

CHAPTER II BACKGROUND AND LITERATURE REVIEW

2.1 Adsorption of Surfactant on Solid Oxide Surface

The adsorption isotherm of an ionic surfactant onto an oppositely charged substrate is typically S-shaped when one plots the log of adsorbed surfactant density versus the log of the equilibrium surfactant concentration (Scamehorn *et al.*, 1982). The isotherm can be divided into four regions, as shown in Figure 2.1.

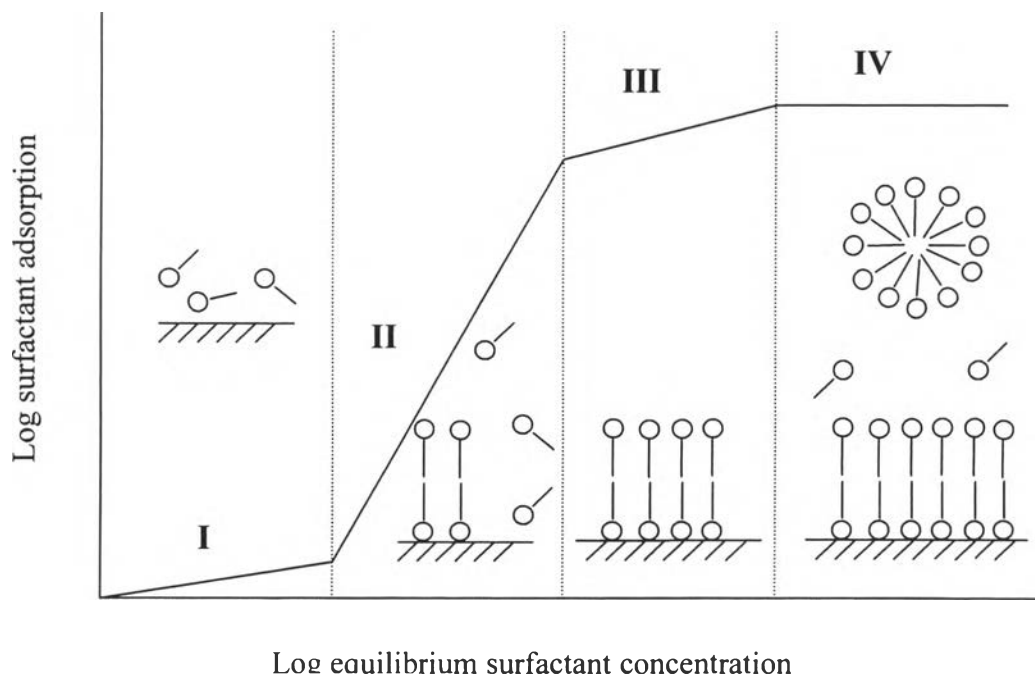


Figure 2.1 Typical adsorption isotherm of surfactant on solid oxide surface.

Region I corresponds to both very low concentration and low adsorption of surfactant. This region does not have lateral interactions between the adsorbed surfactant molecules. In many systems where conditions are favorable to surfactant adsorption, this region may not even be detectable because it occurs at such low surfactant concentrations, i.e., below the detection limits of many methods.

Region II is characterized by a rapid increase in adsorption, resulting from interactions of the hydrophobic chains of oncoming surfactant molecules with those

of previously adsorbed surfactant molecules. These adsorbed surfactant aggregates have been called hemimicelles or admicelles, depending on the assumed morphology. 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 admicelle is a 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 point of transition from region I to region II, representing the first formation of adsorbed surfactant aggregates is called the critical hemimicelle concentration (HMC) or critical admicelle concentration (CAC). All of the factors that result in the lowering of the CMC of surfactant can be expected to decrease the CAC also.

In region III, the adsorption increases more slowly with concentration than in region II. Possible reasons for this are the saturation of the high energy surface sites, neutralization of the surface charge, and repulsive lateral interactions between molecules in the admicelle.

Region IV is the plateau region and begins at approximately the CMC. This region is characterized by a near zero slope (Scamehorn *et al.*, 1982). At the CMC the first micelle forms at the same chemical potential as the last admicelle forms. When the surfactant concentration is increased further, additional molecules form micelles.

2.1.1 Adsorption of Single Surfactant

Yeskie and Harwell (1988) studied 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 surfaces 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 hydrophobic 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 admicelles, was formed (Harwell *et al.*, 1985).

The adsorption of a number of surfactants has been studied on solid oxide surfaces, including cationic, anionic and nonionic surfactants. For example, Somasundaran and Fuerstenau (1965) studied the adsorption of alkyl sulfonates at the alumina-water interface. By combining measurements of potentials with determination of surfactant adsorption isotherms at various pH values they were able to suggest a combined adsorption mechanism involving coulombic attraction of the charged surfactant head groups for charged sites on the alumina surface plus an enhancement due to the tail-tail interactions of adsorbed surfactants.

The adsorption of cationic and anionic surfactants on rutile as a function of surfactant concentration and ionic strength was investigated (Lee and Koopal, 1996). The result showed that the adsorption behavior of sodium nonyl benzene sulfonate (SNBS) and dodecyl or tetradecyl pyridinium chloride (DPPC/TPC) on rutile were broadly similar. Isotherms could be divided in two regions by the common intersection point (cip) between isotherms measured at different salt concentrations. Before the cip adsorption occurred head-on (hemimicelles); after the cip both head-on and head-out adsorption (admicelles) occurred.

Kira'ly *et al.* (1997) investigated the adsorption of nonionic surfactants, n-octyl tetraethylene glycol monoether (C_8E_4) and n-octyl β -D-mono-glucoside (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 increases 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.

Esumi (2001) studied the 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). 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 XN_m occurred mainly due to both electrostatic attraction force and hydrophobic interaction, depending on the alkyl chain length on XN_m . On the other hand, the adsorption of cationic surfactants, DTAC and 2RenQCl (their counter ions are chloride ions), on XN_m was much smaller than that of SDS due to electrostatic repulsion force.

2.1.2 Adsorption of Mixed Surfactants

Adsorption from surfactant mixtures onto solids includes the adsorption of binary surfactant mixtures of anionic-cationic surfactants, anionic-nonionic surfactants, and cationic-nonionic surfactants. The behavior of a mixture is often quite different from that of a single surfactant, and in most cases synergistic effects, better properties of the mixture than those attainable with the individual components by themselves, are observed.

For example, the adsorption of cetyltrimethylammonium bromide (CTAB) and nonylphenyl ethoxylates (NP-n, where $n=13, 20$ and 30) onto polystyrene powder has been investigated (Desai and Dixit, 1997). In a single surfactant system, only the cationic surfactant (CTAB) was found to adsorb significantly while nonionic surfactants showed negligible adsorption. In mixed surfactant systems, the cationic surfactant was found to induce coadsorption of nonionic surfactants. The increased adsorption of nonionic surfactants has been attributed to the formation of non-ideal mixed hemimicelles due to lateral interactions between the two types of surfactants. However, nonionic surfactants with longer hydrophilic chains did not form mixed hemimicelles with CTAB. In general, zeta potential measurements support the adsorption results.

2.2 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). The suggested definition of adsolubilization is “the incorporation of compounds into surfactant surface aggregates, which compounds would not be in excess at the interface without surfactant.” (Wu *et al.*, 1987).

Figure 2.2 shows the structure of an admicelle, characterized by the presence of three regions. The outer region is the most polar, called the head group region, consists of the surfactant headgroups. The inner region, called the core, consists of the hydrocarbon chains and is nonpolar in nature. The region between the headgroups and the core is the palisade region that is intermediate in polarity. It consists of the carbons near the headgroups and is characterized by water molecules that have penetrated the admicelle (Dickson and O’Haver, 2002).

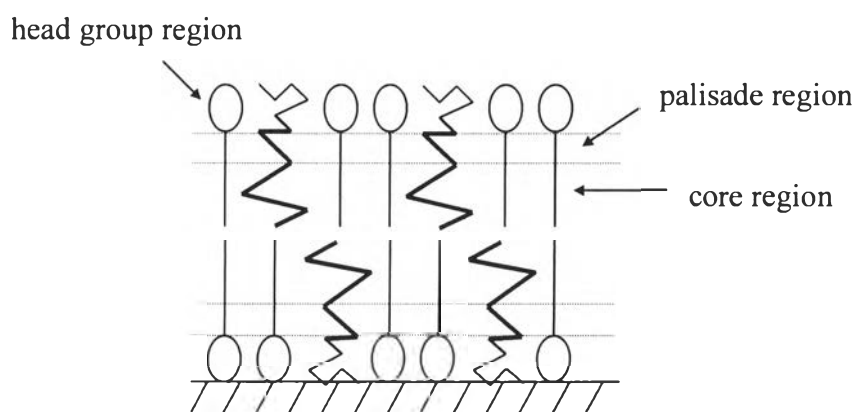


Figure 2.2 The admicelle structure.

The adsolubilization phenomenon is the surface analog of solubilization, with adsorbed surfactant bilayer playing the role of micelle, as shown in Figure 2.3.

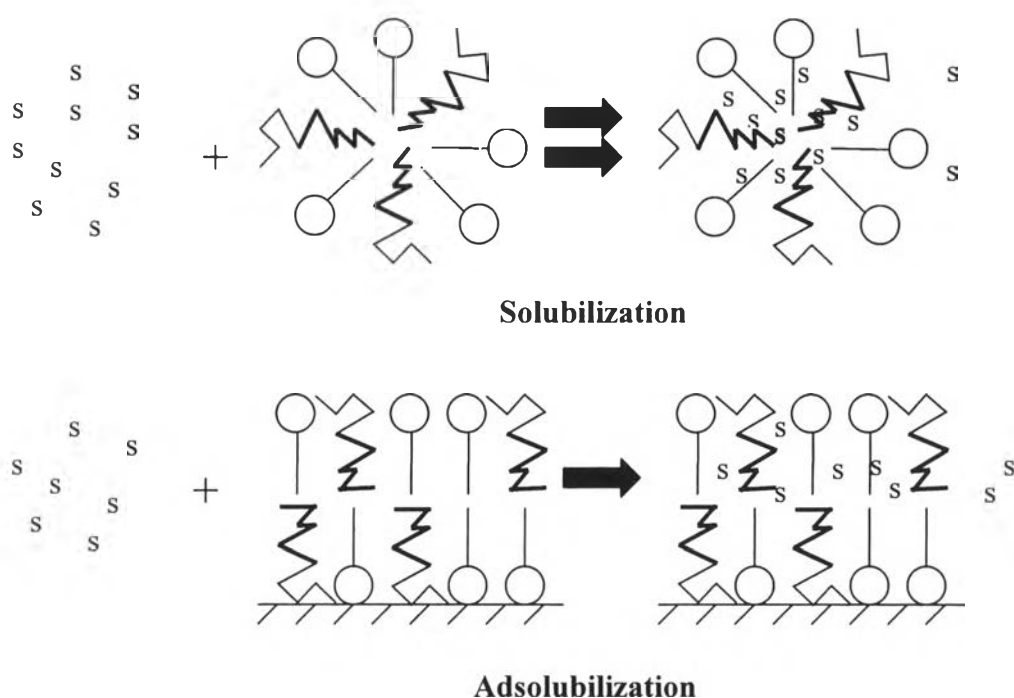


Figure 2.3 The phenomena of solubilization and adsolubilization.

Kitiyanan *et al.* (1996) investigated the adsolubilization of styrene and isoprene and mixtures of styrene and isoprene into cetyltrimethylammonium bromide (CTAB) bilayers (admicelle) on precipitated silica. The results showed that the partition coefficients for styrene remained constant while the mole fraction of styrene increased. The partition coefficients for isoprene decreased with increasing mole fraction of isoprene. The study concluded that styrene partitioned to both the palisade and core regions, while isoprene adsolubilizes primarily into the palisade region. In the mixed-solute system, the total amount of styrene adsolubilization was found to increase slightly in the presence of isoprene; however, isoprene adsolubilization was significantly enhanced in the presence of styrene.

The adsorption of sodium perfluoroheptanoate and adsolubilization of small aliphatic fluorocarbon alcohols into surface aggregate formed on alumina was

investigated by Lai and his co-workers (1997). They found that higher concentrations and increasing hydrophobicity of the solutes enhanced surfactant adsolubilization below the plateau region. Partitioned amounts of the fluorocarbon alcohols rose with the alcohol supernatant concentration and chain length. Aggregation numbers were estimated by using the two-site adsolubilization model.

Thakulsukanant *et al.* (1997) studied adsolubilization characteristics and stability characteristics of hydrocarbon aggregates chemically bonded to porous silica. In this study, octadecyltrichlorosilane (ODS) was chemically bonded with silinol groups of silica surface. The adsolubilization capabilities and stability of the bonded ODS were evaluated and compared to those of physically adsorbed aggregates of cetyltrimethylammonium bromide (CTAB). The adsorption of ODS increased with increasing ODS concentration in the bulk phase and reached a constant value when the equilibrium ODS concentration was higher than 1700 μm .

2.2.2 Factors Affecting Adsorption and Adsolubilization

The adsorption and adsolubilization of surfactant on the mineral oxide surface is determined by several factors.

2.2.2.1 *Nature of the Structural Groups on the Solid Surfaces*

Adsorption of surfactant at the solid-liquid interface is related to the nature and number of the structural groups on the solid surface responsible for the adsorption whether the surface contains highly charged sites or essentially nonpolar group, and the nature of the atoms of which these sites or grouping are constituents.

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 surface onto silica. The adsorption of DTAB (dodecyltrimethyl ammonium bromide) and of the dimeric surfactant 12-2-12 (ethanediyl-1,2-bis(dodecyldimethyl ammonium bromide)) on raw silica (SiNa) and on HCl washed silica (SiH) has been investigated under “free” system conditions. The results have been shown that the amount of surfactant adsorbed at the point of zero charge and at saturation of the silica particles, the sodium ions released by the surface and the decrease in critical

micelle concentration (CMC) of the supernatant with respect to pure water were all larger for the raw silica than for the treated silica.

2.2.2.2 *Molecular Structure of the Surfactant being Adsorbed*

The key parameter affecting the adsorption mechanism is the molecular structure of the surfactant, which includes the type of surfactant and the length and number of its alkyl chains.

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 decrease with increasing chain number of the surfactants. Under a constant feed concentration of 2-naphthol, the adsolubilized amount of 2-naphthol increased, reached a maximum, and then decreased with single-chain or double chain surfactant concentration, whereas only a slight decrease in the adsolubilized amount of 2-naphthol is observed for the triple-chain surfactant. The ratio of amount of 2-naphthol adsolubilized to the adsorbed amount of surfactant on silica for the double-chain and triple-chain surfactants were not so different and were quite large compared to that for the single-chain surfactant. In addition, from the two-step adsorption-adsolubilization procedure, it was found that the double-chain or triple-chain surfactant adsorbs strongly on the silica surface (Esumi *et al.*, 1996).

Subsequently, Esumi *et al.* (1997) studied the adsorption of and adsolubilization into cationic surfactants with different structures on clay (laponite). As an adsolubilize, 2-naphthol was employed as a representative toxic substance. The results showed that adsorption of cationic surfactant increased from 3RdienQ to 1RQ in the layer of laponite, resulting in the layer broadening, where the adsorption by 2RenQ and 3RdienQ made the layer much larger than that by 1RQ. Most of 2-naphthol molecules as the feed concentrations were adsolubilized in the surfactant-adsorbed layer.

2.2.2.3 *Environmental of the Aqueous Phase (pH and ionic strength)*

Properties of the aqueous phase such as pH that usually causes marked changes in the adsorption of ionic surfactants onto charged solid substrate. As the pH of the aqueous phase is lowered, a solid surface will usually become more positive, or less negative, because of adsorption onto charged sites of

protons from the solution, with consequent increase in the adsorption of anionic surfactants and decrease in the adsorption of cationic. The reverse is true when the pH of the aqueous phase is raised. These effects are shown markedly for mineral oxide, such as silica and alumina, and by wool and other polyamide. Change in the pH also may affect surfactant molecules, notably those containing carboxylate group (soap) or nonquaternary ammonium group. In these cases, change in the 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. Moreover, the effect of the ionic strength on the adsorption is also very important to study because it can change the CMC, counterions stabilize ionic surfactant micelles by binding to the micelle surface and screening the electrostatic repulsions between the ionic headgroups, the effect being more pronounced for anionic and cationic than for zwitterionic surfactant and more pronounced for zwitterionic than for nonionic.

Esumi *et al.* (1996) investigated the adsorption of a dimeric (1,2-bis(dodecyldimethylammonio) ethane dibromide, 2RenQ) on silica from its aqueous solution in the presence of added NaBr. The adsorbed amounts of 2RenQ at saturation increase with increasing amount of NaBr added. With a constant feed concentration of 2-naphthol, the adsolubilized amounts of 2-naphthol were greater when NaBr was added, but the ratios of adsolubilized amount of 2-naphthol/adsorbed amount of 2RenQ at maximum adsolubilization decrease with increasing NaBr concentration.

The adsolubilization of anthracene on cationic surfactant hexadecyl trimethyl ammonium (HDTMA) covered silica as a function of adsorption density of HDTMA and in dependence on pH is investigated (Behrends and Herrmann, 2000). It was observed that the partitioning constant, K , normalized on the content of organic carbon in the surfactant coverage is not only a function of the surface concentration but also depends on pH. At low concentrations of adsorbed HDTMA no adsolubilization of anthracene was measured.

Talbot *et al.* (2003) studied the adsolubilization of 4-nitrophenol at a kaolinite/water interface as a function of pH and surfactant surface coverage. This work showed that the influence of the pH on adsolubilization was very much dependent upon surfactant surface coverage. 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.

2.2 Adsorption and Adsolubilization in Mixed Systems

2.3.1 Mixed-Solute System

The effects of ionic strength on surfactant adsorption and the adsolubilization of toluene and acetophenone were investigated using CTAB on precipitated silica (Kanjankhuthakul, 2002). The adsolubilization of the model organic compounds was measured both in single-solute and mixed-solute systems. For both adsorption and adsolubilization, batch experiments were carried out at two different pH values (5 and 8) under various ionic strengths (1, 10 and 100 mM). The results showed that the adsorption of CTAB on the silica surface increased with increasing ionic strength. In the single-solute system, increasing ionic strength had little effect on the adsolubilization of toluene. However, the adsolubilization of acetophenone significantly increased with increasing ionic strength, especially at 100 mM. In the mixed-solute system, the synergistic effect was observed in the adsolubilization of acetophenone in the presence of toluene and the effect was more pronounced with increasing ionic strength. In contrast, the presence of acetophenone had little effect on the adsolubilization of toluene.

Asvapathanagul (2003) investigated the adsorption of a cationic surfactant, cetyltrimethylammonium bromide (CTAB), on precipitated silica and the

adsolubilization of organic solutes into the adsorbed surfactant as a function of surfactant adsorption at two pH 5 and pH 8. Focusing on three different surface adsorptions corresponding to the equilibrium concentrations in regions I, II and III of the adsorption isotherms, adsolubilization of toluene and acetophenone were investigated both in single- and mixed-solute systems. The results showed that the adsorption of CTAB depended strongly on pH and for each pH the adsolubilization increased with increasing surface adsorption. However the adsolubilization behaviors of the adsorbed CTAB aggregates in different adsorption regions were quite distinct, suggesting that the structural arrangement of the surfactant aggregates may play an important role in adsolubilization, as well as on the amount of adsorbed surfactant. This phenomenon was more noticeable at low surfactant adsorption than at higher adsorption. In mixed-solute systems, the presence of acetophenone had little effect on the toluene adsolubilization. In contrast, a synergistic effect was observed for the adsolubilization of acetophenone in the presence of toluene. With regard to differences in surface adsorption, the effect was more pronounced at higher adsorbed amounts of surfactant.

Pradubmook *et al.* (2003) studied the effect of pH on adsolubilization of a cationic surfactant, cetyltrimethylammonium bromide (CTAB), on precipitated silica and adsolubilization of toluene and acetophenone in CTAB at two pH values. 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. In the single solute system, the adsolubilization of both solutes increased with increasing equilibrium concentration of the solute in the aqueous phase. 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 increase in the acetophenone adsolubilization when pH was increased from 5 to 8. In the mixed solute system, the presence of acetophenone had insignificant effect on toluene adsolubilization whereas the presence of toluene had synergistic effect on acetophenone adsolubilization. Moreover, the analyses through the use of the adsolubilization equilibrium constant (K) suggested that toluene adsolubilized into

both the palisade layer and core of admicelle while acetophenone adsorbed into palisade layer only.

2.3.2 Mixed-Surfactant System

Mixtures of two or more different types of surfactants often show a synergistic interaction, i.e., the interfacial properties of the mixture are more pronounced than those of the individual components by themselves. As a result, in many industrial products and processes, mixtures of different types of surfactants, rather than individual materials, are used.

The adsorption of 2-naphthol by surfactant mixture of an anionic surfactant, sodium dodecyl sulfate, and a nonionic surfactant, hexaoxyethylenedodecyl ether on alumina was studied. In a single surfactant system, only the anionic surfactant had an appreciable adsorption capacity. A mixed surfactant adsorbed layer enhanced the adsorption of 2-naphthol compared to the anionic single-surfactant system. The adsorption became greater with an increase in the anionic surfactant content in the initial mixtures. However, the ratios of adsorbed amount to surfactant adsorbed amount become smaller when the anionic surfactant content in the initial mixtures increased (Esumi *et al.*, 2000).

The adsorption of 2-naphthol by binary mixture of cationic and nonionic surfactants on silica was investigated (Esumi *et al.*, 2001). Two cationic surfactants used were hexadecyltrimethylammonium bromide (HTAB) and 1,2-bis(dodecyldimethylammonio)ethane dibromides (2RenQ), and a nonionic surfactant used was hexaoxyethylenedodecyl ether ($C_{10}E_6$). In the HTAB/ $C_{10}E_6$ system, the ratios of adsorbed amount of 2-naphthol and adsorbed amount of surfactant for the mixtures of different compositions were greater than those of the single surfactant systems. On the other hand, in the 2RenQ/ $C_{10}E_6$ system the ratios for mixtures were intermediate between those of single surfactant systems. This study showed that the alkyl chain length of cationic surfactants is an important factor for the adsorption of 2-naphthol.