CHAPTER II
BACKGROUND AND LITERATURE SURVEY

2.1 Silica

Silica is widely used as reinforcing filler for polymer matrices. Use of silica in rubber compounds provides beneficial properties such as increase in tensile strength, modulus, and resilience. Two fundamental properties of silica that influence their use in rubber compounds reinforcement are particle size and extent of hydration. (Mark *et al.*, 1994). The siloxane (SiOSi) surface of silica (SiO_2) reacts with water so that at ordinary temperature the surface of silica becomes covered with silanol groups (SiOH) (Iler, 1979). These silanol groups on the silica surface can react with oxygen or nitrogen containing materials such as alcohol, water, and amine. The silanol to silanol reaction by hydrogen bonding (Fig 1.1) is responsible for the formation of an extensive network that produces a stiff and highly viscous mixture. This type of structure makes processing more difficult because the presence of silanol groups makes silicas hydrophilic. Thus, they do not interact well with most polymers (being hydrophobic) and they require high amounts of shear and energy to incorporate them evenly.

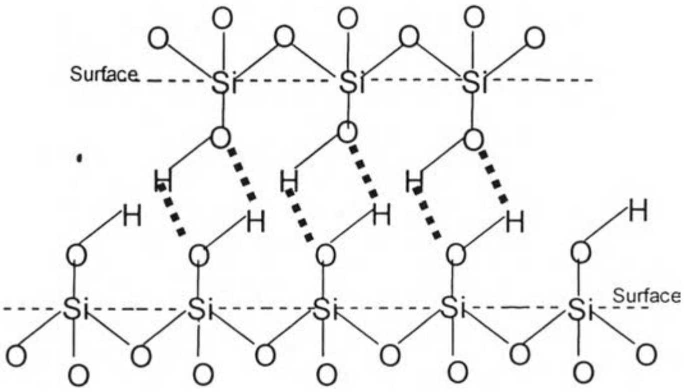

Figure 2.1 The silanol to silanol reaction by hydrogen bonding.

2.2 Non-ionic Surfactant

Surfactant is an abbreviation for surface active agent, which literally means active at a surface. The driving force for a surfactant to adsorb at an interface is to lower the free energy of that phase boundary. The name amphiphile is sometimes used synonymously with surfactant. The term relates to the fact that all surfactant molecules consist of at least two parts, one which is soluble in a specific fluid (the lyophilic part) and one, which is insoluble (the lyophobic parts). When the fluid is water one usually talks about the hydrophilic and hydrophobic parts, respectively. The hydrophilic part is referred to as the head group and the hydrophobic part as the tail (see Figure 2.2) (Holmberg *et al.*, 2003). Depending on the nature of the hydrophilic group, surfactants are classified into four categories; anionic cationic non-ionic and zwitterionic (Rosen, 1989).

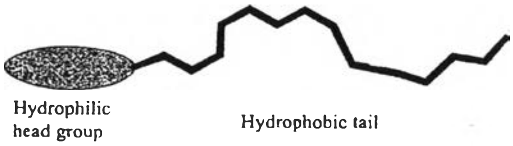

Figure 2.2 Schematic illustration of a surfactant.

In the case of non-ionic surfactants, they have either a polyether or a polyhydroxyl unit as the polar group. In the vast majority of non-ionic surfactants the polar head group is a polyether consisting of oxyethylene units. The typical number of oxyethylene units in the polar chain is between five to ten units but may be higher than one hundred. The single most important type of non-ionic surfactants is fatty alcohol ethoxylate which are hydrolytically stable in the pH range 3-11. They undergo a slow oxidation in air producing some oxidation products such as aldehydes and hydroperoxides which are more irritating to the skin than the intact surfactant.

Some important facts about non-ionic surfactants are

1. They are normally compatible with all other types of surfactants.
2. They are not sensitive to hard water.
3. Unlike ionic surfactants, their physicochemical properties are not markedly affected by electrolytes.
4. The physicochemical properties of ethoxylated compounds are very temperature dependent, unlike ionic surfactants compounds they become less water soluble, more hydrophobic, at higher temperatures. (Holmberg *et al.*, 2003)

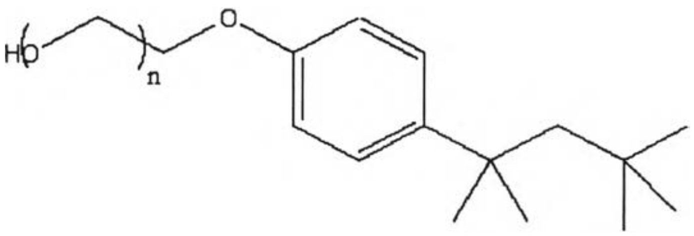

Figure 2.3 Structure of Triton X-100, an ethoxylated octylphenol non-ionic surfactant (n=9-10).

2.3 Surfactant Adsorption on Hydrophilic Surface

The adsorption of non-ionic surfactants on hydrophilic surfaces (i.e. silica) is dictated by the interaction between the surface and the polyoxyethylene chain. If there is an interaction present, the adsorption behavior will be similar to the adsorption of ionic surfactant on hydrophilic surfaces. The adsorption of a non-ionic surfactant on a silica surface is shown schematically in Figure 2.4. Surface aggregation will begin at concentrations well below the CMC (critical micelle concentration) of the surfactant. The concentration at which this surface aggregation starts to appear is called the critical surface aggregation concentration (CSAC) or critical admicelle concentration (CAC) and is of the order of one tenth of the CMC of the surfactant. (Holmberg *et al*, 2003)

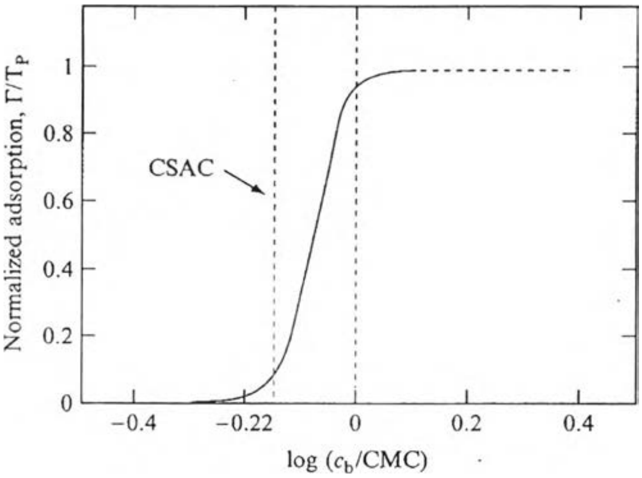

Figure 2.4 Schematic illustration of the adsorption of non-ionic surfactants on a silica surface, where c_b is the surfactant concentration is solution and the left-hand dashed vertical line indicates the critical surface aggregation (CSAC).

Figure 2.5 shows region (I) corresponds to both very low concentration and low adsorption of surfactant. Region (II) indicates the beginning of lateral interaction between surfactant molecules, which results in the formation of surfactant aggregates on the most energetic surface patches. These adsorbed surfactants are called admicelles or hemimicelles depending upon whether the aggregates are viewed as bilayers or monolayers. The admicelle is a local bilayer structure with a lower layer of head groups adsorb on the substrate surface and an upper layer of head groups exposed to the solution. The hemimicelle is a monolayer structure having the head groups adsorb on the surface while the tail groups expose to the solution. The transition point from region I to region II, representing the critical admicelle concentration (CAC) or critical surface aggregation concentration (CSAC).

A marked decrease in the slope of the isotherm indicates the beginning of region III. This is thought to be caused by the repulsion between the like-charged head groups on the surface or the beginning of adsorption onto lower energy surface patches, thus making additional adsorption less favorable. It could also represent the full coverage of high energy sites and the beginning of adsorption on lower energy sites. Region IV is the plateau adsorption region, having almost constant surfactant adsorption with increasing surfactant concentration at which micelles first form is the critical micelle concentration (CMC) (Rosen, 1989).

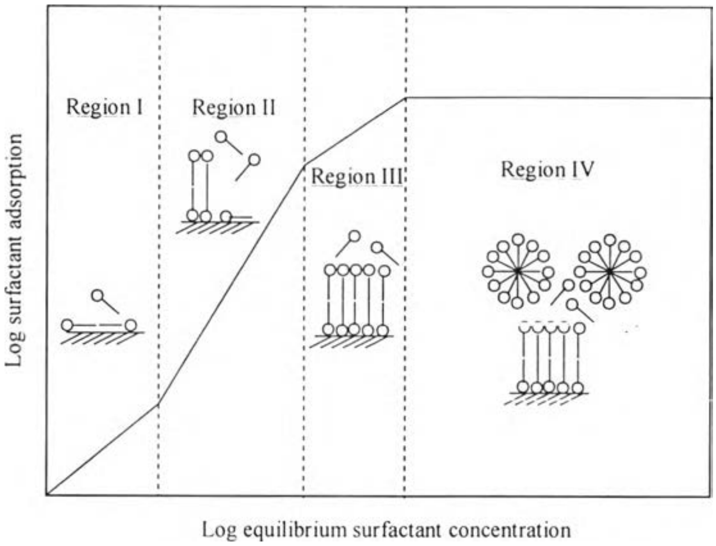

Figure 2.5 Schematic representations of the adsorption of an ionic surfactant on a charged surface as a function of surfactant concentration.

Figure 2.6 shows the adsorption behaviors of some non-ionic surfactants of fatty alcohol ethoxylated C_mE_n (m = number of observed carbon atom in alkyl chain, n = number of oxyethylene unit) type on silica. It was that the adsorbed amount abruptly increases well below the CMC, which are indicated by small arrows. It was also shown that plateau adsorption is reached at concentrations around the CMC of the surfactant. The size of these aggregates increases with increasing hydrocarbon chain length of the surfactant.

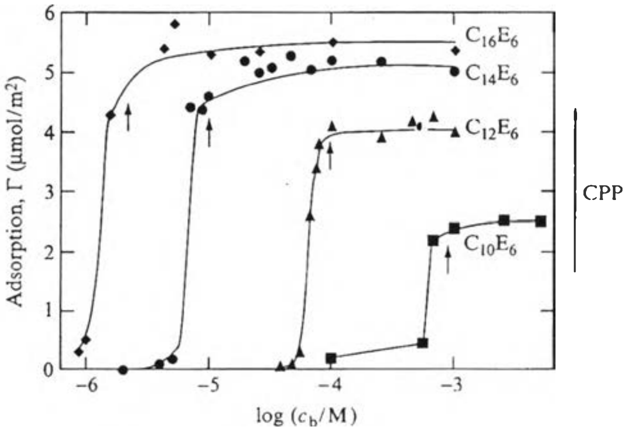

Figure 2.6 Adsorption of various poly(ethylene glycol) monoalkyl ethers, C_mE_n on silica at 25°C showing an increase adsorption.

Figure 2.7 illustrates the fact that the interaction between the surfactant and the surface is important in order for adsorption to take place. This figure shows that for the adsorption of two non-ionic surfactants on silica the adsorption decreases to zero at pH levels of *ca.* 10 and above. It is interesting to note that for the more hydrophobic surfactant, i.e. $C_{12}EO_5$ the pH dependence is very strong at pH levels above pH 9. This indicates that only a small interaction between the surfactant and the surface is sufficient to adsorb hydrophobic surfactants. Once a few molecules are adsorbed on the surface, they form the nuclei for further adsorption and surface aggregation.

This effect is less pronounced for the more hydrophilic surfactant, i.e. $C_{12}EO_8$, as expected. These can be interpreted in two ways. First, in these alkaline solutions the surface hydroxyl groups are ionized and cannot form hydrogen bond with the surfactant and hence no adsorption takes place. Secondly, hydroxyl ions from solution compete for the adsorption sites and at pH levels above *ca.* 10 all surfactants are displaced from the surface.

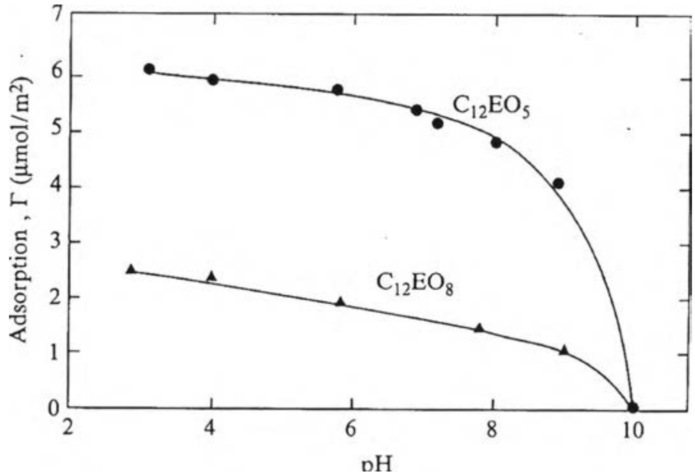

Figure 2.7 Adsorption of two non-ionic surfactants on silica as a function of pH.

2.4 Adsolubilization

Solubilization is the one of the most important phenomena for surfactant solutions that is directly related to micelle formation. Surfactant solutions 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 solute within the micelle. Solubilization can be defined as the spontaneous dissolving of substances (solid, liquid, or gas) by reversible thermodynamically stable isotropic solution with reduced thermodynamically activity of solubilized material (Rosen, 1989).

Similar to the solubilization of organics into micelles, organic molecules will be incorporated into surfactant aggregates adsorbed at the solid-liquid interface. The phenomenon is termed adsolubilization. Adsolubilization is defined as the incorporation of compounds into surfactant aggregates adsorbed on surfaces, of which compounds would not be in excess at the solid-solution interface in the absence of the surfactant. (Scamehorn and Harwell, 1988) as shown in Figure 2.8

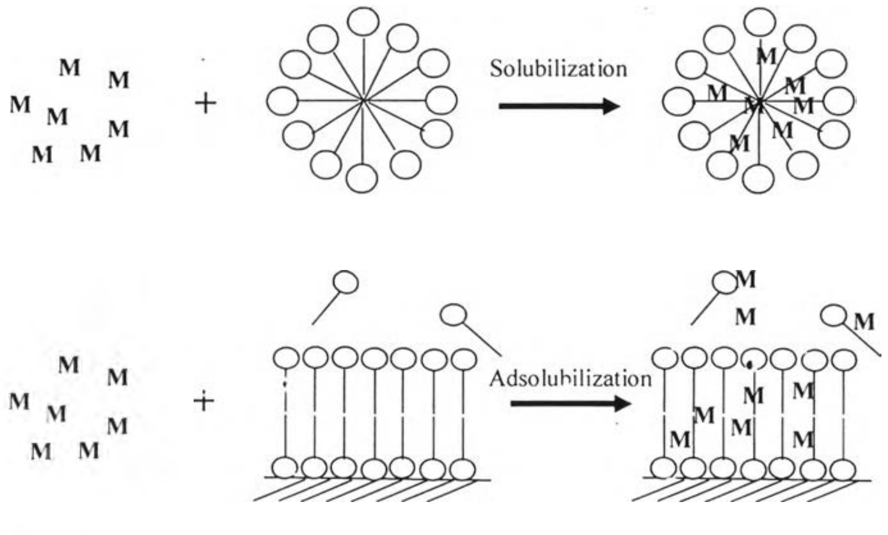

Figure 2.8 Schematic of solubilization and adsolubilization.

2.5 Admicellar Polymerization

The admicellar polymerization method developed from a fundamental understanding of the interaction between surfactant and surfaces. The conditions of the aqueous solution containing surfactant and suspended inorganic particle can be tailored to favor the formation of ultra-thin films in adsorbed surfactant aggregates on the surface of the particles. The formation of ultra-thin films in adsorbed surfactant bilayer has been first investigated by Wu *et al.* (1987).

The method utilized for modification of inorganic powder by admicellar polymerization can be considered to occur in four steps (Figure 2.9)

Step one : Adsorption of surfactant on solid surface

The first step consists of admicelle formation by the adsorption of a surfactant to form surface aggregates on the substrate. Adsorption is accomplished through the use of a suitable surfactant under appropriate system conditions. The choice of a surfactant is influenced by the point of zero charge of the substrate (the pH value at which the surface charge is completely neutralized is called the point of zero charge, or PZC) the chemical nature of the polymer to be formed, and the chosen polymerization initiator system. A study of the PZC for the substrate provides information of the pH ranges in which cationic or anionic surfactant might be utilized. At a pH solution above the PZC, the surface of the substrate will be negatively charged; while below the PZC, the surface will be positively charged. Silicon dioxide has a PZC of approximately 2.9. (Iller, 1979) Thus at a pH of 8, the SiO_2 surface would have negative charge. Adsorption by ionic surfactants is achieved by adjusting the surface charge on the substrate to be opposite that of the surfactant head group.

Moreover, the equilibrium concentration of surfactant must be lower than critical micelle concentration in order to prevent the formation of micelles in the bulk solution. In the absence of micelles, the organic interior of the surfactant bilayer became the only locus for the adsolubilization of organic monomers.

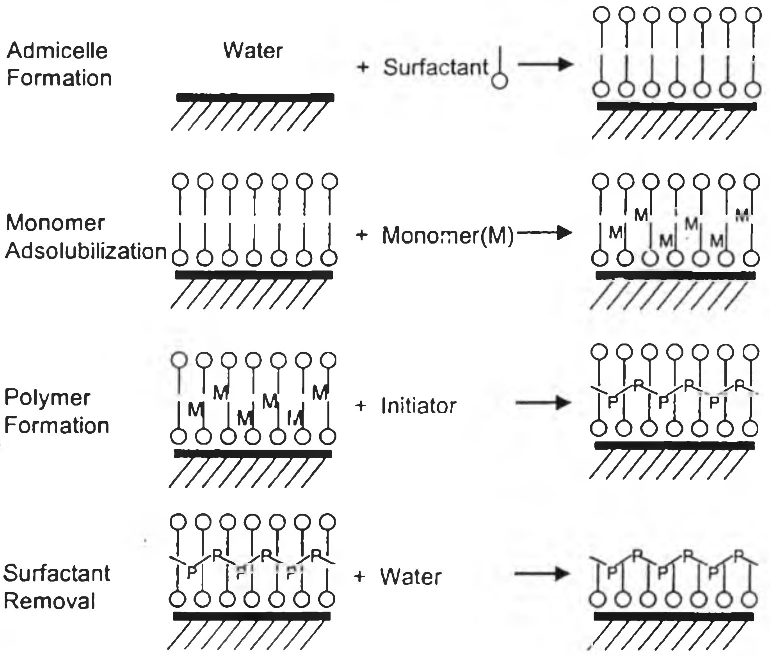

Figure 2.9 Admicellar polymerization process for the formation of an ultra-thin polymer film.

Step two : Monomer adsolubilization

This step can be done subsequently to the first step, or simultaneously with it. It involves the solubilization of monomer into the admicelle, a process called adsolubilization. Many organic monomers are nearly insoluble in water. Thus, when they are introduced into the system, they preferentially partition into the organic solvent interior of the micelle. In the admicelle, the bilayer acts as a two-dimensional solvent to concentrate the monomer near the surface of the substrate.

Step three : Polymerization of adsolubilized monomer

Third step is the in situ polymerization of the monomer. For free radical polymerization, the reaction is started by the generation of radicals from an initiator. Once the reaction has begun, additional monomer from the bulk solution diffuses into the admicelle (Wu *et al.*, 1987). If the reaction is continued for a sufficient length of time, essentially all of the monomer dissolved in the solvent can be converted to polymer.

Step four : Surfactant Removal

The last step is the washing of the treated substrate with water to remove accessible surfactant and to expose the polymer film. The need of this step is optional, depending on the application.

2.6 Literature Survey

2.6.1 Surfactant Adsorption

Surfactant adsorption at the solid-liquid interface is a major event in which the surfactant molecules can interact with the solid interface (Esumi, 2001). The adsorption and concomitant spontaneous organization (self-assembly) of surfactants at interfaces often gives rise to the unique surface properties. The equilibrium structure of adsorbed layers resulted from the balance of many forces, including those that determine the structure of aggregates in bulk solution, e.g., hydrophobic attraction between surfactant tails, repulsive steric headgroup interactions, and geometric packing constraints (Grant *et al.*, 2000). When ionic surfactants adsorb onto metal oxide particles, the stability of dispersed particles is often altered by the surfactant concentration; a high dispersion stability without surfactants decreases by addition of low concentrations of surfactants, but at high surfactant concentration the dispersion stability becomes high. This process is called "dispersion–flocculation–redispersion" and is very useful for the fundamental study of aqueous dispersions of particles by surfactants. This process also illustrates the surface modification of particles by surfactants (Esumi, 2001).

However, early views were that the adsorption process of non-ionic surfactant followed a very similar path to ionic surfactant adsorption, i.e., initial adsorption of monomers, then hydrophobic association, and finally the formation of a bilayer near the CMC (critical micelle concentration), with the hydrocarbon tails intercalating due to the large size of the headgroup.

More recently this approach has been questioned, and many techniques have since been employed to infer the structure of the so-called "solloid" (a surface aggregate of adsorbed surfactant or polymer) (Rutland and Senden, 1993). Levitz *et al.*(1984) used fluorescence decay of pyrene with Triton X-100 and 101 on Spherosil® and determined that at low coverages the adsorption was of a micellar nature but that at high coverages steric interactions caused the micelles to coalesce, forming a single, continuous bilayer. Lee *et al.* (1989) using neutron reflection and hexakis(oxyethylene)dodecyl ether ($C_{12}E_6$) on quartz, proposed a similar scheme where "defective bilayers" at low coverage fused into full bilayers at high coverage with a hydrocarbon layer thickness of a single alkyl chain. In subsequent work Cummins *et al.*(1990), investigated the adsorption of $C_{12}E_6$ to a Ludox TM silica sol using SANS (small-angle neutron scattering). At very low coverages their results were inconclusive, but above a certain (low) coverage value they observed the adsorbate thickness remained constant with increasing coverage. They proposed that the adsorption took place as "islands" of bilayers, which never attained better than 75% coverage (at very low coverage the adsorbate thickness was probably even lower).

Atomic force microscopy has been used to measure surface forces between a spherical silica particle of colloidal dimension and a smooth silica surface in aqueous solution as a function of the concentration of the non-ionic surfactant pentakis(oxyethylene)dodecyl ether. In the absence of surfactant the interaction between silica surfaces was purely repulsive, being composed of electrostatic and hydration forces, whereas at low surfactant concentrations (about one-third the critical micelle concentration (CMC)) the repulsion was replaced at short separations by an attractive force which pulled the surfaces into adhesive contact. At higher concentrations the surfaces still experienced an attractive force at small separations, but the adhesion decreased markedly. At concentrations above the CMC repulsive steric forces are observed. A tentative scheme for the adsorption of poly(oxyethylene) surfactant to silica is presented in figure 2.10 (Rutland and Senden, 1993).

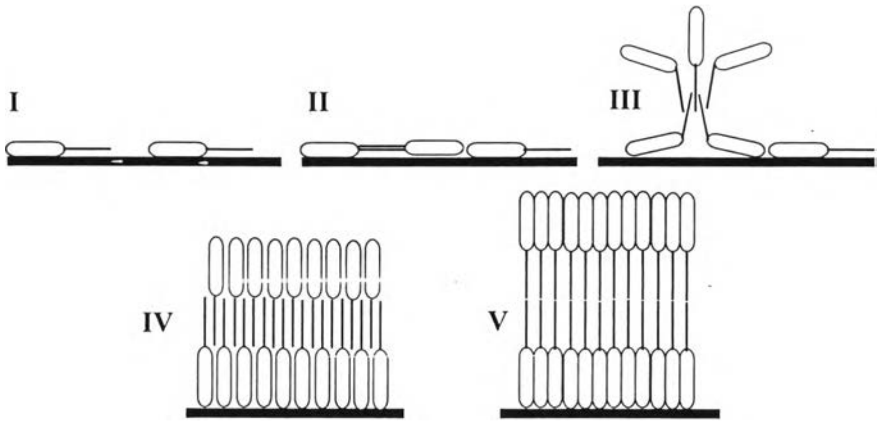

Figure 2.10 Adsorption scheme form on silica. Initially a small amount of adsorption takes place due to hydrogen bonding (I). Then further adsorption takes place through either the direct adsorption of or formation of small aggregates (II, III). At concentrations about the CMC these aggregates have fused sufficiently to form intercalated bilayer structures, with a large headgroup area (IV). Above the CMC and after equilibration a classical bilayer forms (V) with a similar headgroup area to micelles (with which the adsorbate is in equilibrium).

In 2003, Tan and O'Haver studied the adsorption isotherms of various Triton X surfactant systems on precipitated silica (Hi-Sil 233$^{®)}$. From Figure 2.11, the isotherms have the sigmodial shape. The amount of adsorbed surfactant in the plateau region decreases significantly while the CMC increasing slightly with increasing number of EO units. At low levels of adsorption the amount of adsorbed surfactant increased significantly with increasing number of EO units due to the stronger interaction between silica and the larger head groups.

2.6.2 Adsolubilization Isotherm

The adsorption isotherm of styrene in the absence of surfactant and the adsolubilization isotherm of styrene in Triton X-100 surfactant admicelles are investigated by Tan and O'Haver (2003). They found that, in the absence of surfactant, there is negligible styrene adsorption on wet silica until the styrene concentration approaches 3050 μmol/l. At that point, without surfactant, phase separation within the pores of the silica may account for the sudden, erratic increase in "adsorption".

But, in the presence of surfactant the amount of adsolubilized styrene increases slowly with increasing equilibrium styrene concentration in the bulk phase. With the surfactant concentration below the CMC the isotherm was expected to reach its maximum as the styrene concentration approaches its solubility. Using this surface concentration, the mole ratio of adsolubilized styrene to adsorbed surfactant Triton X-100 is about 2.7:1, which differs significantly from the previous studies with ionic surfactants where the maximum ratio was approximately 1.7:1.

Moreover , they compared styrene adsolubilized by the Triton X series surfactants with different hydrophilic group lengths, they also found that the adsolubilization in all systems increased with increasing bulk concentration. As the number of EO units increased from 8.5 to 12.5, the adsolubilization isotherms became less favorable, an expected result which is consistent with their solubilization capacities. At high styrene loading, the adsolubilization capacity increased by as much as 100% as the number of EO groups decreased from 12.5 to 8.5.

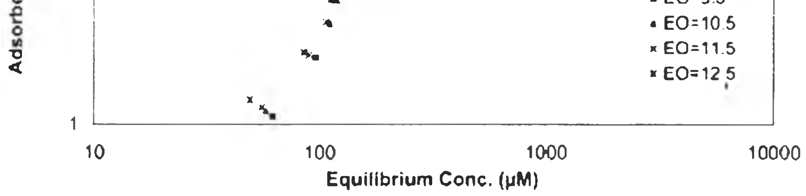

Figure 2.11 Adsorption isotherms of Triton X surfactants with different number of EO units on silica.

2.6.3 Admicellar Polymerization

Admicellar polymerization, or the polymerization of monomers solubilized in adsorbed surfactant aggregates, was first developed in the 1980s (Wu *et al.*, 1987) This novel process has been studied on a variety of inorganic substrates using various type of surfactants and initiators and has been applied to a variety of industrially important substrate (Thammathadanukul *et al.*, 1996). Waddel *et al.* (1995) improved the performance of rubber compounds using precipitated silica as a reinforcing filler. Silica has polar hydroxyl groups on its surface while most polymers, are typically hydrophobic. Thus, silica particles require surface treatment because unmodified silica cannot form efficient physical interaction or chemical bonds with most polymers due to low compatibility of hydrophilic silica with hydrophobic surface polymer. Silane coupling agents are often used to improved the compatibility but increase the cost of the process (Ou-Udomying, 2003).

In 1996 Thammathadanukul *et al.* compared the reinforcement of natural rubber compound by surface-modified precipitated silicas. Either a bifunctional organosilane coupling agent or admicellar polymerization was used in this study. They concluded that both surface modification processes afford materials that dramatically increase the compound cure rate, thereby significantly reducing cure times, while also improving tensile properties, tear strength, abrasion resistance, and compression set of the cured compound.

See and O'Haver (2002) used atomic force microscopy to study polystyrene-modified silica surfaces produced by admicellar polymerization using CTAB as a cationic surfactant. They found that the structure of the polystyrene formed on precipitated silica was insensitive to the surfactant feed concentration. As the initial concentration of CTAB was kept constant at point just below its maximum adsorption, and varied the amount of monomer loading. They also found that at very high feed concentration of styrene, the primary particles are encapsulated by a relatively thick layer of polystyrene film, forming a homogeneous surface that does not show much phase contrast. Whereas at low styrene feed concentration the polystyrene film exists primarily in the pores, with patches extending onto the exposed surface of silica particles. The thickness of polystyrene films is ~6 nm. As the styrene feed concentration is further reduced, thin polystyrene strands can be observed only near the valleys between primary particles.

In 2003 they used the same method to study the characteristics of polystyrene films formed on silica disks. The experimental are divided in two series. In the first series, for which the feed ratio of CTAB to styrene was kept constant and the total feed concentration was varied, a uniform layer of a polystyrene film was observed along with some nanometer size aggregates at high feed concentrations of both CTAB and styrene. These droplets eventually agglomerated with the film beneath and formed larger macrodroplets in a ring arrangement. At lower concentrations, droplets and holes were observed that eventually agglomerated to form a bi-continuous thin film. In the second experimental series, the concentration of CTAB was kept constant, and the feed ratio of CTAB to styrene was varied. A smooth thin film was observed at high concentration of styrene. This film could be deformed and/or removed to expose the silica surface beneath. At lower styrene loadings, the polystyrene film became unstable and formed droplet like aggregates, possibly because of either the uneven adsolubilization of the styrene monomer within the admicelle or the dewetting effect during washing and drying. The structure of the polystyrene film formed on a smooth silica disk was very dependent on the amount of the surfactant fed to the system; this contrasted with the results on precipitated silica.