

CHAPTER II

BACKGROUND AND LITERATURE REVIEW

2.1 Adsorption of Surfactants on Solid Surfaces

The adsorption of surfactants onto solid surfaces is the basis for many technological applications such as ore floatation, pharmaceuticals processes, and wetting. The usual role of surfactant is to modify surface properties for example in the *wetting* application, the main purposed is to make the aqueous solution to spread on the surface. Surfactant adsorption make the hydrophobic surface become more hydrophilic and consequently result in increases the ability of aqueous solution to spread on the surface (Figure 2.1).

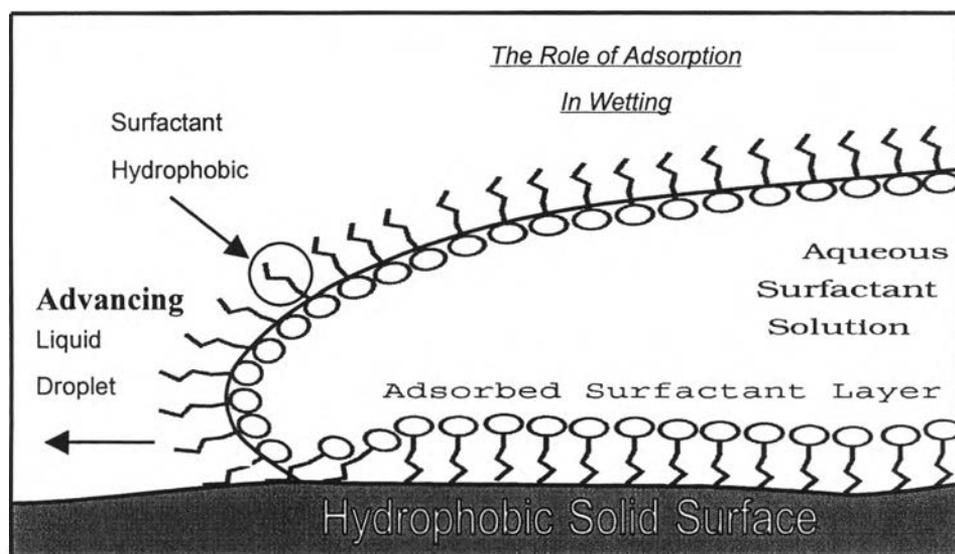


Figure 2.1 The role of adsorption in wetting.

The adsorption of surfactant onto solid-liquid interface is strongly influenced by a number of variables which come from both solid and liquid properties they can be classified as follow:

- (1) The properties of the solid surface such as the specific surface area, surface polarity, electrical charge, and chemical composition.
- (2) Variation in surfactant structure with respect to the type and size of the hydrophilic or hydrophobic group.
- (3) Environment of the aqueous phase such as pH, temperature, and additives for example electrolytes, short-chain alcohol.

These factors control the adsorption *mechanism* and also determine the *structure* of the adsorbed surfactant on the solid adsorbent.

2.1.1. Mechanisms of Surfactant Adsorption

Because of the variables mentioned above, there are several different adsorption mechanisms, which influence the enrichment of surfactants at the solid/liquid interface. The adsorption mechanisms of the surfactants can be classified as follow (Rosen, 1989).

1. *Ion exchange.*
2. *Ion pairing.*
3. *Acid-Base Interaction.*
4. *Adsorption by Polarization of π Electrons.*
5. *Adsorption by Dispersion Forces.*
6. *Hydrophobic Bonding.*

Ion Exchange

This mechanism involves the replacement of counter ions adsorbed onto the substrate from solution by similarly charged surfactant ions.

Ion Pairing

Adsorption of surfactant ions take place from solution onto oppositely charged sites unoccupied by counterions.

Acid-Base Interaction

This mechanism occurred via either hydrogen binding formation between substrate and adsorbate or Lewis acid-Lewis base reaction.

Adsorption by Polarization of π Electrons

Adsorption on solid surfaces is the result of attractive interaction forces between electron-rich aromatic nuclei of the adsorbate and positive sites located on the substrate.

Adsorption by Dispersion Forces

Adsorption by this mechanism occurs via London-Van der Waals dispersion forces acting between adsorbent and adsorbate molecules (Figure 2.2). Adsorption by this mechanism generally increases with increase in the molecular weight of the adsorbate.

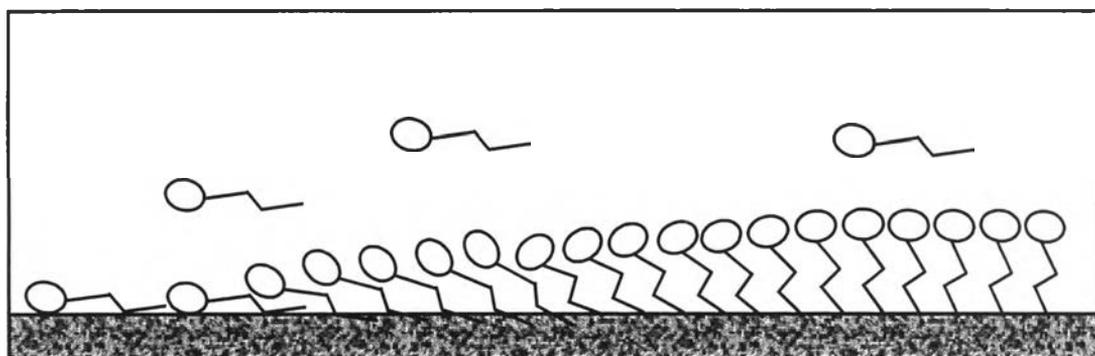


Figure 2.2 Surfactant adsorption via dispersion force on non polar surface.

Hydrophobic Bonding

This mechanism occurs when the combination of mutual attraction between hydrophobic groups of the surfactant molecules and their tendency to escape from an solution environment becomes large enough to permit them to adsorb onto the solid adsorbent by aggregating their chains (Rosen, 1989). These interactions may become stronger when more surfactant molecules are adsorbed (Zollars, 2001). Adsorption of the surfactant molecules from the liquid phase onto or adjacent to other surfactant molecules already adsorbed on the solid adsorbent also may occur by this mechanism .

2.1.2 Adsorption Isotherm

Adsorption on Noncharged Hydrophobic Substrates

The substrate in this class can be considered as low-energy surface where as a result from the method of production there are essentially no ionizable groups on the surface. Typical examples would be paraffin wax, polymers such as polypropylene, etc.

Typically, adsorption isotherms for ionic surfactants on these substrate are of the Langmuir type. They appear to show surface saturation near the critical micelle concentration of the adsorbate. Adsorption onto these substrates is mainly by dispersion forces.

In Figure 2.3. an isotherm is illustrated for the adsorption of hexadecyltrimethylammonium ions (cationic) onto the sample of polystyrene without any ionic surface groups (Connor, 1997).

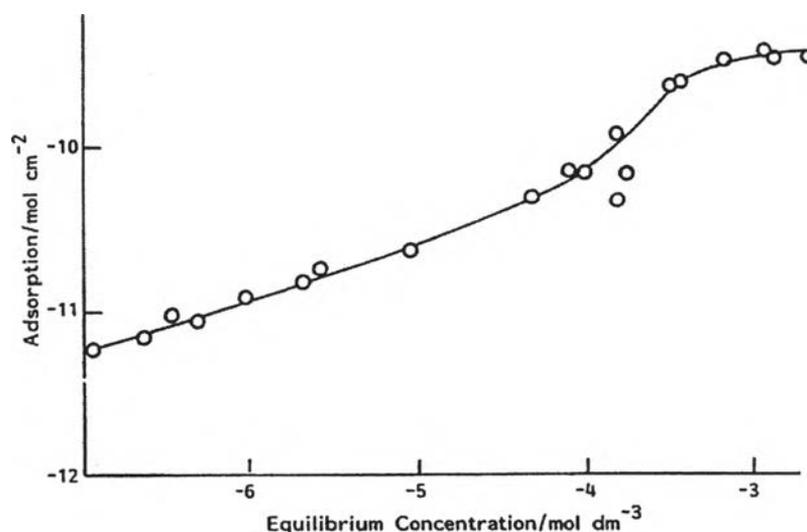


Figure 2.3 Adsorption isotherm for the hexadecyltrimethylammonium ions on polystyrene (uncharged) at pH 8.0 in 10^{-3} mol/dm³ potassium bromide solution (Connor, 1997).

When ionic surfactants adsorb onto uncharged, hydrophobic surface at the beginning the orientation of the adsorbate may be paralleled to the hydrophobic surface or slightly tilted, with hydrophobic group close to surface of the solid and hydrophilic part pointed toward the aqueous phase. Subsequently the adsorbed molecules may become oriented more and more perpendicular to the surface with hydrophilic portion pointed toward the aqueous phase (Zollars, 2001). The concentration of charged groups at the outer edge of the of the adsorbed layer becomes great enough to block any further adsorption due to electrostatic repulsion between the adsorbed surfactant and the surfactant molecules approaching the surface.

Adsorption on Charged Hydrophobic Substrates

A good example of this type of surface could be a polymer with relatively low surface charge densities

- Adsorption with attractive electrostatic interactions

Several adsorption studies have been conducted in which an ionic surfactant has been adsorbed onto a hydrophobic surface containing bound electric charges of the opposite sign. In this situation the first surfactant molecules adsorbed are assumed to adsorb by the attractive electrostatic forces present and therefore adsorb with their hydrophilic head groups extent toward the charged site on the surface. Because of the hydrophobic tails will pointed toward the aqueous solution, the surface becomes increasingly more and more hydrophobic. Finally a second layer of surfactant starts to adsorb, this time with the hydrophobic part interacting with the hydrophobic portion of the electrostatically bound surfactants and the head groups pointing toward the solution.

This type of behavior was observed by Gurses *et al.* (2003) for the adsorption of cetyltrimethylammonium bromide (CTAB), a cationic surfactant, onto powdered active carbon (PAC) by investigated adsorption isotherm and surface zeta potential measurement and also some thermodynamic quantities they suggested that the adsorption of CTAB mainly takes place through ion exchange, ion pairing between positive head group of CTAB and negative charged site of PAC for the lower CTAB concentrations while for the higher concentration hydrophobic bonding seem to be the main driving force.

The isotherm for this kind of adsorption can be compared with the isotherm obtained from the uncharged material. The first striking feature is a well-defined “knee” was observed in the isotherm. A comparison of the adsorption result with the electrophoretic mobility measurement show that the knee occurred at the pointed where the surface charge of the particle reversed (Zollars, 2001). Above the knee the adsorption isotherm closely resembled that observed for adsorption onto uncharged surface.

Connor and Ottewill (1997) studied the adsorption of hexadecyltrimethylammonium (HTAB), a cationic surfactant, on polystyrene particled with carboxylic acid groups on the surface at pH 8.0 in the presence of 10^{-3} mol/dm³ potassium bromide (Fig 2.4). The adsorption isotherm illustrated a well-defined knee at the low equilibrium concentration. Following the knee a slow increase in adsorption occurred. Subsequently a more rapid increase in adsorption occurred which reached a plateau value just below CMC.

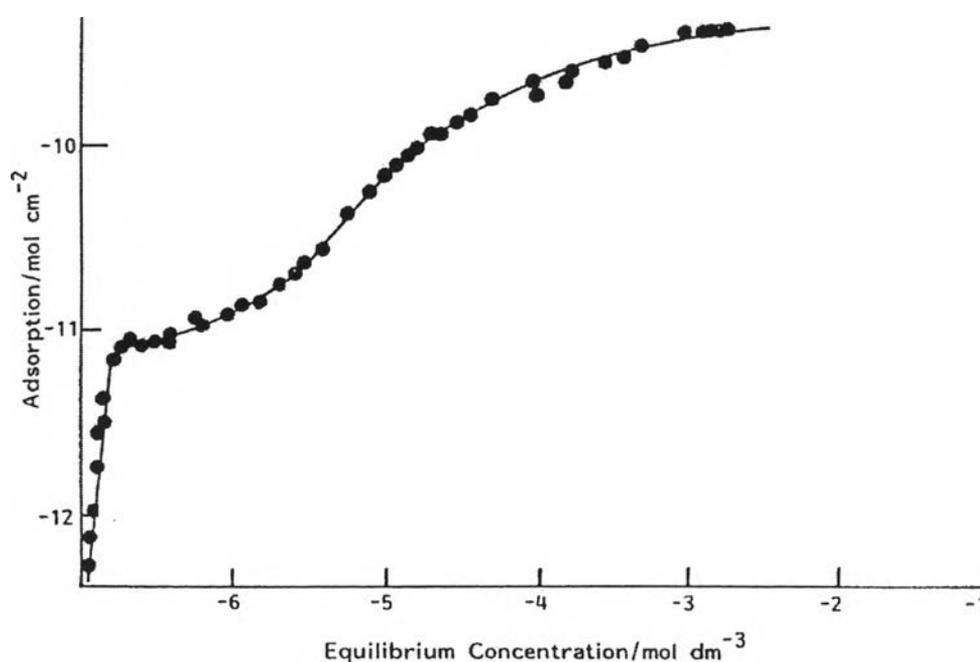


Figure 2.4 Adsorption isotherm for the hexadecyltrimethylammonium ions on polystyrene latex particles (carboxyl) at pH 8.0 in 10^{-3} mol/dm³ potassium bromide solution (Connor, 1997).

- Adsorption with repulsive electrostatic interactions

For the situation where both the ionic surfactant and the adsorbing substrate have the same charge, there will be a repulsive electrostatic force tending to prevent the surfactant from adsorbing onto surface. Any adsorption must then take place via hydrophobic interaction between the hydrophobic part of surfactant and the surface. Because adsorption must occur through the hydrophobic portion of the surfactant, the expected conformation of the adsorbed molecule would have the hydrophilic head group pointing toward the solution. This conformation would seem to preclude multilayer coverage instead to monolayer formation.

This type of behavior was observed by Day *et al.* (1984) for the adsorption of sodium-dodecyl sulfate (SDS), an anionic surfactant on the graphitised carbon black, Graphon. The adsorption isotherm shows two separate steps. The first plateau occurs at an area per molecule of 0.7 nm^2 , equivalent to a close-packed monolayer with molecules lying flat on the hydrophobic surface. The second plateau, near the CMC, corresponds to monolayer oriented perpendicular to the surface and occupying around 0.4 nm^2 per molecule, with the head group point to the aqueous phase.

2.1.3 Structure within the Adsorbed Layer

The surfactant layer properties have been characterized by using many surface-specific techniques, for example ellipsometry, neutron reflectivity, fluorescence spectroscopy, and atomic force microscopy (AFM). It has been found that surfactants frequently organize themselves to be a monolayers or hemi-micellar aggregates on hydrophobic surfaces (Figure 2.5). This resulting from large contact area between surfactant hydrophobic and the solid substrate is thermodynamically favorable (Grosse *et al.*, 2000).

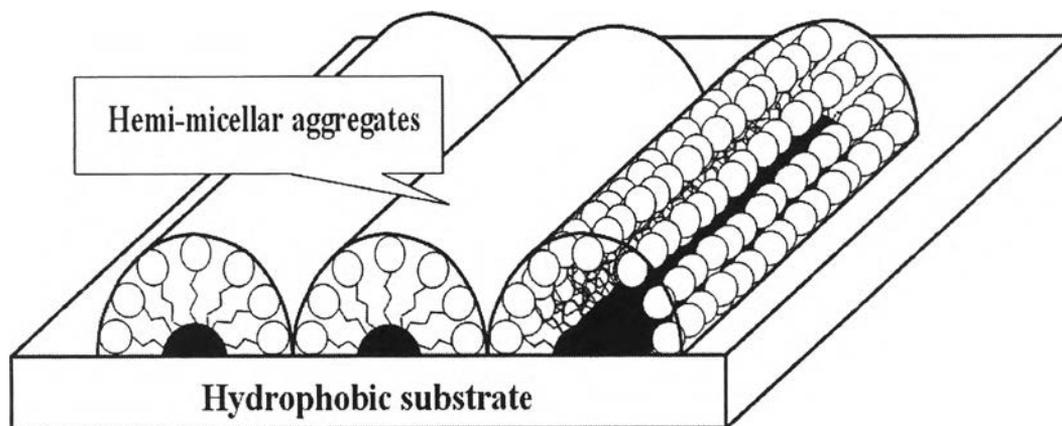


Figure 2.5 Hemi-micellar aggregates at hydrophobic surfaces.

For the non-ionic surfactants several studies show that they tend to form ordinary monolayers at hydrophobic non-crystalline surfaces similar to those observed at the air-water interface. With increasing solute concentration, the surfactants become more erect at the surface until the adsorption is stabilized around the CMC (Tilberg *et al.*, 2000).

Fragneto *et al.* (1996) reported the investigation of tetraethyene glycol monododecyl ether, a nonionic surfactant, onto carbon black. From the neutron reflection study it has been found that surfactant performs ordinary monolayer on the surface at the equilibrium concentration above CMC.

For the ionic surfactants, the AFM results have demonstrated that surfactants at low concentration (approx. 0.3 CMC) lie flat on the surface and organize into monolayer with molecules lying parallel to the surface. At higher concentration, the structure occurs in hemicylinder form.

Grant *et al.* studied the adsorption of cetyltrimethylammonium bromide (CTAB), a cationic surfactant, onto graphite. The AFM measurements have demonstrated that the surfactants at low equilibrium concentration lie flat on the surface and organize into monolayer with molecule lying parallel to the surface plane. At slightly higher concentrations, orientation occurs resulting in hemicylinders formation.

2.2 The Double Layer

The diffuse layer can be visualized as a charged atmosphere surrounding the colloid as in Figure 2.6 (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 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 ion. They have high concentration near the surface, which gradually decreases with distance, until it reaches equilibrium counter-ions 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 are 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 referred to as the double layer. The thickness of this layer depends upon the type and concentration of ions in the solution.

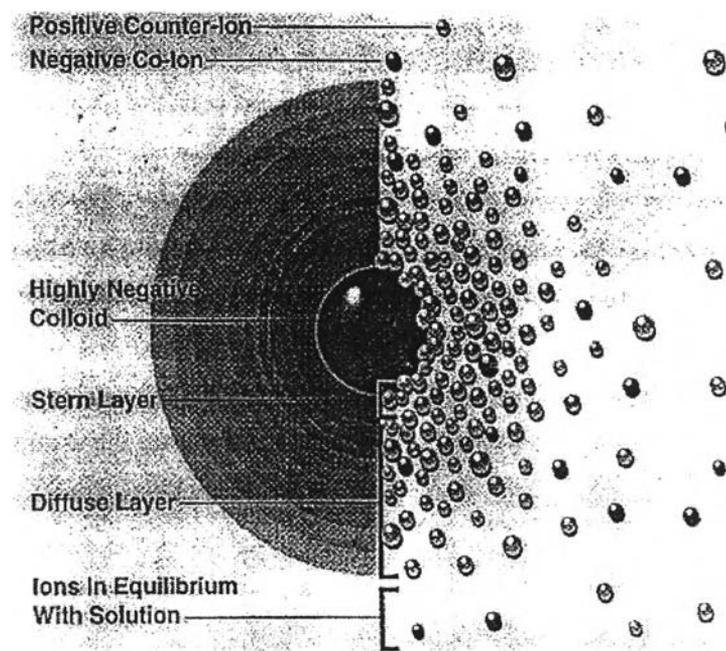


Figure 2.6 Visualization of the Double Layer.

2.3 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 2.7 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. 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 particles at which this force comes into play.

A charge 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 zeta potential.

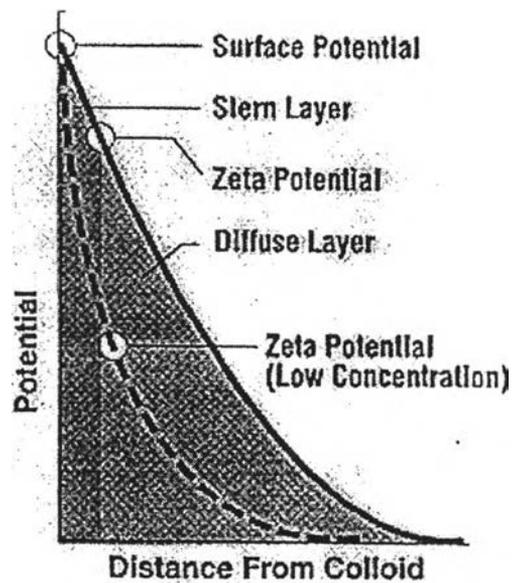


Figure 2.7 Relationship between zeta potential and surface potential.