# CHAPTER II
## BACKGROUND AND LITERATURE REVIEW

### 2.1 Surfactant Adsorption on Solid Oxide Surfaces

The adsorption isotherm of an ionic surfactant on an oxide surfaces 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). Normally, this 'S'-shaped isotherm can be separated into four regions, as shown in Figure 2.1. Region I is a low adsorption density region in which the surfactant adsorption shows a linear dependence on surfactant concentration. This is an indicative of the absence of lateral interactions between the adsorbed surfactant molecules (Rosen, 1988).
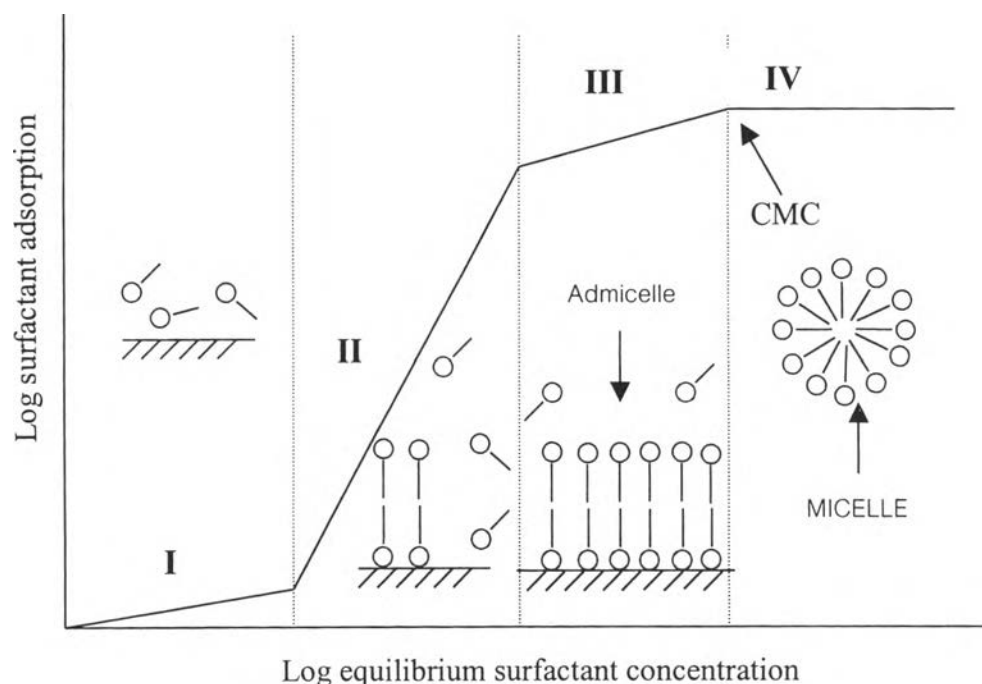


**Figure 2.1** Typical adsorption isotherm of surfactant on solid oxide surface.

Region II is indicated by an increase in the slope of the adsorption isotherm caused by the onset of aggregate formation due to attractive lateral interactions between surfactant tail groups. These "adsorbed micelles", admicelles, are the

surface analog of micelles in bulk. These aggregates are called hemimicelles or admicelles, depending upon who refers to them and whether or not they are monolayers or bilayers. All of the factors that result in the lowering of the CMC of a surfactant can also be expected to lower the concentration at which admicelles form (Yeskie and Harwell, 1988).

In region III the slope of the isotherm decreases because either the surface charge has been neutralized or all of the high energy surface sites have been covered (Tiberg, 2000). Region IV is where adsorption reaches a maximum and all added surfactant goes into the solution to form micelles. It is thought that the surface has become saturated with admicelles or that adsorption stops because the surfactant concentration has reached the CMC. At the CMC, the first micelle forms at the same chemical potential as the last admicelle to form; if the surfactant concentration is increased further, this only results in the formation of more micelles at the same chemical potential as that of the first micelle to form, without an increase in the adsorption of surfactant.

While Figure 2.1 is a typical surfactant adsorption isotherm, only parts of it may be present in some situations. For example, at a very low surfactant adsorption when there is electrostatic repulsion between the surfactant and the surface the CMC may be reached before the onset of lateral interactions between adsorbed surfactants; in this case regions II and III will be missing from the isotherm (Rosen, 1988). If a very high surfactant adsorption occurs on the surface, the Region I/II transition may occur below the concentration at which the surfactant can be detected such that Region I may exist, adsorption at that level cannot be measured.

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 are principally in the form of monolayers, formed on patches of the surface. Individual surfactant molecules or monomers in these aggregates are viewed as being oriented such that the hydrophilic groups of the surfactants are next to the surface, with the surfactant tail groups forming a hydrophilic film in contact with the aqueous solution. Aggregates of this

structure are commonly referred to as hemimicelles while it has been proposed that a bilayered aggregate, termed an admicelle, is formed (Scamehorn *et al.*, 1982).

## 2.2 Solubilization and Adsolubilization

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, 1988). A 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." (Scamehorn and Harwell, 1988). This phenomenon is the surface analog of solubilization, with adsorbed surfactant bilayer playing the role of micelle, as shown in Figure 2.2.
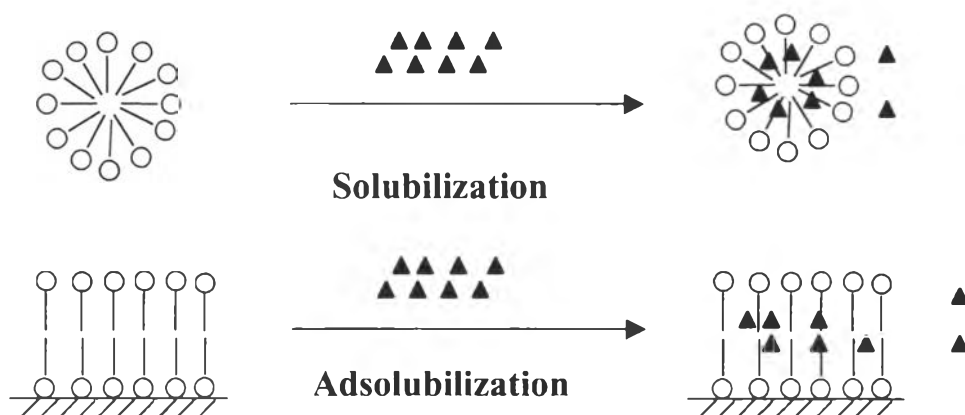


**Figure 2.2** The phenomena of solubilization and adsolubiliation.

Nguyen *et al.* (1988) evaluated several different methods which can be used to study the solubilization of an organic solute in aqueous micellar solutions. The methods which are successfully used to study the solubilization isotherms of organic solutes in micellar solutions are the vapor pressure method, head-space gas chromatography, semi-equilibrium dialysis, micellar-enhanced ultrafiltration, UV-absorbance methods and NMR methods. The selection of the best method to study a particular solubilization isotherm is dependent on the requirement of the research.

Kitiyanan *et al.* (1996) studied adsolubilization of styrene and isoprene into cetyltrimethylammonium bromide (CTAB) admicelle on precipitated silica. The results from a single adsolubilizate systems showed that styrene adsolubilization increases with increasing styrene equilibrium concentration in aqueous phase, and isoprene adsolubilization increases with increasing isoprene partial pressure. The adsolubilization equilibrium constants or partition coefficient (K) of both adsolubilizates were calculated. The adsolubilization equilibrium constant of isoprene decreases with increasing isoprene mole fraction in the admicelle which can suggested that isoprene is adsolubilized into palisade layer. But the adsolubilization equilibrium constant of styrene is almost constant with increasing styrene concentration which suggests that styrene is adsolubilized into both the palisade layer and the core of the admicelle.

Lai *et al.* (1997) investigated sodium perfluoroheptanoate adsorption and adsolubilization of small aliphatic fluorocarbon alcohols into surface aggregate formed on alumina. They found that higher concentrations and increasing hydrophobicity of the solutes enhanced surfactant adsorption below the plateau region. Partitioned amounts of the fluorocarbon alcohols rose with the alcohol supernatant concentration and chain length. Aggregation numbers were estimated using the two-site adsolubilization model.

## 2.3 Factors Affecting Surfactant Adsorption and Adsolubilization

As mentioned in the precious section, surfactant adsorption and adsolubilization of solutes into adsorbed surfactant are strongly influenced by many factors, such as:

-The nature of the structure groups on the solid surface-whether the surface contains highly charged sites or essentially nonpolar group, and the nature of the atoms of which these sites or grouping are constituted.

In 1999, Chorro *et al.* studied 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 showed 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 are all larger for the raw silica than for the treated silica.

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

Esumi *et al.* (1996) studied the adsorption of quaternary ammonium cationic surfactants with one, two, and three alkyl chains on silica by measuring adsorption density, and dispersion stability. The adsorbed amount at saturation decreased with increasing chain number of the surfactant. 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. 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.

Subsequently, Esumi *et al.* (1997) studied adsorption and adsolubilization of cationic surfactant with different structures on clay (laponite). As an adsolubilizate, 2-naphthol, one of the representative toxic substances, was employed. The results showed that adsorption of cationic surfactant increased from methyldodecylbis[2-dimethyldodedecylammonioethyl] ammonium tribromide (3RdienQ) to dodecyltrimethylammonium bromide (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.

-The environment 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 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.

Behrends and Herrmann (2000) studied the adsolubilization of anthracene on surfactant covered silica in dependence on pH: indications for different adsolubilization in admicelle and hemimicelle. They studied the distribution of anthracene between aqueous solution and silica gel covered with the cationic surfactant hexadecyltrimethylammonium bromide (HDTMA) in batch experiments as a function of the adsorption density of HDTMA and in dependence on pH. It was observed that the partitioning constants (K), normalized on the content of organic carbon in the surfactant coverage, are not only a function of the surface concentration but also depend on pH. At low concentrations of adsorbed HDTMA, no adsolubilization of anthracene was detected.

- Surface adsorption and structural arrangement of adsorbed surfactant

Velegol *et al.* (2000) studied the effect of the surfactant counterion on the adsorption isotherms, kinetics, and layer structure for cationic hexadecyl trimethylammonium surfactant on negatively charged silica surfaces. The adsorption

kinetics suggest that the adsorption mechanism changes at CMC. A change in mechanism is also suggested by differences observed in the state of interfacial self-assembly on either side of the CMC. Above the CMC, increasing the binding affinity of the counterion (from chloride to bromide) increased the surface excess concentration by approximately 60% and changed the structure of the adsorbed surfactant layer from aggregates with circular projections to wormlike micelles. Below the CMC, the counterion has only a small effect on the structure of the adsorbed layer, and the isotherms are similar, provided the surfactant concentration is scaled by the appropriate cmc.

Atkin *et al.* (2001) studied the effect of pH, electrolyte, and surface preparation on the surface excess and adsorption kinetics of cetylpyridinium bromide to the silica by using optical reflectometry and atomic force microscopy (AFM). AFM imaging above the critical surface aggregation concentration (CSAC) elucidates spherical surface structures in the absence of electrolyte and elongated cylindrical structures with added electrolyte. At all other concentrations and even at the CSAC, adsorption proceeds slowly in the absence of salt and takes hours to reach an equilibrium value but when electrolyte is present, the adsorption is complete within minutes. Moreover AFM imaging of surfactant adsorption in the slow adsorption region suggests that the slow adsorption kinetics are due to the gradual formation of surface structures in this region. At moderate to high surfactant concentration with added electrolyte, pH increases have little effect on surface excess. In the absence of electrolyte, the surface excess increases with pH as expected, but it is suggested that these increases are primarily due to increased solution ionic strength and not due to increased charge on the substrate. At low surfactant concentration, added cations compete effectively with the cationic surfactant for adsorption sites, resulting in no detectable adsorption until pH ~8 is reached.

Zajac *et al.* (1996) studied the influence of the alkyl chain length and the concentration of exchangeable sodium cations at the solid/water interface on the energetics of cationic surfactant adsorption on a hydrophilic silica surface at free pH. The adding of NaBr to the system prevents the surfactant tails from adopting the orientation parallel to the surface. The growth of the adsorbed layer through local

bilayered admicelles results in a greater effectiveness of adsorption. If the adsorption density is sufficiently high, lateral interactions between adsorbed ions induce a change in the surfactant tail conformation toward a more perpendicular orientation. This favors the hydrophobic bonding mechanism of adsorption and leads to the formation of various adsorbate structures on the silica surface. For high densities of charged sites, many experimental arguments support the existence of a compact bilayered structure at surface saturation. For low charge densities, a great increase in the chemical potential of the solute in the bulk phase is necessary to initiate surface aggregation. As a result, the final structures are less compact.

## 2.4 Previous Works

Pradubmook (2001) studied the effect of pH on adsolubilization of a cationic surfactant, cetyltrimethyl ammonium 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 adsolibilization. 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 equilibruim constant (K) suggested that toluene adsolubilized into both the palisade layer and core of admicelle while acetophenone adsolibilized into palisade layer only.

Kanjanakhunthakul (2002) studied the effects of ionic strength on the adsolubilization of toluene and acetophenone into CTAB admicelles on precipitated silica. The adsolubilization of the model organic compounds, toluene and

acetophenone, was investigated 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 synergetic 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.