CHAPTER II

BACKGROUND AND LITERATURE REVIEW

2.1 Adsorption of Surfactant at Solid-Liquid Interface

2.1.1 Adsorption Isotherm for Ionic Surfactants on Polar Surfaces

Adsorption isotherms are commonly seen for ionic surfactants adsorbing from aqueous solution on surfaces with a charge opposite to the charge on the surfactant. In aqueous solution, the protonation or deprotonation of chemically adsorbed water will cause the solid surface to be charged with a charge dependent on the pH value of the solution. In mildly basic environments, cationic surfactants readily adsorb onto silica; in mildly acidic environments, anionic surfactants adsorb on alumina. The adsorption isotherm of an ionic surfactant onto an oppositely charged substrate is typically an elongated sigmoid curve ('S'-shaped) when the amount of adsorbed surfactant is plotted log-log versus the equilibrium concentration of the surfactant (Scamehorn *et al.*, 1982). The shape of the isotherm is commonly subdivided into four regions, as shown in Figure 2.1.

In region I, marked by very low bulk concentration, surfactants are adsorbed by electrostatic interactions between ionic surfactants and oppositely charged substrates through ion exchange. Adsorbed surfactant molecules in this region are thought to be singly adsorbed, that is, that they do not form aggregates. This is an indicative of the absence of lateral interactions between the adsorbed surfactant molecules (Rosen, 1989).

Region II is distinguished by a rapid increase in adsorption shown as a sharp increase in the slope of the isotherm. This occurs due to hydrophobic interactions between surfactant chains. These adsorbed surfactant aggregates are called hemimicelles or admicelles, depending upon their morphology. The term hemimicelle is used to describe surfactant molecules that are arranged in a monolayer with the head group next to the surface and the tail group exposed to the solution. The term admicelle is used to describe surfactant molecules adsorbed in bilayered aggregates resembling adsorbed micelles with headgroups facing both toward the surface and into the solution (Yeskie and Harwell, 1988). The bulk

surfactant concentration at the region I-to-II transition is called the critical admicelle concentration (CAC) or the hemimicelle concentration (HMC).
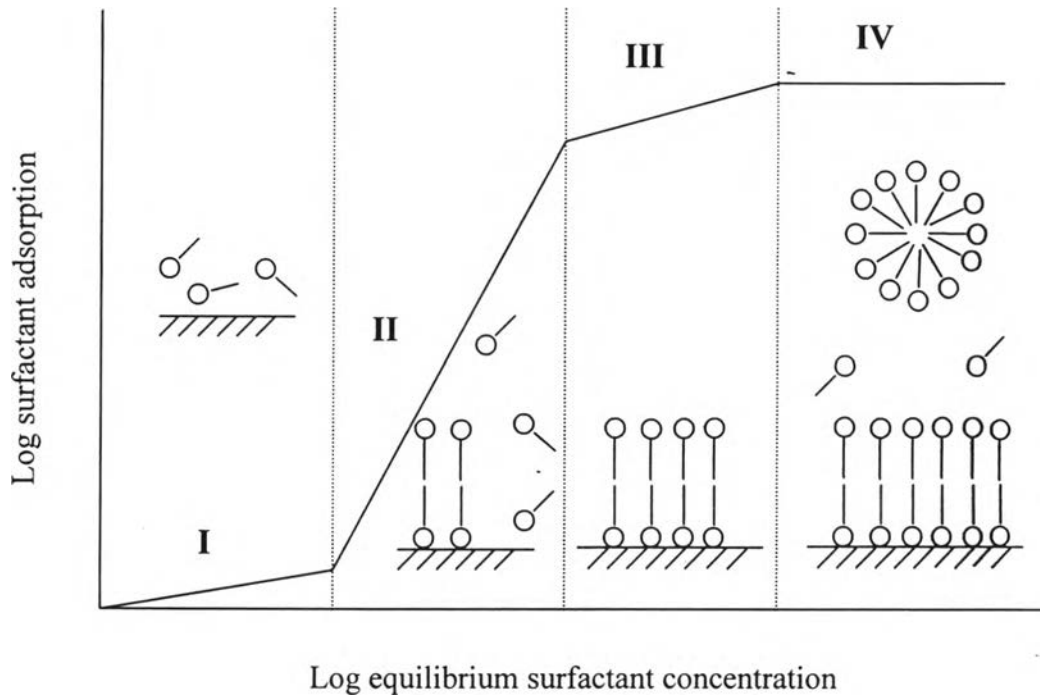

Figure 2.1 Typical adsorption isotherm of surfactant on solid oxide surface.

The slope of the isotherm decreases in region III for one perhaps two reasons, because the extent of adsorption is sufficient to neutralize the surface charge, or adsorption is now beginning on lower energy surface sites (Tiberg, 2000). This region the surfactant concentration is below the critical micelle concentration (CMC) of the surfactant. The region II-to-III transition does not always correspond to a change in the charge of the surface; however it is also noticed in systems of nonionic surfactant adsorbed on silica (Rosen, 1989).

Adsorption reaches a maximum in Region IV, having almost constant surfactant adsorption with increasing surfactant concentration. Thus, this region is often called the plateau region. The point of transition region III to region IV occurs at or near the critical micelle concentration (CMC). At the CMC, the first micelle forms at the same chemical potential as the last admicelle to form because the

chemical potential of the surfactant monomers remains nearly constant despite an increase of surfactant concentration (Holzheu *et al.*, 2000).

2.1.2 Adsorption Isotherm for Nonionic Surfactants on Polar Substrates

Adsorption isotherms of nonionic surfactants from aqueous solutions on polar substrates are sigmoidal in shape, indicative of a cooperative adsorption mechanism (Levitz and Damme, 1986). Nonionics adsorb onto these surface by hydrogen bonding, for example, polyoxyethlenated surfacatants (POE nonionics) may adsorb onto silica surfaces via hydrogen bonding between SiOH groups on the surface and the oxygens of the oxyethylene groups. On negatively charged silica surfaces, the oxygens of the POE chain may interact electrostatically with negative sites on the surface by picking up protons from the water and acquiring positive charges. Adsorption isotherms for POE nonionics are of the Langmuir type with both efficiency and effectiveness decreasing with increase in the length of POE group. The latter effect is due to the larger area occupied by the surfactant molecule at the interface as the length of the POE group is increased. At low coverage, the surfactant molecule may lie prone on the surface; at higher coverage, the hydrophobic group may be displaced from the surface by the hydrophilic group and lateral interactions between adjacent hydrophobic groups (hemimicelle formation) may occur. Maximum adsorption, which occurs near the critical micelle concentration of the surfactant, has been ascribed to both monolayer and bilayer formation (Rosen, 1989).

Kira'ly *et al.* (1997) investigated the adsorption of nonionic surfactants, n-octyl tetraethylene. glycol monoether (C_8E_4) and n-octyl β-D-monoglucoside (C_8G_1), at the hydrophilic silica glass/aqueous solution interface by simultaneous measurements of the adsorption isotherm. Both surfactants displayed pronounced cooperative adsorption behavior ('S'-shaped isotherms). While in the low-affinity region the amount adsorbed was only slightly smaller for C_8G_1 than for C_8E_4, the deviation increased to an order of magnitude in the aggregative adsorption region. The observed difference in the adsorption behavior was interpreted in terms of the different hydrophilic head groups of the two amphiphiles.

The adsorption of nonionic surfactants, alkyl (C_{Na} E_{Np}) and alkyl phenol polyoxyethylene glycol ($C_{Na}PE_{Np}$) at the solid/water interface has been studied (Levitz, 2002). He found that the reversible adsorption of nonionic surfactants occurred onto hydrophilic or polar solids below the critical micelle concentration (CMC), all adsorption isotherms reached a plateau around the CMC. This plateau amount decreased with increasing polar chain length. A step isotherm can be observed for very short polar chains, whereas for long polar chains, the adsorption isotherm appeared to have a 'Langmuir shape' with no clear inflection point. In between, typical sigmoidal isotherms that reach plateau below but near the CMC are observed. Generally speaking, adsorption appeared to be a cooperative process involving strong lateral interaction between surfactants and weak interaction with the solid surface.

A systematic study on the adsorption behavior of decylethoxylene nonyl phenol (NP-10) on silica has been carried out in order to elucidate the mechanism that governed the formation of the adsorbed layer of the nonionic surfactants (Misra *et al.*, 2005). NP-10 adsorbed on silica mainly due to hydrogen bonding and lateral alkyl chain association, the latter leading to masking of the surface potential. Effect of pH and silica-water ratio on adsorption isotherms indicated that the adsorption of NP-10 at silica-water interface resulted from the contribution of both hydrophobic and hydrophilic parts of the surfactant and the surface charge of a silica. The adsorption density of NP-10 was found to be unchanged within the range of experiment pH. The adsorption isotherms in all cases were found to be sigmoidal nature. NP-10 evolved hemimicelles of lower aggregation number at silica-water interface compared to ionic surfactants with relatively small head group, such as sodium dodecyl sulfate at alumina-water interface possibly due to size of the large polyoxyethylene head group of the former.

2.1.3 Factors Affecting Surfactant Adsorption

The adsorption of surfactants at the solid-liquid interface is strongly influenced by a number of factors:

- The nature of the structural groups on the solid surface. This factor plays an important role in determining adsorption depending on whether the surface

has highly charged sites, weakly charged sites or is nonpolar, and the nature of the atoms of which these sites or grouping are constituted.

Chorro *et al.* (1999) investigated the effect of the state of the silica surface and of the surfactant molecular structure on the adsorption of cationic surfactant onto silica. The adsorption of dodecyltrimethylammonium bromide (DTAB) and of the dimeric surfactant 12-2-12 (ethanediyl-1,2-bis (dodecyldimethylammonium bromide)) on raw silica (SiNa) and on HCl washed silica (SiH) has been studied under "free" system conditions. The results showed that the amount of surfactant adsorbed at the point of zero charge and at saturation of silica particle, the sodium ions released by the surface and the decreased in CMC of the supernatant with respect to pure water were all larger for the raw silica than for the treated silica.

- The molecular structure of the surfactant being adsorbed. The properties of surfactants, which determine the adsorption, are as follow: (1) number and length of hydrocarbon chain; (2) branching and double bonds present in hydrocarbon chain; (3) presence of polar ionic group; (4) the cross section area of the polar group; and (5) the orientation of the chains with respect to one another and the surface (Dixit *et al.*, 2002).

For example, Esumi *et al.* (1996) studied the adsorption of quaternary ammonium cationic surfactant with one, two, or three alkyl chains on silica has been studied by measuring adsorption density and dispersion stability. The adsorbed amounts at saturation decreased with increasing chain number of the surfactants because of the structure of the double-chain or triple-chain surfactant in the adsorbed layer on silica was different from that of the single-chain surfactant: the molecular packing of the multi-chain surfactants was higher, and the desorption of these surfactants was hardly observed compared with those of single-chain surfactant.

- The environment of the aqueous phase-its pH, its electrolyte content, the presence of any additives such as short-chain polar solutes (alcohol, urea, etc.), and its temperature. Together these factors determine the mechanism by which adsorption occurs, and the efficiency and effectiveness of adsorption (Rosen, 1989).

The effect of added salt on adsorption and adsolubilization by a dimeric (1, 2-bis (dodecyldimethylammonio) ethane dibromide, 2RenQ) on silica

from its aqueous solution has been investigated (Esumi *et al.*, 1996). They found that the adsorption of 2RenQ on silica was enhanced by increasing amount of added NaBr but the ratios of adsolubilized amount of 2-naphthol/adsorbed amount of 2RenQ at maximum adsolubilization decreased with increasing NaBr concentration. This result can be related to the packing of 2RenQ molecules in the adsorbed layer.

2.1.4 Adsorption of Single Surfactant

The adsorption of a number of surfactants, including cationic, anionic, and nonionic surfactants, has been studied on solid oxide surfaces.

For example, adsorption isotherms for three isomerically pure alkylbenzene sulfonates on alumina and kaolinite from aqueous solutions were examined (Scamehorn *et al.*, 1981). A patchwise adsorption model, which incorporated bilayer adsorption, lateral interactions, and two-dimensional phase transitions, was developed and showed to describe the observed isotherms below the CMC. As expected, Henry's law describes the adsorption at sufficiently low surfactant concentrations. In this region, only unassociated, first layer, surfactant molecules were present on the surface in addition to the charged head surface electrostatic attraction. The adsorption increased rapidly beyond a certain concentration. At this concentration, hemimicelles resulting from lateral interaction between adsorbed surfactants first appeared on the most energetic surface patches. At still higher concentrations, successively less energetic patches were sites for two-dimensional phase transitions forming hemimicelles. Above the CMC, adsorption was independent of concentration. This indicated that micelles did not adsorb significantly and that the pseudo-phase separation model was a good approximation for these systems.

Yeskie and Harwell (1988) investigated the structure of the adsorbed surfactant aggregates, focusing on the surface charge density at the hemimicelle/admicelle transition. They found that surfactants adsorbed from aqueous solution onto mineral oxide surface formed micelle-like aggregates at the interface. It has long been viewed that at low coverage these surfactant aggregates

were principally in the form of monolayers, formed on patches of the surface. Individual surfactant molecules or monomers in these aggregates were viewed as being oriented such that the hydrophilic groups of the surfactants were next to the surface, with the surfactant tail groups forming a hydrophilic film in contact with the aqueous solution. Aggregates of this structure were commonly referred to as hemimicelles while it has been proposed that a bilayered aggregate, termed an admicelle, was formed (Scamehorn *et al.*, 1981).

The adsorption of cationic surfactant, dodecyl pyridinium chloride, on monodisperse porous silica in an aqueous solution has been studied as a function of pH and electrolyte concentration. It was concluded that the proton charges of these silica particles can be distinguished in charges on the outer surface, charges in the mesopores and charges in a microporous region. From a comparison with the adsorption on non-porous silica it was concluded that dodecyl pyridinium cations can penetrate the mesopores, but were excluded from the (highly charged) microporous region. On the outer surface, adsorption of cationic surfactant led to a maximum in a hydrophobicity at about 50% of the maximally adsorbed amount. Charge reversal has already taken place at about 10% of the plateau value. It was concluded that, after charge reversal, head-on adsorption proceeded until monolayer coverage, after which bilayer formation sets in (Szekeres *et al.*, 1998).

The adsorption of ionic surfactants on titanium dioxide with dodecyl chain groups or quaternary ammonium groups (XNm, where m is the carbon number of alkyl chain, 4-16) was studied (Esumi, 2001). The result showed that the adsorbed amount of cationic surfactants (dodecyltrimethylammonium bromide, DTAB; 1,2-bis(dodecyldimethylammonio)ethane dibromide, 2RenQ) on titanium dioxide with dodecyl chain groups increased with increasing concentration of the dodecyl chain due to hydrophobic interaction, where the adsorbed amounts of DTAB at saturation was considerably greater than those of 2RenQ. Adsorption of an anionic surfactant (sodium dodecyl sulfate, SDS) on XNm occurred mainly due to both electrostatic attraction force and hydrophobic interaction, depending on the alkyl chain length on XNm. On the other hand, adsorption of cationic surfactants, DTAC and 2RenQCl (their counter ions are chloride ions), on XNm was quite smaller compared with that of SDS due to electrostatic repulsion force.

Fleming *et ai.* (2001) studied the organization of cationic surfactant, hexadecyltrimethylammonium bromide (CTAB) to silica from solution far below the CMC by using optical reflectometry and AFM. The results have been shown that the lower critical surface aggregation concentration, CSAC, results from the increased surface charge of the silica. This confirms that a threshold surface concentration of adsorbed surfactant was required to initiate surface aggregation. Specifically, on silica an adsorbed density must be sufficient for hydrophobic interactions between neighboring adsorbates. This promoted adsorption beyond that required to balance the surface charge, and hence the formation of surface aggregates. In addition, slow adsorption was observed did not a simple function of the bulk surfactant concentration, but rather a complex function of surface charge characteristics in the case of oppositely charged surfactants adsorbed to silica.

González-Garciá *et al.* (2004) studied the adsorption of nonionic surfactants, TX-100, TX-305, and TX-405 with a different length of the hydrophilic tail on activated carbon over a wide concentration range. Adsorption isotherms showed a two-step increase which was limited at the critical micelle concentration (CMC) of the surfactants. The adsorption depended on the oxyethylenic chain length in such way that the amount adsorbed decreased with increasing the chain length (TX-100>TX-305>TX-405), although the effect was much lower for the longest polar chains. In the concentration range below the CMC of the surfactant, the molecules were adsorbed by direct interactions with the activated carbon surface, but different configuration of the polyoxyethylene chain (POE) directed to the aqueous phase. For concentrations above the CMC, the adsorption took place by the interactions between the adsorbed surfactants molecules and differences related to the length of the hydrophilic chain.

2.1.5 Adsorption of Mixed Surfactants

Mixed surfactant adsorption from aqueous solution onto solids includes the adsorption of binary mixtures of anionic surfactants, anionic-nonionic surfactants, and cationic-nonionic surfactants. Mixed surfactant systems have gained increasing interest since the adsorption of one surfactant is often enhanced by addition of a small amount of the other surfactant. Mixed surfactants are widely used

in industry since they can in most cases provide superior performance for specific applications over single surfactant systems. The adsorption of mixed surfactant systems on solids can be controlled using appropriate surfactant and solution properties (Esumi *et al.*, 2000).

For example, the adsorption of ethoxylated octyl phenol (Triton X-100 and Triton X-305) and cetyltrimethylammonium bromide (CTAB) from their single and mixed aqueous solutions on silica gel and methylated silica gel has been investigated (Huang and Gu, 1987). They found that the adsorption from mixed solutions of CTAB/Triton X-100 or CTAB/Triton X-305 on silica gel exhibited a synergistic effect at low concentrations and an antagonistic effect at high concentrations, but the effects were less pronounced for the latter system. It was suggested that the synergistic effect was due to the additional interaction between the hydrocarbon chains of adsorbed Triton X- molecules and adsorbed CTA^+ ions. The antagonistic effect, which occurs at high concentrations, was believed to result from the formation of mixed micelles in the bulk solution. In contrast with that on the silica gel, the adsorption from mixed solution of Triton X-100/CTAB on methylated silica gel showed no synergistic effect at low concentrations since the CTA^+ ions were not adsorbed. At high concentrations, although the adsorption of Triton X-100 was obviously depressed in the presence of CTAB, the adsorption of CTA^+ ion became significant in the presence of Triton X-100. It was suggested, as above, that the decrease in the adsorption of Triton X-100 was due to the formation of Triton X-100/CTA^+ mixed micelles in the bulk solution. At high concentrations of Triton X-100, some CTA^+ ions may be incorporated into the adsorbed Triton X-100 layer by the hydrophobic interaction between neighboring hydrophobes (surface solubilization). However, the results showed that neither Triton X-305 nor CTAB were adsorbed onto methylated silica gel either from their respective single solution or from their mixed solution.

The adsorption of dodecyltrimethylammonium bromide (DTAB), dodecylpyridinium bromide (DPB), sodium dodecylbenzenesulfonate (SDBS), and sodium dodecyl sulfate (SDS) from their single aqueous solutions and DTAB-SDBS and DPB-SDS binary mixed solutions on silica gel has been investigated (Huang *et al.*, 1989). They found that the individual cationic surfactants can be adsorbed

strongly onto the silica gel, but no significant adsorption of anionic surfactants can be detected. However, in the mixed systems, the adsorption amounts of both the cationic and anionic surfactant ions were enhanced, and the excess adsorption of cationic surface-active ions was exactly equal to the adsorption of anionic surface-active ions. Thus, it was reasonable to suggest that the excess adsorption of cationic and anionic surface-active ions was in the form of ion-pairs.

Xu *et al.* (1991) studied the mixed surfactants adsorption from dodecyl trimethylammonium chloride (DTAC) as a cationic and octaethylene glycol *mono-n*-decyl trimethyl ammonium chloride as nonionic on sodium kaolinite surface. The results from below CMC showed that the adsorption of cationic surfactant increased in the presence of nonionic surfactant whereas above the CMC the adsorption level of the cationic surfactant decreased with increasing in the mole fraction of nonionic surfactant. The decrease adsorption of cationic surfactant has been attributed to the formation of mixed micelles of cationic and nonionic surfactant.

The adsorption of the mixed cationic and nonionic surfactants of hexadecyltrimethylammonium bromide ($C_{16}TAB$) and hexaethylene glycol monododecyl ether ($C_{12}E_6$) at the hydrophilic silicon-solution interface has been measured by specular neutron reflection. The effect of solution composition and concentration on the adsorbed amount, surface structure, and composition has been investigated. The results showed that the variation in surface composition with solution composition revealed the role of the different specific interactions of the two surfactants with the solid surface which the adsorbed amount was a maximum at an equimolar solution composition. For cationic-rich solutions, the surface and solution compositions were identical (consistent with ideal mixing). Whereas for nonionic-rich solutions, the surface was richer in cationic surfactant, reflecting the greater affinity of the cationic for that surface (Penfold *et al.*, 2000).

Dixit *et al.* (2002) studied co-adsorption by using mixed quaternary ammonium compounds CTAB, TTAB and nonyl phenyl ethoxylates (NP13, NP20, NP30). Three solid substrates, quartz, polystyrene and PTFE were chosen for investigation. They found that the 'S' shaped adsorption isotherms were obtained in the case of all the three substrates. The presence of nonionics had varied effects on

the adsorption of CTAB/DTAB depending on concentration which in all the cases the adsorption of CTAB was increased due to the presence of nonionics, NP_n in the pre-plateau region. Similarly there was a decrease in the adsorption of CTAB in the plateau region in all case of all the substrates due to mixed micellization.

The structure and composition of the mixed anionic and nonionic surfactants adsorbed at the hydrophilic silicon solid-solution interface was studied by Penfold *et al.* (2002). This study showed that the anionic surfactant sodium dodecyl sulfate (SDS) alone did not adsorb at the hydrophilic silicon-solution interface. In the presence of the nonionic surfactant hexaethylene glycol monododecyl ether ($C_{12}E_6$), co-adsorption was observed for solutions rich in $C_{12}E_6$. The adsorbed amount and mole fraction of SDS decreased markedly with increasing mole fraction of SDS in solution, and for solutions richer than equimolar there was little surfactant adsorption at the interface. The adsorption of SDS at the interface in the presence $C_{12}E_6$ was due to the synergistic interaction between the two surfactants.

2.2 Solubilization and Adsolubilization

2.2.1 Fundamentals

Solubilization is defined as the spontaneous dissolving of a substance (solid, liquid or gas) by reversible interaction with the micelle of the surfactant in a solvent to form a thermodynamically stable isotropic solution with reduced thermodynamic activity of the solubilized material (Rosen, 1989). A micelle is a transient aggregate of 10 to 100 surfactant molecules. The concentration of surfactant at which micelles begin to form is called critical micelle concentration (CMC); the CMC is a function of the structure of the surfactant, the temperature of the surfactant solution, the concentration of added electrolytes, and the concentration of solubilizates and other amphiphiles (Harwell, 1991).

For example, Zhu and Feng (2003) investigated the solubilization of polycyclic aromatic hydrocarbons (PAHs) by mixed anionic-nonionic surfactants. In single surfactant system, solubilities of PAHs in water were greatly enhanced in a linear fashion by the addition of TX100, TX305, Brij 35, and sodium dodecyl sulfate (SDS). Solubility enhancement efficiencies of surfactants above CMC follow the

order of TX100 > Brij 35 > TX305 > SDS. PAHs were solubilized synergistically in mixed anionic-cationic surfactant solutions, especially at low surfactant concentrations. The synergistic power of the mixed surfactants was SDS-TX305 > SDS-Brij 35 > SDS-TX100.

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). Factors influencing adsolubilization behavior are as follow: (a) surfactant structure; (b) kind of water-insoluble compound; and (c) kind of particles. The adsolubilization phenomenon is the surface analog of solubilization, with adsorbed surfactant aggregate taking the place of micelle, as shown in Figure 2.2.
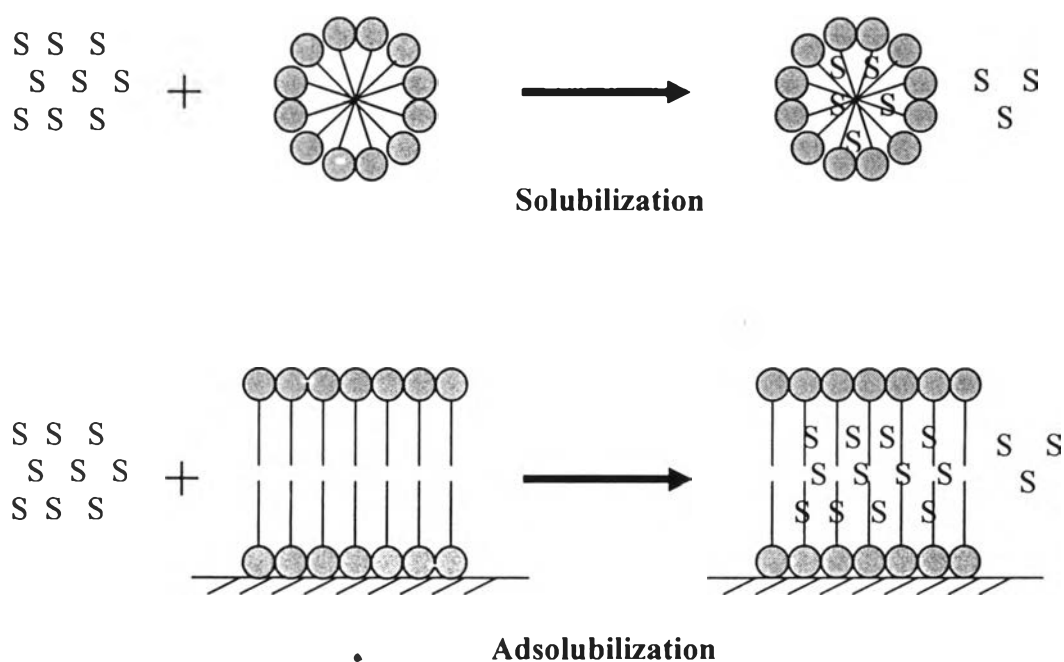

Figure 2.2 The phenomena of solubilization and adsolubilization (Dickson and O'Haver, 2002).

2.2.2 Effect of Nature of Organic Compounds on Adsolubilization Behavior

Surfactants adsorbed on a solid surface can be used to increase the sorption of organic compounds. There are basically three locations within an

admicelle where contaminants may be adsolubilized: the polar head region, the hydrophobic core region which this region consists of the hydrocarbon chains and is nonpolar in nature, and the so-called "palisade region" which is intermediate in polarity (Dickson and O'Haver, 2002), as shown in Figure 2.3.
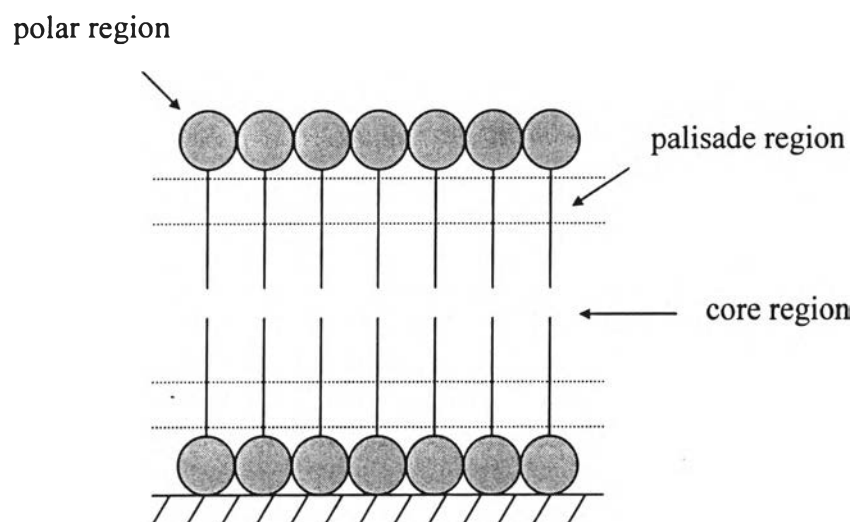

Figure 2.3 The admicelle structure.

Surfactant aggregates on solid/liquid interface, admicelles, are capable of removing hydrophobic organic compounds from solution (benzene, toluene, etc.) and enjoy a higher selectivity over other conventional technologies such as filtration and activated carbon adsorption (Lee, 2002). The location or combination of locations within the admicelle at which a particular contaminant will be adsolubilized depends primarily on the water solubility of the contaminant molecules and the structure of the compound. When the contaminant is non-polar and has low solubility in water, such as the alkanes or other hydrophobic organic compounds are preferentially adsorbed in the core region of surfactant aggregates, whereas the polar organic compounds stay in the palisade layer or at the interface between surfactant aggregate and aqueous solution.

As mentioned, it has been suggested that partition coefficients can be used to elucidate the locus of adsolubilization in admicelles. The following trends have been observed concerning the locus of adsolubilization and partition

coefficients: (1) if the solute partitions primarily to the core, the partition coefficients will increase as the mole fraction of the adsolubilizate increases; (2) if the solute partitions primarily to the palisade region, the partition coefficients will decrease as the mole fraction of the adsolubilizate increases; and (3) if the solute partitions to both the core and the palisade, the partition coefficients will remain constant as the mole fraction of the adsolubilizate increases (Harwell, 1991).

For example, Kitiyanan *et al.* (1996) studied the adsolubilization isotherms for styrene and isoprene into cetyltrimethylammonium bromide (CTAB) bilayers (admicelles) on precipitated silica. The results showed that the partition coefficients for styrene remained constant while the mole fraction of styrene increased, and the partition coefficients for isoprene decreased with increasing mole fraction of isoprene. The study concluded that styrene partition to both the palisade and core regions, while isoprene adsolubilizes into palisade region.

The adsolubilization capabilities and stability of the bonded octadecyltrichlorosilane (ODS) were evaluated and compared to those of physically adsorbed aggregates of cetyltrimethylammonium bromide (CTAB) on porous silica were studied. The adsolubilization of two organic solutes, trichloroethylene (TCE) and phenol, was also measured. Both bonded ODS and CTAB admicelles on silica showed almost the same trend in adsolubilzation of TCE due to the nonpolar property of TCE, while the phenol adsolubilized to a greater extent in CTAB than in bonded ODS may be due to interaction of the polar phenol with the palisade layer of the CTAB admicelles, which palisade layer did not exist in the bonded (Thakulsukanant *et al.*, 1997).

Holuzheu *et al.* (2000) investigated the distribution ratios of aromatic compounds between aqueous solution and surfactant-covered silica by chromatographic method. In this work equilibrium constants of 26 aromatic compounds were determined as a function of pH and of the adsorption density of hexadecyltrimethylammonium bromide (HDTMAB) on silica. Formation of core regions in the surfactant aggregates due to hydrophobic aggregation favors adsolubilization of non-polar compounds. At the same time equilibrium constants of

polar organic compounds decreased because of the reduced interfacial area per surfactant molecule

The adsolubilization of the organic compounds, toluene and acetophenone into CTAB admicelles on precipitated silica as a function of ionic strength was investigated (Kanjanakhunthakul, 2002). It was observed that, for toluene, the partition coefficient decreased with increasing ionic strength. In contrast, the partition coefficient of acetophenone increased with increasing ionic strength. This may be due to the difference in the polarity of the two solutes and also the difference in the structural characteristics of the adsorbed CTAB on silica surface at different ionic strength. At the partition coefficient (K) predicted that location adsolubilization for acetophenone was in the palisade regions, while toluene was both the core and palisade regions.

Dickson and O'Haver (2002) investigated the adsolubilization of naphthalene and α-naphthol with have the similar structures but different in polarities in C_nTAB (n=12, 14, 16) admicelles. They investigated the adsolubilization capacities of the core and palisade regions within the admicelle and their interactions within the admicelle. The partition coefficients for α-naphthol remained constant as the mole fraction of α-naphthol in the admicelle increased, implying that α-naphthol adsolubilized to both the core and palisade regions. The partition coefficients for naphthalene in the $C_{16}TAB$ and $C_{12}TAB$ system remain essentially constant as the mole fraction in the admicelle increased due to the intermediate polarity of naphthalene, indicating that naphthalene adsolubilized to both the core and palisade regions. In the $C_{14}TAB$ system, the partition coefficient increased slightly as the mole fraction of naphthalene in the admicelle increased. This increase in the partition coefficient implied that the component was partitioning primarily to the core of admicelles.

2.2.3 Adsolubilization in Single-surfactant and Mixed-Surfactant Systems

2.2.3.1 Single-Surfactant System

The adsolubilization of phenoxyalcohols and four cationic surfactants with various headgroups at the silica/water interface as a function of both

solute and surfactant concentration was investigated by Monticone and Treiner (1994). The necessary adsorption isotherms of the cationic surfactants hexadecylpyridinium, trimethyltetradecyl, trimethyexadecylammonium bromides, and benzyldimethyltetradecylammonium chlorides on silica have also been studied at low pH and ionic force. It was showed in the case of phenoxyalcohols that the adsorption profile of the solutes was very similar to that of the surfactants: at low alcohol concentration a plateau adsorption was observed followed by a rapid increase of adsolubilization above a solute threshold concentration and a new plateau at higher concentration. This type of isotherm was obtained at low surfactant concentration and may be fitted with the same theoretical adsorption isotherms as the cationic surfactants.

Lai *et al.* (1997) studied the adsolubilization of small aliphatic fluorocarbon alcohols into perfluoroheptanoate admicelle formed on alumina. They found that at low fluorocarbon surfactant adsorption, the high ratios of fluorocarbon alcohols adsolubilizated to fluorocarbon surfactant adsorbed. Higher concentrations and increasing hydrophobicity of the adsolubilizate enhanced surfactant adsorption below the plateau region. Partitioned amounts of the fluorocarbon alcohols rose with the alcohol supernatant concentration and chain length. The above results led to the conclusion that the two-site adsolubilization, which seems to be reasonable by the estimates of aggregation numbers with linear relation to adsorption densities.

Wang *et al.* (1999) studied the adsolubilization of 2-naphthol by tetradecyltrimethylammonium bromide (TTAB) and by mixtures of TTAB and hydrophobically modified polyacrylamide (HMPAM) on Na-kaolinite. It was found that the presence of HMPAM strongly affects the amounts of 2-naphthol adsolubilized onto the clay surface. At high TTAB concentrations, the adsolubilization efficiency of 2-naphthol by the mixture did not higher than with TTAB alone. At lower TTAB concentrations, however, the amount of 2-naphthol adsolubilized was much higher in the presence of HMPAM than in the absence of HMPAM, at a given concentration of TTAB. Finally, the degree of clay dispersion was greatly influenced by the presence of HMPAM.

The impact of lipophilic linkers (long chain linear alcohols) on the adsorption of and styrene adsolubilization in polyethyoxylated alkylphenols

(Triton X) nonionic surfactants with varying EO units on amorphous precipitated silica was also investigated (Tan and O'Haver, 2004). The study showed that the presence of lipophilic linkers increased both surfactant adsorption and styrene adsolubilization. The adsolubilization capacity of surfactants increased, up to a certain value, with increasing lipophilic linkers tail length or concentration. Styrene adsolubilization decreased with increasing numbers of ethyoxylated (EO) units in the surfactant, especially at higher styrene loading levels. The enhancement of adsorption and styrene adsolubilization was thought to be caused by the linkers increasing interactions between styrene and surfactant hydrophobic groups. Partition coefficient data supports initial styrene adsolubilization into both the palisade and core regions of the admicelles while at higher concentrations it appears to go primarily into core. Styrene adsolubilization increased with increasing styrene bulk concentration, as did the ratio of adsolubilized styrene.

2.2.3.2 Mixed-Surfactants System

The behavior of a mixture is often quite different from that of a single surfactant, and in most case of synergistic effect. Mixed surfactants give various advantages over single surfactant system due to lower quantities of surfactants needed to achieve the same effect or performance. As a result, applications include detergency, fabric conditioning, dyeing and mineral floatation among many.

For example, Esumi *et al.* (2000) examined the adsolubilization of 2-naphthol by surfactant mixtures of an anionic surfactant, sodium dodecyl sulfate (SDS), and a nonionic surfactant, hexaoxyethylenedodecyl ether ($C_{10}E_6$) on alumina. They showed complex behavior compared to those obtained with a single surfactant system. In single-surfactant system, only the anionic surfactant was found to show an appreciable adsolubilization. In the mixed-surfactants system, the adsolubilization grew with an increase in the total amount of adsorbed surfactant, whereas the adsolubilization became greater with an increase in the anionic surfactant content in the initial mixtures. Thus, surfactant mixtures of anionic and nonionic surfactants with low concentrations have great possibilities for enhancing adsolubilization of solutes.

Subsequently, Esumi *et al.* (2001) investigated the adsolubilization of 2-naphthol by binary mixtures of cationic surfactants, 1, 2-bis (dodecyldimethylammonio) ethane dibromides (2RenQ) and hexadecyltrimethylammonium bromide (HTAB) and nonionic surfactant, hexaoxyethylenedecyl ether ($C_{10}E_6$) on silica. In the single surfactant systems, adsolubilization of 2-naphthol for HTAB and 2RenQ was similar and was greater than that for $C_{10}E_6$. In the HTAB/$C_{10}E_6$ system, the ratios of adsolubilized amount of 2-naphthol and adsorbed amount of surfactant for the mixtures of different compositions were greater than those of the single surfactant systems. However, in the 2RenQ/$C_{10}E_6$ system the ratios for mixtures were intermediate between those of single surfactant systems. It was suggested that the hydrophobic properties in the mixed surfactant adsorbed layer for adsolubilization of 2-naphthol were effected by the structure of cationic surfactant.

2.3 Effect of pH on Adsorption and Adsolubilization

The adsorption of surfactants depends on many parameters such as the type of surfactant molecule, the electrochemical nature of the substrate, and the pH value of the solution. Adjusting the pH value of the contacting aqueous solution can change the charge on solid oxide surface to be either positive or negative because both hydrogen (H^+) and hydroxyl (OH^-) ions are potential determining ions of mineral oxides. The pH value that makes the charge on the solid oxide surface equal zero is called the point of zero charge (PZC). When the pH of the contacting aqueous solution is below the PZC of the solid oxide surface, the surface will be protonated and positively charged, with consequent increase in the adsorption of anionic surfactants and decrease in the adsorption of cationic. The reverse is true when the pH above the PZC. These effects are showed markedly for mineral oxide, such as silica and alumina, and by wool and other polyamide. Change in the pH also may affects surfactant molecules, notably those containing carboxylate group (soap) or nonquaternary ammonium group. In these cases, change in pH may convert the surfactant from one containing an ionic group capable of strong adsorption onto oppositely charged sites on the adsorbent to a neutral molecule capable of adsorption

only through hydrogen bonding or dispersion forces. Change in pH also may affect nonionic surfactants, notably those having polyoxyethylene chain, because the ether linkage in these chains can be protonated at low pH, yielding positively charged grouping that may adsorb onto negatively charged substrate.

Sharma *et al.* (1996) investigated the morphology of adsorbed cationic surfactant, cetyltrimethylammonium bromide (CTAB), on mica. It appeared that at low CTAB concentration and low pH values, discrete aggregates of adsorbed surfactants were found on the surface. As the surfactant concentration was increased, these aggregates become more organized into elongated cylindrical shapes. The continuity of the network of patches increased until a concentration just below the CMC. At this concentration, the patches became continuous wormlike admicelle on the surface. It was clear that the formation of dense continuous monolayers or bilayers did not occur as postulated earlier. Indeed observations suggested the formation of discrete surfactant aggregates on the surface which under certain conditions (high pH and high surfactant concentration) became continuous and formed wormlike admicelles on the mica surface. This change in surfactant morphology from adsorbed surfactant aggregates to more continuous structures was also responsible for the transition from hydrophilic to hydrophobic surface properties. It was also showed that pH and salt concentration played an important role in this transition.

In 2001, Atkin *et al.* investigated the effect of pH, electrolyte, and surface preparation on the surface excess of cetylpyridinium bromide to the silica by using optical reflectometry and AFM. At concentrations around the critical surface aggregation concentration (CSAC), adsorption proceeded slowly in the absence of salt and taken hours to reach an equilibrium value. At all other concentrations and even at the CSAC when electrolyte was presented, the adsorption was completed within minutes. At moderate to high surfactant concentration with added electrolyte, pH increased has little effect on surface excess. In increases were primarily due to increased solution ionic strength and not due to increased charge on the substrate. At low surfactant concentrations, added cations complete effectively with the cationic surfactant for adsorption sites, resulting in no detectable adsorption until a pH ~8 was reached.

The adsolubilization of anthracene on hexadecyltrimethylammonium (HDTMA) cationic surfactant covered silica as a function of pH was studied by Behrends and Hermann (2000). This work indicated that the partitioning constant, K, normalized on the content of organic carbon in the surfactant coverage did not only a function of the surface concentration but also depends on pH. At low concentrations of adsorbed HDTMA no adsolubilization of anthacene was measured.

Pradubmook (2001) investigated the effect of pH on adsolubilization of toluene and acetophenone into adsorbed surfactant on precipitated silica. Both single-solute and mixed-solute systems were investigated using batch liquid adsorption at pH 5 and pH 8. The results from the adsorption of CTAB revealed that increasing pH led to high amounts of surfactant adsorbed on the precipitated silica. For toluene, pH appeared to have little effect on the adsolubilization. In contrast, the pH effect was more pronounced in the case of acetophenone as indicated by significant increased in the acetophenone adsolubilization when pH was increased from 5 to 8.

The adsolubilization of 4-nitrophenol at a kaolinite/water interface as a function of pH and surfactant surface coverage was investigated by Talbot *et al.* (2003). It was observed that the solute was incorporated into the adsorbed surfactant aggregates as neutral species at low pH. As the pH was raised, the adsolubilization increased slightly as the result of the dissociation of the weak acid studied. At low surfactant concentration: the adsolubilization decreased with increasing pH as the result of the repulsive interaction between the deprotonated solute molecule and the negatively charged sites on kaolinite particles. At high surfactant concentrations increasing pH induced increased adsolubilization as a consequence of the favorable interaction which took place between the deprotonated weak acid and the positively charged surface surfactant aggregated. Hence, depending upon the extent of surface coverage, increasing the pH may retain 4-nitrophenol at the kaolinite/water interface or reject it into the bulk micellar solution.

Okamoto *et al.* (2004) reported that the adsolubilization of 2-naphthol, biphenyl, and their binary solutes in the hexadecyltrimethyl ammonium bromide (HTAB) adsorbed layer formed on silica was significantly affected by the feed concentration of HTAB and solution pH. At the low feed concentrations of HTAB,

competitive adsolubilization between 2-naphthol and biphenyl was observed at above pH 4.5. In contrast, the adsolubilization of biphenyl was clearly enhanced over the whole region by incorporation of 2-naphthol at a high feed concentration. The competitive adsolubilization between 2-naphthol and biphenyl may be derived from sharing the same adsolubilization site, i.e., hydrocarbon chains of HTAB. On the other hand, at the high feed concentration of HTAB, 2-naphthol adsolubilizes the palisade region, while biphenyl incorporates into the core of the layer. In addition, in the high pH region deprotonated 2-naphthol rendered the adsorption layer more compact by increasing interaction with the hydrophilic group of HTAB.