CHAPTER II
LITERATURE SURVEY

Flotation process is one of the surfactant-based separation techniques. Originally it is used in the area of mineral processing. The concept of ore flotation is transferred into the waste paper recycling industry later. The application of flotation of ink from pulpwood was successfully introduced to waste paper mill in the 1980s (Zhu *et al.*, 1998). Both processes have the same concept, i.e., to control the surface hydrophobicity/hydrophilicity of disperse particles in water, but they have several differences in details (Rutland and Pugh 1997).

2.1 Nature of Paper Fiber

Paper means the thin layer object, which is made from fiber and mixed with more than one type of additive.

2.1.1 Source of Paper Fiber

2.1.1.1 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).

2.1.1.2 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

2.1.2 Chemical Composition of Wood

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

2.1.2.1 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.

2.1.2.2 Hemicellulose

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

2.1.2.3 Lignin

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

2.1.2.4 Extractive

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

2.1.3 <u>Composition of Paper Fiber</u>

2.1.3.1 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.

2.1.3.2 Non Fibrous Materials

They are additives, which are added for improving the quality of paper. They are classified into 4 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 is not added sizing agent, is easy for adsorbing water such as tissue paper, blotting paper. Sizing agent used 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 filler used 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 common

used in paper process is cationic starch and polyacrylamide.

- Wet strength agent is added for increasing toughness at 15 percent of originally toughness, 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 wavelenght 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.

2.2 Characteristic Features of Surfactants

The contraction term of surfactant comes from surface-active agent. When surfactants are presented at low concentration, surfactants have the property of adsorbing onto the surfaces or interfaces of the system. At sufficiently high concentration in solution, surfactant molecules will form aggregates called micelles. The concentration at which this occurs is called critical micelle concentration (CMC), which depends on each surfactant.

2.2.1 <u>General Structure of Surfactants</u>

Surfactants have a characteristic molecular structure consisting of a structure group that has very strong attraction for water, known as hydrophilic or lipophobic together with a group that has strong attraction for oil called the lipophilic or hydrophobic structure.

The hydrophobic group is usually a long chain hydrocarbon and less often a halogenated or oxygenated hydrocarbon or siloxane chain. The hydrophilic group is an ionic of highly polar group. Surfactants are classified as following.

2.2.1.1 Anionic

The head group of surfactant bears negative charge, for example, $RCOO^-Na^+$ (soap) $RC_6H_4SO_3^-Na^+$ (LAS or linear alkyl benzene sulfate).

2.2.1.2 Cationic

The head group of surfactant bears positive charge, for example, $CH_3(CH_2)_{15}N^+(CH_3)_3$ Br^- (CTAB or Cetyl trimethylammonium bromide) $RNH_3^+Cl^-$ (salt of a long chain amine) $RN(CH_3)_3^+Cl^-$ (quarternary ammonium chloride).

2.2.1.3 Zwitterionic

The head group of surfactant bears both positive and negative charges, for example, $RN^+H_2CH_2COO^-$ (long-chain amino acid) RN^+ $(CH_3)_2$ (sulfobetain).

2.2.1.4 Nonionic

The head group of surfactant bears nonionic charge, for example, $RCOOCH_2CHOHCH_2OH$ (monoglyceride of long-chain fatty acid) $RC_6H_4O(CH_2CH_2O)_mH$ (nonyl phenol polyethoxylate).

2.3 Role of Surfactant on Flotation Deinking

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

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

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

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

2.4 Adsorption Isotherm of Surfactant

The adsorption behavior of surfactant on surface can be presented by an adsorption isotherm. The curve of an adsorption isotherm for an anionic surfactant on a strongly charged site substrate is shown in Figure 2.1 (Rosen, 1989). The curve can be divided into 4 regions.

In region 1, the surfactant is adsorbed mainly by ion exchange, The charge density or potential at the Stern layer of the substrate remains almost constant.

In region 2, there is a marked increase in adsorption, resulting from interaction between the hydrophobic chains of the previously adsorbed surfactants. This aggregation of the hydrophobic groups, which may occur at concentration well below the critical micelle concentration (CMC) of the surfactant, has been called hemimicelle formation or cooperative adsorption.

In region 3, the slope of the isotherm is reduced, because adsorption now must overcome electrostatic repulsion between the oncoming ions and the similarly charged solid.

In region 4, adsorption in this fashion is usually complete when the surface is covered with a monolayer or bilayer of the surfactant. In many cases this occurs approximately at the CMC of the surfactant, since adsorption appears to involve single ions rather than micelles. Above CMC, the pseudo phase separation model predicts that the monomer concentration is constant and that the concentration of micelles increases linearly with total surfactant concentration (Scamehorn *et al.*, 1982).
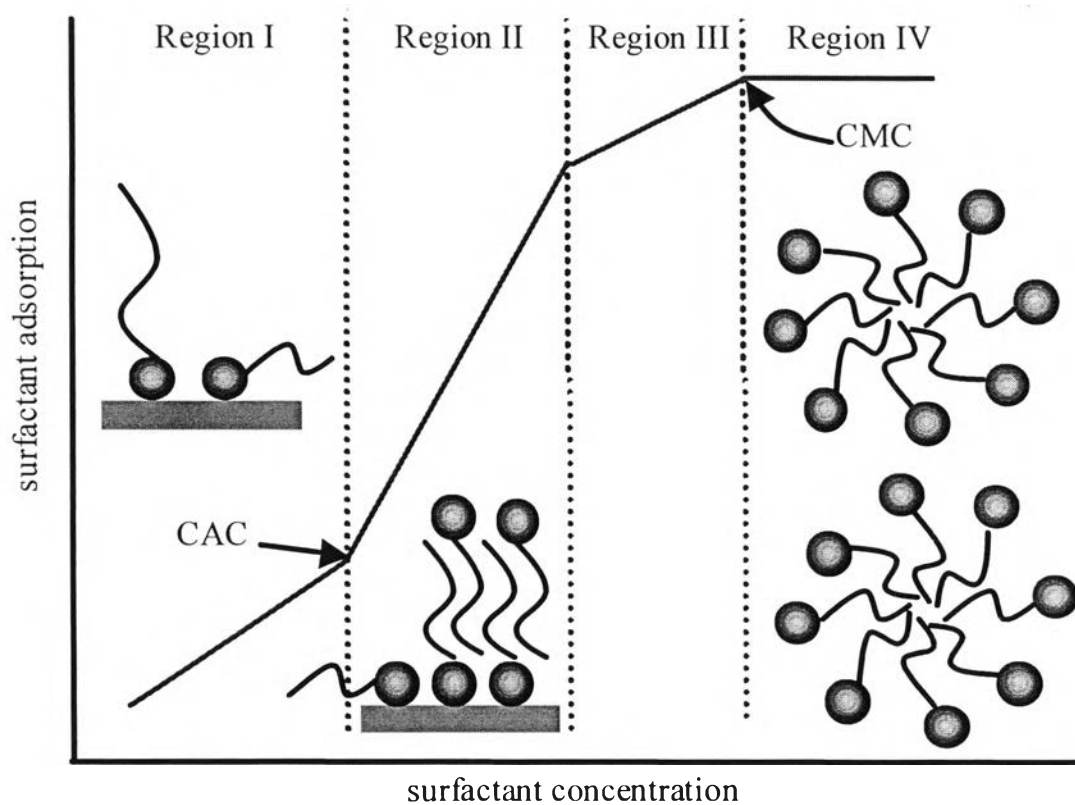

Figure 2.1 S-shaped adsorption isotherm for an anionic surfactant on a strong charge site substrate.

2.5 Roles of Calcium Ions in Flotation Deinking

The system, which had only paper and calcium, was studied by Rivello *et al.* (1997). 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.

In addition, the effect of calcium on flotation deinking was studied by Drabek *et al.* (1998). The deposition of fines and fillers on an air-water interface was studied by impinging jet technique. This system was comparable to the mechanism of fiber on air bubbles in flotation deinking. Calcium soap had an effect to adsorb on all fibers and linked all of them together. By the time, the deposition of fiber continued, fiber forms entangled web at the interface. The large ones were presumably captured by small fiber, since large ones were not adhered by themselves. Finally the large entangled webs were removed from air bubbles by hydrodynamic force. The strength of bridging between fiber and air bubbles depended on many factors, for instance; concentration of surfactant and calcium, size of fiber floc which was one of the important effect had influenced to stock loss effect.

2.6 Effect of pH in Flotation Deinking

A site-binding model (Hankins *et al.*, 1996) described the effect of pH on the adsorption of an anionic surfactant species at a mineral oxide/water interface. A model used to account for effects of pH, surfactant, and counterions is incorporated into patchwise making it was possible to predict both the surface charge and the counterion association beneath an adsorbed surfactant aggregate.

According to Azevedo *et al.* (1999), the results showed that caustic pulping caused the toner to be released from the fibers as larger particles and a poor flotation response was obtained. On the other hand, neutral pulping not only caused the toner to be released as smaller particles but also increase the simultaneous flotation removed of toner and mineral filler particles.

In the flotation experiment of Oliveira and Torem (1995), the results of microflotation tests indicated that in the presence of calcium cation, an increase in flotability at pH 8.0 was verified, probably due to calcium collector salt precipitation on the ink particle surface.

2.7 The Double Layer

The diffuse layer can be visualized as a charged atmosphere surrounding the colloid as in Figure 2.2. (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 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.
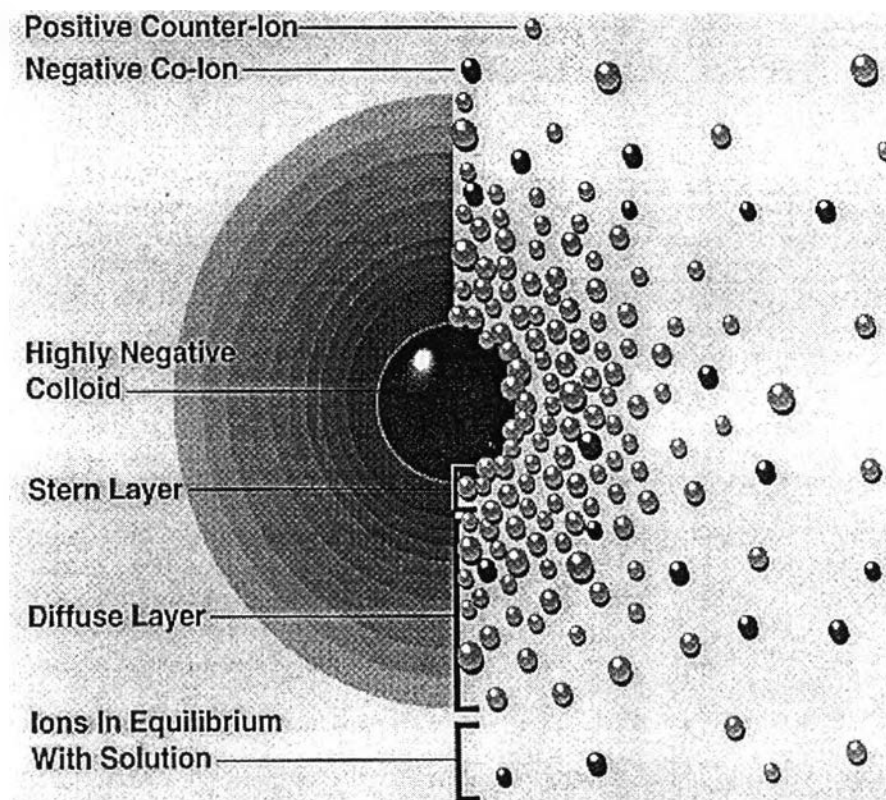

Figure 2.2 Visualization of the Double Layer.

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 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 2.3 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.
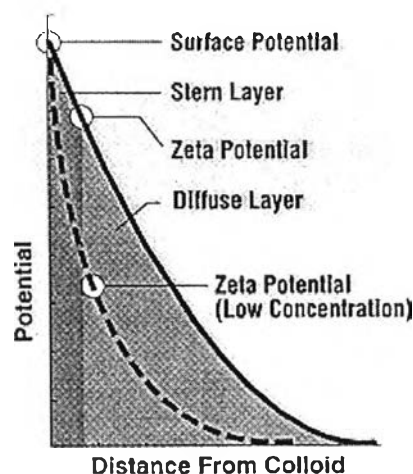
Figure 2.3 Relationship between zeta potential and surface potential.