

CHAPTER II

LITERATURE REVIEW

2.1 Surfactant

A surfactant or a surface-active agent is a chemical substance that is the most versatile product in the chemical industry. It is used in automobiles, detergents, pharmaceuticals, and also applied to many high technology areas. In a system with low surfactant concentration, the surfactant tends to adsorb at a surface or interface.

The molecular structure of a surfactant is called an amphipathic structure (Figure 2.1) because it consists of a lyophobic and a lyophilic group (a hydrophobic and a hydrophilic group, respectively in the case of aqueous solution). In general, the molecules at the surface or interface have higher potential energy than that in the interior because the interaction between the same substance is stronger than that between different substances. When the surfactant is dissolved in a solvent, the lyophobic group of the surfactant in the interior of the solvent causes an increase in free energy of the system. Therefore, displacement of the surfactant molecules to the surface or interface is easier than that of the solvent molecule. From these reasons, the amphipathic structure of the surfactant is the cause of (1) high concentration of surfactant at the surface, (2) reduction of the surface tension of water and (3) orientation of the surfactant molecules at the surface or interface. The chemical structure of surfactant molecule must have an amphipathic structure in the solvent under the condition used for good surface activity in a particular system. The lyophobic group of surfactant is usually a long-chain hydrocarbon while the lyophilic group is an ionic or highly polar group.

The surfactant can be divided into 4 types. It depends on the nature of the hydrophilic group.

1. Anionic surfactant: The hydrophilic group consists of negative charge, for example, $\text{RC}_6\text{H}_4\text{SO}_3^- \text{Na}^+$ (alkylbenzene sulfonate).
2. Cationic surfactant: The hydrophilic group consists of positive charge, for example, $\text{RNH}_3^+ \text{Cl}^-$ (salt of long chain alkyl amine).

3. Zwitterionic surfactant: The hydrophilic group may give both negative and positive charge, for example, $\text{RNH}_2^+\text{CH}_2\text{COO}^-$ (long-chain amino acid).

4. Nonionic surfactant: The hydrophilic group does not contain any ionic charge, for example, $\text{RCOOCH}_2\text{CHOHCH}_2\text{OH}$ (monoglyceride of long-chain fatty acid).

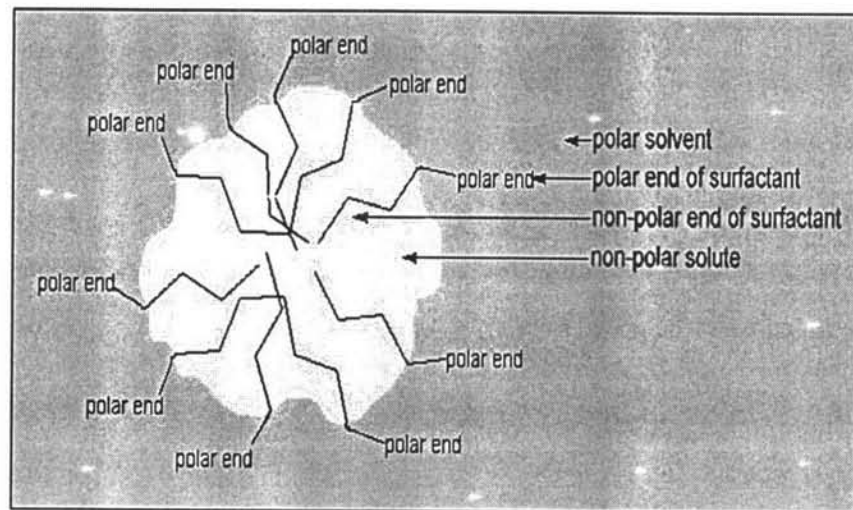


Figure 2.1 Molecular structure of a surfactant

2.2 Surfactant Adsorption

The adsorption of surfactant have influenced from this factors:

1. The nature of the structural groups on solid surface (e.g. polar group, or nonpolar group).
2. The molecular structure of the surfactant (e.g. anionic, cationic, or nonionic surfactant).
3. The environment of the aqueous phase (e.g. pH, electrolyte content and temperature).

The point of zero charge (PZC) or the net surface charge of zero is the most critical parameter to manipulate the surfactant adsorption (Figure 2.2). The point of zero charge is specific for a substrate. It is known from the intersection of the electrophoretic mobility curve and the zero axis. When the solution pH is equal to

PZC, the substrate surface has zero charge. At pH value below the PZC, the substrate surface exhibits a positive charge, while pH value above the PZC, the charge of the surface becomes negative. The PZC value can determine the type of surfactant adsorbed on the substrate surface. Anionic surfactants are adsorbed below PZC, while cationic surfactants are adsorbed above the PZC.

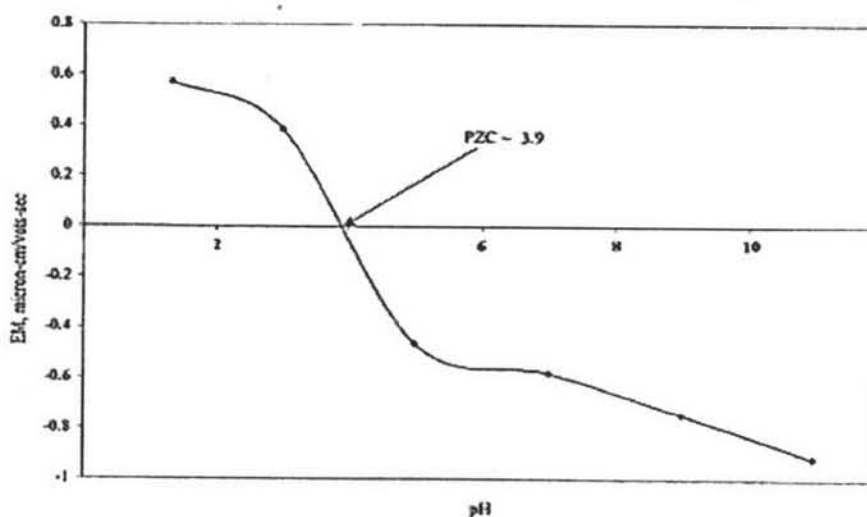


Figure 2.2 The point of zero charge on natural rubber surface (Bunsomsit. K. *et. al.*, 2002).

Furthermore, surfactant absorption is interesting to determine; (1) The amount of surfactant adsorbed per unit mass or unit area of the solid adsorbent, i.e. the surface concentration of the surfactant at the given temperature, since this is a measure of how much of the surface adsorbent has been covered and hence changed by the adsorption. (2) At the liquid-solid interface, the adsorption isotherm is used to help explain the mechanism of surfactant adsorption. The adsorption isotherm curve is plot between the log of adsorbed surfactant and the log of equilibrium concentration of surfactant in the bulk solution.

The shape of an adsorption isotherm curve can be classified into 2 type depend on the adsorbent

1. Adsorption isotherm of surfactant from aqueous solution onto strongly charged site adsorbents.

The adsorption isotherm curve is typically an S-shape curve and can be separated into four regions.

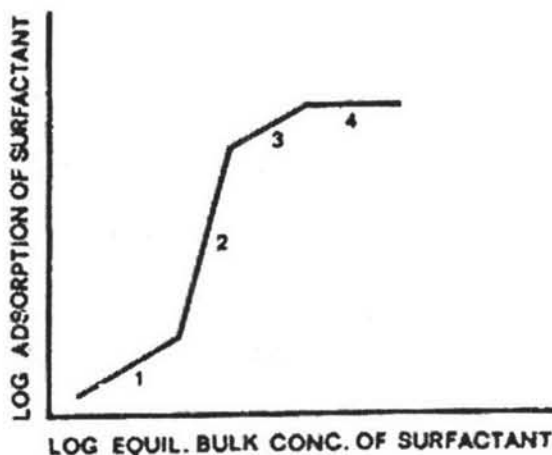


Figure 2.3 Adsorption isotherm of surfactant from aqueous solution onto strongly charged site adsorbents (Rosen. *et. al.*, 1989).

In region I, the surfactant adsorbs mainly by ion exchange. In region II, it is a marked increase in adsorption, resulting from interaction of the hydrophobic chain of oncoming surfactant ions with those of previously adsorbed surfactant and with themselves. In region III, the slope of isotherm is reduced because adsorption now must overcome electrostatic repulsion between the oncoming ions and the similarly charged solid surface. In region IV, Adsorption is usually complete when the surface is covered with a monolayer or bilayer of the surfactant and micelles are starting.

2. Adsorption isotherm of surfactant from aqueous solution onto nonpolar, hydrophobic adsorbents.

The adsorption isotherm curve is in the form of Langmuir type or L-shape curve as shown in Figure 2.4

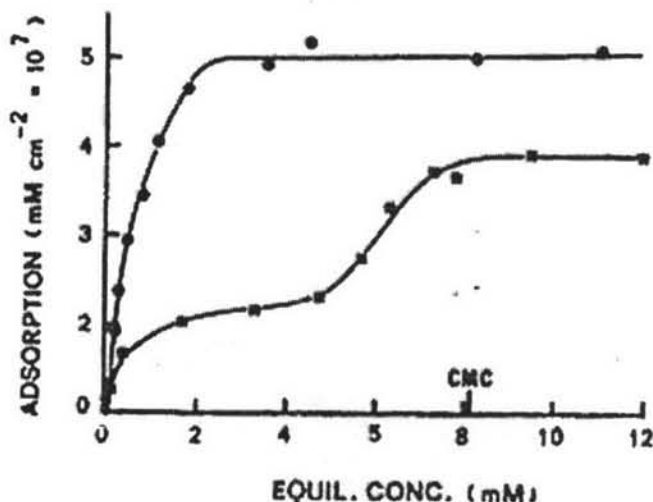


Figure 2.4 Adsorption isotherm of surfactant from aqueous solution onto nonpolar, hydrophobic adsorbents (L-shape, Rosen. *et. al.*, 1989).

The hydrophobic tail of surfactant is adsorbed on the solid surface, so the orientation of the molecule of surfactant is mostly parallel to the surface. When the molecules of surfactant continue to adsorb on the surface, the orientation is more and more perpendicular to the surface. The inflection point may be from the change of orientation from parallel to perpendicular. The concentration of surfactant on the adsorbent at surface saturation at a given temperature, since these determine the effectiveness with the surfactant is adsorbed. The orientation of the adsorbed surfactant and any other parameters that may shed light on the mechanism by which the surfactant is adsorbed, since a knowledge of the mechanism allows us to predict how a surfactant with a given molecular structure will adsorb at the interface and the effect of adsorption on other properties of the adsorbent.

2.3 Admicellar Polymerization Technique

An admicellar polymerization technique is based on the physically adsorbed surfactant onto the substrate, so called admicelle. The feasibility of the phenomena of admicelle formation, adsolubilization to form polymerized and organized ultra

thin film of molecular dimension of substrates has been investigated continually for several years.

Admicellar polymerization consist of four steps (showed in Figure 2.5)

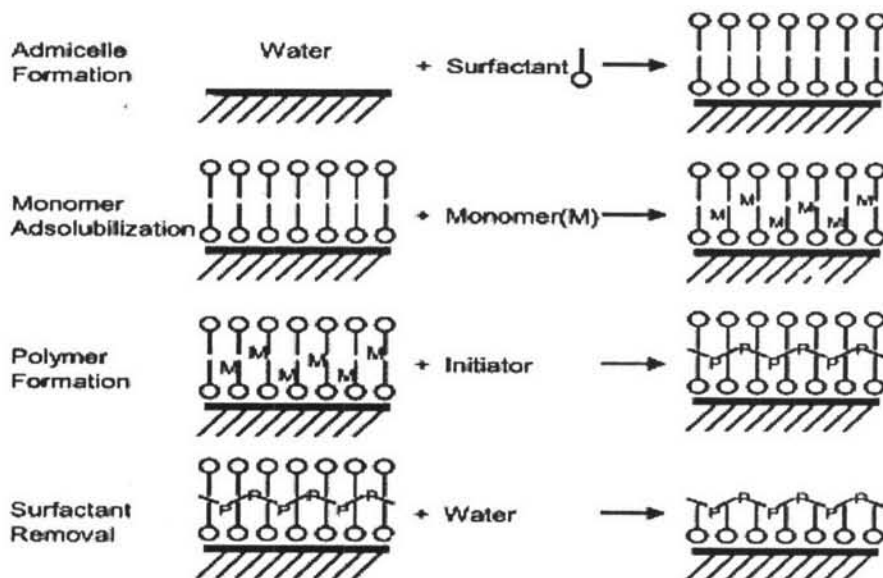


Figure 2.5 Admicellar polymerization process (Xin. *et al.*2003).

Step I. Admicell formation

The formation of an admicelle is occurred by the adsorption of a surfactant bilayer at the solid/aqueous solution interface. The surface aggregate formation at the surfactant concentration below the critical micelle concentration (CMC) is manipulated by the solution pH, counter-ion concentration and surfactant structure. The most parameter may be used to facilitate the admicelle formation is the solution pH at which the substrate surface exhibits a net surface charge of zero. (The point of zero charge or PZC) The PZC is benefit for the wide selection of surfactant type to adsorb on substrate.

Step II. Monomer adsolubilization

The partitioning of organic solutes from aqueous solution into interior of adsorbed surfactant aggregates is termed adsolubilization. The suggested definition of adsolubilization is "the incorporation of compound into surfactant surface

aggregates, which compound would not be in excess at the interface without surfactant.” This phenomenon is analogue of solubilization, with adsorbed surfactant bilayer playing the role of micelles as showed in Figure 2.6

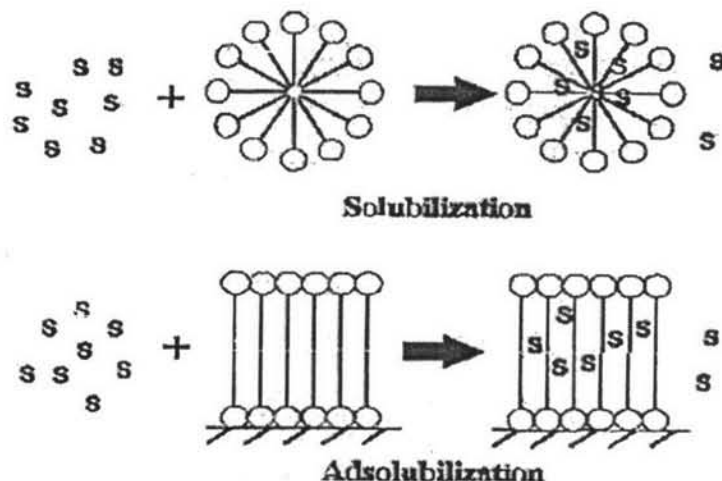


Figure 2.6 Phenomena of solubilization and adsolubilization (Arayawongkul. *et. al.*, 2002).

The adsolubilization is described as the solubilization of monomer into the admicelle. The adsorption of a surfactant bilayer at the solid/aqueous solution interface (step I) acts as a two-dimension solvent. Consequently, the hydrophobic monomer is adsolubilized or partitioned into the adsorbed surfactant aggregates.

Step III. Polymer formation

The monomer concentrated at the surfactant bilayers (step II) is reacted with a water-soluble initiator. The polymerization is occurred and the monomers are transferred to polymer.

Step IV. Solvent removal

From this previous step obtain the ultra thin polymer films, the excess surfactant is removed by washing with water.

Admicellar polymerization was developed about two decades ago. It has many researches involving this technique. Each of the researches studied in many different systems of monomer, surfactant and substrate.

In 1987, Wu *et al.* tried to use admicellar polymerization to form ultrathin polymer film on a solid surface. They used styrene monomer, sodium dodecyl sulfate (SDS) for surfactant and alumina for solid substrate. Their experiments illustrated that admicellar polymerization consists of three steps including admicelle formation, monomer adsorption and polymer formation. From the adsorption isotherm of SDS, the presence of styrene was found to increase SDS adsorption. Ultrathin film of polystyrene of several nanometers thick was formed on the alumina surface.

Polymerization of styrene adsorbed in a surfactant bilayer on alumina was investigated by Esumi *et al.* (1991). They used styrene monomer, sodium 10-undecenoate surfactant and alumina for solid substrate. They found that the adsorbed amount of styrene increases with the equilibrium concentration of styrene and reaches a plateau. The polymerization of such a system with UV irradiation in the presence of an initiator enhances the dispersion stability of the alumina compared with the polymerization of a bilayer of sodium 10-undecenoate alone on the alumina.

In 1995, Waddell *et al.* improved silica-reinforcing filler by admicellar polymerization. In composite material, silica is an important component used as a reinforcing filler, especially in rubber compounds. A problem with silica-reinforcing filler is the non-bond interaction between silica and polymer functionalities. Modified surface silica was developed to improve compatibility between hydrocarbon elastomers and precipitated silica. They used many types of polymers and copolymers for coating. After admicellar polymerization, modified silica can improve the mechanical properties of rubber compounds and improve cure time. The different chemical substances and reaction conditions give a result in different properties of modified silica.

Polypyrrole is a conductive polymer. It is used in electrical conductivity applications such as electrodes, sensors and others. Funkhouser *et al.* (1995) was successful in coating polypyrrole on the alumina surface using SDS surfactant. They studied the adsorption isotherm of SDS surfactant, the effects of electrolyte and pyrrole

concentration on adsorption isotherm. They found pyrrole cause a decrease in SDS adsorption while salt caused an increase in SDS adsorption.

In 1995, Sakhalkar *et al.* found coating glass fiber with polystyrene via admicellar polymerization technique. Glass fiber can form unhomogenous surface. The result showed that styrene in supernatant reduced with time after equilibrium of bilayer surfactant was formed on the substrate because styrene moved to the interior of micelle and polymerize. In addition, polymerization also occurred in aqueous phase but it was lower than that in micelle. The reasons of nonuniformity of glass fiber surface were unhomogeneous of fiber surface.

In 1996, O'Haver *et al.* studied the mechanical properties of modified silica surface. They were used polar comonomer and a cetyltrimethylammonium bromide (CTAB) that produced new classes of reinforcing fillers. It improved the physical properties of rubber compound.

In 1996, Kitiyanan *et al.* tried to study adsolubilization mechanism of styrene and isoprene in CTAB surfactant admicell on precipitated silica. The adsolubilization equilibrium constant is important because it indicated amount of styrene adsolubilized into the palisade layer, the core of the micelle and isoprene adsolubilized into the palisade layer. In comonomer systems, slope of adsolubilization isotherm dramatically increased. It can be concluded that comonomer adsolubilization is better than monomer system.

In 2002, Polypyrrole coated on natural rubber latex and used sodium dodecyl sulfate (SDS) surfactant was investigated by Bunsomsit *et al.* They studied admicellar polymerization process under each of step and found the influence of chemical substance to reaction. In this work, they found the PZC of natural rubber latex and absorption isotherm. They studied the effect of salt concentration to SDS adsorption isotherm and pyrrole adsolubilize. They found salt concentration cause an increase SDS adsorption and pyrrole adsolubilize. Moreover, they studied the effect of pyrrole concentration to SDS adsorption isotherm. They found, increase pyrrole concentration cause a decrease in SDS adsorption at equilibrium. From this studied conductivity of polypyrrole coat natural rubber without salt was the lowest, it can improve significantly with addition salt.

Thin film polystyrene coated on cotton fiber using linear alkylbenzene (LAS) surfactant was investigated by Pongprayoon *et al.* (2002). They studied the rate of LAS adsorption on cotton, effects of pH and electrolyte on adsorption of LAS on cotton. At high pH, LAS adsorption was low but at high concentration of salt, LAS adsorption was high. The cotton after coated with polystyrene shows increase in water resistance.

Arayawongkul *et al.* (2002) tried to characterize polystyrene produced by admicellar polymerization. They used cetyltrimethylammonium bromide (CTAB) surfactant and extracted polystyrene from the surface of modified silica with tetrahydrofuran (THF). This research focused on the effect of surfactant loading, monomer loading and reaction time on the characteristics of polymer. The result showed the reaction time for conducting admicellar polymerization should not be shorter than two hours to obtain relatively high molecular weight polystyrene. The extent of the polystyrene film and amount of polystyrene forming on silica particles increase with increase CTAB adsorption and adsolubilized styrene.

In 2003, Atomic force microscopy was used to investigate ultrathin polystyrene films formed by admicellar polymerization on silica disks by See (2003). Their goal was to examine changes in the properties and morphology of the formed polymer films due to changes in the surfactant and monomer feed levels. They found a smooth thin film that occurred at high concentrations of styrene but at lower styrene loadings, the polystyrene film became unstable and formed droplike aggregates. When samples were examined again after 1 year, the polystyrene films had agglomerated, forming larger aggregates arranged in straight-line or ringlike structures at higher feed concentrations.

Xin *et al.* (2003) used X-ray photoelectron spectroscopy to study hydrophilic surfaces of a rough solid and porous solid modified via admicellar polymerization. They studied the removal of polymer after admicellar polymerization with water and water followed by Soxhlet extraction with toluene. They found organic material can be removed only 30% after water wash and 50% if followed by Soxhlet extraction with toluene. Moreover, on the outside surface, the ratio of surfactant to polymer after admicellar polymerization and the solvent washes is approximately 1:1 whereas the ratio on the interior surface is approximately 3:1.

Preparation and characterization of natural rubber dispersed in nano-matrix was studied by Kawahara *et al.* (2003). They were investigated in terms of graft-copolymerization of deprotenized natural rubber latex with styrene, using tert-butyl hydroperoxide/tetraethylenepentamine as an initiator. They used H-NMR spectroscopy, size-exclusion-chromatography and transmission electron microscopy after staining the films with OsO₄ for characterization. They found natural rubber particle of about 0.5 μm in diameter was dispersed in polystyrene-matrix of about 15 nm in thickness and the stress at break was found to be the highest due to not only nano-matrix of polystyrene but also the highest grafting efficiency.

In 2004, Srinarang. *et al.* studied admicellar polymerization of polystyrene on natural rubber particle with using CTAB surfactant. This research found the point of zero charges (PZC) of natural rubber, the suitable pH, time for surfactant adsorption, CTAB concentration and styrene concentration. Moreover, the effect of salt on CTAB adsorption and monomer adsolubilization was studied. The FTIR showed the characteristic peaks of polystyrene and natural rubber. Thermogravimetry analysis (TGA) results showed that the degradation temperature of the products was altered a little depending of the amount of polystyrene.

Thin polystyrene film coated on cotton with and without a cross-linking agent was characterized by Pongprayoon. *et al.* (2004). They are used divinylbenzene (DVB) as a cross-linking agent to formed network polystyrene. It can be improved film coverage. The result showed, fiber improved in a wettability property. The optimum amount of cross-linking agent was around 1%. Above this, both the coverage and wettability began to decrease.