

CHAPTER II

LITERATURE REVIEW

2.1 Adsorption of surfactant on solid oxide surface

Just as it would not be possible to understand solubilization without an understanding of micelle formation, it is not possible to understand adsolubilization without understanding the formation of admicelles.

Figure 2.1 is a schematic of a typical surfactant adsorption isotherm. Such isotherms are commonly seen for ionic surfactants adsorbing from aqueous solution on surfaces with a charge opposite to the charge on the surfactant. In aqueous solution, the protonation or deprotonation of chemically adsorbed water will change the solid surfaces to be charged, depending on the pH value of solution. Numerous studies have indicated the adsorption of surfactant on high surface area solids such as silica or aluminum oxide (Scamehorn *et al.*, 1982; and Wu *et al.*, 1988). The adsorption isotherm of ionic surfactants on oxide surfaces is typically an 'S'-shape graph when one plots the log of adsorbed surfactant versus the log equilibrium concentration of surfactant (Somasundarun and Fuerstenau, 1966; and Scamehorn *et al.*, 1982).

Isotherms like those in Figure 2.1 are commonly divided into four regions. Region I is a region of low concentration and low surfactant adsorption densities. This region is generally referred to as the Henry's law region because the adsorbed surfactant is considered to be in infinite dilution in the surface phase. The adsorbed surfactants in this region are adsorbed as monomers and do not interact with one another. The most important point, though, is that there are no aggregates of adsorbed surfactants in this region. In many systems where conditions are favorable to surfactant adsorption, region I may not even be detectable because it occurs at such low surfactant

concentrations.

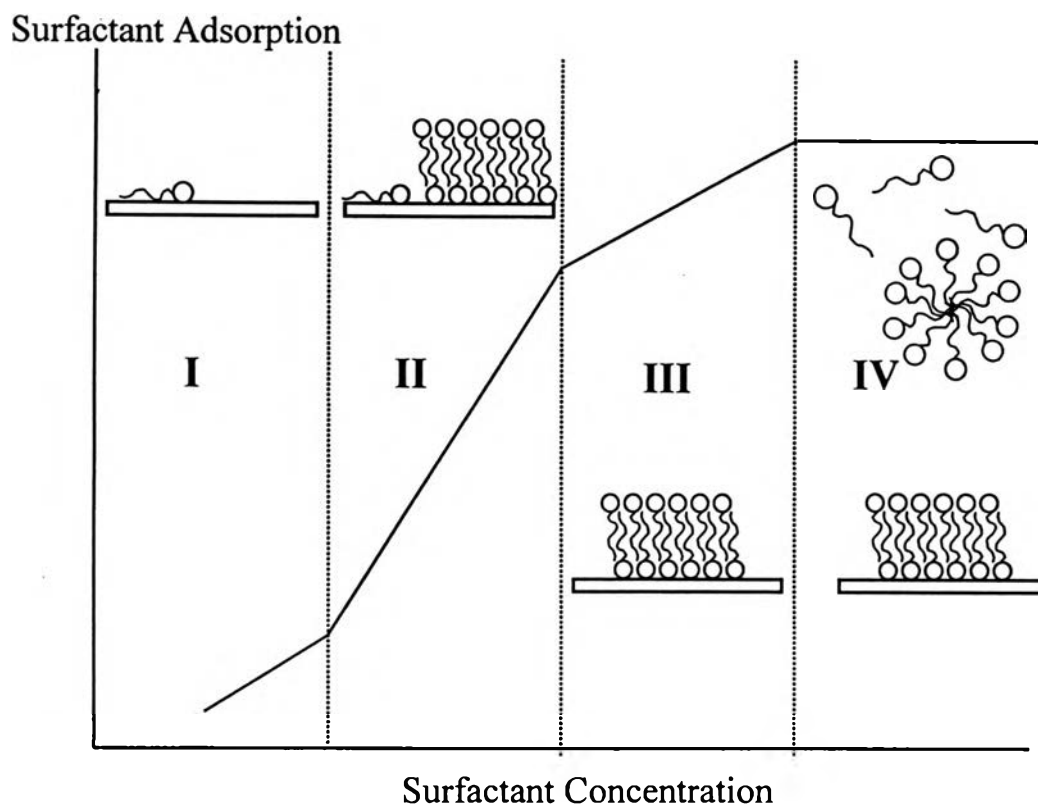


Figure 2.1 Typical surfactant adsorption isotherm on solid oxide surface

Region II is indicated by the sharp increase in the slope of the isotherm that occurs at the transition between region I and region II. This increase in slope indicates the initiating of lateral interaction between surfactant molecules, which results in the formation of micelle-like aggregates of adsorbed surfactants (Scamehorn *et al.*, 1982). These adsorbed surfactant aggregates in this region are called hemimicelles (Somasundarun and Fuerstenau, 1966) or admicelles (Harwell *et al.*, 1985). The hemimicelle is a monolayer structure having the head group adsorbed on the solid surface while the tail group is in contact with the aqueous phase. The admicelle is viewed as the local bilayer structure with head group of lower layer adsorbed on solid surface and the head group of upper layer is in contact with the aqueous phase.

The surfactant concentration at the transition between region I and region II point is labeled the critical admicelles concentration (CAC) (Harwell *et al.*, 1985) or the hemimicelle concentration (HMC) (Somasundarun and Fuertenau, 1996).

The transition between region II and III point is marked by the decrease in the slope of the isotherm. In some systems, the change in slope can be quite dramatic. The most generally given explanation is that the change in slope coincides with the cancellation of the charge on the solid surface by the charge on the absorbed surfactant aggregates.

Region IV is the plateau adsorption region where surfactant adsorption is almost constant with increasing surfactant concentration. In most systems, the region III and region IV transition occurs approximately at the critical micelle concentration (CMC). That means micelles are instantaneously formed in the aqueous phase.

The adsorption of surfactants depends on many parameters such as the type of surfactant molecule, the electrochemical nature of the substrate, and the pH value of the solution. The adjustment of pH value of the contacting aqueous solution can manipulate the charge on solid oxide surface to be either positive or negative because both hydrogen (H^+) and hydroxyl (OH^-) ions are potential determining ions of mineral oxides. The pH value that makes the charge on the solid oxide surface equal zero is called the point of zero charge (PZC). When the pH of the contacting aqueous solution is above the PZC of the solid oxide surface, the surface will be deprotonated and negatively charged. On the other hand, the solid oxide surface will be positively charged at pH value below the PZC.

2.2 Adsolubilization

Adsolubilization is a term describing the partitioning of the organic solutes from the aqueous solution into the hydrophobic environment between

the hydrocarbon chains of the adsorbed surfactant aggregates. This phenomenon is the surface analog of solubilization, with the adsorbed surfactant bilayer playing the same role as micelles. Figure 2-2 indicates the phenomenon of solubilization and adsolubilization. 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.” (Scamehorn and Harwell, 1988).

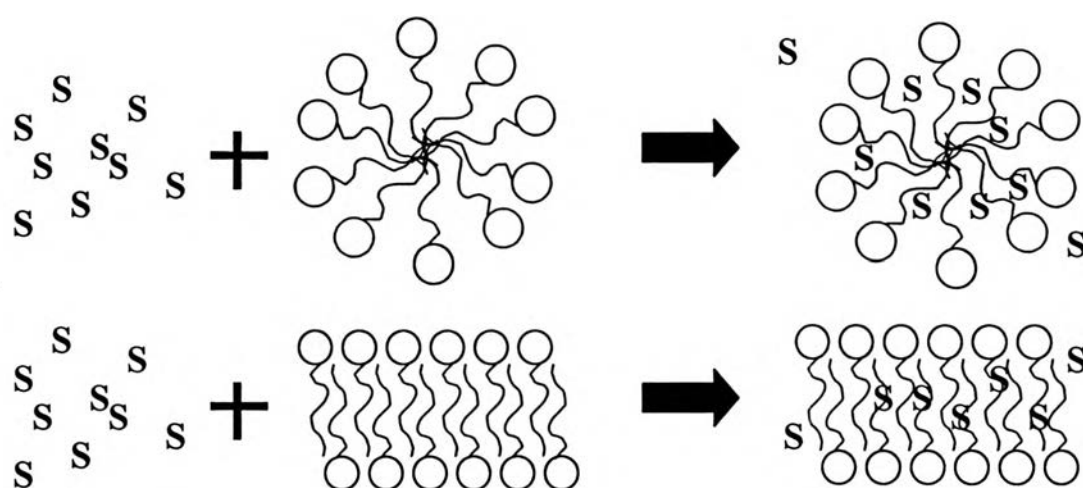


Figure 2.2 The phenomena of solubilization and adsolubilization

The phenomenon of adsolubilization has been studied for a variety of reasons. Nunn *et al.* (1982), gathered evidence about the nature of the adsorbed layer by adsolubilizing the dye pinacyanol chloride in an adsorbed layer of sodium *p*- (1-propylonyl) benzenesulfonate on γ -alumina. Pinacyanol chloride is red in aqueous media and blue in organic surroundings. The dissolved pinacyanol chloride in aqueous solution in which the surfactant was below the CMC gave red color while alumina remained white, indicating that the dye was in an aqueous environment. When the solution also contained surfactant at an equilibrium concentration in bulk solution below the CMC, the solution was clear and the alumina became blue. When the concentration of

the surfactant was raised so that the equilibrium concentration was above CMC, both the alumina and the solution were blue. This indicated the partitioning of pinacyanol between micelles and admicelles, and showed that the interior of the admicelles is similar in the nature to the interior of micelles.

A study of the structure of adsorbed surfactant bilayer of Triton X-100 (octylphenoxyethanol with an average of 9 to 10 oxyethylene units) on silica using adsolubilized pyrene was done (Levitz *et al.*, 1984; Levitz and Van Damme, 1986). Levitz and co-workers used fluorescence decay spectroscopy and pyrene as a probe to determine the structure of adsorbed surfactant bilayer of Triton X-100. This study also supported the existence of condensed assemblies of surfactant molecules on the surface of the silica. These assemblies gave rise, by the interaction of the aliphatic tails, to a hydrophobic, organic environment in their core. The environment of the admicellar layer for pyrene was found to be similar to that of pyrene in Triton X-100 micelles, regardless of the extent of coverage of the surfactant layer on the silica surface.

In 1986, a study used ESR spectroscopy and the nitroxide spin probe 16-doxylstearic acid to study sodium dodecyl sulfate, SDS, adsorbed onto aluminum oxide. They found that at low equilibrium SDS concentrations in the bulk solution, below 150 M, the probe tended to aggregate onto the surface of aluminum oxide along with the SDS. When SDS concentrations in the bulk exceeded 10 mM, giving bilayer coverage on the surface of the alumina, the probe aggregates were broken up. This is consistent with the probe being adsolubilized into the interior of the bilayer.

Admicellar polymerization is the successful application of admicelles. Wu *et al.* (1987), who studied the application of an ultrathin polystyrene film onto the surface of alumina using the in situ polymerization of styrene monomers adsolubilized within sodium dodecyl sulfate (SDS) admicelles. Styrene was found to adsolubilize into SDS admicelles to a maximum value of

one styrene monomer to approximately two adsorbed SDS molecules over a range of styrene concentrations. After washing, the modified alumina was found to be very hydrophobic.

Barton *et al.* (1988) studied the use of admicellar chromatography as a means of separating and concentrating three of isomers of heptanol. Alumina was used as the particulate to pack a chromatography column while the anionic surfactant sodium dodecyl sulfate (SDS) was used to form the admicelles. Immobilized surfactant aggregates at a solid/liquid interface can act as two-dimensional solvents to increase the interfacial concentration of organic compounds' selectivity. The results showed that n-heptanol could be separated from 3-heptanol or 2-methyl-2-hexanol at the low end of isotherm. At the upper end of isotherm, it appears that 2-methyl-2-hexanol could be separated from the other isomers. Each of the alcohols in a ternary mixture might be isolated in a two-stage process operated at opposing ends of the isotherm.

Yeskie (1988) systematically studied the adsolubilization of both series of alcohols and alkanes into admicelles on alumina. For the adsolubilization of alcohols at low levels of surfactant adsorption, the ratios of alcohol to SDS molecules in the admicelles were very high. The increase of surfactant adsorption will reduce the ratios to a value similar to the ratios of alcohol to surfactant molecules in SDS micelles. Below the CMC (in regions I, II, and III) the amount of surfactant adsorption was not only considerably increased in the presence of alcohol but also increased with increasing alcohol molecular weight. Even though surfactant adsorptions were increased below the plateau region, adsorptions in the plateau region were slightly decreased. The high amount of adsolubilized alkane into SDS admicelles was also observed. Furthermore, alkane adsolubilization increased with increasing surfactant adsorption. It was observed, as predicted, that the standard-state free energy of adsolubilized alkanes into the SDS admicelles is approximately the

approximately the same as for the alkanes solubilized into micelles. This further showed that interior of admicelles is similar to the interior of micelles.

Lee *et al.* (1990) proposed a “patchy bilayer” of adsorbed surfactant to explain the results of adsolubilization of alcohol. They further proposed that the adsorbed surfactant in region II and region III of the adsorption isotherm are presented as disk-shaped aggregates. Because of the polar end-group of alcohol, the disk-like admicelles model explained how alcohol could be adsolubilized into two sites of these admicelles. One site is between the head groups of surfactant, and this site is also presented in micelles. The other site, which is not presented in micelles, is the hydrophobic perimeter arising from the formation of the patchy, disk-like admicelles. The fraction of alcohols adsolubilized at the perimeter will be meaningful when the patchy aggregates are small, thus the very high ratios of adsolubilized alcohols to adsorbed surfactant are obtained at low surfactant adsorption. Moreover, the adsolubilized alcohols at the perimeter increased the hydrophobicity of the surface phase so the surfactant adsorption is higher in the presence of alcohols. As the chain length of alcohol increased, this hydrophobic contribution became greater and, therefore, resulted in enhanced surfactant adsorption.

Subsequently, admicelles have been occupied for the reactions as two-dimensional templates. Yu *et al.* (1992) presented a process called admicellar catalysis to catalyze the hydrolysis reaction of trimethylortho-benzoate (TMOB) by using of sodium dodecyl sulfate (SDS) adsorbed on high surface area alumina. The results indicated that the highest specific activity of admicelles is less than that the maximum specific activity of the corresponding micelles, nevertheless the admicelles activity is increased with increasing surface coverage above a specific value.