and 135 ppm water hardness, the maximum detergency was obtained at around 150-170 rpm and around 15-20 min washing cycle.

Obendorf *et al.* (1982) reported that mechanical action and detergent concentration affected the soil removal. An increase in either mechanical action or detergent concentration resulted in increasing removal of triolein from inter fiber capillaries, but the concentration of triolein in the cotton fibers remained high.

In 1987, Raney *et al.* studied the correlation of PIT with optimum detergency. The maximum detergent action in ternary systems was found to occur when the temperature was near the PIT of the system composed of water, the surfactant and the hydrocarbon soil itself. The combination of solubilization and emulsification was also proposed as the predominant mechanisms for oily soil removal rather than the roll-up mechanism.

As known, builder is another interesting factor for enhancing the cleaning efficiency. Webb *et al.* (1988) also found the largest difference in soil removal and appearance among the formulations of detergents was based on the presence or absence of builder. Builder enhances the cleaning efficiency of the surfactant.

Jakobi and Lohr (1987) found that particulate soil also acquires a negative charge of pigments and fibers is further increased by adsorption of anionic surfactants. The corresponding increase in mutual repulsion is responsible for an increase in the washing effect. Dispersing power for pigments also increases for the same reason, whereas the redeposition tendency of removed soil is diminished. In contrast to anionic surfactants, cationic surfactants can cause a decrease in washing effect below that observed with pure water that is devoid of additives. Significant soil removal then occurs only at high surfactant concentrations, at which a complete charge reversal takes place on both fabric and soil.

Jakobi and Lohr (1989) found that fibers and pigments in an aqueous medium acquire negative charges. Essential similar results are obtained for all major pigment soil components. This is one of the reasons for enhancement of wash performance.

The assumption that soil adhesion is dependent on electrostatic interactions has led to attempts to correlate soil removal with the zeta potential of the fibers in the wash liquid. Since most textile fibers and soil particles are negatively charged in solutions of anionic surfactants, Gotte (1949) proposed that the resultant repulsive forces between the similar charges of fiber and soil contribute to the detachment of soil. Kling and Lange (1952) suggested that these repulsion forces also prevent redeposition of soil on the fibers.

In 1963, Wagner studied the effect of wash temperature on soil deposition which depends on the nature of soil, and the fiber. He studied desorption and sorption of Degussa No.100 carbon on cotton and concluded that a higher bath temperature increased the rates of both soil desorption and adsorption and soil desorption.

In 1973, Vaeck and de Pauw found that an increase in the level of mechanical energy increases the amount of particulate soil removed and the amount of soil redeposited without changing the relative effects of other factors. They also found that electrolytes have a strong effect on soil redeposition, increasing both the deposition rate and the saturation concentration, and that sodium chloride increases the deposition of carbon black over 100 times. The effect was observed with hydrophobic and hydrophilic soils, various surfactants, and on pure cotton and polyester-cotton fabrics. The magnitude of the effect depended only on the number of ions and was independent of the size or mass of the monovalent ions.