

CHAPTER II

LITERATURE SURVEY

The aim of this chapter is to present background information on the adsorption of ionic surfactant at solid-liquid interface and some related works.

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. 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 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 in structure, and of 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.

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.

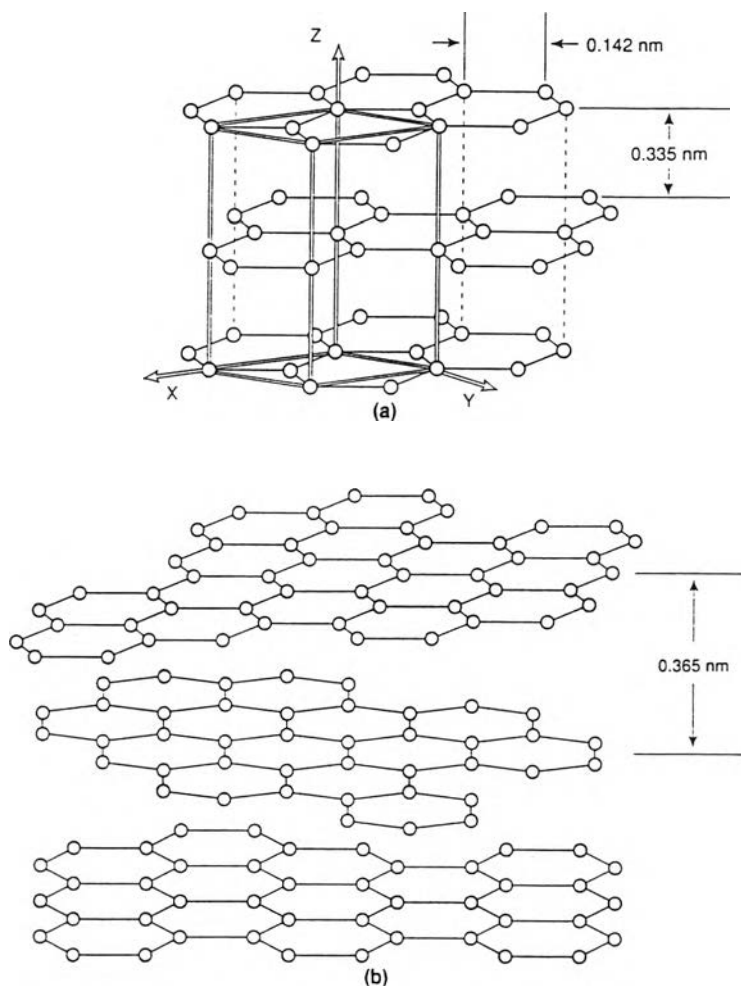


Figure 2.1 Atomic structural models of (a), graphite, and (b), carbon black (Baker *et al.*, 1992).

2.2 Nature of Surfactant

A surfactant or surface-active agent has a characteristic molecular structure consisting of hydrophilic (water-loving) which is usually polar group and hydrophobic (water-hating) which is usually hydrocarbon or non polar

group. One of important properties of surfactant is to adsorb onto the surface or interface of system resulting in decreasing the surface or interfacial tension of the medium in which it is dissolved.

Depending on the nature of hydrophilic group, surfactants are classified into four main groups;

1. Anionic. The surface-active portion of molecule bears a negative charge, for example, sodium dodecyl sulfate ($\text{CH}_3(\text{CH}_2)_{11}\text{SO}_4^- \text{Na}^+$).

2. Cationic. The surface-active portion of molecule bears a positive charge, for example, cetyltrimethyl ammonium bromide ($\text{CH}_3(\text{CH}_2)_{15}\text{N}^+(\text{CH}_3)_3\text{Br}^-$).

3. Nonionic. The surface-active portion bears no apparent ionic charge, for example, polyoxyethylene alcohol ($\text{C}_n\text{H}_{2n+1}(\text{OCH}_2\text{CH}_2)_m\text{OH}$).

4. Zwitterionic. Both positive and negative charge are present in the surface-active portion, for example lauramidopropylbetaine ($(\text{CH}_2)_3\text{N}^+(\text{CH}_3)_2\text{CH}_2\text{COO}^-$).

A single molecule of surfactant is called monomer, and at sufficient concentration in solution, monomers or surfactant molecules will nucleate to form aggregates called micelles. This process is called *micellization* that is demonstrated in Figure 2.2 and the lowest total surfactant concentration at which micelles are present is called critical micelle concentration (CMC).

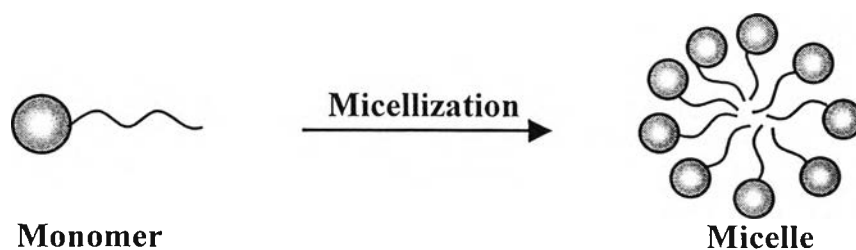
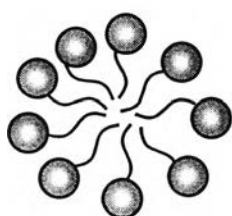
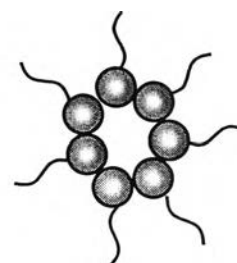


Figure 2.2 Micellization process (Rosen, 1989).

Normal micelles, which have hydrophobic part in the interior and hydrophilic part in the external solvent, are formed in aqueous solutions. Inverse micelles, which have hydrophilic part in the interior and hydrophobic part on the outside, are formed in the non polar solvents. Figure 2.3 illustrates the picture of normal and reverse micelles.



Normal micelle



Inverse micelle

Figure 2.3 Normal and inverse micelle (Rosen, 1989).

2.3 Interaction Involved Surfactant Adsorption

Broadly, the interactions may be classified as being either electrical or specific, often referred to as chemical. Use of the latter term does not necessarily mean that chemical bonds are formed. The surfaces of many solids carry a net charge under a range of solution conditions, and this charge can be expected to have a drastic effect on the adsorption of ionic surfactants.

2.3.1 Electrical Interactions

Because the surface is charged, electroneutrality must be preserved by an equal and opposite charge on the liquid side of the interface. A generally accepted view of the charge distribution on the fluid side of the interface is referred to the electrical double layer approach.

The double layer consists of compacted or adsorbed layer, called Stern layer and diffuse layer. The compact region can be divided into

inner Helmholtz plane, located at the surface of layer of Stern adsorbed ions and *outer Helmholtz plane*, located on the plane of centers of the next layer of ions, marking the beginning of the diffuse layer. The schematic representation of electrical double layer is shown in Figure 2.4, which illustrates the steeply sloped Stern layer and the gradually sloped diffuse layer.

There is a term often associated with electrical double layer is the *zeta potential or electrokinetic potential*. It is the potential of the charged surface at the plane of shear between particle and the surrounding solution as the particle and the solution move with respect to each other. Zeta potential is obtained from electrophoretic measurements.

2.3.2 Specific Interactions

There are a number of potentially important interactions other than electrical one. In adsorbed films at all but low coverages the hydrophobic tails of surfactant molecules are in close mutual proximity and may aggregate in some way at the surface under the influence of hydrophobic interactions. These attractive chain-chain interactions lead to enhanced adsorption, giving a negative contribution to the adsorption energy (Aveyard, 1987).

A similar kind of attractive hydrophobic interaction is possible between surfactant chains and hydrophobic surfaces in water. Whereas chain-chain interactions are largely absent at low surface coverage. The chain-solid interactions will be most in evidence at low coverage, and thus enhance the early stage of adsorption (Aveyard, 1987).

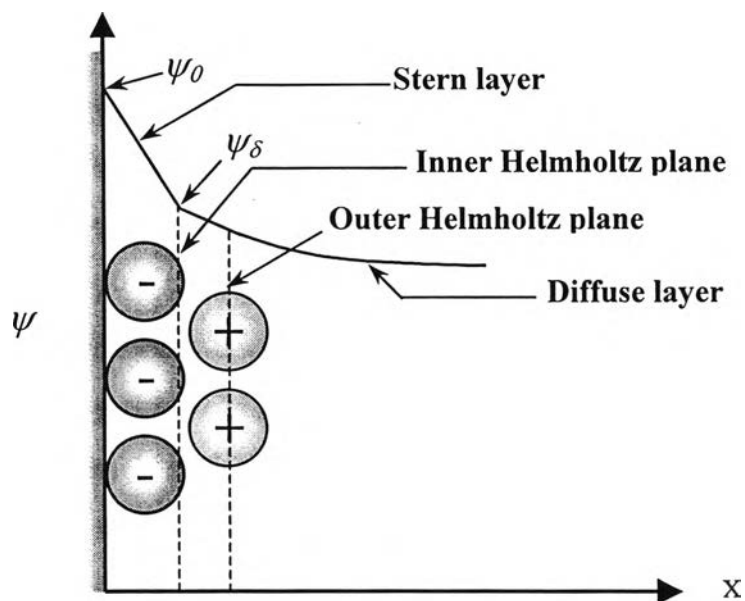


Figure 2.4 The Stern layer (Adamson, 1990).

2.4 Surfactant Adsorption Isotherm

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 2.5. 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.

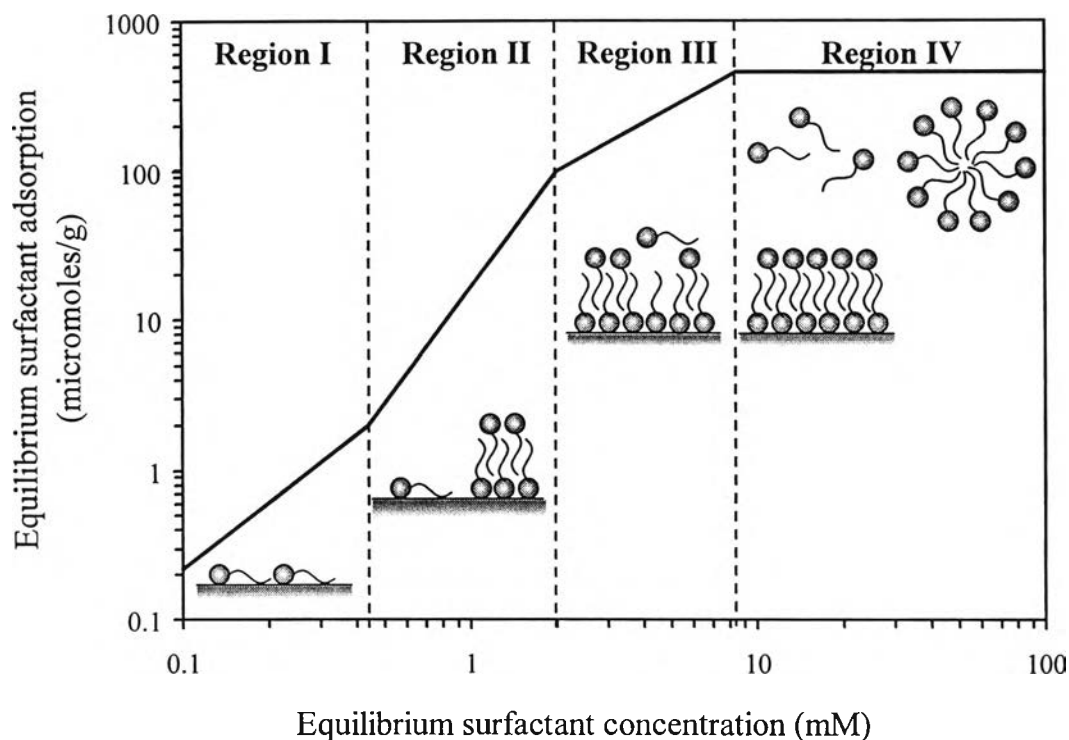


Figure 2.5 Typical surfactant adsorption isotherm.

2.5 Adsorption of Surfactant 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 reported studies 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 work will review research work on adsorption studies onto hydrophobic surface, especially carbonaceous materials.

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 Langmurian shape, and the plateau adsorption occurred at CMC. However, the results for Graphon, heat-treated Spheron 6, 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 interactions, 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 Graphon and 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.

Zettlemoyer (1968) also searched the adsorption of SDS on Graphon but further investigated the sodium adsorption isotherm, followed with radiotagged sodium. The curious phenomenon found from his experiments was that the amount of sodium ions (Na^+) taken up was less than dodecyl ions (DS^-) below the CMC and greater than DS^- above the CMC, where the adsorbed DS^- film took up Na^+ preferentially leaving micelles deficient. Furthermore, the addition of calcium (Ca^{++}) to the SDS/ Graphon system also showed some interesting results. The Ca^{++} enhanced the adsorption of SDS, since Ca^{++} reduced repulsion between the head groups.

For paper industry, the flotation technique has been used as a major technology for obtaining a recycled fiber with similar properties to the original fiber. Ink removal from wastepaper using flotation technique is based on the physicochemical differences between fiber and ink particles. The fundamental aspects of deinking flotation have been investigated by many researchers in order to understand the interaction of the collector chemistry and to solve problems in recycling waste paper.

Oliveira and Torem (1996) investigated the effect of some metallic cations on deinking flotation. Calcium, magnesium, and aluminium ions were used as counterions and sodium stearate used as collector to observe the floatability of inks. The results indicated that in the presence of calcium, an increase in floatability was verified probably due to calcium/collector salt precipitation on ink surface. In the presence of magnesium and aluminium species, an increase in floatability of ink was noted for pH ranges related to the concentration of hydroxy complexes of metals (Mg(OH)^+ , Al(OH)^+ , and Al(OH)^{2+}) and metallic hydroxides ($\text{Mg(OH)}_2(\text{s})$, and $\text{Al(OH)}_3(\text{s})$).

From such work, the mechanism on floatability of ink particles was supported by the precipitation mechanism, but there is no observation of behavior below the precipitation

Riviello (1997) studied the mechanism of the collector chemistry in flotation deinking focusing on the adsorption of surfactants; sodium octanoate (C_8), sodium dodecanoate (C_{12}) and SDS on carbon surfaces and calcium. The results from the experiments demonstrated that cooperative adsorption of surfactants and calcium occurred. All surfactants readily adsorbed on the carbon surfaces, presumably with a tail-down and/or lying-down orientation. Calcium also adsorbed onto the carbon and was responsible for diminished