

## CHAPTER II

### LITERATURE REVIEW

#### 2.1 Surfactant

##### 2.1.1 General Principle

The word surfactant is not only a technical term, but also a diminutive form of the phrase SURFace ACTive AgeNT. Surfactants are amphipathic molecules that consist of a non-polar hydrophobic portion (lipophilic), usually a straight or branched hydrocarbon or fluorocarbon chain, which is attached to a polar or ionic portion (hydrophilic or lipophobic). The hydrocarbon chain interacts weakly with the water molecules in an aqueous environment, whereas the polar or ionic head group interacts strongly with water molecules via dipole or ion-dipole interactions. It is this strong interaction with the water molecules that renders the surfactant soluble in water. When surfactant dissolved in aqueous medium the hydrophobic group distorts the structure of the water. As a result of this distortion, some of the surfactant molecules are expelled to the interfaces of the system, with their hydrophobic groups oriented so as to minimize contact with the water molecules. The surface of the water becomes covered with a single layer of surfactant molecules with their hydrophobic groups oriented predominantly toward the air. Since air molecules are essentially non-polar in nature, as are the hydrophobic groups, this decrease in the dissimilarity of the two phases contacting each other at the surface result in a decrease in the surface tension of the water (Tadros, 2005).

Surfactants can aggregate in solution forming micelles, or micellization. The concentration at which this phenomenon occurs is called the *critical micelle concentration* (CMC). In aqueous solution, the surfactant hydrophobic groups are directed towards the interior of the aggregate and the surfactant hydrophilic groups are directed towards the solvent. In non-polar solution, the structure of the micelle is similar but reversed, the surfactant hydrophilic groups are directed towards the interior of the aggregate and the surfactant hydrophobic groups are directed towards the non-polar solvent (Rosen, 1989).

Surfactants find applications in almost every chemical industry, such as in detergents, personal care and cosmetics, plastics and fibers, agrochemicals, pharmaceuticals, paints, inks, food processing, etc. In addition, they play an important role in the oil industry. The last decades have seen the extension of surfactant applications to such high-technology areas as magnetic recording, biotechnology, and micro-electronics (Tadros, 2005).

### 2.1.2 Basic Surfactant Classifications

A simple classification of surfactants based on the nature of the hydrophilic group is commonly used. The four basic classes of surfactants are defined as follows:

1. *Anionic surfactants*. The hydrophile is a negatively charged group such as carboxyl ( $\text{RCOO}^- \text{M}^+$ ), sulfonate ( $\text{RSO}_3^- \text{M}^+$ ), sulfate ( $\text{ROSO}_3^- \text{M}^+$ ), or phosphate ( $\text{ROPO}_3^- \text{M}^+$ ).

2. *Cationic surfactants*. The hydrophile is a positively charged group, for example, the quaternary ammonium halides ( $\text{R}_4\text{N}^+ \text{X}^-$ ).

3. *Nonionic surfactants*. The hydrophile has no charge, but derives its water solubility from highly polar groups such as polyoxyethylene (PEO or  $\text{R-O-CH}_2\text{-CH}_2\text{-O-}$ ), R-polyol groups including sugars, monoglyceride of long-chain fatty acid ( $\text{RCOOCH}_2\text{CHOHCH}_2\text{OH}$ ), polyoxyethylene alkylphenol ( $\text{RC}_6\text{H}_4(\text{OC}_2\text{H}_4)_n\text{OH}$ ).

4. *Amphoteric (and zwitterionic) surfactants*. The molecule contains, or can potentially contain, both a negative charge and a positive charge, such as the sulfobetaines ( $\text{RN}^+(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{SO}_3^-$ ), long-chain amino acid ( $\text{RN}^+\text{H}_2\text{CH}_2\text{COO}^-$ ).

### 2.1.3 Polymeric Surfactants

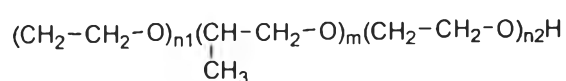
There has been considerable recent interest in polymeric surfactants due to their wide application. Various polymeric surfactants have been introduced and they are marketed under special trade names (such as Hypermers of ICI). One may consider the ethylene oxide-propylene oxide copolymers (EO/PO) as polymeric surfactants, but these generally do not have high molecular weights and they seldom produce speciality properties. Silicone surfactants may also be considered as

polymeric. Graft copolymer of a poly(methyl methacrylate) backbone with several polyethylene oxide (PEO) side chains, which has excellent dispersing and stabilizing properties for concentrated dispersions of hydrophobic particles in water (Tadros, 2005). Another important class of polymeric surfactants that are used for demulsification is those based on alkoxyated alkyl formaldehyde condensates.

Normal polymers can be modified to increase their hydrophobic or hydrophilic characteristics and use as polymeric surfactants. A common example of the modification of a water-insoluble material is the sulfonation of polystyrene for the preparation of polymeric surfactant. In addition, polyacrylic acid and polyacrylamide are typical water-soluble polymers that can be functionalized by the addition of hydrophobic side chains that turn them into amphiphilic materials (Myers, 2006).

#### 2.1.3.1 PEO-PPO-PEO Triblock Copolymer

Water-soluble triblock copolymers of poly(ethylene oxide) (PEO) and poly(propylene oxide) (PPO), often denoted PEO-PPO-PEO or  $(EO)_{n1}(PO)_m(EO)_{n2}$ , are commercially available nonionic macromolecular surface active agents. PEO is hydrophilic part and PPO is hydrophobic part. The general formula of this copolymer can be written as:



Variation of the copolymer composition (PPO/PEO ratio) and molecular weight (PEO and PPO block length) during synthesis leads to the production of molecules with optimum properties that meet the specific requirements in various areas of technological significance. The ratio number of ethylene oxide units by number of propylene oxide units, also known as the hydrophilic/lipophilic balance (HLB) can be changed easily. As a result, PEO-PPO-PEO triblock copolymers are an important class of surfactants and find widespread industrial applications in detergency, dispersion stabilization, foaming, emulsification, lubrication, and formulation of cosmetics and inks, etc., along with more specialized applications in, for example,

pharmaceuticals (drug solubilization and controlled release and burn wound covering), bioprocessing (protecting microorganisms against mechanical damage), and separations (solubilization of organics in aqueous solutions). Commercial names for PEO-PPO-PEO polymeric surfactants are Poloxamers (manufactured by ICI) and Pluronics (manufactured by BASF). In addition, this copolymer can be expected to be environmentally acceptable surfactant with low toxicity.

The notation for the Pluronic triblock copolymers starts with the letters L (for liquid), P (for paste), or F (for flakes). The first one or two numbers are indicative of the molecular weight of the PPO block (multiply by 300 to obtain approximate molecular weight of PPO block in Da unit), and the last number signifies the weight fraction of the PEO block. For example, Pluronics P104 is a paste form which has a PPO block roughly 3000 Da and 40 wt. % of PEO block.

## **2.2 Adsorption of Surfactant on Solid Oxide Surfaces**

Surfactant adsorption is a process of transfer of surfactant molecules from bulk solution phase to the surface/interface. The adsorption phenomenon depends on the interaction between the surface of the adsorbent and the adsorbed species. The interaction may be due to: (1) chemical bonding, (2) hydrogen bonding, (3) hydrophobic bonding, and (4) van der Waals force (Parida *et al.*, 2006). The adsorption of surfactant at the solid-liquid interface plays an important role in many technological and industrial applications, such as detergency, mineral flotation, dispersion of solid, oil recovery and so on.

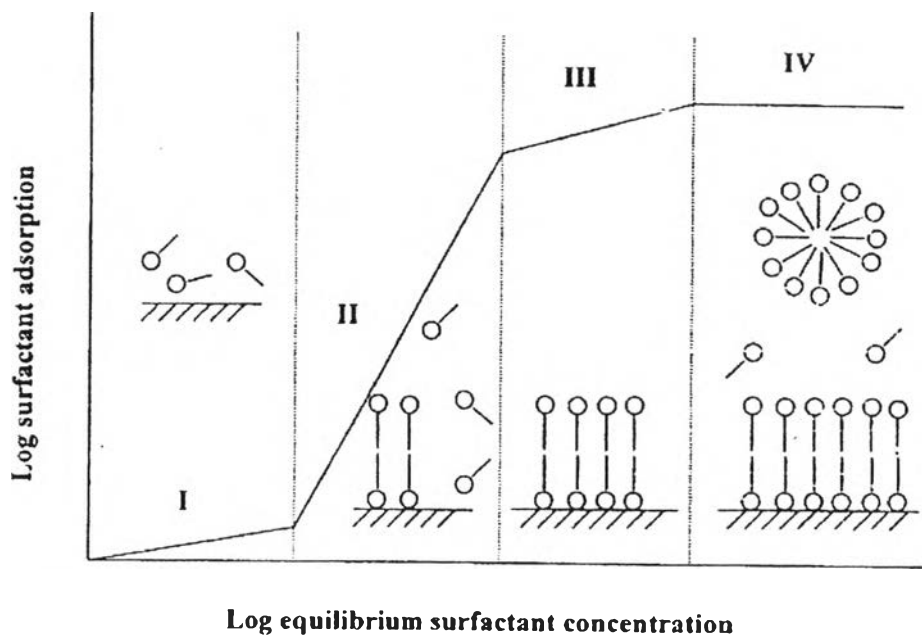
### **2.2.1 Adsorption of Single Surfactant**

The adsorption of single surfactant can be divided into ionic surfactants and nonionic surfactants.

#### **2.2.1.1 *Adsorption of Ionic Surfactants***

The adsorption isotherm of ionic surfactants onto an oppositely charged oxide surface is typically an elongated S-shaped curve when one plots the log of the adsorbed surfactant density versus the log of the equilibrium

concentration of surfactant (Scamehorn *et al.*, 1982). In general, a typical adsorption isotherm can be subdivided into four regions as shown in Figure 2.1.



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

In region I, occur at low concentration and low adsorption of surfactant. In this region, the adsorption obeys Henry's law, adsorption increases linearly with concentration and the slope of the curve is approximately one (Chandar *et al.*, 1987). In addition, 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. This is indicative of an absence of lateral interactions between the adsorbed surfactant molecules (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 sudden increase in the adsorption due to lateral interactions between surfactant molecules, which result in the formation of surfactant aggregates on the surfaces. 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 I to region II, representing the first formation of adsorbed surfactant aggregates, is called the critical admicelle concentration (CAC) or the critical hemimicelle concentration (HMC).

The slope of the isotherm decreases in region III. It indicates the adsorption rate of region III is lower than region II. 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 above the CMC, having almost constant surfactant adsorption with increasing surfactant concentration. This region adsorption reaches a maximum. It is thought that the surface has become saturated with admicelle or that adsorption stops because the surfactant concentration has reached the CMC. Typically, the equilibrium surfactant concentration at the transition point from region III to region IV is approximately at the critical micelle concentration (CMC). At the CMC, the first micelle forms at the same chemical potential as the last admicelle to forms; if the surfactant concentration is increased further, this only results in the formation of more micelle at the same chemical potential as that of the first micelle to form, without an increase in the adsorption of surfactant.

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.*, 1982).

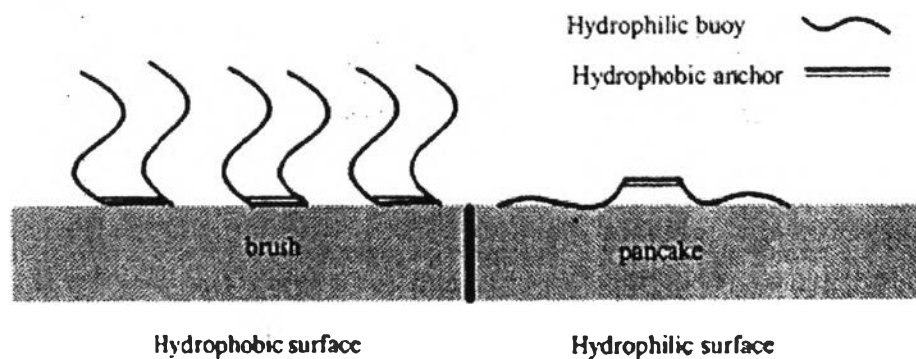
#### 2.2.1.2 Adsorption of Nonionic Surfactants

Nonionic surfactants are physically adsorbed rather than electrostatically or chemisorbed. However, they differ from many other surfactants in that, quite small changes in concentration, temperature, or molecular structure of the adsorbent can have a large effect on the adsorption. This is due to adsorbate-adsorbate and adsorbate-solvent interactions, which causes surfactant aggregation in bulk solution and which leads to change in orientation and packing of surfactant at the surface. 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).

Partyka *et al.* (1984) studied the adsorption of nonionic surfactants of the oxyethylenic alkylphenol, oxyethylenic alkyl ether, and poly(oxyethylene) glycol type on a precipitated silica gel having a small specific surface area. They found that increasing temperatures slightly increased the adsorption. For the adsorption isotherm, with increasing chain length of EO group the amount adsorbed at the plateau decreases. The rate of adsorption is relatively rapid and depends on the length of the oxyethylenic chain. For example, the rate of adsorption of series of ethylene oxide (EO) alkylphenol surfactant on the silica gel increases with increase in the chain length of hydrophilic group (EO).

### 2.2.1.3 Adsorption of PEO-PPO-PEO Triblock Copolymers

If PEO-PPO-PEO triblock copolymer molecules adsorb, the conformation of the block copolymer molecule will depend on the properties of the surface and the quality of the solvent. For block copolymer adsorption from water onto a hydrophobic surface, the propylene oxide block acts as the anchor, being mainly situated near the surface because of its high surface affinity. The ethylene oxide segments (buoy) were found not to adsorb; they have no affinity for the surface. A brush conformation is the result. The thickness of a (saturated) brush layer depends mainly on the length of the ethylene oxide groups. For a hydrophilic substrate like silica, the situation is different. Ethylene oxide has the highest surface affinity and will adsorb preferentially, thus forming a pancake conformation. Compared to a saturated brush layer the pancake layer is in general less thick (Schroën *et al.*, 1995). Schematic representation of PEO-PPO-PEO triblock copolymers adsorbed at a hydrophobic and a hydrophilic surface is shown in Figure 2.2.



**Figure 2.2** Schematic representation of PEO-PPO-PEO triblock copolymers adsorbed at a hydrophobic and a hydrophilic surface (Schroën *et al.*, 1995).

Malmsten *et al.* (1992) studied the adsorption of PEO-PPO-PEO block copolymers on silica. For a number of polymers with a total molecular weight of approximately 15000, it was found that the adsorbed amount is rather low ( $0.35\text{-}0.40\text{ mg/m}^2$ ) and independent of the PPO content in the range 0-30% PPO. For a copolymer with a total molecular weight of 4000 and 50% PPO content, the



adsorbed amount was approximately  $0.20 \text{ mg/m}^2$ . Thin adsorbed layers, with hydrodynamic thicknesses of about 2-5 nm, were performed by all polymers investigated. At higher pH, both the adsorbed amount and the hydrodynamic thickness decrease until complete desorption occurs. This is because, at higher pH, the silica surface becomes increasingly (negatively) charged, thus increasing the affinity of cations for the surface, as well as decreasing the affinity of the polymer for the surface.

Shar *et al.* (1998) investigated the adsorption of a series of PEO-PPO-PEO triblock copolymers onto hydrophobic polystyrene latex. They found that the adsorbed amount of copolymers increases with increasing total molar mass and with the variable block molar mass. The copolymers with PEO block sizes smaller than or equal to the PPO block size adsorb more strongly than the copolymers of the corresponding molar masses predominantly consisting of PEO blocks. The random copolymers (50:50 ratio of PEO/PPO) and the high anchor-fraction of block copolymers adsorb at similar levels but are at substantially higher levels than the PEO homopolymers. In contrast, the low anchor-fraction (high PEO content) of block copolymers adsorb at levels lower than the random copolymers but higher than the PEO homopolymers of the corresponding molar masses. An increase in the adsorbed amount of the copolymers with increasing PPO block molar mass at fixed PEO block size also confirms the strong dependence of adsorbed amount on the anchor content. In addition, the hydrodynamic thickness of the adsorbed layer was determined. An increase in PEO block size increases the number of segments in tails which contribute more towards the hydrodynamic thickness of the adsorbed layer. However, an increase in the PPO block size increases the affinity between the surface and the polymer segments which raises the adsorbed amount, and hence, in turn, the hydrodynamic thickness of the adsorbed layer. Random and block copolymers show higher hydrodynamic layer thickness values than the PEO homopolymers. For the block copolymers at high PPO content the layer thickness is greater than both the PEO homopolymer and the random copolymer.

Shar *et al.* (1999) studied the adsorption of the same series of PEO-PPO-PEO copolymers from aqueous solution onto hydrophilic silica particles. They found that the adsorbed amounts presented in the study are about 5-6 times

lower than those measured for the same copolymers on hydrophobic polystyrene latex. The adsorbed amount increased with increasing the total polymer molar mass. Comparison between the adsorption of these PEO-PPO-PEO triblock copolymers on silica and on polystyrene latex show higher maximum amount adsorbed at the interface ( $\Gamma_{\max}$ ) for the hydrophobic surface. Moreover, much lower adsorbed amounts were observed for PEO homopolymers than the copolymers. In the case of PEO homopolymers show overall lower amount adsorbed values suggests a flatten adsorption configuration for these polymers. In addition, they found that the adsorbed amount depends on both anchor and buoy blocks. Hydrodynamic thickness of the copolymers is found to be approximately 4 times lower for silica surface than that observed for the polystyrene latex surface. Copolymers show higher hydrodynamic thickness values than the PEO homopolymers of the corresponding molar mass. There is an increase in the hydrodynamic thickness of the adsorbed layer with increasing PPO block size for constant PEO block size. This effect, however, is smaller than that observed for the polystyrene latex.

### 2.2.2 Adsorption of Mixed Surfactant

Adsorption of more than one surfactant significantly enhances the efficiency of many interfacial properties compared to the adsorption of a single surfactant. Adsorption of surfactants from the mixed systems mainly depends on the solution properties of mixed surfactant system.

Huang *et al.* (1989) have studied the adsorption of cationic and anionic surfactants on silica from the anionic-cationic surfactant mixture solution. They found that the individual cationic surfactants can be strongly adsorbed onto the silica gel, but no significant adsorption of anionic surfactant can be detected. However, in the mixed systems, the adsorption amount of both the cationic and anionic surfactant ions is enhanced and the excess adsorption of cationic surface-active ions is exactly equal to the adsorption of anionic surface-active ions. From the observations, they assumed that the excess adsorption of cationic and anionic surface-active ions is in the form of ion pairs.

In the case of the adsorption of cationic-nonionic surfactant mixture, the adsorption of tetradacyl-trimethyl-ammonium chloride (TTAC) and

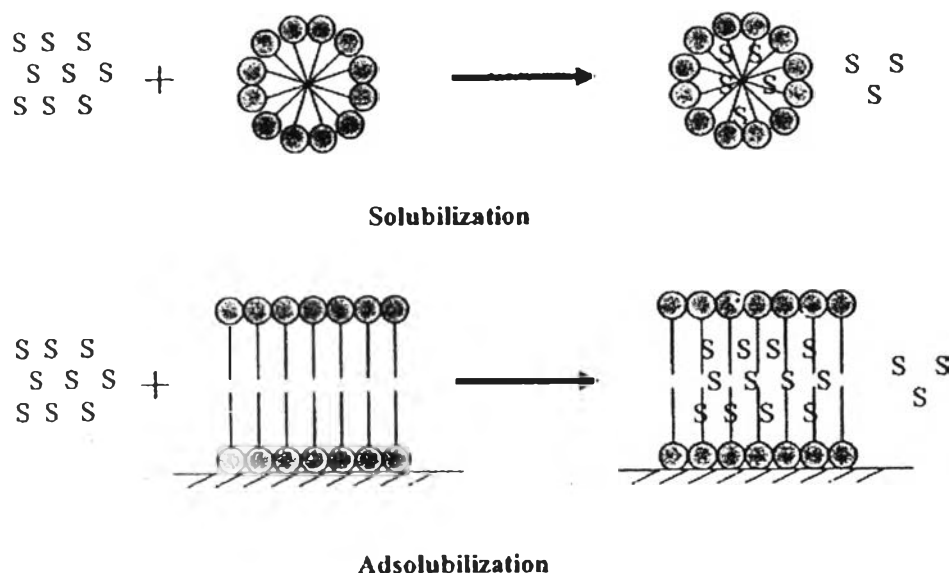
pentadecylethoxylated-nonyl-phenol (NP-15) on alumina from their mixture were studied by Somasundaran and Huang (2000). From the study, it was found that TTAC adsorbed on negatively charge alumina but NP-15 did not adsorb alone on the alumina. The adsorption behavior depends upon the ratio of the two surfactants. With increasing the TTAC concentration of the mixtures, the adsorption of NP-15 is enhanced significantly, and the adsorption isotherms are shifted to lower concentration ranges. In case of adsorption of TTAC, the plateau adsorption decreases markedly upon the addition of nonionic surfactant. This was attributed to the competition of the bulky nonionic NP-15 with TTAC for the adsorption sites under saturated adsorption conditions.

In the case of the adsorption of anionic-nonionic surfactant mixture, the adsorption of nonionic surfactant is enhanced where nonionic alone shows trace adsorption and adsorption of anionic surfactant slightly decreases. Another feature of adsorption isotherm is that with the increasing molar ratio of nonionic surfactant the continuous shift of plateau of isotherm of anionic surfactant towards lower concentration and the hemimicellization concentration of anionic surfactant also shifts towards lower concentration. Adsorption of nonionic surfactant (TX-100) from the mixture of anionic–nonionic surfactant on negatively charged silica gel shows the decreasing amount of adsorbed TX-100 above the CMC with increasing concentration of anionic surfactant and there is no change in isotherm below the CMC between mixed system and the pure TX-100 (Gao *et al.*, 1984). In addition, Somasundaran and Huang (2000) have found that in the case of adsorption of anionic-nonionic surfactant on kaolin, when the hydrocarbon chain length of nonionic surfactant is equal or longer than that of anionic, isotherms of anionic surfactant do not change with changing the chain length of nonionic surfactant. But, if the chain length of nonionic surfactant is shorter than that of anionic, however, different isotherms of anionic surfactant are obtained due to less shielding of anionic surfactant.

## 2.3 Adsolubilization

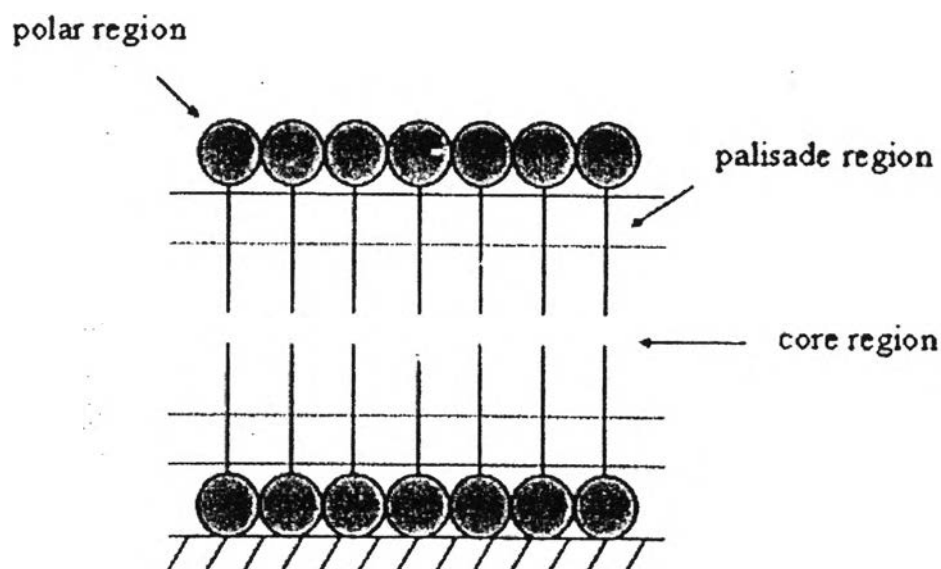
### 2.3.1 Fundamentals

A formal definition of adsolubilization suggested here is “the incorporation of compounds into surfactant surface aggregates, which compounds would not be in excess at the interface in the absence of the surfactant.” (Scamehorn and Harwell, 1988). Accordingly, surfactant adsorbed layers exhibit hydrophobic properties which the organic solutes from aqueous solution can be incorporated. Adsolubilization is the surface analogue of solubilization, which 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). Factors influencing adsolubilization behavior are as follows: (a) surfactant structure; (b) kind of organic solutes; (c) kind of particles. The phenomena of solubilization and adsolubilization are shown in Figure 2.3.



**Figure 2.3** The phenomena of solubilization and adsolubilization.

Figure 2.4 shows the structure of admicelle. This figure indicates that the admicelle is characterized by three regions. The outer region, consisting of the surfactant head groups, is the most polar and forms the admicelle/water and admicelle/solid interfaces. The inner region is referred to as the core region. This region consists of the hydrocarbon chains and is non-polar in nature. The region between the headgroups and the core is the palisade region. This region is intermediate in polarity, consists of the carbons near the headgroups, and is also characterized by water molecules that have penetrated the admicelle (Dickson and O'Haver, 2002).



**Figure 2.4** The admicelle structure.

In order to elucidate the locus of adsolubilization in admicelle, the partition coefficients have been used. The following trends have been proposed concerning the locus of adsolubilization and the partition coefficients: (1) if the solute partitions primarily to the core, the partition coefficients will increase as the mole fraction of the solute increases; (2) if the solute partitions primarily to the palisade region, the partition coefficients will decrease as the mole fraction of the solute increases; (3) if the solute partitions to both the core and the palisade, the partition coefficient will remain constant as the mole fraction of the solute increases (Harwell, 1991).

Kitiyanan *et al.* (1996) studied the adsolubilization of styrene, isoprene and their mixtures into cetyltrimethylammonium bromide (CTAB) bilayers (admicelles) on precipitated silica. The result showed that the adsolubilization equilibrium constant or partition coefficient of styrene is constant. This implies that styrene is adsolubilized into both the palisade region and the core of the admicelle. While the isoprene adsolubilization equilibrium constant decrease with increasing mole fraction implies that isoprene is adsolubilized into the palisade region of the admicelle. In addition, Tan and O'Haver (2004) found that the location of styrene adsolubilization can vary with its amount of loading. They studied the adsolubilization of styrene in polyethoxylated alkylphenols (Triton X) on silica. The result showed that at low concentrations the styrene partition coefficient does not change significantly and then slowly increases at higher concentrations. This implies that styrene initially adsolubilizes into both the palisade region and the core of the admicelle and then primarily into the core region at higher concentrations.

Dickson and O'Haver (2002) investigated the adsolubilization of naphthalene and  $\alpha$ -naphthol with 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  $\alpha$ -naphthol remained constant as the mole fraction of  $\alpha$ -naphthol in the admicelle increased, implying that  $\alpha$ -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.

The adsolubilization has been widely used in the development of various industrial products such as paints, pharmaceuticals, preparation of polymer thin films, and waste water treatment to collect and remove organic pollutants. More recently, Yu *et al.* (1992) have begun to investigate the use of adsolubilization for

admicellar catalysis, a surface analogue of micellar catalysis which may give greater stereo selectivity than micellar catalysis and may be more amenable to development into industrial scale processes because it can be employed in a fixed bed mode.

### 2.3.2 Adsolubilization in Single-Surfactant System

A number of studies have been conducted on the adsolubilization in single-surfactant system. Adsolubilization of hexanol for silica-cationic surfactant systems such as dodecylpyridinium chloride (DPCI) and cetylpyridinium chloride (CPCI) has been studied by Esumi *et al.* (1991). The adsorbed amount of CPCI increases slightly with increasing feed concentration of hexanol. The increase in the adsorption of CPCI is due to an increase of the surface activity of CPCI in the presence of CPCI. A similar trend is observed for the silica-DPCI system. The adsolubilized amount of hexanol increases with the adsorbed amount of CPCI and decreases above the critical micelle concentration of CPCI. Also, the adsolubilized amount of hexanol increases with the feed concentration of hexanol. However, for the silica-DPCI system, hexanol is hardly adsolubilized. Microenvironmental properties such as micropolarity and microviscosity of adsorbed layers have been estimated using the fluofluorescence probe and spin probe techniques. The micropolarity of the CPCI layer on silica is lower than that of the DPCI layer on silica, while the microviscosity of the former is greater than that of the latter. It is reasonable to correlate the adsolubilization behavior with the microenvironmental properties of the adsorbed surfactant layer.

Esumi and Yamamoto (1998) investigated the adsorption of sodium dodecyl sulfate (SDS) on hydrotalcite and adsolubilization of 2-naphthol. They found that the amount of SDS adsorbed increased sharply at low SDS concentration and then reached a plateau. The adsorption of SDS would occur at two sites: one is the external surface and the other is the interlayer. The microenvironment in the SDS adsorbed layer becomes hydrophobic with increasing SDS concentration. The amount of SDS adsorbed in the presence of 2-naphthol was almost the same as that in the absence of 2-naphthol. The amount of 2-naphthol adsolubilized increased with increasing SDS concentration and reached a maximum, and then gradually decreased. This gradual reduction is not correlated with the solubilization in SDS micelles in

aqueous solution. But it come from the 2-naphthol adsorbed would desorb by adsorption of SDS due to electrostatic repulsive interaction between SDS and dissociated 2-naphthol.

A simultaneous sorption of 2-naphthol and copper ions by cationic surfactant-adsorbed laponite was carried out by Esumi *et al.* (1999). Two cationic surfactants, dodecyl trimethylammonium bromide (DTAB) and 1,2-bis(dodecyldimethylammonio) ethane dibromide (2RenQ), were used. The results shown that both the surfactant-adsorbed laponite retained a high sorption capacity for copper ions due to cation exchange, while the 2RenQ-adsorbed laponite completely adsolubilized 2-naphthol in a whole concentration region, but the DTAB-adsorbed laponite one decreased the adsolubilization gradually above the CMC of DTAB.

Esumi *et al.* (2000) examined the adsolubilization of 2-naphthol on alumina with adsorption of sodium dodecyl sulfate (SDS). 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. The result from the experiment 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.

Adak *et al.* (2006) investigated the removal of phenol from water by sodium dodecyl sulfate modified alumina through adsolubilization. The surfactant-modified alumina was found to be very efficient showing 90% removal of phenol from phenol-spiked distilled water under optimized conditions. The removal of phenol from water followed a second order kinetics. The  $\text{pH} < 7$  favors the removal. The removal efficiency was increased due to the presence of anions and was decreased a little due to the presence of cations. Temperature and humic acid had no effect on the removal of phenol. The removal of phenol-spiked in tap water was found to be very much comparable with that obtained for distilled water system. Desorption of both SDS and phenol from the surface was possible using sodium hydroxide solutions. Desorption of only phenol is possible by acetone or rectified spirit.



The adsolubilization of dihydroxybenzenes (catechol and hydroquinone) into cetyltrimethylammonium bromide (CTAB) layers on silica particles have been investigated by Li *et al.* (2007). It was found that the adsolubilization amount of catechol increases with increasing the concentration of CTAB, reaches a maximum value at the critical micelle concentration (CMC), and then decreases with further increment of CTAB concentration. For hydroquinone, different phenomenon is observed. The maximum adsolubilization amount reaches at critical surface aggregation concentration (CSAC) instead of CMC of the CTAB and then decreases until it reaches a plateau at CMC. This is because that the interaction between hydroquinone and CTAB molecules is stronger than the interaction between hydroquinone and CTAB micelle. Hence, the adsolubilization ability of the admicelle is smaller than the monolayer. This will lead to the decrease of the adsolubilization amount of hydroquinone on silica surface. However, the formation of the micelles has no effect on the adsolubilization of hydroquinone because of the weak interaction between CTAB micelles and hydroquinone. This is the reason that the adsolubilization amount remains constant after CMC.

### 2.3.3 Adsolubilization in Mixed-Surfactant System

Surfactant mixtures provide several advantages over single surfactants, because the adsorption of surfactants on particles can be controlled using appropriate surfactants and solution properties. It would be expected that the adsolubilization of organic compounds could be enhanced using a minimum amount of surfactant mixtures. The adsolubilization of 2-naphthol using surfactant mixtures of an anionic surfactant, sodium dodecyl sulfate (SDS), and a nonionic surfactant, hexaoxyethylenedodecyl ether ( $C_{10}E_6$ ), on alumina has been investigated by Esumi *et al.* (2000). In a single-surfactant system,  $C_{10}E_6$  itself showed a very low adsolubilization of 2-naphthol, whereas SDS has an appreciable adsolubilization capacity. In a mixed-surfactant system, the adsolubilization become greater with an increase in the SDS content in the initial mixtures. On the other hand, the ratio of adsolubilized amount to surfactant adsorbed amount become smaller when the SDS content in the initial mixtures increased. They use the ratio of adsolubilized amount to surfactant adsorbed amount to compare the efficiency of adsolubilization. When

the ratio of SDS to  $C_{10}E_6$  becomes small, the efficiency of adsolubilization becomes greater. 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.

Esumi *et al.* (2001) investigated the adsolubilization of 2-naphthol by binary mixtures of cationic and nonionic surfactants on silica. Two cationic surfactants used were hexadecyltrimethylammonium bromide (HTAB) and 1,2-bis(dodecyldimethylammonio)ethane dibromides (2RenQ), and a nonionic surfactant used was hexaoxyethylenedecyl ether ( $C_{10}E_6$ ). In the single surfactant systems, adsolubilization of 2-naphthol for HTAB and 2RenQ was very similar and was greater than that for  $C_{10}E_6$ . In the HTAB/ $C_{10}E_6$  system, the adsolubilization of 2-naphthol was enhanced by surfactant mixtures of HTAB and  $C_{10}E_6$  compared to those of single systems. On the other hand, in the 2RenQ/ $C_{10}E_6$  system the adsolubilization of 2-naphthol by surfactant mixtures of 2RenQ and  $C_{10}E_6$  was rather smaller than that of 2RenQ alone but still larger than that of  $C_{10}E_6$ . It is suggested that the hydrophobic properties in the mixed surfactant adsorbed layer for adsolubilization of 2-naphthol are affected by the structure of cationic surfactant.

#### 2.3.4 Adsolubilization in PEO-PPO-PEO Triblock Copolymer System

The use of polymeric surfactants as an adsorbate is more practical important because replacement of the solution phase may cause desorption of the adsorbed surfactants away from the interface. This desorption will necessarily result in subsequent release of the adsolubilized solutes. Polymeric surfactants have an advantage over low molecular surfactants: the desorption rate of the former types is generally lower than that of the latter. In other words, the adsorbed layer of polymeric surfactants is able to remain at the interface, overcoming a problem of replacement of the supernatant by the surfactant free solution.

Montarges *et al.* (1998) studied the adsorption of organic toxicants from water onto  $Al_{13}$ -pluronic modified clay. This organic toxicants are 4-monochlorophenol (4-MCP) and 2,5-dichlorophenol (2,5-DCP). In the case of 4-MCP, the presence of co-intercalated PEO-PPO-PEO triblock copolymers leads to higher adsorbed amounts than what is observed for a classical aluminum-pillared clay. In acid conditions the highest adsorbed amounts are obtains for the clay

modified with the most hydrophobic polymer. In basic conditions a reverse trend is observed as the highest adsorbed amounts are obtained for the clay modified with the most hydrophilic polymer. In the case of 2,5-DCP, the highest adsorbed amounts are obtained in the case of clay modified with the most hydrophobic polymer for both pH domains.

Tsurumi *et al.* (2006) investigated the adsolubilization of 2-naphthol into an adsorbed layer of PEO-PPO-PEO triblock copolymers on hydrophilic silica. The result showed that the order of the adsorption in the saturation level was found to be  $P123 \approx P103 > P105 \gg F108$ , meaning that copolymers with higher hydrophobicity can adsorb preferentially to the silica surface. In other words, the adsorbed amount increases as the HLB value decreases. Indeed, this order was parallel to the order of the adsolubilization amount of 2-naphthol. This suggests that an enhancement of copolymers adsorption provides a number of hydrophobic sites that is sufficient to enable adsolubilization of 2-naphthol. In the case of co-addition of copolymers and 2-naphthol, the adsolubilization amount increased gradually at lower surfactant concentration regions, reached a maximum, and then decreased with increasing concentration of copolymers. The maximum amount appeared at CMC of each copolymer. The decrement in the adsolubilization amount is interpreted as incorporation of the 2-naphthol takes place not only into the adsorbed layer but also into the solution micelles simultaneously. On the other hand, the final decrement was not observed when 2-naphthol was added after replacement of the copolymers supernatant by free surfactant solution.

The same experimental was investigated on hydrophobically modified silica particles by Tsurumi *et al.* (2006). The result showed that the amount of the PEO-PPO-PEO adsorbed of the maximum/saturation adsorption level was increases with a decrease in the HLB value, suggesting that the more hydrophobic copolymers (P103 and P123) adsorb preferentially onto the hydrophobic silica surface over the more hydrophilic copolymers (P105 and P108). The greater adsorbed amount of the more hydrophobic surfactants resulted in a greater amount of 2-naphthol adsolubilized into the adsorbed copolymers layers. In the case of simultaneous addition of the copolymer and 2-naphthol, the amount adsolubilized into the adsorbed P123 and P103 layers increased, reached a maximum, and

then decreased. On the other hand, for both P105 and P108, a decreased in the adsolubilized amount was not observed. When 2-naphthol was added after replacement of the copolymers supernatant by a surfactant free solution, the final decrease was insignificant for all copolymers.

As mentioned earlier, when compare both researches of Tsurumi *et al.* the adsorption and adsolubilization of the more hydrophilic copolymers (P105 and P108) on the hydrophobic silica particles is expected to be greater than that on the hydrophilic silica particles.

Wattanaphan (2008) studied the adsorption of EO/PO block copolymers L31, P123, L64, 17R2, 25R4, and 10R5 onto hydrophilic silica surfaces and adsolubilization of phenol, naphthalene, and 2-naphthol into EO/PO block copolymers adsorbed layer. The results showed that L31 and 17R2 with HLB values lower than 7 could not appreciably adsorb onto hydrophilic silica due to the small number of EO groups capable of interacting with the silica surface. Four factors are considered for the adsorption of block copolymers onto silica; HLB value, configuration, EO/PO ratio, and molecular weight. Consequently, the maximum amount of adsorbed surfactant is thus affected by the copolymer configuration, EO/PO ratio, and molecular weight as well. For adsolubilization study, for a given HLB value, the copolymers which have a larger number of PPO groups and higher molecular weight appear to appreciably adsolubilize organics more than those with a lower number of PPO groups and lower molecular weight. In addition, the effect of size and polarity of organic compounds were investigated. The small molecules prefer to be adsolubilized more than the larger one and the polar compounds tend to have significantly higher in the amounts of organics adsolubilized than the non-polar compounds

#### **2.4 Factors Affecting Surfactant Adsorption and Adsolubilization**

Many factors affecting surfactant adsorption at solid-liquid interface, as well as adsolubilization of organic molecules have been introduced in this section. These factors determine the mechanism, efficiency and effectiveness of the adsorption and adsolubilization.

#### 2.4.1 Nature of the Structural Groups on the Solid Surfaces

Adsorption and adsolubilization is related to the nature of the structural groups on the solid surface whether the surface contains highly charged sites or essential nonpolar group, and the nature of atoms of which this site or grouping are constituted.

Esumi (2001) investigated 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) and 1,2-bis(dodecyltrimethylammonio)ethane dibromide (2RenQ)) on titanium dioxide with dodecyl chain groups increased with increasing the concentration of dodecyl chain due to hydrophobic interaction. The adsolubilized amount of 2-naphthol on DTAB- titanium dioxide with dodecyl chain groups increased with increasing the concentration of dodecyl chain, but not observed for 2RenQ. Adsorption of an anionic surfactant (sodium dodecyl sulfate (SDS)) on XNm occurred mainly due to both electrostatic attraction force and hydrophobic interaction. On the other hand, adsorption of cationic surfactants, DTAC and 2RenQCl, on XNm was quite smaller compared with that of SDS due to electrostatic repulsion force. In the case of adsolubilization of XNm, the amount of 2-naphthol adsorbed in the absence of surfactants increased with increasing alkyl chain length on XNm. Further, an appreciable increase in the adsolubilization of 2-naphthol on XNm with adsorption of 2RenQCl was observed.

#### 2.4.2 Molecular Structure of the Surfactant being Adsorbed

The chemical structure of surfactant influences on the adsorption and adsolubilization. The surface-active properties of a surfactant are therefore determined by its numerous structural characteristics, which includes the type of surfactant (ionic or nonionic surfactant) and whether the number, length, straight chain or branched of the hydrophobic part.

Esumi and Yamanaka (1995) studied the adsorption of sodium dodecyl poly(oxyethylene) sulfate, SDE<sub>n</sub>S (n = 0, 3, 5, and 8), on positively charged alumina in aqueous solution. The adsorption of SDE<sub>n</sub>S decreases with increasing

oxyethylene chain length of  $SDE_nS$ . In particular, the decrease in the adsorption of  $SDE_8S$  is markedly large. The adsorption of  $SDE_nS$  was considerably influenced in the presence of 2-naphthol. In particular, the enhancement in the adsorption of SDS is probably due to the decrease in the electrostatic repulsive force between the adsorbed SDS molecules. In addition, the adsolubilization of yellow OB and 2-naphthol have been investigated. It is found that yellow OB is preferably partitioned into the  $SDE_nS$  adsorbed layer on alumina as the oxyethylene chain length of  $SDE_nS$  decreases. The adsolubilized amount of 2-naphthol in the case of SDS,  $SDE_3S$ , and  $SDE_5S$  increased sharply at low concentration of  $SDE_nS$  and reached a maximum, then decreased. On the other hand, in the case of  $SDE_8S$ , the adsolubilized amount of 2-naphthol increased gradually. Further, the adsolubilization capacity for 2-naphthol increased from  $n = 0$  to  $n = 8$  of  $SDE_nS$ .

Esumi *et al.* (1996) investigated the adsorption and adsolubilization by monomeric (1RQ), dimeric (2RenQ), or trimeric (3RdienQ) quaternary ammonium surfactants at silica/water interface. They found that the amount adsorbed at saturation decrease with increasing dodecyl chain number of the surfactant from 1RQ to 2RenQ and 3RdienQ. The amounts of 2-naphthol adsolubilized increase, reach a maximum, and then decrease for the three surfactants. The ratio of amount of 2-naphthol adsolubilized to the adsorbed amount of surfactant increases with increasing the chain number from 1RQ to 2RenQ and 3RdienQ. However, it is interesting that the ratio of amount of 2-naphthol adsolubilized to dodecyl chain decreases with increasing chain number from 1RQ to 2RenQ and 3RdienQ. In addition, the result suggested that 2RenQ and 3RdienQ adsorb strongly on the silica surface, incorporating 2-naphthol firmly compared to 1RQ.

#### 2.4.3 Environmental of the Aqueous Phase (pH and Ionic Strength)

It is well known that the surface charge density of disperse hydrophilic solid in water is governed primarily by the pH of the system. Thus, the amount of adsorption and adsolubilization is affected by change in the pH of the solutions. The point of zero charge (pzc) is the pH value at which a solid submerged in an electrolyte exhibits zero net electrical charge on the surface. When the pH is lower than the pzc value, the surface is positively charged. Conversely, above pzc the

surface is negatively charged. Pradubmook *et al.* (2003) studied the effect of pH on the adsorption of cetyltrimethylammonium bromide (CTAB) on silica and the adsolubilization of toluene and acetophenone. The adsorption and adsolubilization were investigated at pH values 5 and 8. The CTAB adsorption at pH 8 was higher than the adsorption at pH 5. The point of zero charge for silica is between 2 and 3. Thus, the higher above pH 3 the more negative the surface, and the greater the adsorption of cationic surfactant. Increasing the pH leads to higher amounts of head on adsorbed surfactant on the silica. The adsolubilization of toluene and acetophenone at pH 8 was higher than the adsolubilization at pH 5. For toluene, pH had little effect on the adsolubilization. In contrast, the pH effect on acetophenone was much more pronounced.

For effect of ionic strength, the adsorbed amount of ionic surfactants apparently increases with increasing ionic strength due to a decrease in the electrostatic repulsion force between the surfactants. Esumi *et al.* (1996) studied the effect of added salt, NaBr, on adsorption and adsolubilization of 2-naphthol by gemini surfactant on silica. The gemini surfactant was used in this study is 1,2-bis(dodecyldimethylammonio) ethane dibromide (2RenQ). They found that the adsorbed amounts and the plateau adsorption of 2RenQ increase with increasing amount of NaBr added. The adsolubilized amounts of 2-naphthol with added NaBr were greater than that with no added NaBr, but the ratio of the adsolubilized amount of 2-naphthol to the adsorbed amount of 2RenQ decrease with increasing NaBr concentration may occur because incorporation of 2-naphthol molecules into the 2RenQ adsorbed layer is prevented by the increasing density 2RenQ molecular packing caused by the added NaBr. In addition, from a two steps process of adsorption-adsolubilization, the results shown the adsolubilized amounts of 2-naphthol with no added NaBr markedly decreases, accompanying the significant desorption of 2RenQ, while the adsolubilized amounts of 2-naphthol and adsorbed amounts of 2RenQ with NaBr added are almost the same. Therefore, it is inferred that 2RenQ adsorbs strongly on the silica surface with added NaBr, incorporating 2-naphthol more firmly compared to the situation with no added NaBr.