CHAPTER II
LITERATURE SURVEY

2.1 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. Carbon black manufacturing plants 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 blacks differ from other forms of bulk carbon such as diamond, graphite, cokes and charcoal in that they are particulate, composed of aggregates having complex configurations, quasi-graphitic structure and colloidal 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 soots that are impure by-products from the combustion of coal and oils and from use of diesel fuels. Carbon black are essentially free of the inorganic contaminants and extractable organic residues characteristic of most forms of soot.

A number of processes have been used to produce carbon black including the oil-furnace, impingement (channel), lampblack, and the thermal decomposition of natural gas and acetylene. These processes produce different grades of carbon and are referred to by the process by which they are made, e.g., oil-furnace black, lampblack, thermal black, acetylene black and channel-type impingement black. A small amount of by-product carbon from

manufacturing synthesis gas from liquid hydrocarbons has been found applications in electrically conductive compositions. The different grades from the various processes have certain unique characteristics, but it is now possible to produce reasonable approximations of most of these grades by the oil-furnace process. Since over 95% of the total output of carbon black is produced by the oil-furnace process, this article emphasizes this process.

2.1.1 Physical Structure of Carbon Black

The arrangement of carbon atoms in carbon black has been well established by x-ray diffraction method. Carbon black can have a degenerated graphitic crystallite structure. Whereas graphite has three-dimensional order, as seen in the model structure of Figure 2.1, carbon black has two-dimensional order. The x-ray data indicated that carbon black consists of well-developed graphite structure platelets stacked roughly parallel to one another but random in orientation with respect to adjacent layers.

2.1.2 Chemical Composition

Oil-furnace blacks used by the rubber industry contain over 97% elemental carbon. Thermal and

acetylene black consist of over 99% carbon. The ultimate analysis of rubber-grade blacks is shown in Table 2.1. The elements other than carbon in furnace black are hydrogen, oxygen, and sulfur, and there are mineral oxides and salts and traces of adsorbed hydrocarbons. The oxygen content is located on the surface of the aggregates as C_xO_y complexes. The hydrogen and sulfur are distributed on the surface and the interior of the aggregates. Some special blacks used for pigment purposes contain larger quantities of oxygen than normal furnace blacks. These blacks are made by oxidation in a separate process step using nitric acid, ozone, air and other oxidizing agents. They contain from 2 to 6% oxygen. Oxidation improves

dispersion and flow characteristics in pigment vehicle systems such as lithographic inks, paints, and enamels.
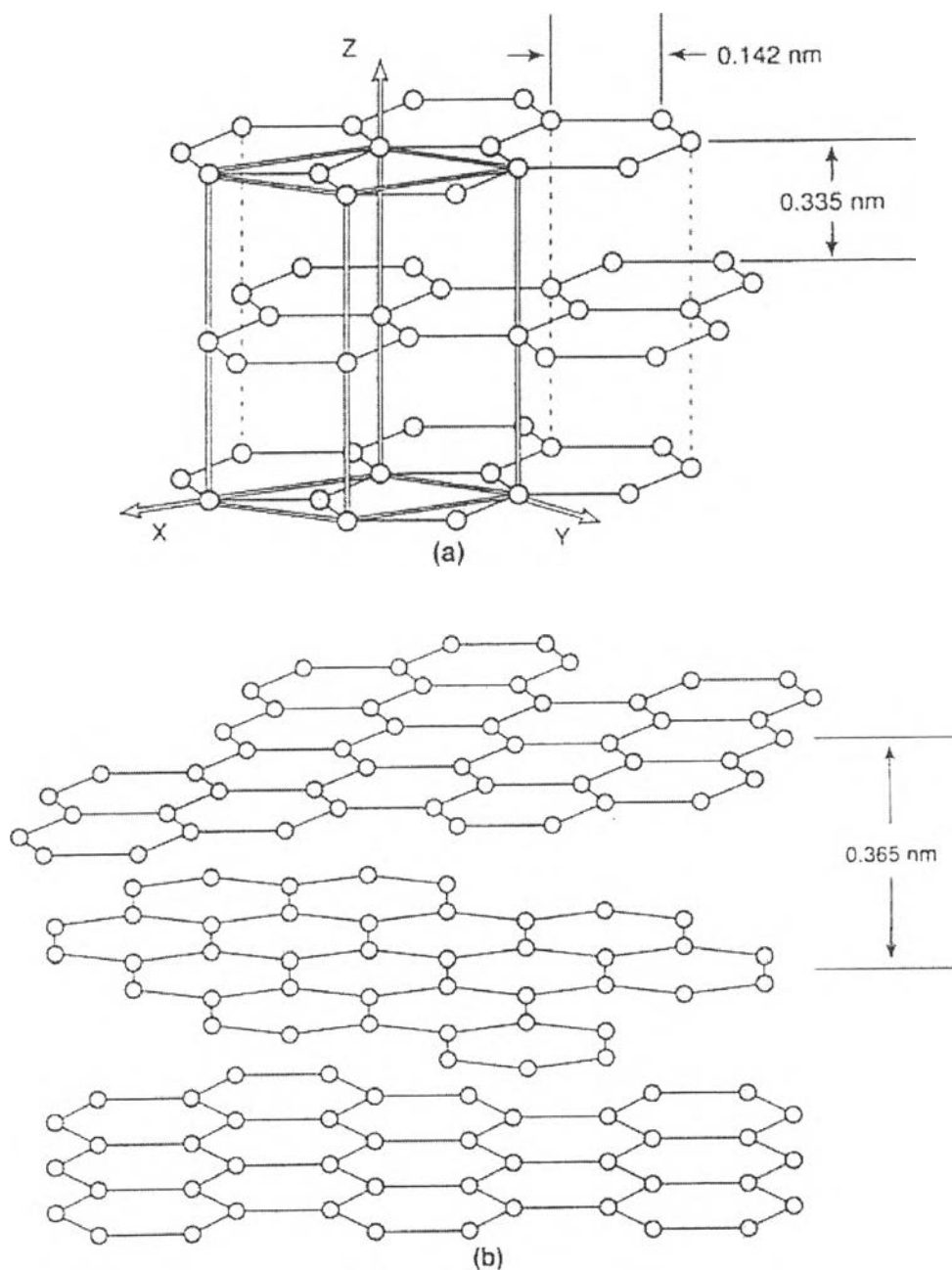
Figure 2.1 Atomic structural models of (a) graphite and (b) carbon black (Baker *et al.*, 1992)

Table 2.1 Chemical composition of carbon blacks, % (Baker *et al.*, 1992).

Type	Rubber-grade furnace	Medium thermal	Acetylene
Carbon	97.3-99.3	99.4	99.8
Hydrogen	0.20-0.40	0.30-0.50	0.05-0.10
Oxygen	0.20-1.20	0.00-0.12	0.10-0.15
Sulfur	0.20-1.20	0.00-0.25	0.02-0.05
Ash	0.10-1.00	0.20-0.38	0.00
Volatile	0.60-1.50		<0.40

2.2 Paper Fiber

Paper means a thin layer object, which is made from fiber and mixed with more than one type of additives (Watanawong, 2000).

2.2.1 Source of Paper Fiber

2.2.1.1 Wood

- Softwood is coniferous or gymnosperm species such as spruce, pine, fir. The trade name of paper normally has N (needle) at the initial name, for example, NBKP (Needle Bleached Kraft Pulp)

- Hardwood is angiosper species such as Eucalyptus, birch, aspen. The trade name of paper normally has L (leaved) at the initial name, for example, LBKP (Leaved Bleached Kraft Pulp).

2.2.1.2 Non-Wood

- Agriculture residue such as millet, bagasse
- Natural growing plants such as bamboo

- Crop fibers - Paper fiber is produced from bast or stem such as hemp, ramic, sute, kenaf.
  - Paper fiber is produced from leaf fiber such as abaca, sisal, and pineapple.
  - Paper fiber is produced from seed fiber such as cotton

2.2.2 Chemical Composition of Wood

Chemical composition of some variety of sources fiber composes of cellulose, hemicellulose, lignin and extractive.

2.2.2.1 Cellulose

It is a straight chain homopolymer of d-glucose, which is connected with 1,4 β glucosidic bond. It comprises of 10,000 units and H-bond link between row.

2.2.2.2 Hemicellulose

It is heteropolymer which is combined approximately 200 units of many types of sugars such as glucose, mannose, xylose and arabinose.

2.2.2.3 Lignin

It is amorphous, which has approximately 2,500 units of phenyl propane units. The function of lignin is the binder between fibers.

2.2.2.4 Extractive

It is the compound, which can be soluble in organic solvent, for instance, acetone, alcohol, dicholomethane and chloroform.

2.2.3 Composition of Paper Fiber

2.2.3.1 Fibrous Materials

Generally, paper composes of fiber in 70 to 95 percent of paperweight. The quality of paper depends on quantity of fiber. Fibers comprise of plant cells such as parenchyma cell, vessel cell.

2.2.3.2 Non Fibrous Materials

They are additives, which are added for improving the quality of paper. They are classified into 2 parts.

* Functional additive is added to improve the specific property of paper. It can be divided into 6 types as following.

  * Sizing agent is the chemical which increase the tolerance of water. Paper which contains no added sizing agent is easy for adsorbing water such as tissue paper, blotting paper. Sizing agents use in paper process are alum/rosin size, wax, asphalt, AKD (Alkyl Ketone Dimer) and ASA (Alkenyl Succinic Anhydride).

  * Filler is added in order to increase surface area of paper. It also improves the properties of paper such as increase in ore particle-air and ore particle-fiber, light scattering, smoothness, brightness and decrease in budget of paper production. The fillers use in paper process are kaolin or clay, TiO_2 (Titanium dioxide) and $CaCO_3$ (Calcium carbonate)

  * Dry strength agent is added for increasing toughness of paper. The agent which is commonly

used in paper process is cationic starch and polyacrylamide.

- Wet strength agent is added for increasing toughness at 15 percent of originally toughness. They are, for instance, urea-formaldehyde, melamine-formaldehyde, polyamide and polyamine
- Dyes is added for colouring paper, tinting dyes.
- Optical brightenings agent is fluorescent dyes that adsorbs UV ultraviolet and desorbs wavelength in range of blue.

* Chemical processing aids

- Retention aids
- Deformers help preventing foam formation.
- Microbiological control agent prevent the slime formation.
- Pitch control agent
- Drainage aids increase the rate of leaving water from paper.
- Formation aids decrease the aggregate of fiber.

2.3 General Structure of Surfactants

The term surfactant is a contraction of surface-active agent which has a characteristic molecule consisting of groups of opposing solubility tendencies, typically an oil-soluble hydrocarbon chain, known as a hydrophobic group, and a water-soluble ionic group, called hydrophilic group. This is known as an amphipathic structure.

Depending on the nature of the hydrophilic group, surfactants are classified as:

2.3.1 Anionic

The surface-active portion of the molecule bears negative charge, for example, $RCOO^-Na^+$ (soap) $RC_6H_4SO_3^-Na^+$ (LAS or linear alkyl benzene sulfate).

2.3.2 Cationic

The surface-active portion of the molecule bears positive charge, for example, $CH_3(CH_2)_{15}N^+(CH_3)_3Br^-$ (CTAB or Cetyl trimethylammonium bromide), $RNH_3^+Cl^-$ (salt of a long chain amine) $RN-(CH_3)_3^+Cl^-$ (quarternary ammonium chloride).

2.3.3 Zwitterionic

The surface-active portion of the molecule bears both positive and negative charges, for example, $RN^+H_2CH_2COO^-$ (long-chain amino acid) $RN^+(CH_3)_2$ (sulfobetaine).

2.3.4 Nonionic

The surface-active portion of the molecule bears nonionic charge, for example, $RCOOCH_2CHOHCH_2OH$ (monoglyceride of long-chain fatty acid), $RC_6H_4(OC_2H_4)_xOH$ (polyoxyethylenated alkylphenol).

2.4 Roles of Surfactant on Flotation Deinking

According to Ferguson (1992b), surfactants used in flotation deinking take three important roles.

- Acting as a dispersant to separate ink particles from the fiber and prevent redeposition of separated ink particles on the fiber.

- Acting as a collector to agglomerate the small ink particles to floc by controlling the surface of ink into hydrophobic surface.

- Acting as a frother to generate foam on the top layer of flotation cell for ink removal.

2.5 Adsorption Isotherm of Surfactant

The adsorption 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 2.2 (Harwell and Scamehorn, 1993). 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.
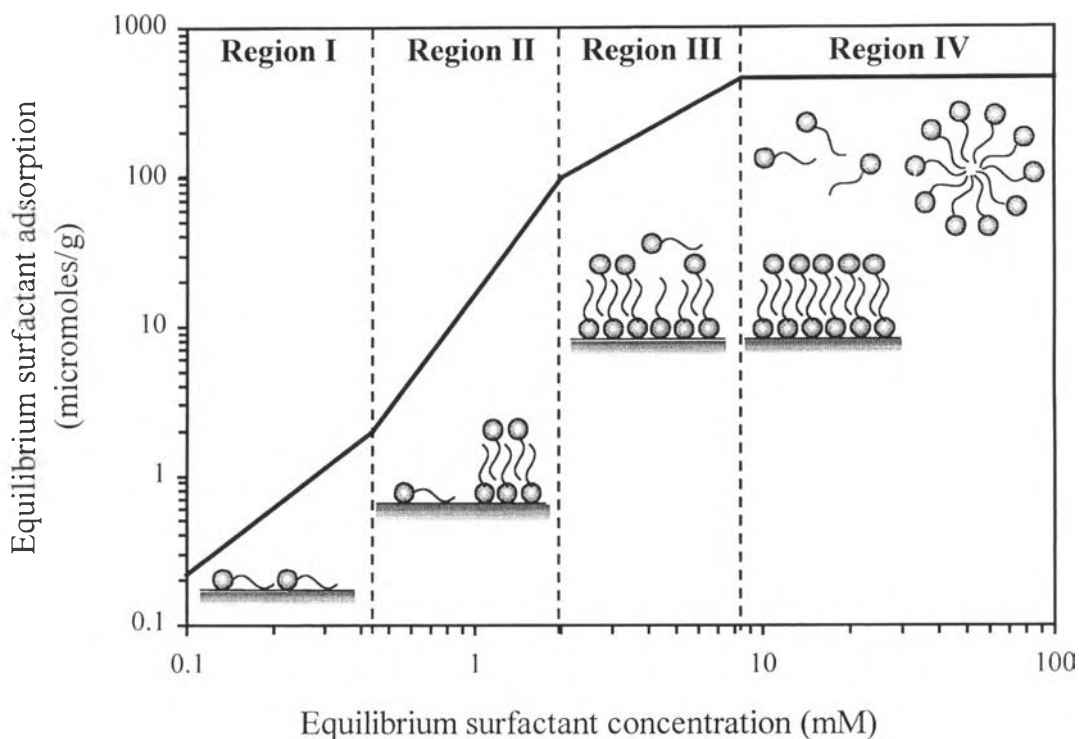
Figure 2.2 Typical surfactant adsorption isotherm.

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.

2.6 Roles of Calcium Ions in Flotation Deinking

The collector chemistry implies the use of anionic surfactant and a "collector" ion, such as calcium, to impart the desired properties to the ink particles. The fundamental aspects and the roles of calcium ions in flotation deinking have been proposed.

Larsson *et al.* (1984) studied the zeta potential and flotation efficiency as a function of the addition of calcium ion concentration to model ink dispersions in the presence of sodium stearate. They verified that the absolute value of the negative zeta potential of the ink particles decreased with increasing calcium concentration while flotation efficiency increased. It was suggested that, in alkaline medium, generally adopted industrially, the highly negative charge of the ink particle promoted its electrostatic stabilization.

This stabilization facilitated the liberation of the ink particle from the fiber. Nevertheless, this charge prevented the adhesion of ink particles on the air bubbles. It was observed that when calcium chloride was added to the flotation pulp, the salt of calcium/collector was partially precipitated on the surface of ink particles and hence became less negatively charged. The precipitation of calcium dicarboxylate was necessary to create a micro-encapsulation of the ink particles causing aggregation, hydrophobicity, and subsequent flotation.

There are a few problems occurring in flotation deinking and leading to less efficiency, for example, fiber loss. A major cause of fiber loss is the presence of calcium ion in the deinking system. A hypothesis to explain how fibers float was reported by Turvey (1993). He suggested that calcium ions form a complex with print components which sticks to fibers and gives them a hydrophobic surface, the fiber will have an increasing tendency to float during flotation deinking.

In addition, Dorris and Ngugen (1995) studied flotation of model inks (flexographic inks) without fibers. Flexographic inks which composed of a pigment, usually carbon black that dispersed in water with the use of water soluble carboxylic derivatives, which also performed as binder. The results showed that, in basic condition, the floatability of flexographic inks at alkaline condition improved with the addition with calcium ions and much more so with the addition of both sodium oleate and calcium ions, under turbulent agitation. The results suggested that conventional calcium soaps of fatty acids were effective flotation collectors for flexographic inks. Contrary results obtained in flotation deinking mills suggest that the problem of deinkability of flexo inks may not be due only to poor floatability, but also to other phenomena such as ink redeposition on fibers.

Oliveira and Torem (1996) investigated the fundamentals of ink flotation with sodium stearate, oleic acid and sodium dodecyl sulfate

collectors as well as the influence of metallic cations such as Ca^{2+}, Mg^{2+} and Al^{3+} on floatability. The results indicated that, with sodium stearate, an increase in floatability was probably associated with the precipitation of stearate species on the ink surface. It was suggested that a non-specific adsorption mechanism had occurred with sodium dodecyl sulphate, whilst a specific adsorption mechanism was associated with oleic acid. In the presence of calcium cation, an increase in floatability was verified, probably due to calcium/collector salt precipitation on the ink particle surface. In the presence of magnesium and aluminum species, an increase in floatability of ink was noted for pH ranges related to the concentration of hydroxy complexes and to the predominance of metallic hydroxides at pH values below their the isoelectric points (IEPs).

In the above references, the mechanism on the floatability of ink particles was supported by the precipitation mechanism. Conditions under which no surfactant precipitated was presented were not considered.

Rutland and Pugh (1997) studied mechanism of surfactant and calcium in adsorption by surface force and coagulation technique. The surface force technique concerned the invention of fatty acid flotation collectors and calcium activator with a negatively charged mica substrate at high pH. Since the surface of ink particles under deinking conditions are enriched by negatively charged groups, these experiments enabled some details of the fundamental mechanisms involved in deinking flotation to be clarified. The results (carried out at relatively low calcium and fatty acid concentrations) are summarized as follows: (a) At pH greater than 10, the negatively charged surface generated a long range DLVO double-layer repulsion and the potential at the mica/electrolyte interface could be estimated. However, at short distances, a repulsive non-DLVO hydration barrier was detected due to adsorbed Na^+. (b) On addition of $CaCl_2$, the Na^+ was replaced by the specific adsorption of the less strongly hydrated $Ca(OH)^+$ solution species or more

strongly hydrolyzable calcium species. This resulted in the elimination of the hydration forces and mica-mica contact. On addition of fatty acid, no change in the force profile was detected, suggesting no calcium was removed from the surface and there was no evidence of calcium soap formation in the surface region. This result implies that under alkali conditions, the calcium does not induce a bridging mechanism in the presence of fatty acid (below the calcium soap precipitation level). In fact, the calcium could be only operated as bridging agents if they can specifically bind to the surface, as well as to the carboxylated fatty acid. The "calcium dehydration/destabilization mechanism" was verified by coagulation studies with quartz suspension. At higher concentrations of fatty acid and calcium, calcium soap was precipitated in bulk solution. It was suggested that microencapsulation of the ink particles with hydrophobic species occurs through heterocoagulation with the bulk precipitated calcium soap particles.

Rivello *et al.* (1997) studied ink removal from secondary fiber by flotation deinking. The underlying mechanism of " collector chemistry " are elucidated and found to be complex combinations of the ink particle interactions stemming from the nature of the surfactant/calcium relationship. This study was focused on two medium chain-length fatty acids (sodium octanoate and sodium dodecanoate) and a comparable chain-length sulfate (sodium dodecyl sulfate). The system behavior are observed below the K_{sp} of the surfactant/calcium complex by investigating the adsorption isotherms of the surfactants on both model inks and fibers, the associated zeta potentials, the aggregation characteristics of the model ink and the flotation of the ink and fibers. The fundamental mechanisms were found to be adsorptive rather than precipitative. It was proposed that the surfactant adsorbed with a tail-down and/or lying down geometry on the carbon surfaces and the calcium strongly associated with the anionic head groups without bulk phase precipitation. The specific interactions between the carboxylate, the Ca^{2+} and the fiber result in

decreased calcium adsorption with increasing C8 concentration (a "calcium exclusion" effect). The interaction between paper fiber and calcium ions was purely electrostatic and non-associative adsorption. The calcium ions were attracted by the negatively charged sites on paper surface resulting from ionization of carboxyl and hydroxyl group.
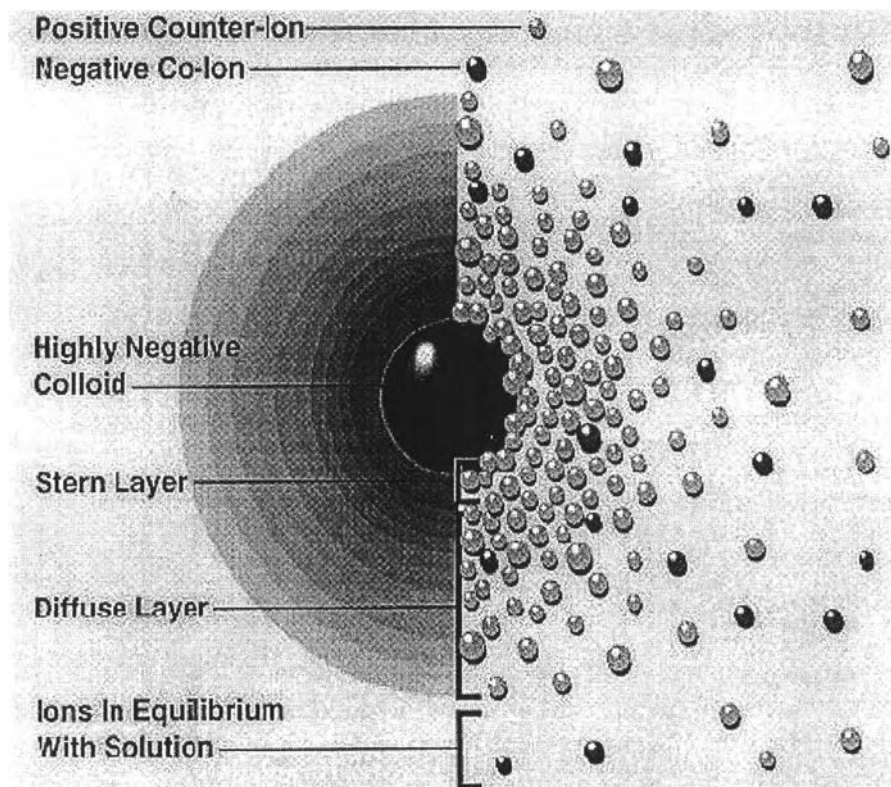
2.7 The Double Layer

The diffuse layer can be visualized as a charged atmosphere surrounding the colloid as shown in Figure 2.3 (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. The effect of the colloid on the positive ions (often called counter-ions) in solution was studied. 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 at the same time they are repelled by the stern layer as well as other positive ions 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.

Similarly, 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 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 2.3** Visualization of the double layer.

2.8 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 points in the mass of the suspending liquid. This voltage

difference is on the order of millivolts and referred to as the surface potential. Figure 2.4 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 be moved 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 plan 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.
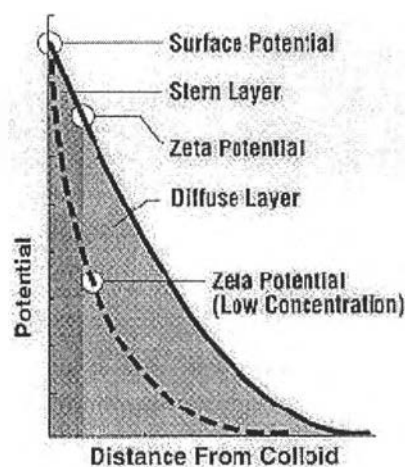
Figure 2.4 Relationship between zeta potential and surface potential.