

CHAPTER II

THEORETICAL 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 2.1 (Kitiyanan *et al.*, 1996).

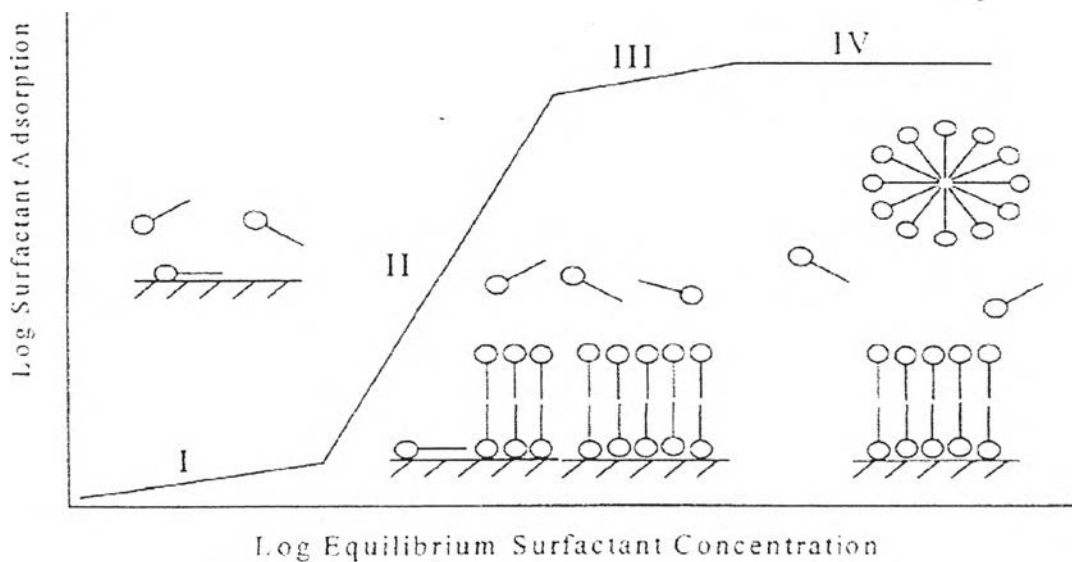


Figure 2.1 Typical adsorption isotherm of surfactants on solid oxide surfaces.

Region I corresponds to both very low concentration and low adsorption of surfactant. This region is commonly referred to as the Henry's law region because the adsorbed surfactant is considered to be in infinite dilution in the solid phase and, thus, the interaction between molecules of surfactants is negligible. Adsorbed surfactants in this region are viewed as being adsorbed alone and not forming any aggregates. 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 a sharp increase in the isotherm slope, which indicates the beginning of lateral interactions between surfactant monomers resulting in the formation of surfactant aggregates. In this region, these adsorbed surfactant aggregates are called hemimicelles or admicelles due to the electrostatic attraction between the surfactant ions and the charged solid surface. The hemimicelle is a monolayer structure having the head group adsorbed onto the solid surface while the tail group is directed towards the aqueous solution. The admicelle is a local bilayer structure with a lower layer of head groups adsorbed onto the solid surface and an upper layer of head groups in contact with the aqueous solution as shown in Figure 2.2 (Pradubmook *et al.*, 2003). The concentration at which the transition point from region I to region II occurs is called the hemimicelle concentration (HMC) or the critical admicelle concentration (CAC).

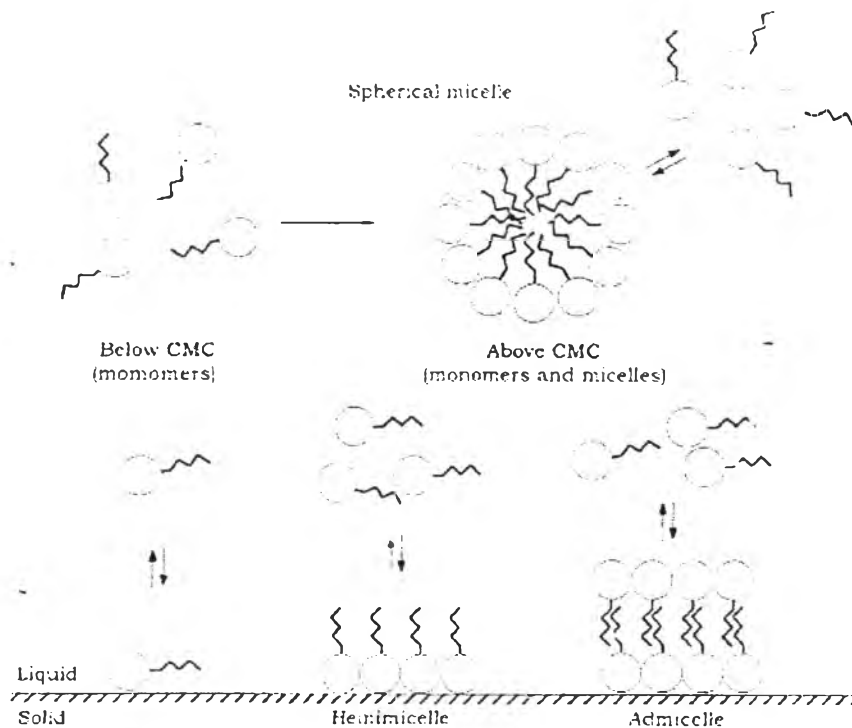


Figure 2.2 Example of surfactant micellization.

Region III is the region that has the isotherm slope decreasing from region II. This decrease in slope is attributed to lateral electrostatic repulsion between adjacent surfactant molecules or the like-charged head groups adsorbing on the surface. The transition point from region II to region III is marked by a decrease in the slope of the isotherm.

Region IV is called the plateau adsorption region usually occurring above the critical micelle concentration (CMC) of the surfactant. In most systems, the transition point from region III to region IV occurs approximately at the CMC and represents the first formation of micelles after the interface is saturated with admicelles. While increases in the surfactant concentration contribute to the micellization in solution by which the surfactants go into the micellar pseudophase in order to form more micelles, so that it does not change the adsorption density and the adsorption becomes nearly constant above the CMC. The adsorption in this region is mainly through lateral hydrophobic interactions between the hydrocarbon chains (Lewlomphaisan, 2009). 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).

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 aggregates is termed adsolubilization. This phenomenon is the surface analog of solubilization, with adsorbed surfactant bilayers playing the role of micelles, as shown in Figure 2.3. 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.” (Kitiyanan *et al.*, 1996).

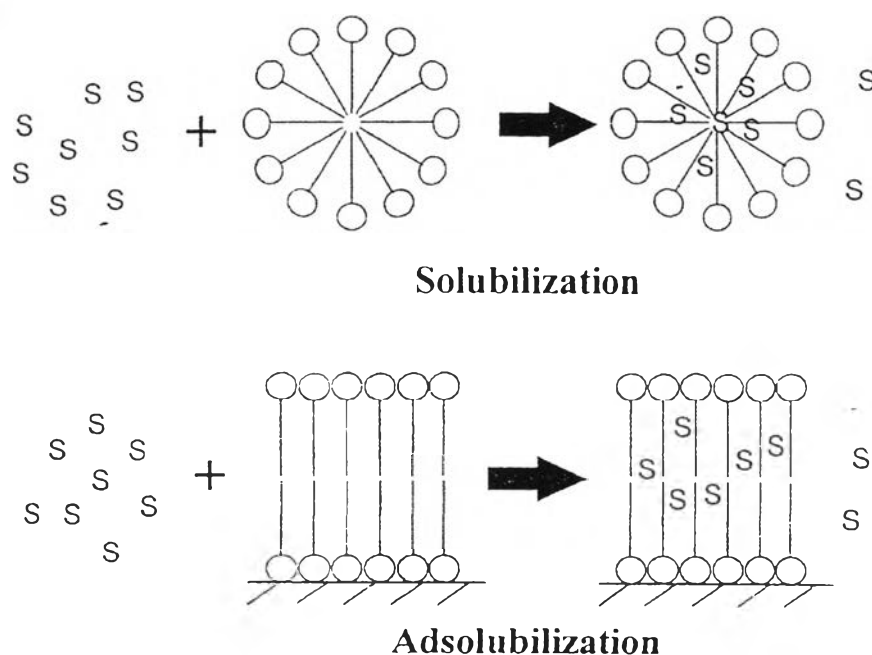


Figure 2.3 The phenomena of solubilization and adsolubilization.

Figure 2.4 shows that admicelles having a bilayer structure can be divided into three regions, similar to micelles. These regions consist of an outer region, an inner region, and a palisade region. The outer region is the most polar or ionic region because it consists of surfactant head groups and forms the liquid-solid interfaces. The inner region or the core region is a nonpolar region because it consists of the surfactant tail groups' hydrocarbon chains. Nonpolar solute is expected to partition primarily within the core region. The palisade region defines the transition region between the head group and the core. It has an intermediate polarity since the carbons near the head groups and it is also characterized by water molecules that have penetrated the admicelle. Polar solute is expected to preferentially adsorb in the palisade layer (Arpornpong, 2008).

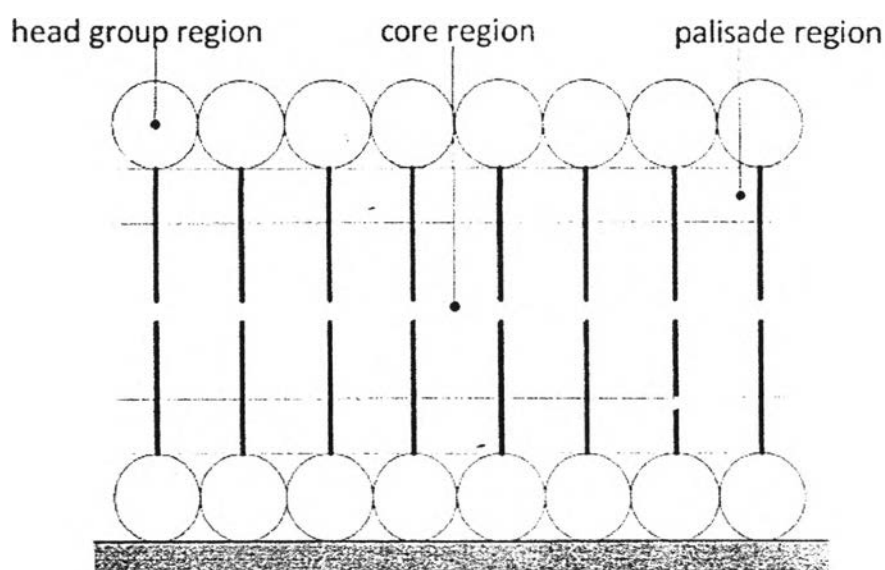


Figure 2.4 The bilayer structure of surfactant admicelles at the solid-liquid interface.

Kitiyanan *et al.* (1996) studied adsolubilization of styrene and isoprene into cetyltrimethylammonium bromide (CTAB) admicelle on precipitated silica. The results from single adsolubilization systems showed that styrene adsolubilization increases with increasing styrene equilibrium concentration in the 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 adsolubilized only into the palisade layer.

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 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 .

2.3 Factors Affecting Surfactant Adsorption

The adsorption of surfactants on solid surfaces is controlled by several parameters, including the electro-chemical nature of the solid surface, the type of surfactant molecule, the pH of the solution, the ionic strength and electrolyte, and the temperature.

2.3.1 Nature of the Structural Groups on the Solid Surface

Adsorption of surfactants on solid surface is related directly to the nature and number 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 grouping are constituted.

2.3.2 Type of Surfactant Molecule

The molecular structure of the surfactant being adsorbed onto solid surface is another critical factor affecting adsorption. It is important whether it is ionic or nonionic, and whether the hydrophobic group is long or short, straight chain or branched, aliphatic or aromatic (Kanjanakhunthakul, 2002). Moreover, the size of the hydrophilic group may be used to determine the effectiveness of adsorption when the cross-sectional area of that group is greater than that of the hydrophobic chain:the

larger hydrophilic group, the smaller amounts of adsorbed surfactants at surface saturation (Lewlompaisan, 2009).

Attaphong *et al.* (2010) studied adsorption and adsolubilization of polymerizable surfactants on aluminum oxide. In this study, a bilayer of anionic polymerizable surfactant (Hitenol BC 05, Hitenol BC 10 and Hitenol BC 20) and non-polymerizable surfactant (Hitenol N 08) was adsorbed onto alumina. The results of adsorption studies showed that as the number of ethylene oxide (EO) groups of the surfactants increased, the area per molecule increased and the maximum adsorption decreased. The lowest maximum adsorption onto alumina was for Hitenol BC 20 (20 EO groups) while the highest level of adsorption was for Hitenol BC 05 (5 EO groups). This variation in adsorption was attributed to the increased bulkiness of the head group with increasing number of EO groups. Relative to the adsolubilization capacity of organic solutes, ethylcyclohexane is more adsolubilized than styrene. Styrene and ethylcyclohexane adsolubilization were both independent of the number of EO groups of the surfactant.

2.3.3 Solution pH

The pH of an aqueous solution is an important parameter for the adsorption of ionic surfactants onto charged solid surfaces. The net charge on a solid oxide surface can be manipulated to be either positive or negative by adjusting the pH of the contacting aqueous solution because both hydrogen and hydroxyl ions are potential determining ions for metal oxides. The pH that makes the charge on the surface equal to zero is called the point of zero charge (PZC). When the pH of the contacting aqueous solution is below the PZC of the solid oxide surface, the surface will be protonated and positively charged. On the other hand, the solid oxide surface will be negatively charged at a pH above the PZC. For instance, silica, having $2 \leq \text{PZC} \leq 3$, will be negatively charged when the pH of the aqueous solution exceeds 3. Therefore, cationic surfactants such as cetyltrimethylammonium bromide (CTAB) adsorb readily on the surface of silica when the pH of the contacting aqueous phase is greater than 3 (Kitiyanan *et al.*, 1996).

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 adsolubilized into the palisade layer only.

2.3.4 Ionic Strength and Electrolyte

The addition of a neutral electrolyte (such as NaCl, NaBr, KBr) to the solution of ionic surfactant can affect the adsorbed surfactants by reducing the electrostatic repulsion between the similarly charged ionic surfactant head groups. When the electrolytes are present in the system, the micelles and admicelles are formed more easily due to the decreased repulsion between ionic surfactant head groups resulting in a larger aggregation number of the surfactant micelles and admicelles. Furthermore, electrolytes can enhance solubilization by decreasing CMC. When the concentration of electrolytes in the aqueous solution increases, maximum surfactant adsorption also increases (Arpornpong, 2008).

Kanjanakhunthakul (2002) studied the effect of ionic strength on adsorption of a cationic surfactant, cetyltrimethylammonium bromide (CTAB), on precipitated silica and adsolubilization of toluene and acetophenone into CTAB under various ionic strengths. Both single-solute and mixed-solute systems were investigated under various ionic strengths (1, 10, and 100 mM) by using NaBr. 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.

2.3.5 Temperature

The increase of temperature causes a decrease in the adsorption of ionic surfactants but the effect of temperature is small compared to the effect of solution pH. On the contrary, the increased temperature often enhances the solubilizing ability of ionic micelles. However, a rise in temperature usually results in an increase in the adsorption of nonionic surfactants containing a polyethylene chain as the hydrophobic group (Lewlomphaisan, 2009).

Saphanuchart *et al.* (2008) examined the effect of temperature on the adsolubilization partition coefficient of polar solutes into cetylpyridinium chloride admicelles adsorbed on precipitated silica. The investigated adsolubilization temperatures were 20, 35, 50, and 65 °C. The results were found that increasing temperature led to loosening molecular packing and increasing solute–surfactant headgroup attraction enhancing the ability of solutes to partition into admicelles, increasing the partition coefficient, whereas increasing aqueous solubility of solute reduced the partition coefficient. For slightly polar solutes, diphenylmethane and 4-bromotoluene, the partition coefficient tended to decrease as temperature increased due to the dominance of the impact of increasing aqueous solubility. For more polar diphenylether, the impact of increasing solubility was offset by loosening of admicelle and increasing solute–surfactant headgroup attraction, resulting in nearly unchanged partition coefficient with increasing temperature. For highly polar solute *p*-tolunitrile, the partition coefficient initially decreased (thus the solubility effects dominated) and then increased as temperature increased in the examined range, suggesting that looser molecular packing and solute–surfactant attraction dominated.