CHAPTER II
BACKGROUND AND LITERATURE SURVEY

2.1 Natural Rubber

Natural rubber (NR) is a natural polymeric material that exhibits excellent physical and chemical properties. Natural rubber latex could be found in many plants. The white sap of the common milkyweed and dandelion is rubber latex. The most important source of natural rubber latex is the *Hevea brasiliensis* tree. The latex from this tree contains hundreds of proteins, including enzymes that are involved in the biosynthesis of the rubber molecules. NR exhibits excellent mechanical properties under both normal and dynamic loadings, but it is subservient to environmental damage (for examples, by ozone and organic oils). Raw NR contains 93-95 wt.% of *cis*-1,4-polyisoprene of about 5×10^5 g/mol, 2-3 wt.% of proteins, 2 wt.% acetone-soluble resins (including fatty acids), small amount of sugars, and trace amount of mineral matters and water (Nontasorn, 2002). Hydrocarbon component of NR, which consists of over 99.99 wt.% of linear *cis*-1,4-polyisoprene, is shown in Figure 2.1(Lim-ochakun, 2000).

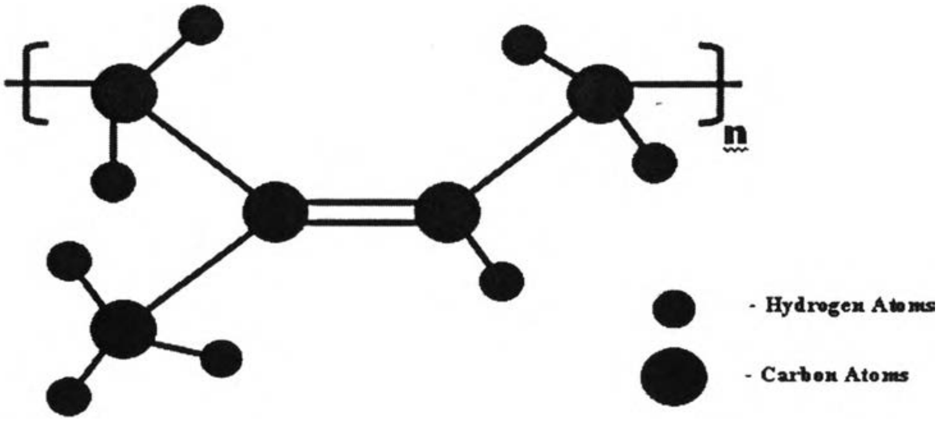

Figure 2.1 Chemical structure of NR (cis-1,4-polyisoprene).

Average molecular weight of the polyisoprene in NR ranges from 200,000 to 400,000 with a relatively broad molecular weight distribution, which is responsible for the observed excellent processing behavior. There is one double bond for each isoprene part, along with the α-methylene groups contained in an NR molecular chain, is the active place where vulcanization with sulfur takes place. The glass transition temperature (T_g) - the temperature or range of temperature that the polymer exhibits a marked change in its physical properties - of uncured NR is approximately -76.2 ± 0.5°C, which is far below room temperature. As a result, NR appears to be soft and can be soften under heat. Conversely, it is rigid and brittle at low temperatures. Hence, NR can be utilized in a narrow temperature range.

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

O'Haver *et al.* (1996) reported the use of admicellar-modified silica to improve the performance of rubber compounds. The silica was modified by in situ admicellar polymerization of both nonpolar and polar monomers to obtained copolymers of different properties on its surface The admicellar-modified silica serves to improve the rubber cure properties and the physical properties of the cured compounds.

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 Clay and Clay Mineral

Clay or layered silicate is a natural, earthy, fine-grained material composed largely of a limited group of crystalline minerals known as the clay minerals. Generally, it can be classified into many types according to differences in its structure and composition. The clay minerals are hydrous silicates, which contain tetrahedral silicate sheet and octahedral aluminum or magnesium sheet. The clay minerals were classified based on their layer type (either 1:1 or 2:1) .

Clay minerals find almost innumerable applications, and the diversity of uses is still increasing. The reason is the large variety of clays and clay minerals and the ease that these materials can be modified. Swelling behavior, adsorption properties, colloidal and rheological phenomena can be optimized and adjusted to the intended used. In addition to applications well known for a long time, new uses are found and new types of materials are created. Clay minerals and clays are more and more involved in material science studies and are parent materials of organic-inorganic composites. Among several types of clays, the smectite is usually used as additive in polymer composites. The layered silicates are the most attractive because it can be intercalated by organic molecules.

Smectites are a group of clay minerals, which possess expandability, taking up water or organic molecules between their structural layers, and also marked cation exchange properties. The structure can be either dioctahedral or trioctahedral depending upon the type of substituted cationic atoms. Dioctahedral signifies that two of octahedrons are filled with trivalent cations, such as Al^{3+} or Fe^{3+}. Trioctahedral signifies that all of the octahedrons were filled with divalent Mg^{2+} or Fe^{2+}.

Table 2.1 Classification of phyilosilicates, emphasis on clay minerals

Layer type	Group	Subgroup	Species
1:1	Serpentine-Kaolin (z~0)	Serpentines (Tr)	Chrysotile, antigorite, lizardite, berthierine, odinite
		Kaolins (Di)	Kaolinite, dickite, nacrite, halloysite
2:1	Talc-pyrophyllite (z~0)	Talc (Tr)	
		Pyrophyllite (Di)	
	Smectite (z~0.2-0.6)	Tr smectites	Saponite, hectorite
		Di smectites	Montmorillonite, beidellite, nontronite
	Vermiculite (z~0.6-0.9)	Tr vermiculites	
		Di vermiculites	
	Illite (0.6>z<0.9)	Tr illite	Illite, glauconite
		Di illite	
	Mica (z~1.0)	Tr micas	Biotite, phlogopite, lepidolite
		Di micas	Muscovite, paragonite
	Brittle mica (z~2.0)	Di brittle micas	Margarite
	Chlorite (z variable)	Tr,Tr chlorites[a]	Common name based on Fe2+, Mg2+, Mn2+, Ni2+
		Di,Di chlorites	Donbassite
		Di,Tr chlorites	Sudoite, cookeite (Li)
		Tr,Di chlorites	No known examples

[a] 2:1 layer first in name of chlorite; Tr = trioctahedral and Di = duictagedrak; z = charge per formula unit.

Table 2.2 Chemical formula of clay in 2:1 phyllosilicates types

Subgroup	Species	General formula
Dioctahedral Smectites	Montmorillonite	$M_{x/n}^{n+} \cdot yH_2O[Al_{4.0-x}Mg_x](Si_{8.0})O_{20}(OH)_4$
	Beidellite	$M_{x/n}^{n+} \cdot yH_2O[Al_{4.0}](Si_{8.0-x}Al_x)O_{20}(OH)_4$
	Nontronite	$M_{x/n}^{n+} \cdot yH_2O[Fe_{4.0}](Si_{8.0-x}Al_x)O_{20}(OH)_4$
Trioctahedral Smectites	Saponite	$M_{x/n}^{n+} \cdot yH_2O[Mg_{6.0}](Si_{8.0-x}Al_x)O_{20}(OH)_4$
	Hectorite	$M_{x/n}^{n+} \cdot yH_2O[Mg_{6.0-x}Li_x](Si_{8.0})O_{20}(OH, Fe)_4$

The principal smectites are montmorillnite, beidellite and nontronite. all of which are dioctahedral 2:1 layer silicate, and saponite, hectorite and sanconite, which are trioctahereal. Their chemical structure is illustrated in Table 2.2.

The smectite clay minerals consist of many layers of octahedral aluminates sheets sandwiched between tetrahedral silicate layers. Oxygen atoms reveal the layer edge of tetrahedral site and octahedral site. Illustration in Figure 2.2 is the structure of smectite clays.

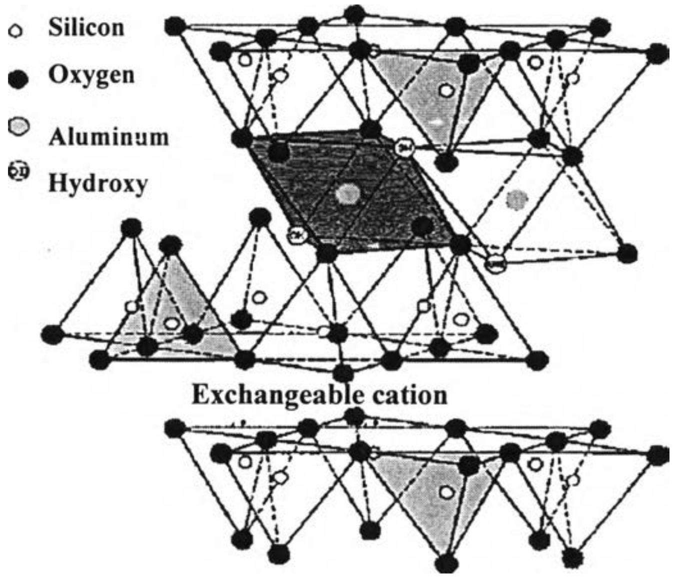

Figure 2.2 Structure of 2:1 phyllosilicates.

The 2:1 type layers of smectites have various cation substitutions in both the tetrahedral and octahedral positions. Substitutions of ions of the same valence, notably Mg-Fe(II) and Al-Fe(III) substitutions, are common in octahedral positions. Coupled substitutions also occur such as $Fe^{3+} + O^{2-}$ replacing $Fe^{2+} + (OH)^-$ which is equivalent to a combined oxidation-dehydration process. Anion substitutions, particularly F^- for $(OH)^-$, are not common in natural smectites but it is utilized in synthetic materials.

The isomorphic substitutions within metal oxide sheets with the lower valency species give the silicate layer slightly negative charges, and it is counterbalanced by interlayer cations namely Na^+ and K^+. As the forces that hold the stacks together are relatively weak, the intercalation of small molecules between the layers is easy.

Montmorillonite (MMT), categorized in smectite group, is normally applied to polymer nanocomposites because of its suitable layer charge density.

2.3 Montmorillonite

MMT has a low thermal expansion coefficient and a high gas barrier property. Stacking of this structure leads to a regular weak dipolar or Van der Waals interaction between the layers. Isomorphic substitution in each layer generates negative charges that are counterbalanced by hydrated sodium or potassium ions residing in the interlayer spacing. In aqueous suspension, cations in interlayer may exchange with ions in the bulk solution. They are known as *exchangeable cations*. The total amount of cations adsorbed in the clay interlayer, expressed in milli-equivalents per hundred grams of dry clay, is called the cation exchange capacity (CEC). It is an important characteristic of clay minerals. The cation exchange capacity is high for sodium montmorillonite, in comparison with other clay minerals.

There are many ways to investigate the CEC values. The principle method suggested by Rhoades in 1982 is displacement of saturating index cation and then displacement the saturating index cation after washing free from saturating salt. The last step, detect the saturating index cation by many techniques such as titration, atomic emission spectroscopy depending on the type of index. Methylene blue index is the simple method to detect the CEC values. It is used in a standard test method ASTM C 337-99 for characterizing the property of clays.

On a larger scale of MMT, each layer can be seen as a high aspect ratio lamella about 100-200 nm in diameter and 1 nm in thickness (Figure 2.3).

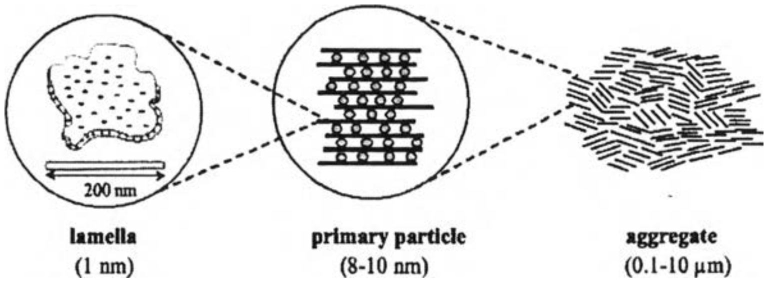

Figure 2.3 Microstructure of montmorillinte.

Five to ten lamellae are associated by interlayer ions in primary particles (8-10 nm in the "transverse" direction which, in turn, form larger irregular aggregates (0.1 – 10 μm in diameter) giving the clay its turbostatic structure. Due to this special characteristic, MMT can be easily dispersed in water resulting in a stable colloid. Typically, the natural MMT is too hydrophilic to disperse in an organic matrix. Its dispersibility can be improved by several ways: (1) adsorption, (2) ion exchange with inorganic cations and cationic complexes, (3) ion exchange with organic cations, (4) binding of inorganic and organic anions, mainly at the edges, (5) grafting of organic compounds, (6) reaction with acids, (7) pillaring by different types of poly(hydroxy metal) cations, (8) interlamellar or intraparticle and interparticle polymerization, (9) dehydroxylation and calcinations, (10) delamination and reaggregation of smectitic clay minerals, and (11) physical treatment such as lyophilication, ultrasound, and plasma. Ion exchange with organic cations is the principle reaction to convert clay mineral to organophillic clay or organoclay.

2.4 Polymer Nanocomposite

Nanocomposites are a combination of two or more phases containing different compositions or structures, where at least one of the phases is in the nanoscale regime. These materials exhibit behavior different from conventional composite materials with microscale structure, due to the small size of the structural unit and the high surface-to-volume ratio. The properties of composite materials are greatly influenced by the degree of mixing between the two phases. In conventionally filled polymers, the constituents are immiscible. This is resulting in a coarsely blended macrocomposite with chemically distinct phases which causes a poor physical attraction between the organic and inorganic components which leads to an agglomeration of the inorganic phase, thus weakens the materials. In addition, the micrometer-size particles act as stress concentrators. In nanocomposites, chemically dissimilar components are combined at the nanometer scale and are too small to act as a stress concentrator. Stronger interactions between the polymer and silicate clay often leads to an improvement in the mechanical properties. The structure of the composites depends on the extent to which the organic and inorganic components is being made.

Depending on the nature of the components used (layered silicate, organic cation, and polymer matrix) and the method of preparation, three main types of composite maybe obtained when layered clay is associated with a polymer (Figure 2.4).

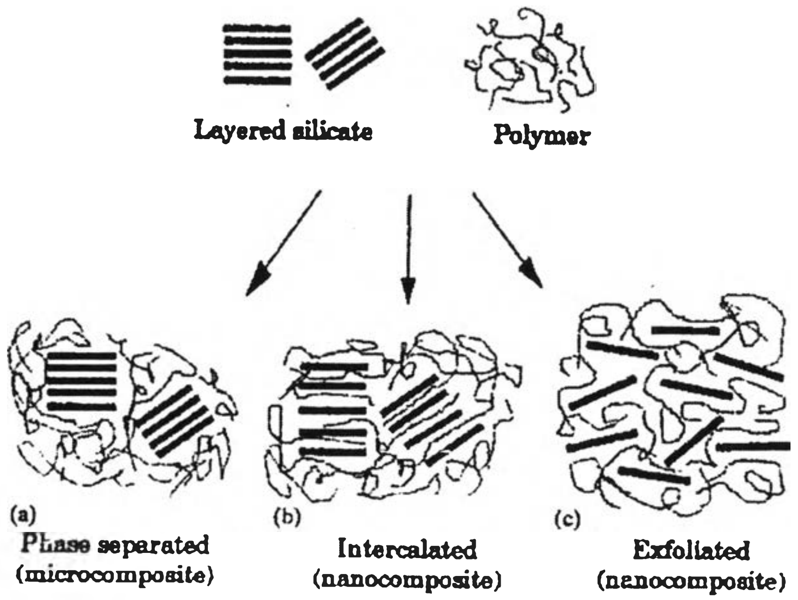

Figure 2.4 The different types of composite arising from the interaction of layered silicates and polymer.

(a) phase-separated microcomposite;
(b) intercalated nanocomposite and
(c) exfoliated nanocomposite.

Phase Separated Microcomposite

Phase separated microcomposite is where the clay acts as conventional filler. When the polymer is unable to intercalate between the silicate sheets, normal microcomposite is obtained, whose properties stay in the same range as traditional microcomposites.

Intercalated Nanocomposite

Intercalated structure in which a single (and sometimes more than one) extended polymer chain is intercalated between the silicate layers results in a well multilayer morphology built up with alternation polymeric and inorganic layers.

Exfoliated Nanocomposite

Exfoliated or delaminated structure is obtained when the silicate layers are completely and uniformly dispersed in a continuous polymer matrix.

2.4.1 Nanocomposite Preparation

Synthesis of polymer/clay nanocomposite can be carried out by one of the four methods which are exfoliation-adsorption (solution method), *in situ* polymerization, melt intercalation and template synthesis.

Exfoliation-Adsorption

The layered silicate is exfoliated into single layers using a solvent in which the polymer (or a prepolymer in case of insoluble polymers such as polyimide) is soluble. It is well known that such layered silicates, owing to the weak forces that stack the layers together, can be easily dispersed in an adequate solvent. The polymer then adsorbs onto the delaminated sheets and when the solvent is evaporated (or the mixture precipitated), the sheets reassemble, sandwiching the polymer to form, in the best case, an ordered multiplayer structure. The process also includes nanocomposites that are obtained through emulsion polymerization where the layered silicate is dispersed in the aqueous phase.

In situ Polymerization

In situ polymerization was the first method used to synthesize polymer-clay nanocomposites based on polyamide 6 in 1987 by a Toyota research group. In this technique, the layered silicate is swollen within the liquid monomer (or a solution containing monomer) so the polymer can be formed in between the intercalated sheets. Polymerization can be initiated either by heat or radiation, by the diffusion of a suitable initiator or by an organic initiator or a catalyst fixed through cationic exchange inside the interlayers prior to the reaction.

Melt Intercalation

The melt intercalation process was first reported by Vaia et al. in 1993. In this method, the layered silicate is mixed with the polymer matrix in the molten state. Under these conditions and if the layer surfaces are sufficiently compatible with the chosen polymer, the polymer can diffuse into the interlayer space and either an intercalated or an exfoliated nanocomposite results. In this technique, no solvent is required.

The melt intercalation process has become increasingly popular due simply to its great potential for industrial applications. Indeed, polymer-clay nanocomposites have been successfully produced by extrusion. A wide range of thermoplastics; from strongly polar polyamide-6 to styrene, have been intercalated between clay layers. However, polyolefins, which represent the biggest volume of polymers produced, have so far only been successfully intercalated to a limited extent.

Template Synthesis

This technique, where the silicates are formed *in situ* in an aqueous solution containing the polymer and the silicate building blocks, has been widely used for the synthesis of double-layer hydroxide-based nanocomposites, but is far less developed for layered silicates. In this technique, based on self-assembling principles, the polymer aids the nucleation and growth of the inorganic host crystals and gets trapped within the layers as they grow.

2.4.2 Characterization of Polymer-Clay Nanocomposites

There are mainly two methods to characterize the structure of polymer-clay nanocomposites. The most straightforward is X-ray diffraction (XRD) due to the capability for indirect evaluation of the interlayer spacings. The sample preparation is relatively easy and the X-ray analysis can be performed within a few hours. However, one needs to be very careful with the interpretation of the results. Lack of sensitivity of the analysis and limitation of the equipment can lead to a wrong conclusion about the nanocomposite structure. Therefore, transmission electron microscopy is a necessary complement to XRD. TEM gives a direct measure of the spatial distribution of the layers but requires substantial skills in specimen preparation and analysis.

X-Ray Diffraction

XRD is used to identify intercalated structures. In such nanocomposites, the repetitive multilayer structure is well preserved, allowing the interlayer spacing to be determined. The intercalation of the polymer chains usually increases the interlayer spacing, in comparison with the spacing of the organoclay used, leading to a shift of the diffraction peak towards lower angle values.

The scattering angle and the layer spacing are related through the Bragg's relation:

$$\lambda = 2d \sin \theta$$

where λ corresponds to the wave length of the X-ray radiation used in the diffraction experiment, d is the spacing between diffractional lattice planes and θ is the measured diffraction angle.

As far as exfoliated structure is concerned, no diffraction peaks are visible in the XRD diffractograms either because of a much too large spacing between the layers (i.e. exceeding 8 nm in the case of ordered exfoliated structure) or because of the complete disintegration of the layers.

Transmission Electron Spectroscopy

Transmission electron microscopy (TEM) is used to characterize the nanocomposite morphology. Besides these two well-defined structures, other intermediate organizations can exist presenting both intercalation and exfoliation. In this case, a broadening of the diffraction peak is often observed and one must rely on TEM observation to define the overall structure.

2.4.3 Properties of Polymer-Clay Nanocomposite

Layered silicate nanofillers have proved to trigger a tremendous property improvement of the polymers in which they are dispersed. Amongst those properties, unexpected large increase in moduli (tensile or Young's modulus and flexural modulus) of nanocomposites at filler contents sometimes as low as 1 wt.% has drawn a lot of attention. Thermal stability and fire retardancy through char formation are other interesting and widely searched properties displayed by nanocomposites. Those new materials have also been studied and applied for their superior barrier properties against gas and vapor transmission. Finally, depending on the type of polymeric materials, they can also display interesting properties in the frame of ionic conductivity or thermal expansion control.

2.5. Surfactant Structure

The word surfactant is a contraction of the term “surface-active agent”. The surfactants are among the most unique and versatile materials due to their chemical structure. Generally, these are water-soluble surface-active agents comprised of a hydrophobic portion, usually a straight or branched hydrocarbon or fluorocarbon chain containing 8-18 carbon atoms (Tadros, 1995), attached to hydrophilic or water solubility enhancing functional groups. 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.

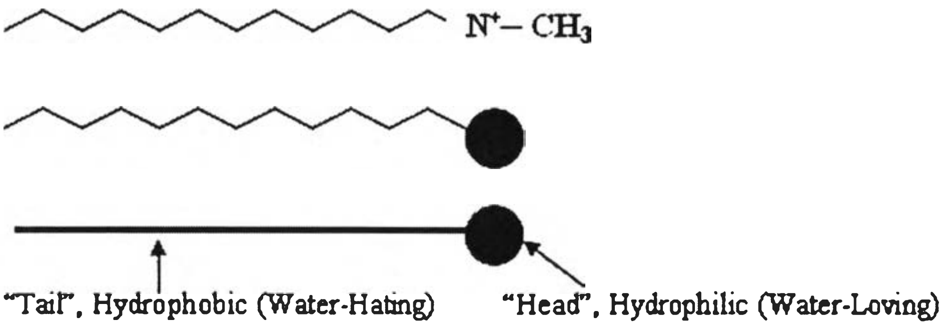

Figure 2.5 Surfactant structure.

Surfactants can be 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: surfactant molecule, whose polar group is negatively charged. Some examples are alkylbenzene sulfonate and sodium dodecylsulfate.
Nonionic surfactant: no ionic charge appears on the hydrophilic portion, some of the examples are polyoxyethylenated alkylphenol. Cationic surfactant: positive charge of the surfactant molecules is appeared on the hydrophilic portion. Some examples are quaternary ammonium chloride and laurylamine hydrochloride. Ampholytic or zwitterionic surfactant: surfactant molecule, which has both positively and negatively 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 the

solution. At low pH's (acidic solutions), they form cations. But, at high pH's (alkaline solutions), they form anions. Some examples are polyoxyethylenated alkylphenol and lauramidopropylbetaine. Normally, cationic surfactants are more expensive than anionic or nonionic surfactants (Rosen, 1989).

2.5.1 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. Cationic surfactant depends upon the chemical structure, it is possible to make a hydrophilic solid to behave as if it was hydrophobic or make hydrophobic solid to behave as if it was 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 2.6.

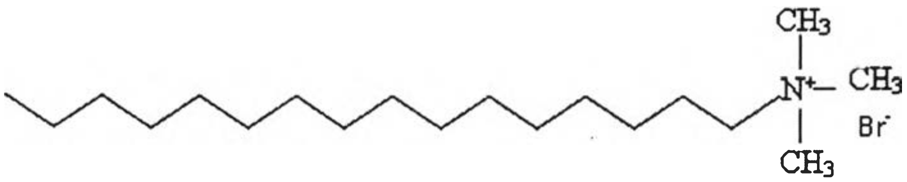

Figure 2.6 Cetyltrimethylammoniumbromide (CTAB).

Actually, fatty amine salts (or ammonium salts) were developed as the first cationic surfactants as shown in Figure 2.7. With very few exceptions, commercially available cationics are based on the nitrogen atom carrying the positive charge (Porter, 1994).

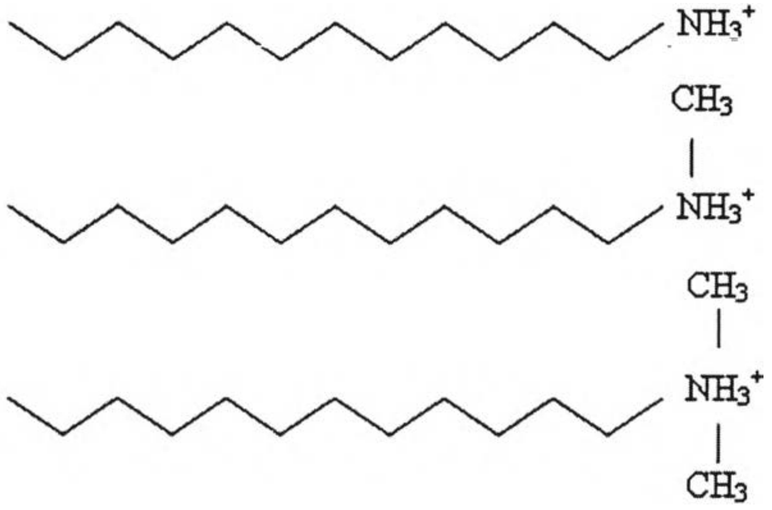

Figure 2.7 Fatty amine salts.

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 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 ($C_nH_{2n+1}(CH_3)_3NBr$) 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 at high pH conditions. As latter 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 as well as dynamic properties by minimizing the energy loss and improved silica dispersion.

2.5.2 Nonionic Surfactants

Nonionic surfactants are surface-active compounds with both head and tail are hydrophobic groups. They are good performance in hard water and with high electrolyte concentration and soluble in both water and organic solvent. Solubility decreases with increasing temperature. Terric X10 is a familiar nonionic surfactant, which is often used in biochemical applications to solubilize proteins. Terric X10 has no antimicrobial properties. It is considered as a comparatively mild detergent, non-denaturing. It is clear to slightly hazy, colorless to light yellow liquid. Terric X10 structure is shown in Figure 2.8.

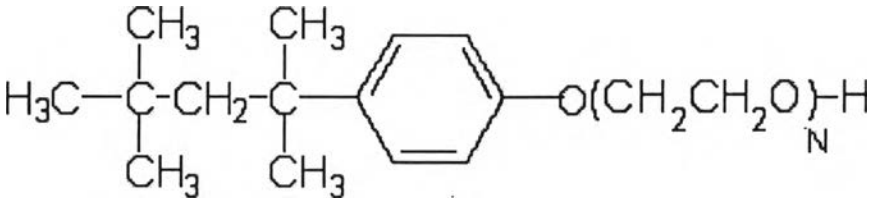

Figure 2.8 Octyl phenol ethylene oxide (Terric X10).

2.6 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 of substrate (Kitiyanan *et al.*, 1996). It involves molecular attraction at the surface as shown in Figure 2.9. 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.

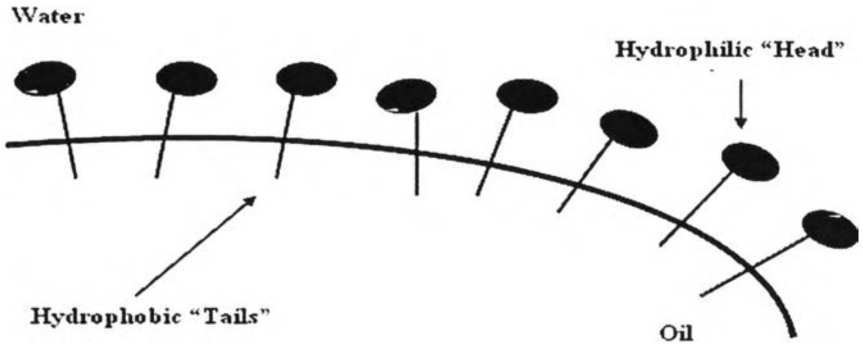

Figure 2.9 Surfactant molecules lean to adsorb to the surface of oil droplets. The hydrophilic heads expose to the water phase, while the hydrophobic tails stick into the oil phase.

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 2.10.

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 sharp increase in the slope of the isotherm relative to the slope in the Henry's Law region, indicates the beginning of the 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 tail groups of approaching surfactant ions and those of previously adsorbed surfactant, which caused the adsorbed surfactant to form a micelle like aggregate on the solid surface. The aggregation of the adsorbed surfactants are called admicelles (Harwell *et al.,* 1985) or hemimicells (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 hexposed 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 being adsorbed on the surface whereas the tail groups orienting 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 increases, the concentration, at which the transition from one type of aggregate to the other takes place, depends mainly on the 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 favor the formation of hemimicelles at lower surfactant concentration than essential for admicelles to form.

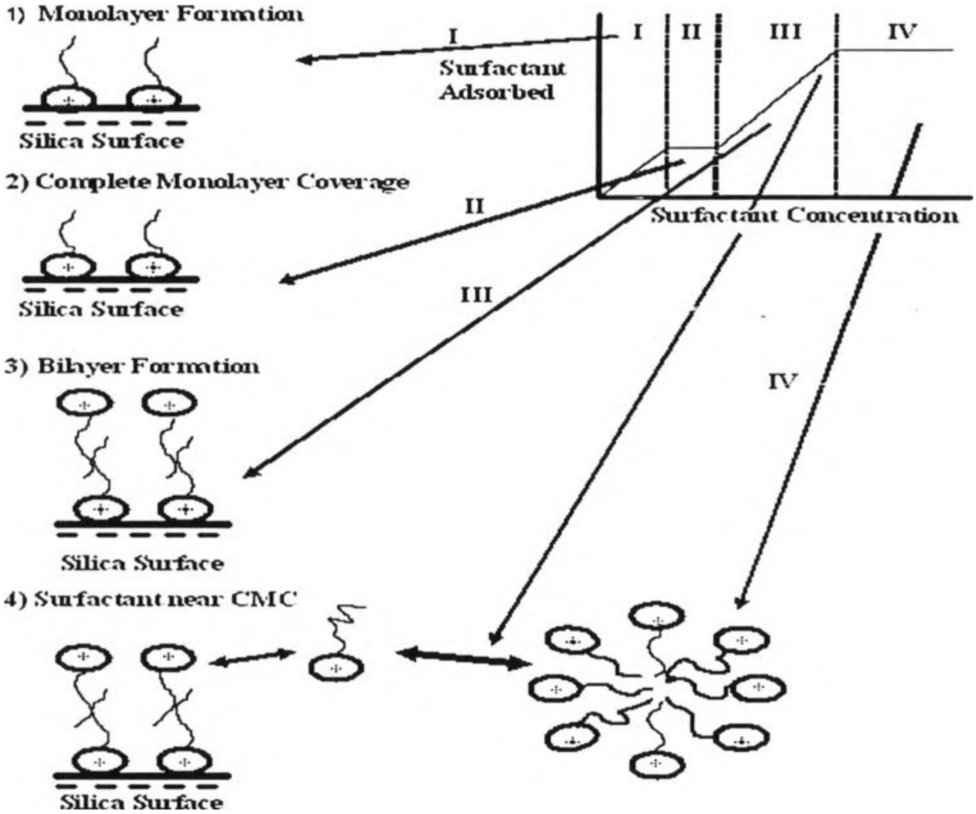

Figure 2.10 Adsorption isotherm for an ionic surfactant on an oppositely charged substrate.

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In region III, the slope of the isotherm decreases rapidly because of the competition between admicelles 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 2.11). While these patches are filled up, lower energy patches become energetically more favorable for adsorption at slightly higher equilibrium surfactant concentration.

Figure 2.11 Surfactant bilayer (www.kcpc.usyd.edu.au).

Region IV is referred to 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 2.12. The electrostatic repulsive force between the charged head groups at the surface of the aggregates is an important parameter ultimately determining the aggregation number (Sharma *et al.*, 1996).

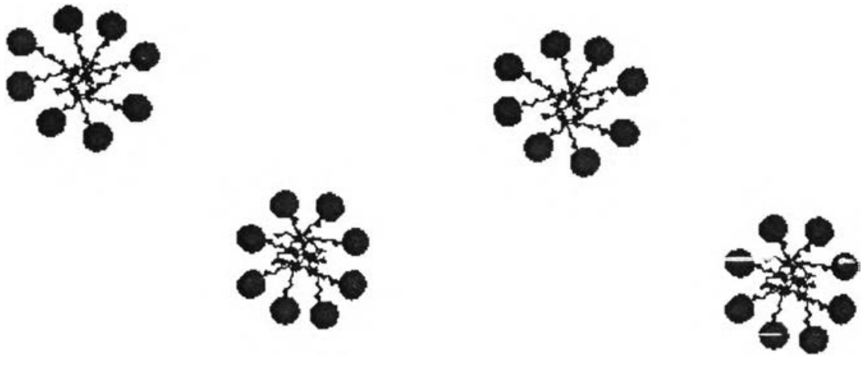


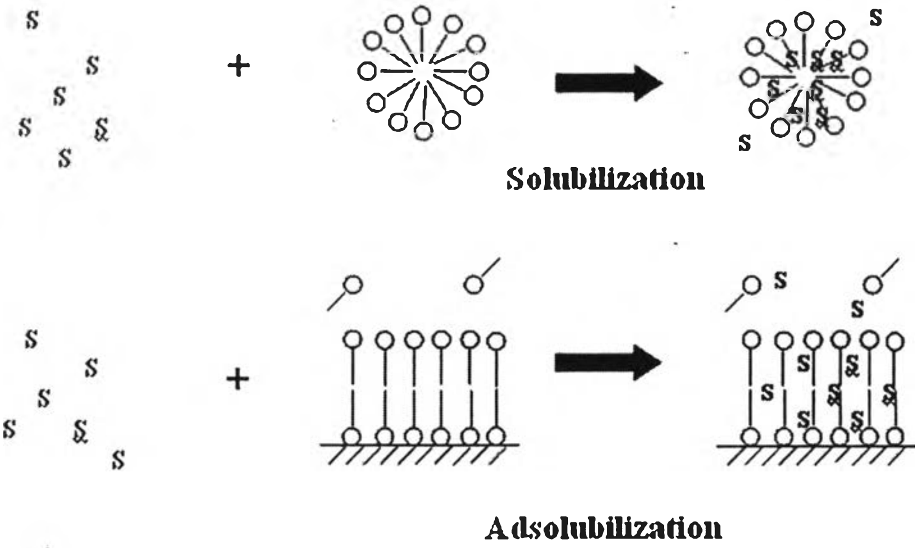
Figure 2.12 Structure of micelles (www.kcpc.usyd.edu.au).

2.7 Solubilization

Solubilization is an important property of surfactants that is directly related to the presence of micelles (Figure 2.10). 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.

2.8 Adsolubilization

Similar to the solubilization of organic molecules into micelles, organic molecules will 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 2.13 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.

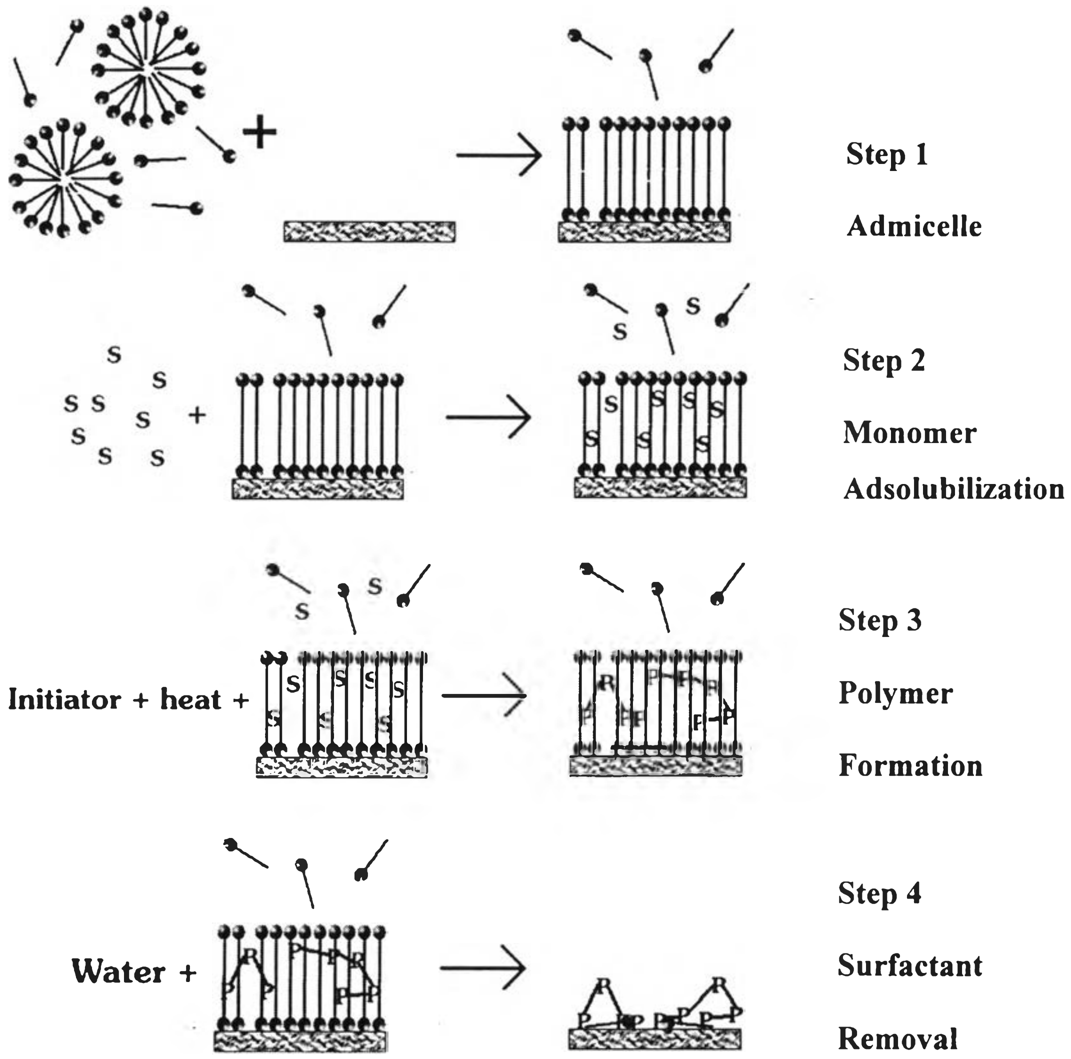
Kitiyanan *et al.* (1996) studied the adsolubilization of styrene, isoprene, and mixtures of styrene and isoprene into CTAB bilayers (admicelles) on precipitated silicas. The styrene adsolubilization constant is nearly unchanged with increasing styrene equilibrium concentration in the aqueous phase while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

2.9 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, is called admicellar polymerization (Wu *et al.*, 1987). Admicellar polymerization can be considered to occur in four basic steps as show in Figure 2.14.

Step 1 is admicelle formation by the aggregation of surfactants at solid/liquid interfaces to form bilayers (admicelles) through adsorption from an aqueous solution of surfactants. 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 admicelle or concurrently with surfactant adsorption.



“S”s represent solute molecules, monomers.

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

Figure 2.14 Admicellar polymerization process for the formation of a thin polymer film.

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 deionized water, followed by drying in a vacuum at a temperature below the boiling point of polymer.

2.10 Mixtures of Surfactants

Nonionic surfactant can enhance micelle formation with either anionic or cationic surfactants. It seem reasonable that nonionic surfactants could also enhance 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 showed 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 has been 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 appears 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/$C_{12}E_6$ and 2RenQ/ $C_{12}E_6$. In the HTAB/$C_{12}E_6$ system, the ratios of adsolubilized amount of 2-naphthol and adsorbed amount of surfactant for the mixtures of different compositions are greater than those of single surfactant systems. On the other hand, in the 2RenQ/ $C_{12}E_6$ system, the ratios for the mixtures are intermediate between those of the single surfactant systems. It is suggested that the hydrophobic properties in the mixed surfactant adsorbed layer for adsolubilization of 2-naphthol are 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.