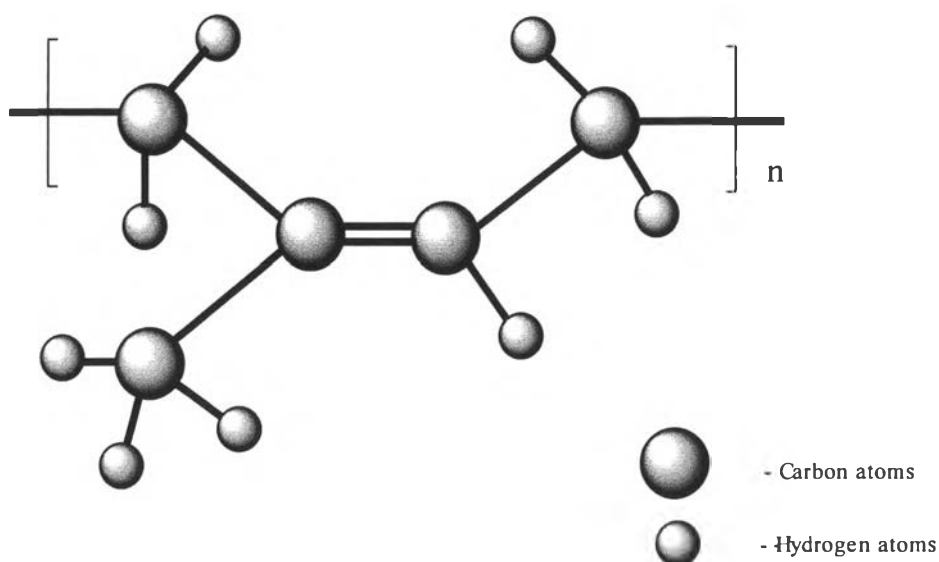




## CHAPTER II BACKGROUND AND LITERATURE SURVEY

### 2.1 Natural Rubber

Natural rubber (NR) which is found in several plants is a renewable polymer material exhibiting excellent physical and chemical properties. The white sap of the common milkweed and dandelion is rubber latex. The most important source of natural rubber latex is *Hevea brasiliensis* tree. The latex contains hundreds of proteins, including enzymes that are involved in the biosynthesis of the rubber molecules. NR has excellent dynamic properties. Such as resistance to fatigue though it is less resistant to environmental damage (under ozone exposure and oils) than some synthetic rubbers. Raw NR contains 93-95% *cis*-1,4-polyisoprene of about  $5 \times 10^5$  g/mol, 2-3% proteins, 2% acetone-soluble resins (including fatty acids), small amounts of sugars, a little mineral matter and water. The Hydrocarbon components of NR consist of over 99.99% of linear *cis*-1,4-polyisoprene as shown in Figure 2.1.



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

The Average molecular weights for polyisoprene in NR ranging from 200,000 to 400,000 with a relatively broad molecular weight distribution resulting in excellent processing behavior. One double bond for each isoprene. Along with the  $\alpha$ -methylene groups contained in an NR molecular chain provides the groups for vulcanization with sulfur. This double bond is easily oxidized resulting in the poor thermal properties. Thus, the NR cannot be used in a wide range of applications.

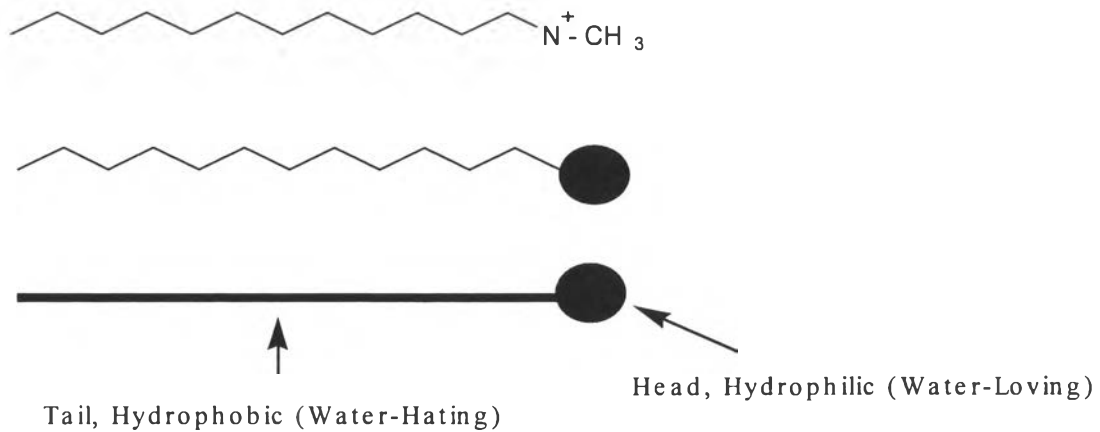
Moreover, NR has many undesirable properties, like low hardness, abrasion, stiffness and tear resistances. Consequently, fillers are utilized to improve performance of unfilled NR.

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 silica obtained from admicellar polymerization process was served to improve the rubber cure properties and the cured compound physical properties.

Kudisri (1997) produced polystyrene-isoprene copolymer on clay by *in-situ* polymerization of monomer in surfactant admicelle. This research studied the effect of the amount of surfactant and monomer on the process. It was found that the increase in the compound cure rate decreased  $t_{90}$  cure time and improved tensile property, tear strength, hardness, flex cracking resistance and compression set.

## 2.2 Surfactant Structures

The word of surfactant is a contraction of the term "Surface active agent". Surfactants are among the most unique and versatile materials due to their unique chemical structures. Generally, these compounds are comprised of a hydrophobic portion, usually a straight or branched hydrocarbon or fluorocarbon chain containing 8-18 carbon atoms (Tadros, 1995) and a hydrophilic portion which has a different charges. For this reason, we often describe surfactants as 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.



**Figure 2.2** Surfactant structures.

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).

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

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

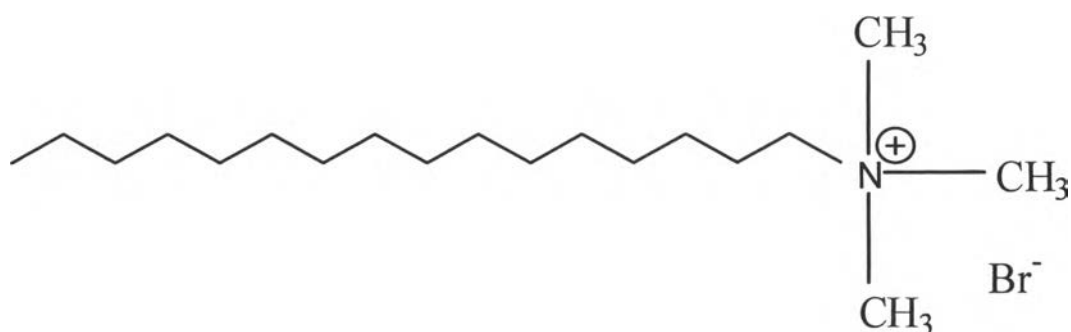
**Cationic surfactant** : positive charge of the surfactant molecules appears on the hydrophilic portion. For example, quaternary ammonium chloride, laurylamine hydrochloride.

**Ampholytic or zwitterionic surfactant** : there have both positive and negative charged portions. The presence of both charged hydrophilic groups in the same molecule leads to the headgroup hydrophilicity being an intermediate between the ionic and conventional nonionic classes (Laughlin, 1991). The charge depends on pH of solution. At low pH (acidic solutions), they form cations. But, at high pH (alkaline solutions), they form anions. For an intermediate pH range. For example, polyoxyethylenated alkylphenol, lauramidopropylbetaine.

However cationic surfactants are more expensive than anionic surfactants or nonionic surfactants (Rosen, 1989).

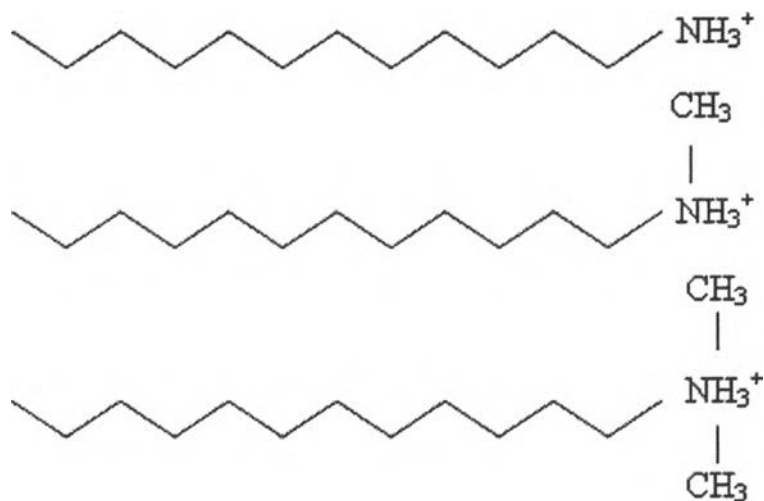
### 2.3 Cationic Surfactants

A cationic surfactant is a surface-active compound with the hydrophilic portion carrying a positive charge. With cationic surfactant adsorbing onto a solid surface, it can alter the surface property from hydrophobic to hydrophilic or vice versa. 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 uncharged and insoluble in water at pH above  $K_A$  (Rosen, 1989). In household products, cationic surfactants are used 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).



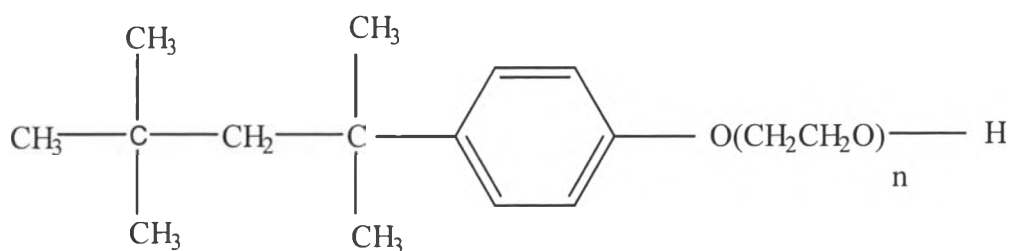
**Figure 2.4** Fatty amine salts.

Unfortunately, if we take these cationic surfactants up to a high pH (10 or 11) ammonium salts can also be sensitive to pH. Then, it is feasible to deprotonate the amine, thus leaving an uncharged molecule. In the same way as fatty acid salts tend to precipitate out once they are deprotonated, these fatty amine salts will precipitate out once deprotonated. Therefore, the quaternary ammonium surfactants ( $C_nH_{2n+1}(CH_3)_3NBr$ ) were 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 provides 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 can enhance mechanical properties of natural rubber, dynamic properties by minimizing the energy loss and improved silica dispersion.

## 2.4 Nonionic Surfactants

Nonionic surfactants are surface-active compounds with good performance in hard water and high electrolyte concentration. They are soluble in both water and organic solvents. Solubility decreases in water with increasing temperature due to the dehydration of  $\text{CH}_2\text{CH}_2\text{O}$  group. Triton X-100 is a common nonionic surfactant which is often used in biochemical applications to solubilize proteins. Triton X-100 has no antimicrobial properties and is considered a comparatively mild detergent, non-denaturing. It is a clear to slightly hazy, colorless to light yellow liquid. Triton X-100 structure is shown in Figure 2.5.

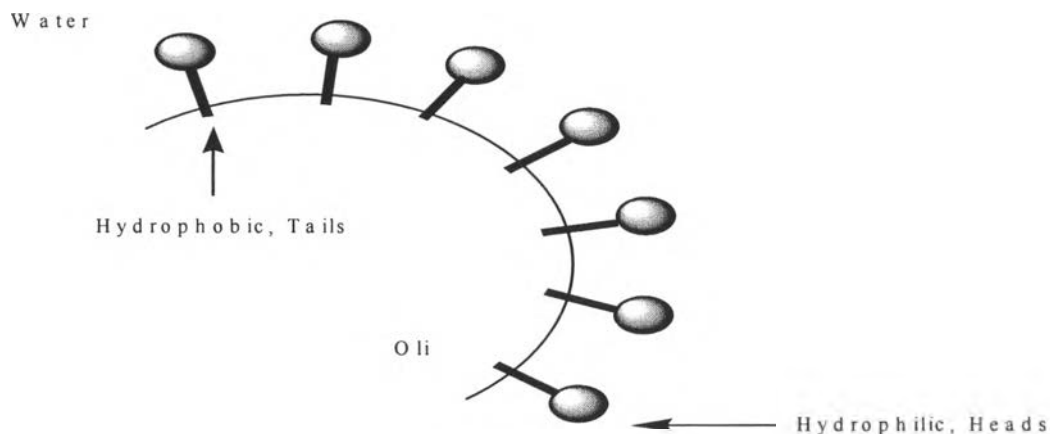


**Figure 2.5** Octyl phenol ethylene oxide (Triton X-100).

## 2.5 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 (Rosen, 1989). It involves molecular attraction at the surface as shown in Figure 2.6. 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).

Actually, 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.



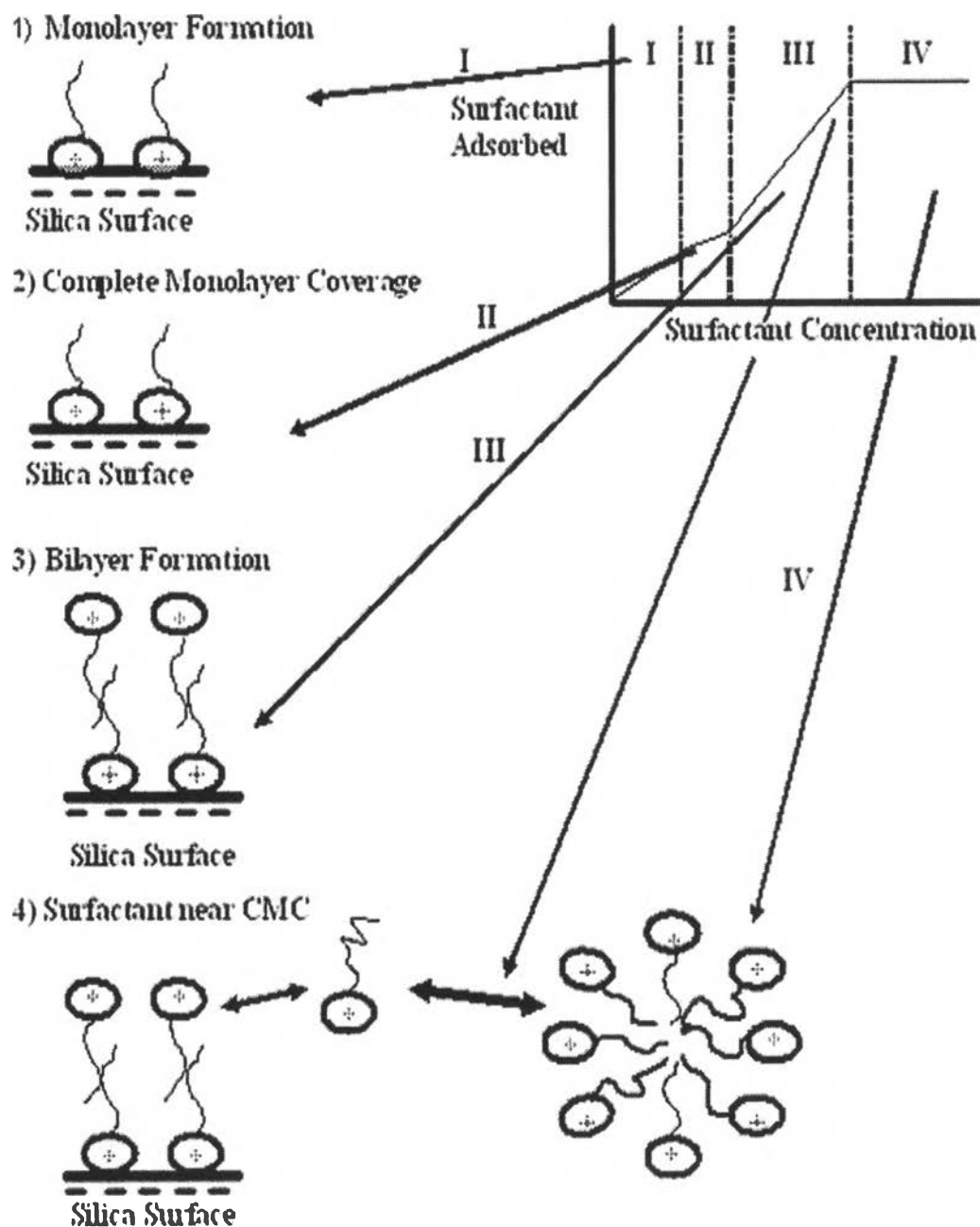
**Figure 2.6** Surfactant molecules adsorbing onto the surface of oil droplets with hydrophilic heads are exposing to the water phase and the hydrophobic tails sticking into the oil phase.

The adsorption isotherm of an ionic surfactant onto an oppositely charged substrate is typically a “S-shaped curve” of 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 2.7.

Region I of the adsorption isotherm corresponding to both very low bulk 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 Law 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 due to the hydrophobic interactions between the tail groups of approaching surfactant ions and those of previously adsorbed surfactant, which cause

the adsorbed surfactants 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.

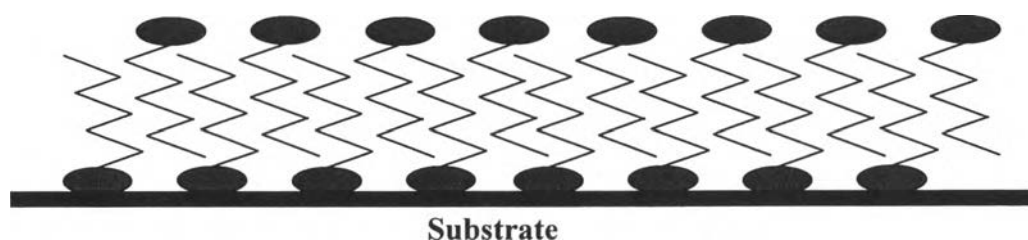


**Figure 2.7** Adsorption isotherm for an ionic surfactant on an oppositely charged substrate.



The admicelle is considered as a local bilayer structure with a lower layer of head groups adsorbed on the oppositely-charged 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 oppositely-charged 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 of surfactant molecules adsorbing on the surface of the beginning of admicelle formation on the lower energy surface patches (Figure 2.8). While these patches become filled, lower energy patches become energetically more favorable for adsorption at slightly higher equilibrium surfactant concentration.



**Figure 2.8** 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 show in Figure 2.9. 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).



**Figure 2.9** Structure of micelles .

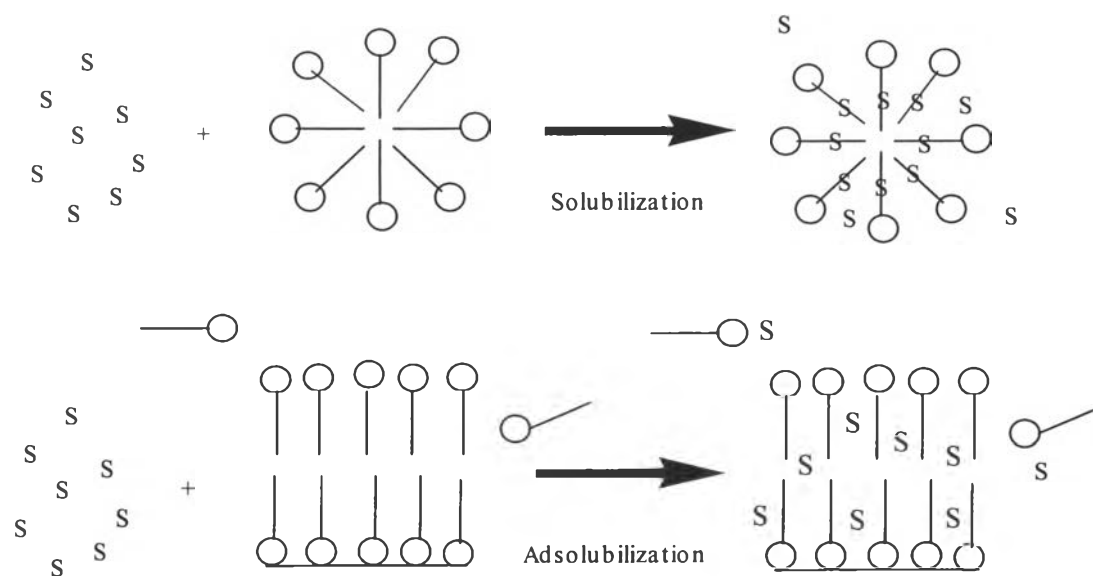
## 2.6 Solubilization

Solubilization is an important property of surfactants that is directly related to the presence of micelle formation (Figure 2.7). 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 solubilize), the exact location in the micelle at which solubilization occurs can vary.

## 2.7 Adsolubilization

Similar to the solubilization of organics into micelles, organic molecules can be integrated into surfactant aggregates at the solid-liquid interface (Figure 2.10). 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).



"S"s represent solute molecules, monomers

**Figure 2.10** 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 known as admicelles and the incorporation of the solute into the aggregates.

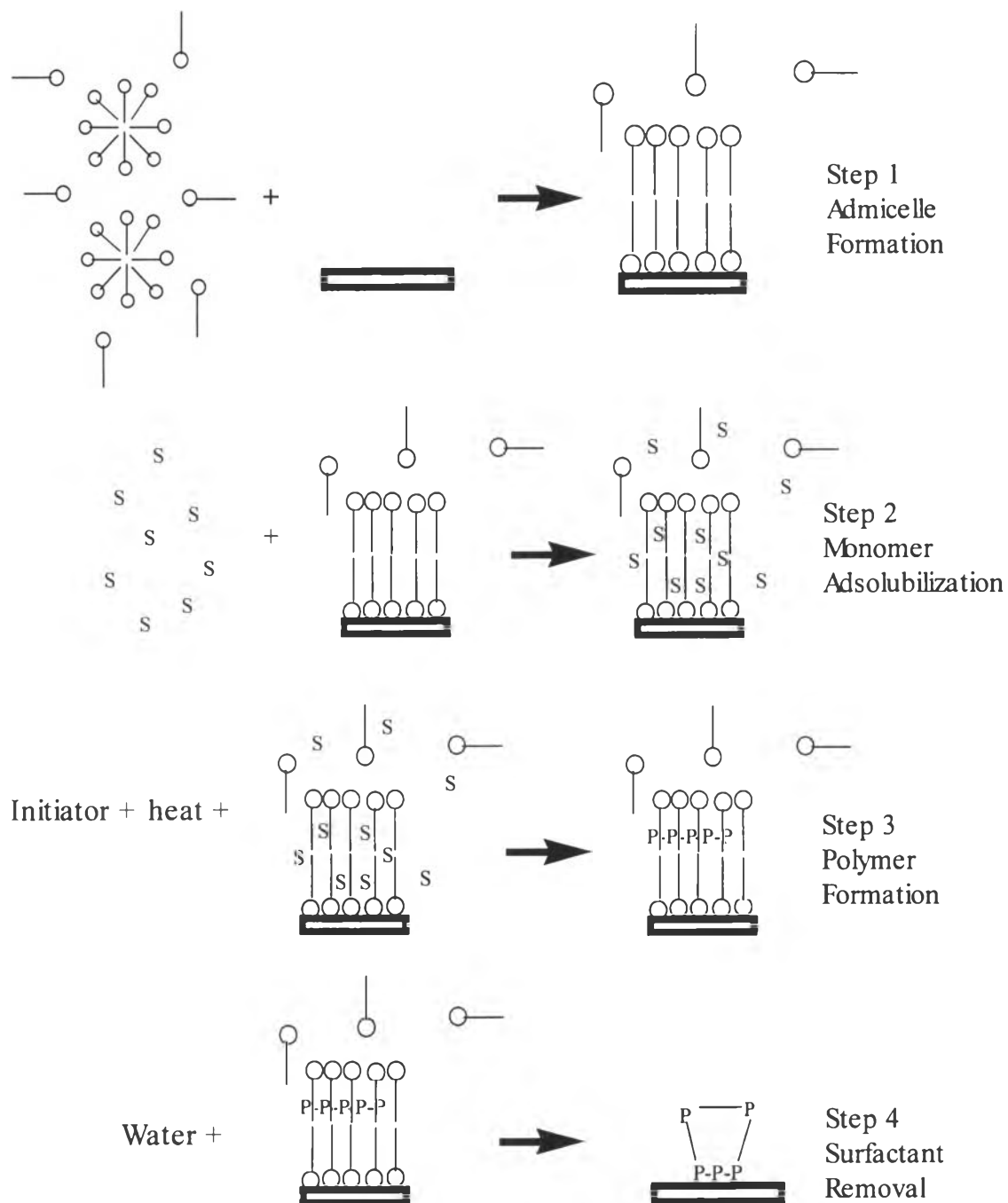
Kitiyanan *et al.* (1996) studied the adsolubilization of styrene, isoprene, and mixtures of styrene and isoprene into CTAB bilayers (admicelles) on precipitated silicas. The styrene adsolubilization constant is nearly unchanged with increasing styrene equilibrium concentration in the aqueous phase while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

## 2.8 Ultra-Thin Film Formation

Formation of ultra-thin films on solid surfaces has been of interest 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 is called admicellar polymerization (Wu *et al.*, 1987). Admicellar polymerization can be considered to occur in four basic steps as show in Figure 2.11.

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.

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 admicelles or concurrently with surfactant adsorption.



“S”s represent solute molecules, monomers.

“P”s connected by lines represent polymer chains formed during the reaction.

**Figure 2.11** Admicellar polymerization process for the formation of a thin polymer film.

Step 3 is the *in-situ* polymerization of adsolubilized monomers. Apart from the purpose of concentrating monomers 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 preferable. In this study, polymer formed was recovered by tetrahydrofuran extraction of the isolated silica after the reaction step, with intermediate washings, if necessary, by deionized water, followed by drying in a vacuum at a temperature below the boiling point of polymer.

## 2.9 Mixtures of Surfactants

Nonionic surfactant can enhance micelle formation with either anionic or cationic surfactants. It seems reasonable that nonionic surfactants could also enhance to the formation of micelles in mixed cationic-anionic systems.

Somasundaran *et al.* (1996) studied the behavior of surfactant mixtures at solid-liquid interfaces using anionic-nonionic and cationic-nonionic surfactants of different structures. The results show that adsorption of nonionic surfactants on alumina was enhanced significantly by the coadsorption of ionic surfactants. The adsorption behavior of these binary surfactant mixtures was dependent upon the ratio of the two surfactants in the mixture. With an increase in the ionic surfactant content, the adsorption of nonionic surfactant increased and the isotherm shifted to lower surfactant concentrations. Synergism and competition between the ionic and nonionic surfactants were observed in different concentration ranges at different mixing ratios

Zajac *et al.* (1996) studied the adsorption of a cationic surfactant, benzyldimethyldodecylammonium bromide (BDDAB), from aqueous solutions on silica S91-16 and crystalline quartz at 298 K and free pH was studied using adsorption microcalorimetry. Differential molar enthalpy of displacement was

correlated with the experimental adsorption isotherm and plotted as a function of the amount adsorbed. The general (qualitative) shape of the enthalpy curve appeared to be dependent upon the crystalline structure of silica (amorphous-crystalline). The experimental calorimetric and adsorption data for BDDAB were compared with those for benzyltrimethylammonium bromide (BTMAB), a molecule containing no alkyl chain, in order to demonstrate an ion-exchange mechanism of individual surfactant adsorption onto silica S91-16 at low surface coverages.

Esumi *et al.* (1996) studied the adsolubilization of 2-naphthol on silica with mixtures of cationic and nonionic surfactants such as HTAB/C<sub>12</sub>E<sub>6</sub> and 2RenQ/C<sub>12</sub>E<sub>6</sub>. In the HTAB/C<sub>12</sub>E<sub>6</sub> system, the ratios of adsolubilized amount of 2-naphthol to adsorbed amount of surfactant for the mixtures of different compositions were greater than those of single surfactant systems. On the other hand, in the 2RenQ/C<sub>12</sub>E<sub>6</sub> system the ratios for the mixtures were intermediate between those of the single surfactant systems. It was suggested that the hydrophobic properties in the mixed surfactant adsorbed layer for adsolubilization of 2-naphthol were affected by the structure of the cationic surfactant. Thus, to enhance the adsolubilization of 2-naphthol at low surfactant concentration, a proper surfactant selection for binary mixtures of cationic and nonionic surfactants is required.