CHAPTER II
BACKGROUND AND LITERATURE REVIEW

2.1 Adsorption of Surfactant on Solid Oxide Surface

The adsorption isotherm for an ionic surfactant onto an oppositely charged substrate, for example, sodium alkanesulfonates or alkylbenzenesulfonate onto oppositely charged Al_2O_3, is typically S-shaped. The shape of the isotherm is believed to reflect four distinct modes of adsorption as shown in Figure 1 (Kitiyanan et al., 1996).
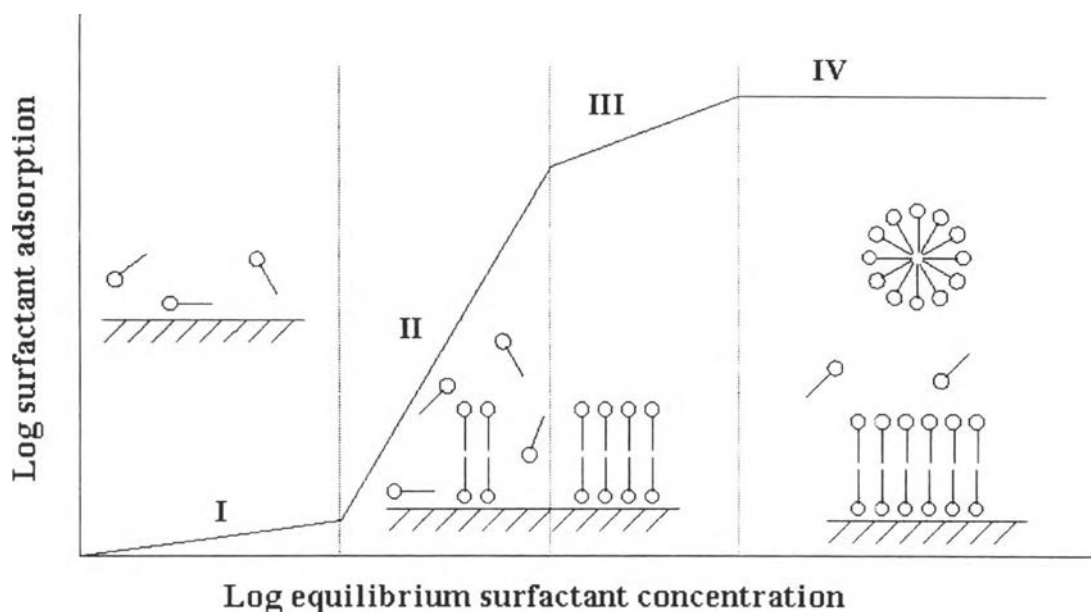

Figure 2.1 Typical adsorption isotherm of surfactants on solid oxide surfaces.

Region I, marked by low adsorption densies, is sometimes referred to as the Henry's law region. In region I the surfactants are individually adsorbed and do not appreciably interact with one another. For nonionic surfactants and for ionic surfactants with some added electrolyte, the slope of the isotherm in this region is 1 when the data is plotted on the log-log plot (Rosen, 1988). For ionic surfactants on a surface of moderate charge density with no added

electrolyte, the slope of the isotherm may be less than 1 because the charge on the surface is being reversed by the adsorption of the charged surfactant ions. 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 indicated by the sharp increase in the slope of the isotherm. All investigators of surfactant adsorption have attributed this increase in slope to the thermodynamically favored formation of micelle-like aggregates of adsorbed surfactant. The transition has been given designations analogous to the critical micelle concentration (CMC), that is, the critical admicelle concentration (CAC) or hemimicelle concentration (HMC), depending upon which theory one subscribes to. An admicelle is a local bilayer structure with a lower layer of head groups adsorbed onto the substrate surface and an upper layer of head groups exposed to the solution. A hemimicelle is a monolayer structure having head groups adsorbed onto the surface while the tail groups are exposed to the solution (Yeskie and Harwell, 1987).

The region II/region III transition is marked by a decrease in the slope of the isotherm, which in some systems, can be quite dramatic. While there is widespread agreement about the mechanism for the change in slope from region I to region II. There is little agreement about the reason for the change in slope from region II to region III. The most commonly given explanation is that the aggregates forming in region II are monolayers adsorbing head down on an oppositely charged surface (Rosen, 1988). The change in slope coincides with the cancellation of the charge on the solid surface by the charge on the adsorbed aggregates so that subsequent surfactants are adsorbing onto a like-charged surface (Rosen, 1988). It is also proposed that a second layer on the aggregate doesn't begin to form until region III occurs (Rosen, 1988). Other workers have presented data to indicate that the second layer forms suddenly

at the CMC of the system. Other workers have attributed the change in slope to the distribution of energies on the surface. That is, in Region II surfactant molecules are adsorbing onto the higher energy sites on the substrate surface, while in Region III they are adsorbing onto lower energy sites (Tiberg, 2000) The region II/region III transition does not always correspond to a change in the charge of the surface, however it is also observed in systems of nonionic surfactants adsorbed on silica (Rosen, 1988).

Region IV is called the plateau adsorption region. In most systems the region III/region IV transition occurs at or near the CMC of the surfactant (Rosen, 1988). When the surfactant is monoisomeric the adsorption becomes nearly constant above the CMC. This phenomenon is easily understood in term of the pseudophase separation model of micelle formation: micelles that form at the CMC have the same chemical potential as the monomer at the CMC (Rosen, 1988). As the concentration of surfactant increases, the surfactants go into the micellar pseudophase at almost the same chemical potential as the surfactant in the first micelle to form and so the chemical potential of the surfactant does not increase as dramatically with surfactant concentration above the CMC as it would in the absence of micelles. Since the admicelles are also in equilibrium with the same monomer phase, the last admicelle to form is also at the same chemical potential as the monomer at the CMC. The only way more admicelles can form is for the chemical potential of the surfactant to increase, but this would occur only slowly because any added surfactant goes to form more micelles . The pseudophase separation model is certainly only an approximation, but in general, the better a surfactant is at forming micelles, the more pronounced will be the region 3/region 4 transition, the closer that transition will be to the CMC, and the less the adsorption will increase above the CMC (Scamehorn et al., 1981).

Yeskie and Harwell (1988) studied the structure of the adsorbed surfactant aggregates, especially focusing on the surface charge density at the hemimicelle/admicelle transition. They found that surfactants adsorbed from aqueous solution onto mineral oxide surfaces form micelle-like aggregates at the interface. It had long been the view 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 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 (Scamehorn *et al.*, 1981) However, Yeskie proposed that a bilayered aggregate, termed an admicelle, is formed (Scamehorn *et al.*, 1981).

Monticone and Treiner (1995a) studied the adsolubilization of naphthalene derivatives and cationic surfactant onto porous silica in aqueous solution. They studied the coadsorption as a function of surfactant concentration, i.e., below and above the critical micelle concentration (CMC) and at two pH values (3.6 and 6.5). Adsorption of cetylpyridinium chloride or cetyltrimethylammonium bromide on the silica induced a considerable adsolubilization of neutral molecules. The effect may be described by a partitioning process. Naphthalene, which is strongly adsorbed on the silica surface in the absence of surfactant, is also desorbed as micelles are formed. Comparison of the micellar solubilization effect as determined from solute desorption or direct micellar solubilization experiments display differences that may be attributed to the retention of some solute on the adsorbed surfactant structure (hemimicelle or admicelle) in the presence of free micelles.

2.2 Solubilization and Adsolubilization

Solubilization is defined as the spontaneous dissolving of a substance (solid, liquid, and 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). The partitioning of organic solutes from aqueous solution into the interior of adsorbed surfactant aggregate is termed adsolubilization. This phenomenon is the surface analog of solubilization, with adsorbed surfactant bilayer playing the role of micelle, as shown in Figure 2.2 (Rosen, 1988).
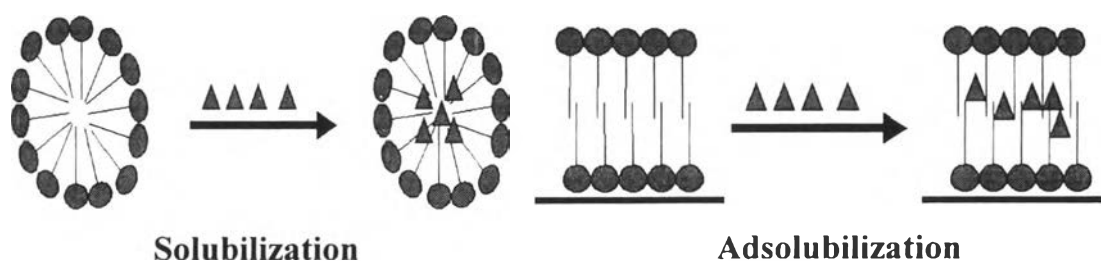

Solubilization   **Adsolubilization**

Figure 2.2 The phenomena of solubilization and adsolubilization.

The presence of adsorbed surfactant aggregates at the solid/liquid interface in aqueous solution may promote the incorporation of hydrophobic solute molecules. This phenomenon demonstrates some of the characteristics of classical micellar solubilization and therefore has been called surface solubilization, adsolubilization, or coadsorption. It has been shown that the distribution of neutral compounds such as alcohol, phenol or naphthalene derivatives between adsorbed surfactant aggregate and the aqueous solution may be described by a partition constant. As the solute concentration in the system may be chosen well below its aqueous solubility, the partition coefficient can be determined under controlled activity conditions so that a true thermodynamic quantity may be derived.

Kitiyanan *et al.* (1996) studied adsolubilization of styrene and isoprene into cetyltrimethylammonium bromide (CTAB) admicelle on precipitated silica. The results from 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 of both adsolubilizates were calculated, and suggested that styrene is adsolubilized into both the palisade layer and the core of admicelle, while isoprene is adsolibilized only into the palisade layer.

Sun and Jaffe (1996) studied the sorption of phenanthrene from water onto alumina coated with di-anionic surfactants (commercial DOWFAX). The results showed that the di-anionic surfactants adsorbed on alumina are effective pseudo-phases for the sorption of nonionic organic compounds (NOCs) such as phenanthrene, increasing the apparent distribution coefficient (K*) of phenanthrene onto the solid phase by up to 3 orders of magnitude. The effectiveness of the surfactants as sorptive phases was shown to increase with their carbon content.

Lai *et al.* (1997) investigated the adsolubilization of fluorocarbon alcohols into perfluoroheptanoate admicelle formed on alumina. The results showed that higher concentrations and increasing hydrophobicity of the adsolubilizate enhanced surfactant adsorption below the plateau region. Partitioned amounts of the fluorocarbon alcohols rose with the alcohol supernatant concentration and chain length. Aggregation numbers were estimated with the two-site adsolubilization model.

Thakulsukanant *et al.* (1997) studied adsolubilization and stability characteristics of hydrocarbon aggregates chemically bonded to porous silica. In this study, octadecyltrichlorosilane (ODS) was chemically bonded with silanol groups on the silica surface. The adsolubilization capabilities and

stability of the bonded ODS were then studied and compared to those of physically adsorbed aggregates of cetytrimethylammonium 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.

Holuzheu *et al.* (2000) studied the distribution ratios of aromatic compounds between aqueous solution and surfactant-covered silica by chromatographic method. In this work equilibrium constants of 26 aromatic compounds were determined by a chromatographic method as functions of pH and of the adsorption density of hexadecyltrimethylammonium bromide (HDTMAB) on silica. The dependency of the retention times on surfactant adsorption changes with increasing HDTMAB coverage and was modified by pH. The changes can be explained by the transition of electrostatically driven surfactant adsorption to hydrophobic aggregation.

Esumi *et al.* (1996) investigated the characterization of adsorption of quaternary ammonium cationic surfactant and their adsolubilization behaviors on silica. Adsorption of quaternary ammonium cationic surfactants with one, two, or three alkyl chains on silica has been studied by measuring adsorption density, ζ potential, and dispersion stability. The amount adsorbed at saturation decreased with increasing chain number. Silica suspensions exhibited a process of dispersion-flocculation-redispersion with the surfactant concentration for three surfactants, which can be well correlated with the change in ζ potential. Fluorescence and ESR measurements using probes showed that the microproperties in the adsorbed layers were considerably affected by their chain numbers of the surfactant.

2.3 Factors Affecting Surfactant Adsorption and Adsolubilization

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

-The nature of the structural groups on the solid surface—whether the surface contains highly charged sites or essentially nonpolar groups, and the nature of the atoms of which these sites or groupings are constituted; and

-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.

Monticone and Treiner (1995b) also studied effect of pH and ionic strength on the adsorption of cetylpyridinium chloride and the coadsorption between cetylpyridinium chloride and phenoxypropanol at a silica/water interface. The effects of pH and ionic strength on both of these phenomena have been investigated. It is shown that the solute partition coefficient between the adsorbed aggregates and the solution was independent of pH and of ionic strength and was equal to the partition coefficient of the classical micellar solubilization effect for the same solute/surfactant system. The partition coefficient is therefore only dependent upon the amount of surfactant adsorbed on the particles and on the solute hydrophobicity.

Monticone *et al.* (2000) investigated the effect of pH on the coadsorption of weak acids to silica/water and weak bases to alumina/water interfaces as induced by ionic surfactants. The effect of changing pH on the coadsorption for both types of systems had been studied in the pH range between 3 and 9. The surfactant concentration was kept constant corresponding to the isotherm region of a low surface coverage. Solute partition coefficient (P_{ads}) and binding constant (K_B) had been determined. It was shown that in all cases the solute coadsorption went through a maximum

at a pH value equal to the pK of the acids or of the bases. It was argued that the initial pH changes induce the dissociation of the solutes and a favorable interaction with the adsorbed surfactant ions. However as the pH further changed and the silica and alumina surfaces became increasingly ionized, these ionic sites were responsible for a repulsive effect on the dissociated solute species, hence the coadsorption maximum. A simple thermodynamic model which depended only upon chemical equilibrium and the corresponding constants P_{ads}, K_B, and pK fit well the experimental data provided K_B was assumed to be a function of the solution proton activity.

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 had 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 measured.

In this study we focused on the effect of pH on the adsorption of CTAB onto precipitated silica and the adsolubilization of toluene and acetophenone in the adsorbed CTAB aggregates at 2 different pH values. It has been reported that pH changes usually cause 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 positively charged (or less negatively charged) because of the adsorption of protons from the solution onto charged sites. The reverse is true when the pH of the aqueous phase is

raised. These effects are shown markedly by mineral oxides such as silica and alumina. Changes in the pH may also affect surfactant molecules, notably those containing a carboxylate group (soap) or a 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 though hydrogen bonding or dispersion forces.