

CHAPTER II

BACKGROUND AND LITERATURE REVIEW

2.1 Adsorption of Surfactant at Solid-Liquid Interface

2.1.1 Adsorption of Single Surfactant

Commonly, types of surfactant can be separated to 2 main types; ionic and nonionic surfactant. And, generally, a number of surfactant is used to adsorb on mineral oxide which is hydrophilic surface to hydrophobic surface for adsorb an organic compound or heavy metal. The adsorption of single surfactants, including ionic and nonionic surfactants, has been studied on solid oxide surface.

2.1.1.1 *Adsorption of Ionic Surfactants*

Typically, adsorption isotherms are seen for ionic surfactants adsorbing from aqueous solution on surfaces with a charge opposite to the charge on the surfactant. The adsorption isotherm of ionic surfactants onto an oppositely charge 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). This 'S'-shaped isotherm can be separated into four regions, as shown in Figure 2.1.

In region I, corresponds to both very low concentration and low adsorption of surfactant. This region is commonly referred to as the Henry's law region because the adsorbed surfactant is considered to be in infinite dilution in the surface phase and, thus, the interaction between molecules of surfactants is negligible. Adsorbed surfactants in this region are viewed as being adsorbed alone by electrostatic interactions between ionic surfactants and oppositely charged substrates through ion exchange and not forming any aggregates (Rosen, 1989).

Region II is distinguished by a sharply increased isotherm slope relative to the slope in region I. This increase in slope indicates the beginning of lateral interactions between surfactant molecules, which result in the formation of surfactant aggregates on the most energetic surface patches. These adsorbed surfactant aggregates are called admicelles or hemimicelles, depending upon whether the aggregates are viewed as bilayers or monolayers. The admicelle is considered as

a local bilayer structure with a lower layer of head groups adsorbed on the substrate surface and an upper layer of head groups in contact with solution. The hemimicelle is a monolayer structure having the head group adsorbed on the surface while the tail group is in contact with the aqueous phase. The transition point from region II to region III, representing the first formation of adsorbed surfactant aggregates, is called the critical admicelle concentration (CAC) or the hemimicelle concentration (HMC).

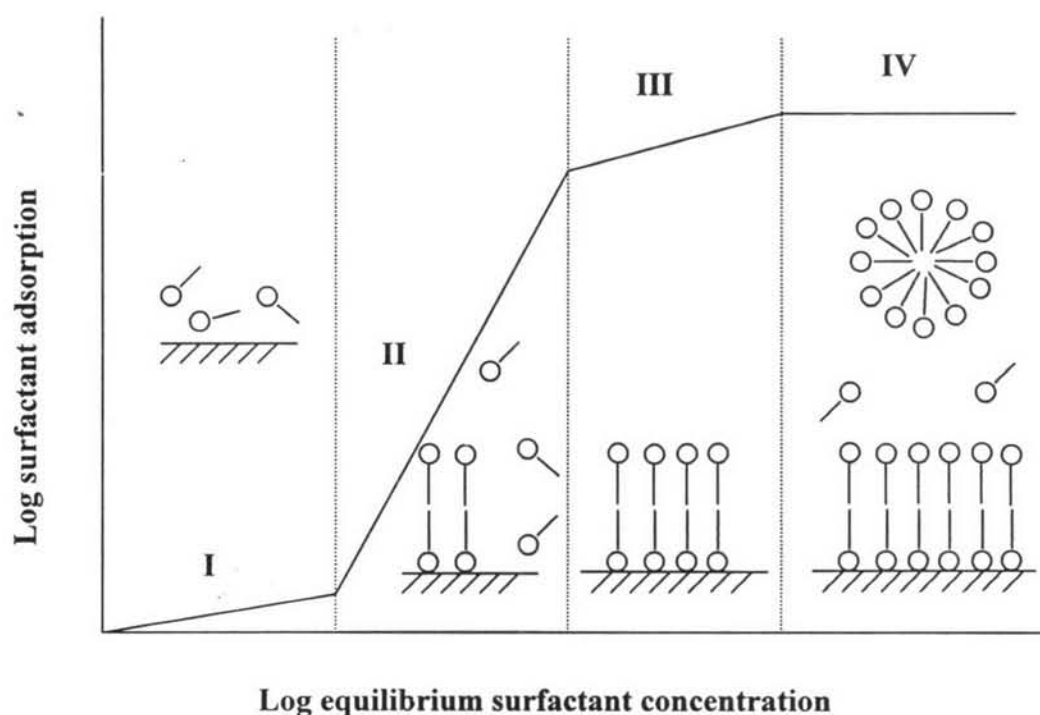


Figure 2.1 Schematic presentation of a typical surfactant adsorption isotherm.

The slope of the isotherm decreases in region III. This is thought to be caused by either repulsion between the like-charged head groups on the surface or the beginning of admicelle formation on lower energy surface patches. The surfactant concentration in this region is below the critical micelle concentration (CMC) of the surfactant.

Region IV is the plateau region, having almost constant surfactant adsorption with increasing surfactant concentration. Typically, the equilibrium surfactant concentration at the transition point from region III to region IV is approximately at the critical micelle concentration (CMC).

Yeskie *et al.* (1988) found that there are conditions under which a second layer of surfactant always forms simultaneously with the first layer of surfactants. Accordingly, there are wide ranges of condition under which only first layer form. This was shown to be resulted from the electrostatic contributions of the free energy of transfer a monomer from a hemimicelle to an admicelle are potentially much larger in magnitude than the largest possible hydrophobic contributions. In addition, admicelles do form little if there is any interpenetrating of the hydrocarbon tails of second layer between the hydrocarbon tails of the first layer because the electrostatic repulsion between the two layers of head groups is larger than the largest possible gain in hydrophobic bonding that could result from the interpenetrating.

Adsorption of sodium dodecyl sulfate on hydrotalcite was studied by Esumi and Yamamoto (1998). The amount of SDS adsorbed increased sharply at low SDS concentration and then reached a plateau above 4 mmol dm^{-3} of SDS which corresponds to the critical micelle concentration of SDS in the presence of 10 mmol dm^{-3} NaCl. The adsorption of SDS would occur at two sites: one is the external surface and the other is the interlayer. They reported that the θ potential of hydrotalcite in the absence of SDS is positive and it changes to negative with SDS concentration and then becomes constant. The result of θ potential suggests that SDS molecules adsorb on positively sites of the external surface, orienting their hydrocarbon chains to the aqueous solution and then a bilayer is formed through hydrophobic interaction between SDS molecules with, increasing SDS concentration, resulting in a negative θ potential. This change in the θ potential by adsorption of SDS affects dispersion stability of hydrotalcite. Although the dispersion stability of hydrotalcite suspension in the absence of SDS was relatively high, the addition of low concentration SDS made the dispersion stability unstable, probably due to monolayer adsorption of SDS. A further addition of higher SDS concentrations considerably enhanced the dispersion stability due to the formation of bilayer. This dispersion stability can be correlated with the change in the θ potential with SDS concentration.

2.1.1.2 Adsorption of Nonionic Surfactants

On strongly hydrated surfaces such as the polar silica/water interface it is to be expected that the principal driving energy for adsorption must originate in some specific interaction between the head group and the polar surface sites rather than through any interactions of the hydrophobic tails with the surface. It is generally accepted that the adsorption of surfactants bearing polyoxyethylene head groups onto the heavily water-structured surfaces of silica proceeds, at least in the initial stages, through the attachment of the head group. Infrared measurements (Grosborne, 1967) support this contention, the mechanism being one of hydrogen bond formation between surface silanol groups and the ether oxygen of the oxyethylene chains (Schick, 1987).

The adsorption isotherms of nonionic surfactants from aqueous solutions on polar substrates are also sigmoidal in shape ('S'-shaped), indicative of a cooperative adsorption mechanism (Livitz and Damme, 1986). 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).

Levitz (2002) investigated the adsorption of nonionic surfactants, alkyl ($C_{Na} E_{Np}$) and alkyl phenol polyoxyethylene glycol ($C_{Na} PE_{Np}$) at the solid/water interface. 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.

The impact of lipophilic linkers (long chain linear alcohols) on the adsorption of and styrene adsolubilization in polyethoxylated alkylphenols (Triton X) nonionic surfactants with varying EO units on amorphous precipitated silica (Hi-Sil[®] 233) was investigated by Tan and O'Haver (2004). The surfactant adsorption and styrene adsolubilization isotherms with and without linkers were compared. Results show that the presence of lipophilic linkers increases both surfactant adsorption and styrene adsolubilization and the percent increase of styrene adsolubilization was greater than the percent increase of surfactant adsorption for all studied systems. The adsolubilization capacity of surfactants increases, up to a certain value, with increasing lipophilic linker tail length or concentration. Styrene adsolubilization at the water-silica interface decreases with increasing numbers of ethoxylated (EO) units in the surfactant, especially at higher styrene loading levels. The enhancement of adsorption and styrene adsolubilization is thought to be caused by the linkers increasing interactions between styrene and surfactant hydrophobic groups.

Misra *et al.* (2005) studied 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. 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.

2.1.2 Adsorption of Mixed Surfactants

Most of earlier studies were performed with a single surfactant. Several factors can influence the efficiency of soil remediation with single surfactant. Too hard sub-surface water may be detrimental to the effectiveness of an anionic surfactant because anionic surfactant may precipitate, while nonionic surfactants are more likely to adsorb onto clay fractions than anionic surfactant (West and Harwell, 1992; Tsomides *et al.* 1995), which leads to a requirement for high concentration of surfactants. These factors may reduce surfactant availability and increase cost of remediation for soils and groundwater. An improved strategy to SER (surfactant-enhanced remediation) is to reduce the concentrations of surfactants and cost level while maintaining the efficiency of remediation.

In practical applications, mixtures of surfactants, rather than individual surfactants are often used. In most cases, when different types of surfactants are purposely mixed, synergism is observed, i.e. the condition when properties of the mixture are better than those attainable with individual components by themselves. For example, addition of nonionic surfactant to an anionic surfactant solution may significantly reduce CMC and may also significantly increase the size of micelle (Dubin *et al.*, 1989), which would result in an increase in solubilization degree. Various kinds of surfactants usually coexist in water and soils. The sorbed surfactants may significantly affect the properties of soils/sediments and suspended particles, and thus the transport and transformation of organic pollutants.

A few studies have indicated the superiority of mixed surfactants to individual ones in subsurface remediation. Anionic-nonionic surfactants reduced precipitation and sorption loss, and enhanced the flushing and washing efficiency for contaminated soils (Sabatini *et al.*, 1995; Xia and Xu, 1997). Mixtures of anionic surfactant with nonionic surfactant suppressed soil dispersion and ensured high recovery for nonaqueous phase liquids (NAPLs). The effectiveness of such progresses can be increased if the contaminant partitioned into the mixed micelle can be biodegraded in either above-ground reactors or in-situ.

Adsorption isotherms for sodium dodecyl sulfate (SDS) and octylphenolpoly(oxyethylene) (Triton X100 or TX100) on acidic γ -alumina from single aqueous surfactant solution and from mixed surfactant solutions are reported

by Wang and Kwak (1999). In the Henry (low surface density) region of the adsorption isotherm, the two surfactants adsorb independently. TX100, which has very low adsorption densities in the absence of SDS, is strongly co-adsorbed in the hemimicellar region for SDS. Above the mixed micellar CMC, SDS adsorption does not reach a plateau, but continues to increase, while TX100 adsorption decreases.

2.2 Solubilization and Adsolubilization

2.2.1 Fundamentals

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

The solubilization of pyrene by four anionic-nonionic mixed surfactants, sodium dodecyl sulfate (SDS) with Triton X-405 (TX405), Brij 35, Brij 58, and Triton X-100 (TX100), has been studied by Zhou and Zhu (2004) from measurements of the molar solubilization ratio (MSR), the micelle-water partition coefficient (K_{mc}), and the critical micelle concentration (CMC). The MSRs of pyrene in mixed surfactants are found to be larger than those predicted according to an ideal

mixing rule. The mixing effect of anionic and nonionic surfactants on MSR for pyrene follows the order of SDS-TX405 > SDS-Brij35 > SDS-Brij58 > SDS-TX100 and increases with an increase in the hydrophile-lipophile balance (HLB) value of nonionic surfactant in mixed systems. In addition, the mixture of anionic and nonionic surfactants cause the K_{mc} value for pyrene to be greater than the ideal value in SDS-TX405 mixed system, but to be smaller than the ideal value in SDS-Brij35, SDS-Brij58, and SDS-TX100 mixed systems. Meanwhile, in the four mixed systems, the experimental CMCs are lower than the ideal CMCs at almost all mixed surfactant solution compositions. The mixing effect of anionic and nonionic surfactants on MSR for pyrene can be attributed to the conjunct or the net result of the negative deviation of the CMCs from ideal mixture and the increasing or decreasing K_{mc} .

Zhao *et al.* (2005) studied solubilization and biodegradation of phenanthrene in mixed anionic-nonionic surfactant solutions. They reported the solubility of phenanthrene was proportional to the concentration of the single surfactants when above the CMC. On the basis of MSR, solubilization capacity for phenanthrene was in the order: TW80 > Brij35 > TX100 > SDS. Given the molar fraction of nonionic surfactant and the total surfactant concentrations, SDS-TW80 enhanced the solubility of phenanthrene most significantly among three mixed systems, while SDS-Brij35 exhibited larger extent of synergistic solubilization.

Surfactant adsorbed layers formed on particles exhibit hydrophobic properties which have been characterized by many techniques. Accordingly, water-insoluble compounds can be incorporated into the surfactant adsorbed layers, which is called "adsolubilization".

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 follows: (a) surfactant structure; (b) kind of water-insoluble compound; (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.

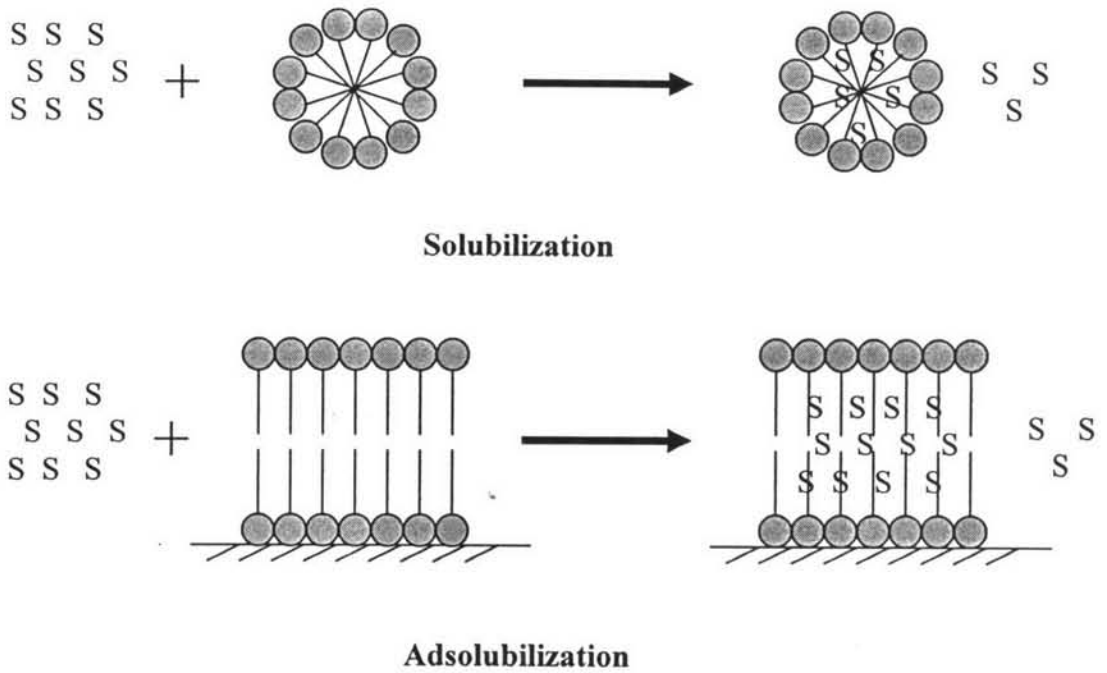


Figure 2.2 The phenomena of solubilization and adsolubilization.

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.

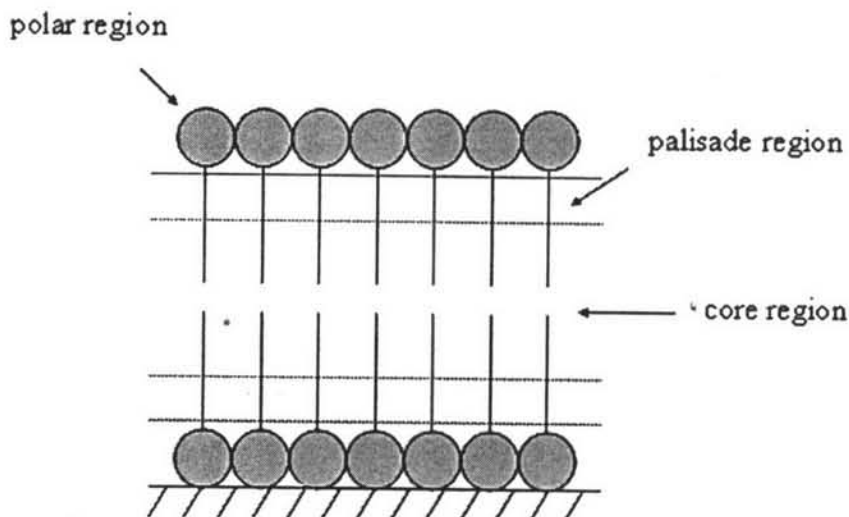


Figure 2.3 The admicelle structure.

Surfactant aggregates on solid/liquid interface, admicelles, is capable of removing hydrophobic organic compounds from solution (benzene, toluene, etc.) and enjoys 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 adsolubilize increases; (2) if the solute partitions primarily to the palisade region, the partition coefficients will decrease as the mole fraction of the adsolubilize 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 adsorbate increases (Harwell, 1991).

Kitiyanan *et al.* (1996) studied the adsorption 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 isoprene. The study concluded that styrene partition to both the palisade and core regions, while isoprene adsorbs into palisade region.

Thakulsukanant *et al.* (1997) studied the adsorption 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 adsorption 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 adsorption of TCE due to the nonpolar property of TCE, while the phenol adsorbed 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

Kanjanakunthakul (2002) studied the adsorption of the organic compounds, toluene and acetophenone into CTAB admicelles on precipitated silica as a function of ionic strength. 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 adsorption for acetophenone was in the palisade regions, while toluene was both core and palisade regions.

Dickson and O'Haver (2002) investigated the adsorption of naphthalene and α -naphthol with have the similar structures but different in polarities in C_n TAB ($n = 12, 14, 16$) 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 C₁₆TAB and C₁₂TAB 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 C₁₄TAB 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.

2.2.2 Adsolubilization in Single-Surfactant and Mixed-Surfactants Systems

2.2.2.1 *Single-Surfactant System*

For adsorption of ionic surfactants, oppositely charged systems of ionic surfactants and particles are well known to show strong interactions between the first surfactant layer and the surfaces of particles. The amount of ionic surfactants adsorbed onto oppositely charged particles increases accompanying the formation of monolayer and bilayer.

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.

Esumi *et al.* (2000) studied the reexamination of 2-naphthol adsolubilization on alumina with sodium dodecyl sulfate adsorption. The

adsolubilized amount of 2-naphthol increased sharply and reached a maximum, then decreased with SDS concentration. The decrement of the adsolubilized amount began below the critical micelle concentration of SDS. From the dispersion state of the alumina suspension and the SDS adsorption isotherm, it is demonstrated that the decrement of adsolubilization of 2-naphthol is not due to the partition of 2-naphthol between the SDS adsorbed layer and SDS micelles, but is due to the difference of SDS adsorption states such as monolayers and admicelles.

Tan and O'Haver (2004) studied the use of the BET adsorption isotherm equation to examine styrene adsolubilization by nonionic surfactants at the water-silica interface. They reported that the impact of EO units, as the number of EO units increases, the surfactant molecule becomes more hydrophilic and the HLB value increases. The interactions between the increasingly hydrophilic surfactant and the comparatively hydrophobic styrene molecule significantly decrease. And the impact of lipophilic linkers, the presence of linkers changes the surfactant-solute interactions but does not significantly effect the solute-solute interactions. The experimental results showed that hexane enhanced styrene adsolubilization, though not as well as alcohols. Hexane, adsolubilizing primarily in the core, has much less impact on styrene adsolubilization which occurs primarily in the palisade region. They expected weak interactions between non-polar hexane and polarizable styrene.

2.2.2.2 *Mixed-Surfactant Systems*

Adsorption from surfactant mixtures onto solids includes the adsorption of binary surfactant mixtures of anionic surfactants, anionic-nonionic surfactants, and cationic-nonionic surfactants. In particular, it is interesting that in ionic-nonionic surfactants, the adsorption of one surfactant is often enhanced by the addition of a small amount of the other surfactant. Surfactant mixtures provide several advantages over single surfactants, because the adsorption of surfactants onto particles can be controlled using appropriate surfactants and solution properties.

Esumi *et al.* (2000) studied mixed surfactant adsolubilization of 2-naphthol on alumina. Their adsolubilization results obtained with mixtures of an anionic (SDS) and a nonionic ($C_{10}E_6$) surfactant on alumina have shown complex behavior compared to those obtained with a single-surfactant system. $C_{10}E_6$ itself

showed a very low adsolubilization of 2-naphthol, whereas SDS had an appreciable adsolubilization capacity. A mixed-surfactant adsorbed layer at the alumina-water interface enhanced the adsolubilization of 2-naphthol compared to the SDS single-surfactant system. The ratio of SDS to $C_{10}E_6$ in the adsorption layer changes with the SDS content in the initial mixtures and is important for adsolubilization. The surfactant adsorbed layer for both SDS: $C_{10}E_6 = 1:3$ and 1:1 provides greater efficiency of adsolubilization than that for SDS alone. Thus, surfactant mixtures of anionic and nonionic surfactants with low concentrations have great possibilities for enhancing adsolubilization of toxic compounds.

2.2.3 Factors Affecting Surfactant Adsorption and Adsolubilization

The adsorption of surfactants at the solid-liquid interface is strongly influenced by a number of factors which these factors determine the mechanism by which adsorption occurs, and the efficiency and effectiveness of adsorption.

(1) The nature of the structural groups on the solid surface whether the surface contains highly charged sites or essentially nonpolar groupings, and the nature of the atoms of which these sites or groupings are constituted.

Adsorption of ionic surfactants on titanium dioxide with dodecyl chain groups or quaternary ammonium groups (XNm , where m is the carbon number of the alkyl chain, 4-16) was investigated by Esumi (2001). 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.

(2) The environment of the aqueous phase i.e. its pH, its electrolyte content, the presence of any additives such as short-chain polar solutes (alcohol, urea, etc.), and its temperature.

Talbot *et al.* (2003) studied the adsolubilization of 4-nitrophenol at a kaolinite/water interface as a function of pH and surfactant surface coverage. They reported that at constant pH, the adsolubilization is at a maximum at a surfactant concentration corresponding to the onset of the saturation plateau. At still higher concentrations, the solute is distributed between the surface and free aggregates. The influence of the pH on adsolubilization is very much dependent upon surfactant surface coverage. At low surfactant concentration the behavior of 4-nitrophenol is very similar to that observed with the same surfactant at a silica/water interface: the adsolubilization decreases with increasing pH as the result of the repulsive interaction between the deprotonated solute molecule and the negatively charged sites on kaolinite particles. At higher surfactant concentrations increasing the pH induces increased adsolubilization as a consequence of the favorable interaction which takes place between the deprotonated weak acid and the positively charged surface surfactant aggregates. 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.

The influence of the temperature on the adsorption of monomeric and micellar solutions of the anionic surfactant sodium dodecyl sulfate (SDS) on phosphatidylcholine (PC) liposomes was investigated by Parra *et al.* (2003) using the fluorescent probe 2-(*p*-toluidinyl)-naphthalene-6-sodium sulfonate (TNS). The number of adsorbed molecules was quantified by measuring changes in the electrostatic potential of the liposomes/probe during an incubation with SDS at varying temperatures. At low surfactant concentrations, the increase in temperature reduced the number of surfactant molecules incorporated per vesicle regardless of the incubation time, whereas at high surfactant concentrations the incubation time has an opposite effect on this process. Thus the surfactant adsorption decreased with temperature, yet it increased progressively with time. The adsorption was linear with temperature below critical micellar concentration (CMC) of SDS and this linear

tendency did not change above CMC. This suggests an adsorption of SDS monomers regardless of the surfactant concentration.

Tronto *et al.* (2004) studied the effect of pH, temperature, and ionic strength on adsorption of sodium dodecylbenzenesulfonate into Mg-Al-CO₃ layered double hydroxides. In the temperature effect, for equilibrium concentrations below the CMC, the higher temperature leads to a decrease in the adsorbed amount. However, above the CMC, there is a competition between the solid surface adsorption and the micelle formation, which cancels the effect of temperature. In the ionic strength effect, at equilibrium concentrations below CMC, the increase in ionic strength leads to a decrease in the repulsive forces between the surfactants polar groups, improving their adsorption on the solid surface. On the other hand, as the equilibrium concentration reaches the CMC, there is a competition between the adsorption and the surfactant aggregation in micelles. This competition leads the adsorption isotherm to a plateau, which will be reached at concentrations above CMC in each case. This competition is more significant when the ionic strength favors the micelle stabilization. So, at higher ionic strength, the plateau is reached at a lower amount of adsorbed surfactant and at lower equilibrium concentration. The pH effect on adsorption was investigated in two different conditions of pH (7.0 and 9.0) at the same ionic strength and at constant temperature. At concentrations above CMC the amounts of SDBS adsorbed are comparatively higher for pH value of 9.0. At lower pH, as the CMC is reached, the equilibrium between the micelles/surface unimers/surfactant adsorbed is displaced toward the micelles formation, thus resulting in an isotherm plateau at lower amount of adsorbed SDBS.

Gawade *et al.* (2005) studied (1) The effect of pH on adsorption of alumina and SDS treated alumina by changing the pH of the solution from 2 to 11. In SDS treated alumina, adsorption decreases as the pH increases from 2 to 11. As pH decreases below PZC i.e. 8.5 on alumina surface positive charge on alumina surface increases and amount of surfactant adsorbed is also increase. It has been reported that at lower pH amount of SDS adsorbed concentration is much greater than at very high pH. This may be attributed by the increase in HMC with increase in pH. Therefore, the extent of Isoproturon solubilized in surfactant aggregates at solid/liquid interface decreases and corresponding decrease in adsorption at higher pH value. In absence of

SDS, the adsorption of Isoproturon increases with increase in pH from 2 to 8.5. Above pH 8.5, adsorption decreases with increase in pH. Increase in adsorption of Isoproturon with respect to increase in pH may be attributed to electrostatic interaction between the AlOH_2^+ groups of alumina and negative charge developed on groups of Isoproturon. (2) The effect of initial concentration, the amount of Isoproturon adsorbed on SDS treated alumina increases as the concentration of Isoproturon increases. (3) The effect of agitation speed, the amount of Isoproturon adsorbed increased with increase in agitation speed. (4) The effect of mass of adsorbent, with increase in adsorbent mass, amount adsorbed per gram decreases. (5) The effect of temperature, the amount of Isoproturon adsorbed decreases with increase in temperature of the system.

(3) The molecular structure of the surfactant being adsorbed (the adsorbate) whether it is ionic or nonionic, and whether the hydrophobic group is long or short, straight-chain or branched, aliphatic or aromatic (the effect of the type of surfactant).

Esumi and Yamanaka (1995) studied the adsorption of sodium dodecyl poly(oxyethylene) sulfate, SDE_nS ($n = 0, 3, 5, \text{ and } 8$) on positively charged alumina in aqueous solution. The enhancement in the adsorption of SDS in the presence of 2-naphthol is probably due to the decrease in the electrostatic repulsive force between the adsorbed SDS molecules. The adsolubilized amount of 2-naphthol was greatly influenced by the SDE_nS concentration: in the cases of SDS, SDE_3S , and SDE_5S , it increased sharply at low concentration of SDE_nS and reached a maximum, then decreased with a further increase in SDE_nS concentration. On the other hand, in the case of SDE_8S , the adsolubilized amount of 2-naphthol increased gradually. This decrease in the adsolubilized amount of 2-naphthol for SDS, SDE_3S , SDE_5S may occur due to solubilization of 2-naphthol into SDE_nS micelles in bulk. Further, the adsolubilization capacity for 2-naphthol increased from $n = 0$ to $n = 8$ of SDE_nS . These results indicate that the adsolubilization of 2-naphthol is also affected not only by the hydrocarbon chain, but also by the oxyethylene chain-length of SDE_nS . In a cationic surfactant adsorbed layer at the silica/water and clay/water interfaces, a similar adsolubilization behavior for 2-naphthol has been observed with the surfactant concentration. It is concluded that the adsorption of SDE_nS on alumina

decreases with increasing oxyethylene chain length of SDE_nS , and this adsorption behavior significantly affects the stability of alumina dispersion and microviscosity in the adsorbed layer. Further, the adsolubilization of 2-naphthol is significantly affected by the oxyethylene chain length of SDE_nS adsorbed on alumina.

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.

Esumi and Yamamoto (1998) studied the adsorption of sodium dodecyl sulfate on hydrotalcite and adsolubilization of 2-naphthol. It is interesting to compare adsolubilization behavior of 2-naphthol for two different systems; SDS/hydrotalcite and DTAB (dodecyltrimethyl ammonium bromide)/laponite. At the same adsorption density of SDS and DTAB, the amount of 2-naphthol adsolubilized for DTAB/laponite system is about 10 times that of SDS/hydrotalcite by intercalation of SDS is about three times that of laponite by intercalation of DTAB. This difference may occur due to different interactions of 2-naphthol with the surfactants. There is also a possibility to delaminate laponite into the individual silicate layers or thin layers for a great adsolubilization capacity.

Paria *et al.* (2004) studied the effect of cationic surfactant on the adsorption characteristics of anionic surfactant on cellulose surface. They reported that in the case of NaDBS only, the adsorption is weak. The reason, most probably, is because the cellulosic surface is expected to be negatively charged and the adsorption of the negatively charged head group of the surfactant is opposed. The adsorption of NaDBS takes place mostly at hydrophobic sites. But in the case of CTAB has a positively charged head group and this, on adsorption, is expected to convert the negatively charged site to a hydrophobic site. The enhancement in adsorption after mixing the two surfactants NaDBS and CTAB in the solution, the enhancements both in rate and amount are smaller compared to the pretreated

surfaces. The main reason for this difference is because cationic and anionic surfactants, in mixture, form an ion pair and this behaves like surfactant with almost no charge and hence less adsorption than CTAB. The adsorption appears to be purely due to hydrophobic interactions. This view is confirmed by the adsorption studies carried out using a nonionic surfactant Triton X-100 (TX-100). It is interesting to notice that the enhancement in adsorption for the ratio of NaDBS:TX-100 (same concentration as the ratio of NaDBS:CTAB) is approximately same and washing and pretreatment gives approximately same result. So, they concluded that, to enhance the adsorption of NaDBS, it is better to pretreat the surface with CTAB than mixing the same in formulation. In the latter case the ion pair formation hinders the adsorption at charged sites.

Lee *et al.* (2004) studied the effect of surfactants on the distribution of organic compounds in the soil solid/water system. The anionic surfactants are preferable for soil remediation due to little adsorption on the soil surface, which leads to easy micelle formation in the solution, causing the contaminants to be released from the soil. Cationic surfactants may adsorb onto the soil surface to form admicelles in which contaminants can partition. This leads to difficulty in obtaining good remediation efficiency unless a very high surfactant concentration is used. The affinity of NOCs to the SOM (soil organic matter) is beyond that to the adsorbed surfactants. Although nonionic surfactants adsorb on the soil mineral surface of the soil, which may also hinder the contaminant desorption, the contaminant partitioning to the SOM can lead to an increased difficulty in soil remediation, especially for the water soluble compounds. This indicates that surfactant washing of low-SOM soils should produce better remediation efficiency under the same conditions. For different S_w compounds, the primary sorptive effects of the relatively water soluble compounds are due primary to the soil properties. For the less water soluble compounds, they are due to the solution properties. Surfactant washing can be used for effective soil remediation because of an increase in the hydrophobic environment of the solution. They concluded that the best choice for soil remediation by surfactant washing is composed of the lower SOM in the soils, the lower polarity of the surfactants (either anionic or nonionic), and the low- S_w contaminants.

Paria *et al.* (2005) studied the adsorption of an anionic surfactant, sodium dodecylbenzenesulfonate (NaDBS) and a non-ionic surfactant, Triton X-100 (TX-100) on filter paper surface, which is negatively charged in neutral aqueous medium. They reported that the equilibrium adsorption isotherms of NaDBS and TX-100 do not show Langmuir-type adsorption but show a typical three or four-region isotherm having a maximum in the region IV. This can be attributed to the presence of shorter chain (different CMC) surfactant molecules. TX-100 molecules show hemimicelle formation while NaDBS molecules do not form hemimicelles. Because hemimicellization of NaDBS is absent due to the electrical repulsion between the head group of the adsorbed NaDBS molecules, where the tail is attached to the surface.

Adsorption behavior of phenol, *ortho*-nitrophenol (ONP), *meta*-nitrophenol (MNP) and *para*-nitrophenol (PNP) on a kaolinite-type clay has been investigated by Pura and Atun (2005). Influence of an anionic surfactant, sodium dodecylsulfate (SDS), on adsorption behavior of phenol and nitro-substituted phenols onto kaolinite is studied by determining their adsorption isotherms. Experimental evidence has shown that phenol does not adsorb to the surface of kaolinite in the presence of SDS due to large repulsive, electrostatic barrier between negatively charged phenol and negatively charged adsorptive SDS micelles or hemimicelles. The adsorption capacity of kaolinite for the aromatic nitro compounds in the SDS system is markedly increased compared with the adsorption onto bare kaolinite surface especially at high-concentration region. Adsorption results were interpreted by comparing isotherms of phenolic compounds and SDS. It is shown that bilayer structure of SDS forms even at low SDS concentrations. In this region, PNP molecules are adsorbed via adsolubilization whereas penetration of ONP and MNP is difficult because of their structural properties and electrical interactions. However, adsolubilization phenomenon dominates adsorption process of all nitrophenol compounds at higher concentrations. Data show that adsorption capacities of the adsorbates in the presence of SDS follow the order $ONP > MNP > PNP$. The differences in the adsorption capacities depending on position of nitro group on phenol ring are correlated with the capacity of SDS.