# CHAPTER II
# BACKGROUND AND LITERATURE SURVERY

## 2.1 Natural Rubber

Natural rubber (NR) is a renewable polymer material exhibiting excellent physical and chemical properties. NR is derived from latex and can extracted from *Hevea brasiliensis* tree as a colloidal polydispersion, which contains hundreds of proteins, including enzymes that are involved in the biosynthesis of the rubber molecules. NR is the strongest of all rubbers and excellent in dynamic properties, such as resistance to fatigue but it is less resistant to environmental damage (example, by ozone in the atmosphere and by oils) than some synthetic rubbers. Raw NR contains 93-95% *cis*-1,4-polyisoprene, 2-3% proteins, 2% acetone-soluble resins (including fatty acids), a small amount of sugars, a little mineral matter and water (Nontasorn, 2002). Hydrocarbon component of NR, which consists of over 99.99% of linear *cis*-1,4-polyisoprene is shown in Figure 2.1 (Lim-ochakun, 2000).
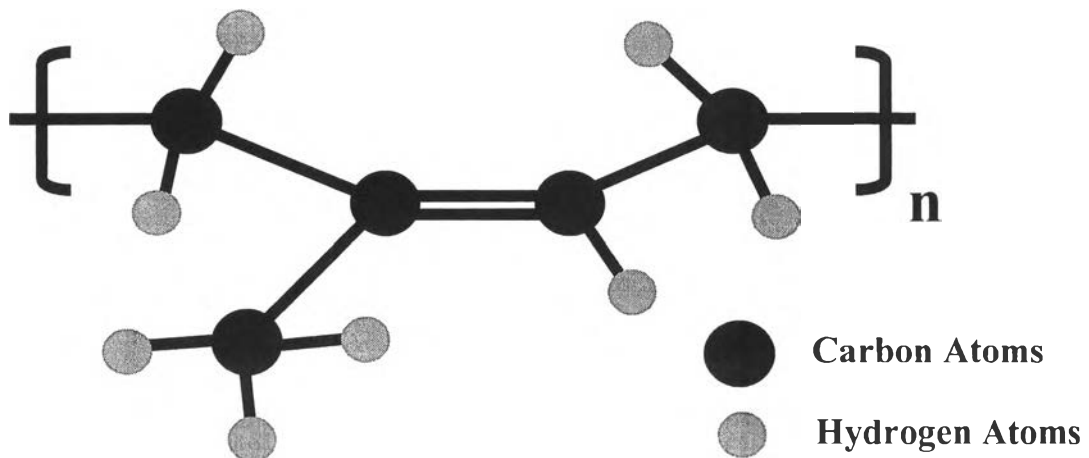


**Figure 2.1** Chemical structure of NR (cis-1,4-polyisoprene).

An average molecular weight of the polyisoprene in NR ranges from 200,000 to 400,000 with a relatively broad molecular weight distribution, the cause of its excellent processing behavior. There is one double bond for each isoprene part, along with the α-methylene groups in an NR molecular chain which is responsible for vulcanization with sulfur. The glass transition temperature (Tg), the temperature or range of temperature, which the polymer exhibits a marked change in several physical properties, of uncured NR is approximately $76.2 \pm 0.5^{O}C$. Therefore, rubber is soft and can be melted by heat. Conversely, it is rigid and brittle at low temperatures. Hence, NR can be utilized in a narrow temperature range (Lim-ochakun, 2000).

The thermal properties of NR can be enhanced by vulcanization with sulfur. Although the vulcanized rubber has many advantages such as low Tg and high impact strength, it also has many undesirable properties, such as hardness, abrasion, stiffness and tear resistances. Consequently, fillers are utilized to improve performance in these properties.

O'Haver *et al.* (1996) studied the modified silica surface by using copolymer prepared with a nonpolar and polar monomer to improve the performance of rubber compounds. The admicellar polymerization process was found to improve the rubber properties and the cured compound physical properties.

Kudisri (1997) studied the effects of the amounts of surfactant and monomer on the physical properties compared with the unmodified clay by using *in- situ* polymerization process. This process increases the compound cure rate, thereby decreasing $t_{90}$ cure time, while also improving tensile properties, tear strength, hardness except abrasion loss, flex cracking resistance fatigue to failure and compression set. The intermediate condition was found to give the highest tensile properties compared with other conditions.

## 2.2 Surfactant Structure

The word surfactant is derived from "SURFace ACTive AgeNT". Surfactants are one of the most unique and versatile materials due to their chemical structure. Generally, these are water-soluble surface-active agents comprised a

hydrophobic portion, usually a straight or branched hydrocarbon or fluorocarbon chain containing carbon atoms greater than eight, attached to hydrophilic or water solubility enhancing functional groups. For this reason, we often describe surfactants to be amphiphilic molecules - they love everything. Surfactants are said to have a "tail" and a "head" as shown in Figure 2.2. The tail is hydrophobic, which means water-hating, therefore oil-loving. It may be depicted either as a straight line or a wavy tail. The head is hydrophilic, which means water loving and generally depicted as a circle.
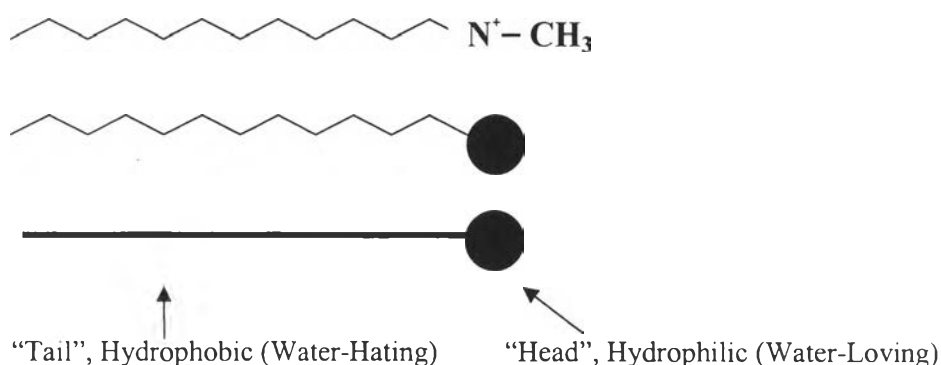


"Tail", Hydrophobic (Water-Hating)          "Head", Hydrophilic (Water-Loving)

**Figure 2.2** Surfactant structure.

Surfactants are classified according to the charge present in the hydrophilic portion of the molecule (after dissociation in aqueous solution). They can be categorized into 4 types (Porter, 1994).

1) Anionic surfactant : surfactant molecule, whose polar group is negatively charged. For example, alkylbenzene sulfonate, sodium dodecylsulfate.

2) Nonionic surfactant : no ion charge appears on the hydrophilic portion; for example, polyoxyethylenated alkylphenol.

3) Cationic surfactant : positive charge of the surfactant molecules is appeared on the hydrophilic portion. For example, quarternary ammonium chloride, laurylamine hydrochloride.

4) Ampholytic or zwitterionic surfactant : surfactant molecule, which have both positive and negative charged portions. The presence of both charged hydrophilic groups in the same molecule leads to adsorb into both negatively charged

and positively charged surface without changing the charge of the surface significantly (Rosen, 1989). The charge depends on solution pH. At low pH (acidic solutions), they form cations. But, at high pH (alkaline solutions), they form anions. For an intermediate pH range, zwitterions (having both positive and negative charges) are formed. For example, polyoxyethylenated alkylphenol, lauramidopropylbetaine.

## 2.3 Cationic Surfactants

Cationic surfactants are surface-active compounds with hydrophobic portion and a hydrophilic portion carrying a positive charge. They are positively charged in aqueous solutions. Using a cationic, it is possible to make a hydrophilic solid behave as if it were hydrophobic or make hydrophobic solid behave as if it were hydrophilic. Thus, the surface properties of solids can be modified by using cationic surfactants (Porter, 1994). Cationic surfactants are very soluble, stable in strongly acidic solutions and sensitive to pH changes - become unchanged and insoluble in water at pH above 7 (Rosen, 1989). In household products, the cationic surfactants are applied in fabric softeners, hair conditioners and other hair products. Cetyltrimethylammoniumbromide (CTAB) is a familiar cationic surfactant and its structure is shown in Figure 2.3.
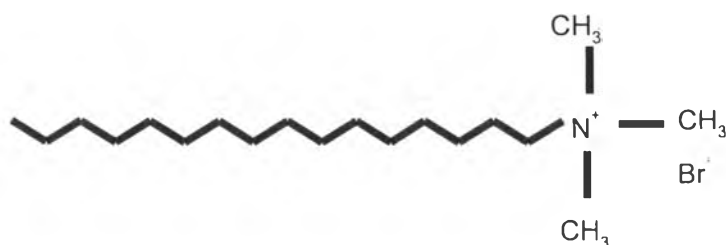


**Figure 2.3** Cetyltrimethylammoniumbromide (CTAB).

Actually, fatty amine salts (or ammonium salts) were developed as the first cationic surfactants as shown in Figure 2.4. With very few exceptions, commercially available cationics are based on the nitrogen atom carrying the positive charge (Porter, 1994).
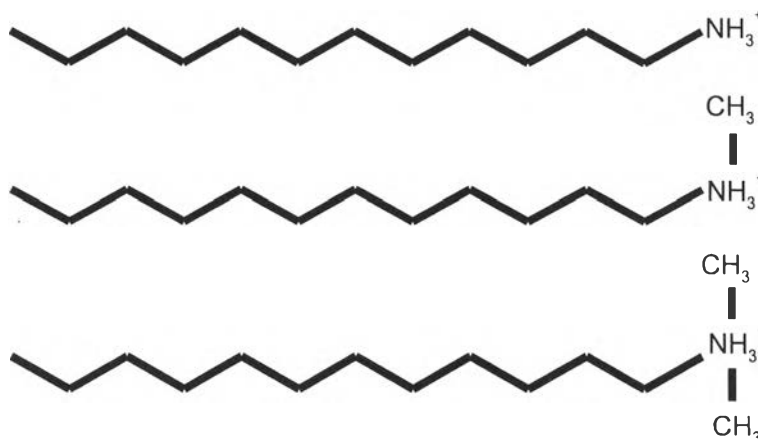


**Figure 2.4** Fatty amine salts.

Unfortunately, if we take these cationic surfactants up to high pH values (10 or 11), ammonium salts can also be sensitive to pH. Then, it is feasible to deprotonate the amine, thus leaving with an uncharged molecule. In the same way as fatty acid salts tended to precipitate out once they were protonated, these fatty amine salts will precipitate out once deprotonated. Therefore, the quaternary ammonium surfactants ($C_nH_{2n+1}(CH_3)_3NBr$) are developed (quaternary means that there are four substituents on the nitrogen atom). These surfactants are incredibly stable because they do not lose their charge in high pH conditions. As a result, quaternary ammonium salts are excellent surfactants that could be used over an extensive range of conditions.

Ismail *et al.* (1997) studied the effect of cationic surfactant (fatty diamine) as a multifunctional additive (MFA) on the mechanical properties of silica filled natural rubber compounds. MFA and silane coupling agent were used not only to enhance mechanical properties of natural rubber, dynamic properties by minimizing the energy loss but also to improve silica dispersion leading to a lower hysteresis.

## 2.4 Surfactant Adsorption

Adsorption of surfactant molecules is controlled by several parameters such as pH of the solution, type of surfactant molecule and electro-chemical nature type of substrate. It involves molecular attraction at the surface as shown in Figure 2.5. Adsorption of ionic surfactants on charged metal oxides is a topic of great industrial and academic interest, and this has led to a large number of studies with different models proposed (Hough and Rendall, 1983).
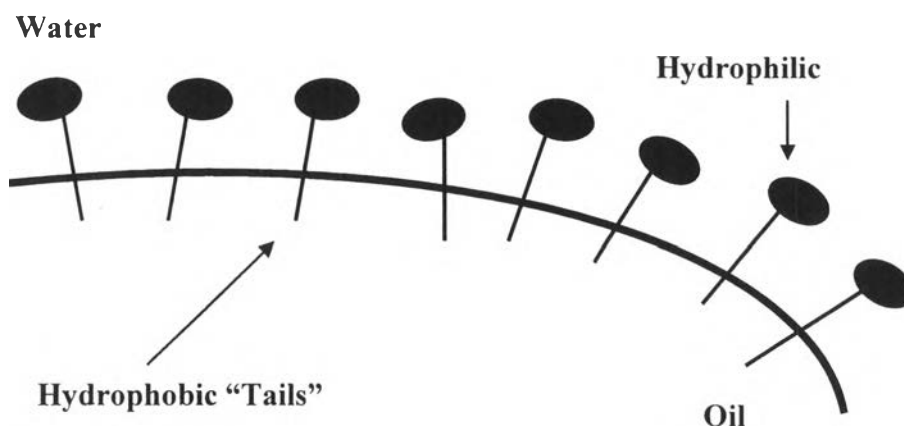
**Water**



**Figure 2.5** Surfactant molecules lean to adsorb to the surface of oil droplets. The hydrophilic heads expose to the water phase, while the hydrophobic tails stick into the oil phase.

Generally, data from adsorption experiments are presented in the form of an adsorption isotherm, which displays the surfactant adsorption (the amount of surfactant adsorbed per gram of adsorbent) as a function of equilibrium bulk concentration of surfactant in the liquid phase. The adsorption isotherm of an ionic surfactant onto an oppositely charged substrate is typically a "S-shaped curve" when one plots the log of the adsorbed surfactant density versus the log of the equilibrium concentration of surfactant. The "S-shaped" isotherm can be divided into four regions (Rosen, 1989), as shown in Figure 2.6.
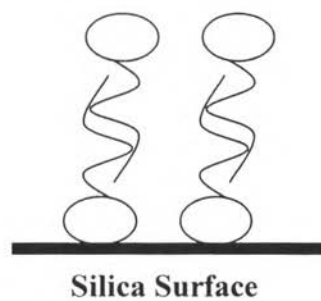
**1) Monolayer Formation**
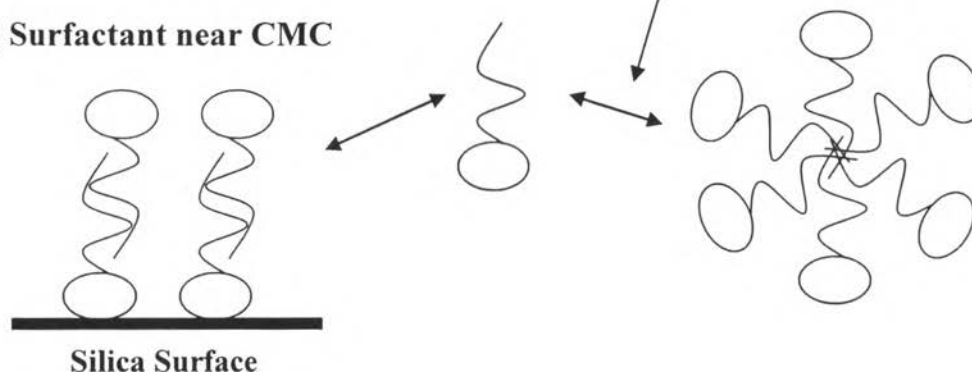
**Surfactant Adsorbed**
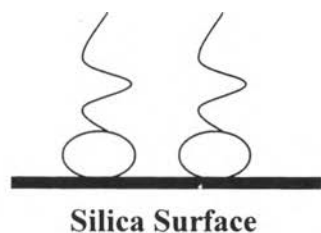
**2) Complete Monolayer Coverage**

**3) Bilayer Formation**

**Surfactant Concentration**
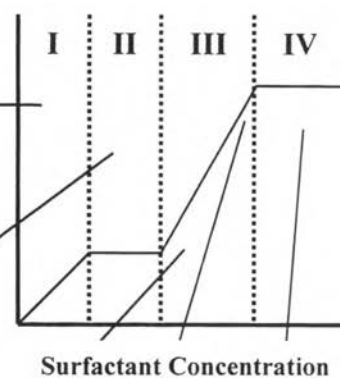
**4) Surfactant near CMC**

**Figure 2.6** Adsorption isotherm for an ionic surfactant on an oppositely charged substrate.

Region I o f t he a dsorption i sotherm c orresponding t o b oth v ery l ow b ulk concentration of surfactant and low adsorption of the surfactant is commonly referred as the Henry's law region. The adsorption driving force is largely due to electrostatic attraction between the surfactant head groups and the oppositely charged surface as well as a significant tail/surface interaction on hydrophobic surfaces. Because the interaction between molecules of the surfactants is negligible, the adsorbed surfactants in this region are viewed as being adsorbed alone and the aggregation of surfactant is not forming.

Region II, distinguishing by a sharply increased isotherm slope relative to the slope in the Henry's L aw region, indicates the beginning of lateral interaction between the surfactant molecules. In this region, adsorption greatly increases while the equilibrium concentration does not change greatly. It is broadly accepted that this increase is resulted from the hydrophobic interactions between tail groups of approaching surfactant ions and those of previously adsorbed surfactant, leading to the adsorbed surfactant to form a micelle like aggregate on the solid surface. The aggregation of adsorbed surfactants are called admicelles (Harwell *et al.,* 1985) or hemimicelles (Somasundarun and Fuerstenau, 1966), depending upon whether the aggregates are viewed as monolayers or bilayers. The admicelle is considered as a local bilayer structure with a lower layer of head groups adsorbed on the substrate surface and an upper layer of head groups exposed to the bulk solution. By growing in number and size, admicelles will eventually form a more or less complete bilayer (Fan *et al.,* 1997). The hemimicelle is a monolayer structure having the head groups adsorb on the surface whereas the tail groups exhibit to the solution. The transition point from the region I to region II, representing the first formation of adsorbed surfactant aggregates, is called the critical admicelle concentration (CAC) (Harwell *et al.,* 1985) or the hemimicelle concentration (HMC) (Somasundarun and Fuerstenau, 1966). In systems where hemimicelles form before admicelles, as surfactant concentration is increased, the concentration, at which the transition from one type of aggregate to the other takes place depending mainly on electrostatic effects (Yeskie and Harwell, 1988). Therefore, high surface charge densities, high counterion binding and higher dielectric constants all favor the formation of admicelles before the formation of hemimicelles. Conversely, low surface-charge

densities, low counterion binding and low dielectric constants all favour formation of hemimicelles at lower surfactant concentration than essential for admicelles to form.

In region III, the slope of the isotherm decreases rapidly because of competition between admicelle due to the repulsion between the like-charged head groups on the surface of the beginning of admicelle formation on the lower energy surface patches (Figure 2.7). While these patches become filled, lower energy patches become energetically more favorable for adsorption at slightly higher equilibrium surfactant concentration.
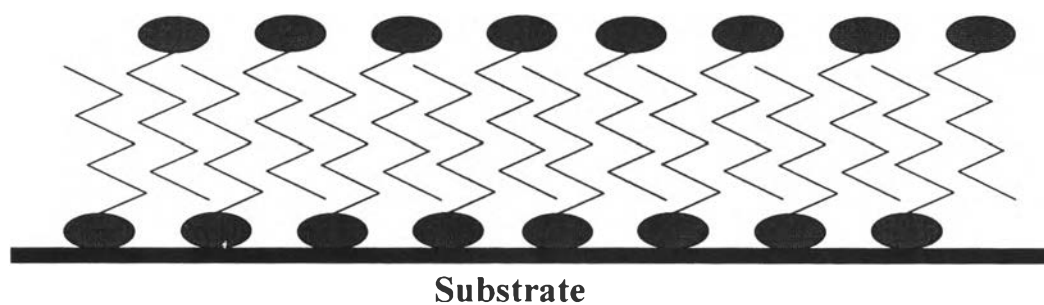


**Substrate**

**Figure 2.7** Surfactant bilayer.

Region IV is referred as the plateau adsorption region. The position of this plateau usually corresponds to a maximum adsorption of either one or two monomolecular layers on the solid surface, having almost constant surfactant adsorption with increasing surfactant concentration. Normally, the equilibrium surfactant concentration at the transition point from region III to IV is roughly at the critical micelle concentration (CMC), at which micelles first form (Rosen, 1989) as shown in Figure 2.8. The electrostatic repulsive force between the charged head groups at the surface of the aggregates is an important parameter, which will ultimately determine the aggregation number (Sharma *et al.*, 1996).

Nunn *et al.* (1982) demonstrated the surface solubilization of the dye pinacyanol hydrochloride by surfactant aggregates adsorbed at the alumina-aqueous solution interface. The dye, which is purple in aqueous media, becomes light blue as it partitions into the organic environment of the adsorbed surfactant aggregates, producing light blue particles.
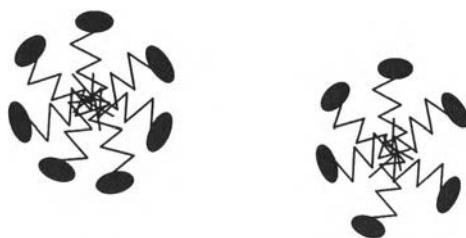
**Figure 2.8** Structure of micelles.

Lee *et al.* (1990) showed that the behavior of adsorbed surfactant aggregates, admicelles, was found to be very similar to that of micelles in the presence of alkanes. However, peculiar phenomena were observed in the incorporation of alcohols into micelles: (i) very high ratios of alcohol to surfactant adsorption at lower coverage, (ii) remarkable increases of surfactant adsorption below the CMC, and (iii) a slight decrease of plateau adsorption. The hypothesis is that while the alkanes are adsolubilized only in the hydrocarbon core of the admicelle, there are two sites at which alcohols are adsolubilized, at the core and at the hydrophobic perimeter of the admicelle.

The four-region model based on electrostatic and hydrophobic interactions adequatedly explains adsorption of anionic surfactants on positively charged solids such as alumina. Fan *et al.* (1997) studied the cationic surfactants adsorption on negatively charged alumina at pH 10 and at a constant ionic strength of 0.03 M NaCl. In this case, only three distinct regions were observed in the adsorption isotherms and there seemed to be lack of adsorption region III. Although the adsorption region III may still exist, the difficulty in detecting it from the adsorption isotherm is probably the result of similar slopes for regions II and III. And this may be attributed to the loose and interpenetrating colloid structure in the case of the cationic amine/negatively charged alumina system.
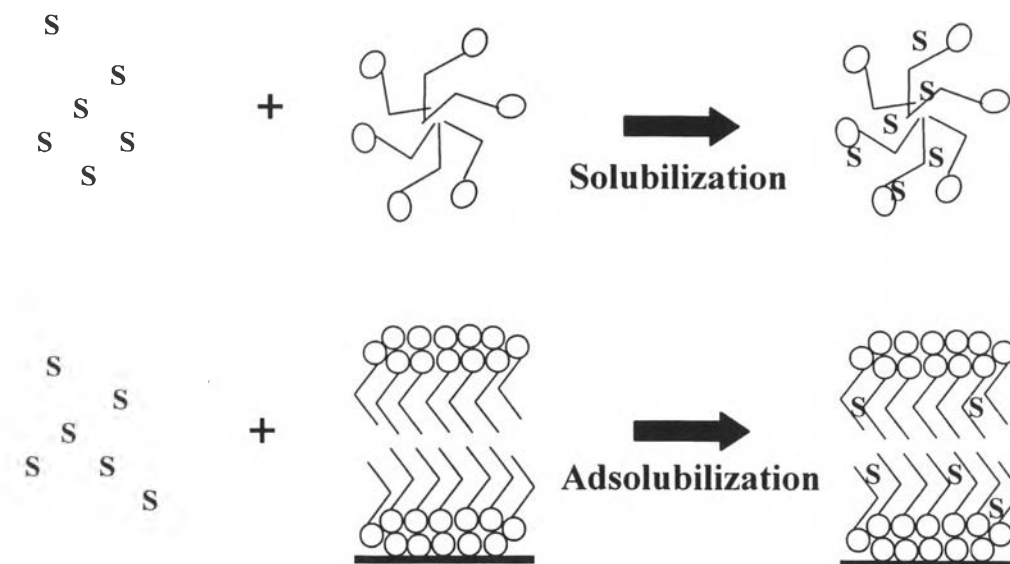
## 2.5 Solubilization

Solubilization is an important property of surfactants that is directly related to the presence of micelle formation (Figure 2.8). The solution of surfactant above

the CMC can dissolve considerably larger quantities of organic materials than pure water or surfactant solutions with concentrations below the CMC. The additional capacity is obtained by solubilizing the solute in the micelles. Solubilization can be defined as "the spontaneous dissolving of substance (solid, liquid or gas) by reversible thermodynamically stable isotropic solution with reduced thermodynamic activity of the solubilized material" (Rosen, 1989). Consequently, a water-insoluble material in a dilute surfactant solution could appreciably increase its solubility when the surfactant concentration surpasses the CMC. Solubility increases approximately linearly with the concentration of surfactant above the CMC. There are a number of different sites in a micelle: (1) on the surface of the micelle; (2) between the hydrophilic head group; (3) in the palisade layer of the micelle located between the hydrophilic groups and the first few carbon atoms of the hydrophobic groups and (4) in the inner core of the micelle. Depending on the nature of the material solubilized (the solubilizate), the exact location in the micelle at which solubilization occurs can vary.

## 2.6 Adsolubilization

Similar to the solubilization of organics into micelles, organic molecules will be integrated into surfactant aggregates at the solid-liquid interface. This phenomenon is termed *adsolubilization*. Normally, adsolubilization is defined as *"the excess concentration of a species at an interface in the presence of an admicelle that would not exist in the absence of the admicelle"* (Wu et al., 1987) as shown in Figure 2.9. This definition conveys the idea that the particular solute of interest does not adsorb onto the adsorbent surface by itself, or adsorbs to a much lower degree. The removal of the solute from bulk solution occurs because of the presence of adsorbed surfactant aggregates and the incorporation of the solute into the aggregates.

"S"s represent solute molecules, monomers.

**Figure 2.9** Phenomena of solubilization and adsolubilization.

For adsolubilization, the particular solute of interest does not adsorb onto the adsorbent surface by itself or adsorbs to a much lower degree. The removal of the solute from bulk solution occurs because of the presence of adsorbed surfactant aggregates and the incorporation of the solute into the aggregates.

Kitiyanan *et al.* (1996) studied the adsolubilization of styrene, isoprene, and mixtures of styrene and isoprene into CTAB bilayers (admicelles) on precipitated silicas. The styrene adsolubilization constant is nearly unchanged with increasing styrene equilibrium concentration in the aqueous phase while the isoprene adsolubilization constant increases with increasing isoprene partial pressure. The adsolubilization constants recommend that styrene adsolubilizes into the palisade layer.

## 2.7 Ultra-Thin Film Formation

Formation of ultra-thin films on solid surfaces has been the object of powerful study in recent years because of a wide variety of possible applications of these films. The method used for the modification of inorganic powders by the

formation of ultra-thin polymer films in adsorbed surfactant bilayers, called admicelles (Wu *et al.*, 1987). Admicellar polymerization can be considered to occur in four basic steps as shown in Figure 2.10. Step 1 is admicelle formation by the aggregation of surfactants at solid/liquid interfaces to form bilayers (admicelles) through adsorption from an aqueous solution. To gain admicelle formation, the most critical parameter to be manipulated is the solution pH, relative to which the surface exhibits a net surface charge of zero (referred to as the point of zero charge or PZC). The surface becomes protonated and more positively charged at pH values below the PZC and surface is negatively charged above the PZC. As a result, anionic surfactants adsorb well below the PZC whereas cationic surfactants above the PZC. In this study, silicas, having $2 \leq PZC \leq 3$, are negatively charged when the pH of the aqueous solution exceeds 3. Consequently, a cationic surfactant (cyltrimethylammonium bromide, CTAB) was chosen to form the bilayer when the pH of the surfactant solution is greater than 3 (Kitiyanan *et al.*, 1996).

Step 2, hydrophobic species are concentrated at the interface in a phenomenon called adsolubilization under conditions favorable for the formation of admicelles on a solid surface and unfavorable for the presence of micelles in an aqueous supernatant (Sakhalkar and Hirt, 1995). The hydrophobic monomers (e.g., styrene and isoprene in this study) adsolubilize or partition into the adsorbed surfactant aggregates of step 1. This step can occur after the formation of admicelle or concurrently with surfactant adsorption.

Step 3 is the *in-situ* polymerization of adsolubilized monomer. Further than the purpose of concentrating monomer at the surface of the substrate, the admicelles function as reaction loci or a two-dimensional reaction solvent for polymerization. Initiators begin the formation of polymer, possibly by mechanisms similar to those occurring in conventional emulsion techniques (Sakhalkar and Hirt, 1995).

Step 4 is the removal of excess surfactant by washing in order to expose the polymer-modified surface. To increase the rate of surfactant removal, Waddell *et al.* (1995) suggested that the continuous, counter-current washing would be preferred. In this study, polymer formed was recovered by tetrahydrofuran extraction of the isolated silica after the reaction step, with intermediate washings, if necessary, by
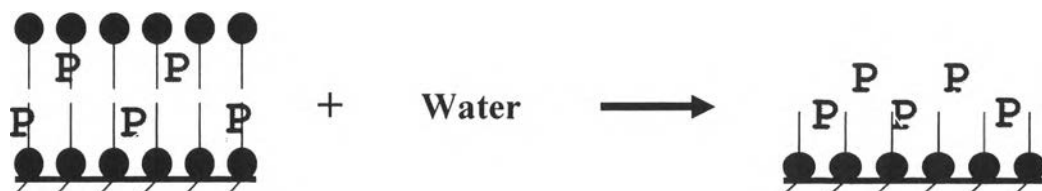
## Step 1  Admicelle Formation
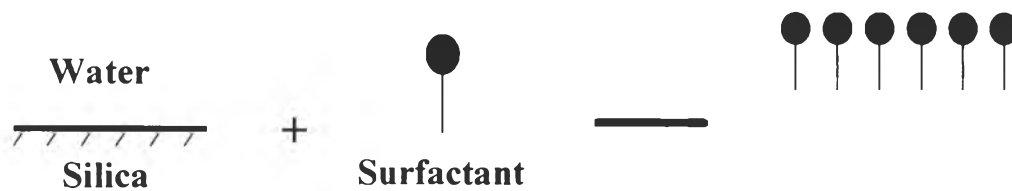


## Step 2  Monomer Adsolubilization
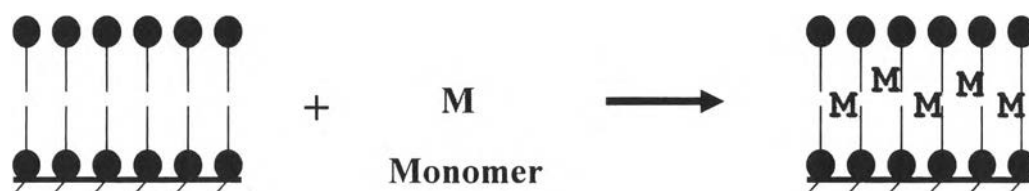


## Step 3  Polymerization



## Step 4  Surfactant Removal



"M"s represent solute molecules, monomers.

"P"s represent polymer chains formed during the reaction.

**Figure 2.10**  Admicellar polymerization process for the formation of a thin polymer film.

deionized water, followed by drying in a vacuum at a temperature below the boiling point of polymer. Figure 2.10 illustrates 4 steps of admicellar polymerization process to form a thin polymer film on the hydrophilic surface.

Wu *et al.* (1987) studied the rate of polymerization of styrene monomers in an adsorbed two-dimensional surfactant bilyer solvent (admicelle) that used a water/ethanol-sodium dodecyl sulfate-styrene-alumina system was found to be proportional to the first order of monomer concentration and half-order of initiator concentration and the average number of radicals per alumina particle is less than unity. The results from polymerization of styrene in sodium dodecyl sulfate bilayers adsorbed on alumina showed 75% and higher conversions of adsolubilized monomer to polymer after 25 min. Uniform films of 3.4-3.6 nm thickness were formed on aluminum oxide layers on glass slides for reaction times of 30-45 min. Under varying conditions, film thicknesses of 13.0 nm were also obtainable (O'Rear *et al.* 1987).

Thammathadanukul *et al.* (1996) studied the comparison of rubber reinforcement using various surface-modified precipitated silicas. The results showed that all copolymer-treated silicas offered greater improvements in the rubber performance than the silicas modified by the silane coupling process. Moreover, the improvement of filler-elastomer interaction by the *in situ* polymerization process was found to depend on both the amount and type of polymer developed on the silica surface.

Chinpan (1996) studied the admicellar polymerization-modified silicas with butadiene and isoprene as co-monomers with styrene. The polymer was capable of forming bonds with the rubber compound during the curing process. Significant improvements in the compound properties were achieved, and it was also found that those lower loading of monomer and surfactant achieved the greatest improvement in the largest number of rubber properties.

Chaisirimahamorakot (2001) studied the effect of retention time and monomer loading on the properties of silicas modified by the *in situ* polymerization using a continuous system. It was concluded that the continuous stirred tank reactor was used successfully. The results showed that the optimum conditions for the modification were 5 g of monomers per kg of the silica at 60 min residence time.

Nontasorn (2002) studied the effects of co-monomer loading and retention time on the modified silicas by *in situ* polymerization of organic monomers in the surfactant layer adsorbed onto the surface of precipitated silicas in order to enhance silica/elastomer interactions leading to improving performance of rubber products. The properties of rubber results from the modified silica surface using continuous system showed that 5 g of monomers per kg of the silica at 30 min retention time offered the superior characteristics in rubber compounding. Moreover, it provided the highest overall improvement for the surface characterization.

**2.8 Silica**

Silica, which is also known as silicon dioxide, $SiO_2$, is colorless to white in its pure form, and accounts for ~25% of the earth's crust. Silica occurs in several forms, slightly soluble in alkalies and soluble in dilute hydrofluoric acid. It exists in two varieties, amorphous and crystalline. For crystalline forms, the structures are characterized by tetrahedral configuration of atoms within the crystals. Whereas in the amorphous forms, the $SiO_4$ (silicate) subunits show no regular lattice pattern in the structures. Chemical element of silica that constituent surface is silanol structure (-Si-OH) as shown in Figure 2.11. Silica has a highly active polar surface because of the silanol structure. It is insoluble in water at 150°C, but its solubility improves to 0.25 weight percent at 500°C (Iler, 1979).
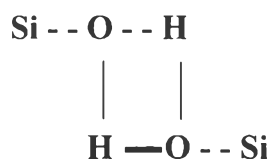
$$Si - - O - - H$$
$$|\qquad|$$
$$H —O - - Si$$

**Figure 2.11** Silanol reaction by hydrogen bonding.

Silica is a non-black reinforcing agent designed for colored compounding and has low thermal coefficient of expansion (melts at a high temperature, 1731°C). It withstands sudden changes in temperature and can be used in parts that are

subjected to wide ranges of heat and cold. Silica is very hard and chemically stable; therefore, it is widely served as filler for rubber. Its presence offers an increase in wire adhesion, abrasion resistance and tear resistance.

Silica surface shape is basically unknown. The only method which allows direct measurement of the surface shape is *Atom Force Microscopy* (AFM). It is based on the scanning of the surface with a special probe and employed only for the outer surface measurement.

Geometry of the inner surface of the adsorbent particles is assumed to be smooth, especially after hydrothermal treatment of silica xerogel. The presence or absence of the small pores, which may produce a steric hindrance to the analyte molecules to penetrate inside. This may be determined from the pore size distribution curve calculated from the gas adsorption isotherm.

O'Haver *et al.* (1993) studied the ultra-thin polystyrene film on silica. Polystyrene was successfully polymerized into cetyltrimethyl ammonium bromide (CTAB) as a cationic surfactant and using 2,2'-azobis-2-methylpropionitrile (AIBN) as a water-insoluble initiator. Extraction and characterization of polymer formed were measured by using techniques including PA-FTIR and GPC. The molecular weight of polymer formed was investigated with respect to polymerization time. Polymeric film on porous silica may slightly increase particle size and decrease surface area of silica. The presence of polystyrene on the silica was shown by PA-FTIR spectra and the distribution of molecular weight of extracted polymer was studied by GPC.