

CHAPTER II

BACKGROUND

2.1 Micelle Formation

Micelle formation or micellization is the fundamental surfactant phenomenon where a large number of separate surfactant molecules (monomer) assemble to form a closed aggregate. At low surfactant concentration in aqueous solution, all surfactant exists as unaggregated molecules. Because of their hydrophobicity, they will accumulate at the air/water interface. At sufficiently high concentrations, surfactant molecules simultaneously aggregate in the bulk solution to form clusters called micelles. The concentration at which micelles first form is the critical micelle concentration (CMC). The surfactants aggregate in such a fashion that their hydrophilic groups are oriented directly toward the aqueous phase and the nonpolar or hydrophobic groups are directed toward the interior of the micelle and thereby shielded from water. Detailed consideration of micelle geometry indicates that the hydrophobic tail groups are randomly arranged in the micelle interior and that they are not totally shielded by the hydrophilic group. In addition, the aggregation number, the average number of monomers that incorporate into one micelle, can vary anywhere from as few as 3 or 4 to hundreds or thousands depending upon the surfactant and system conditions (Rosen, 1989).

2.2 Solubilization

Solubilization is an important property of surfactants that is directly related to the presence of micelles. Surfactant solutions above the CMC can dissolve considerably larger quantities of organic materials than pure water or surfactant solutions with concentrations below the CMC. The additional capacity is obtained by solubilizing the solute in the micelles. Rosen (1989) defines solubilization as "the spontaneous dissolving of a substance (solid, liquid, or gas) by reversible thermodynamically stable isotropic solution with reduced thermodynamic activity of the solubilized material". Consequently, water-insoluble material in a dilute surfactant solution could appreciably increase its solubility when the surfactant concentration surpasses the CMC. Solubility increases approximately linearly with the concentration of surfactant above the CMC. There are a number of different sites in a micelle: (1) on the surface of the micelle; (2) between the hydrophilic head group; (3) in the palisade layer of the micelle located between the hydrophilic groups and the first few carbon atoms of the hydrophobic groups and (4) in the inner core of the micelle. Depending on the nature of the material solubilized (the solubilize), the exact location in the micelle at which solubilization occurs can vary.

2.3 Surfactant Adsorption

Numerous studies have been made on the adsorption of ionic surfactants on oppositely charged surfaces (Rosen, 1989). The adsorption of surfactant molecules from aqueous solution onto an oppositely charged surface is due to many mechanisms and is controlled by several parameters such as the electro-chemical nature type of substrate, the pH of the solution, and the type of surfactant molecule.

Normally, data from adsorption experiments are expressed in the form of an adsorption isotherm, which displays the surfactant adsorption (the amount of surfactant adsorbed per gram of adsorbent) as a function of the equilibrium bulk concentration of surfactant. The adsorption isotherm is typically s-shaped and can be divided into four distinct regions, each of these regions corresponding to a different mechanism of surfactant adsorption. Figure 2.1 shown a schematic presentation of a typical adsorption isotherm.

Region I of the adsorption isotherm is commonly referred to as the Henry's Law region. This region occurs at low equilibrium concentrations and low surfactant adsorption. The equilibrium adsorption in this region is proportional to the equilibrium concentration of the surfactant in the solution with a predicted slope of approximately one (Rosen, 1989). The driving force for the adsorption is largely due to electrostatic attraction between the surfactant head groups and the oppositely charged surface as well as a significant tail/surface interaction on hydrophobic surfaces (Scamehorn, 1982). There is little or no interaction between individually adsorbed surfactant molecules which are viewed as being adsorbed alone, i.e. not forming any aggregates.

Region II is distinguished by a sharply increased isotherm slope relative to the slope in the Henry's Law region. In this region, adsorption greatly increases while the equilibrium concentration does not change greatly. Increased surface coverage increases the tendency of surfactant to adsorb. It is widely accepted that this increase is caused by the hydrophobic interactions between tail groups of oncoming surfactant ions and those of previously adsorbed surfactant, which causes the adsorbed surfactant to form a micelle-like aggregate on the solid surface. These adsorbed surfactant aggregates are called admicelles or hemimicelles, depending upon whether the aggregates

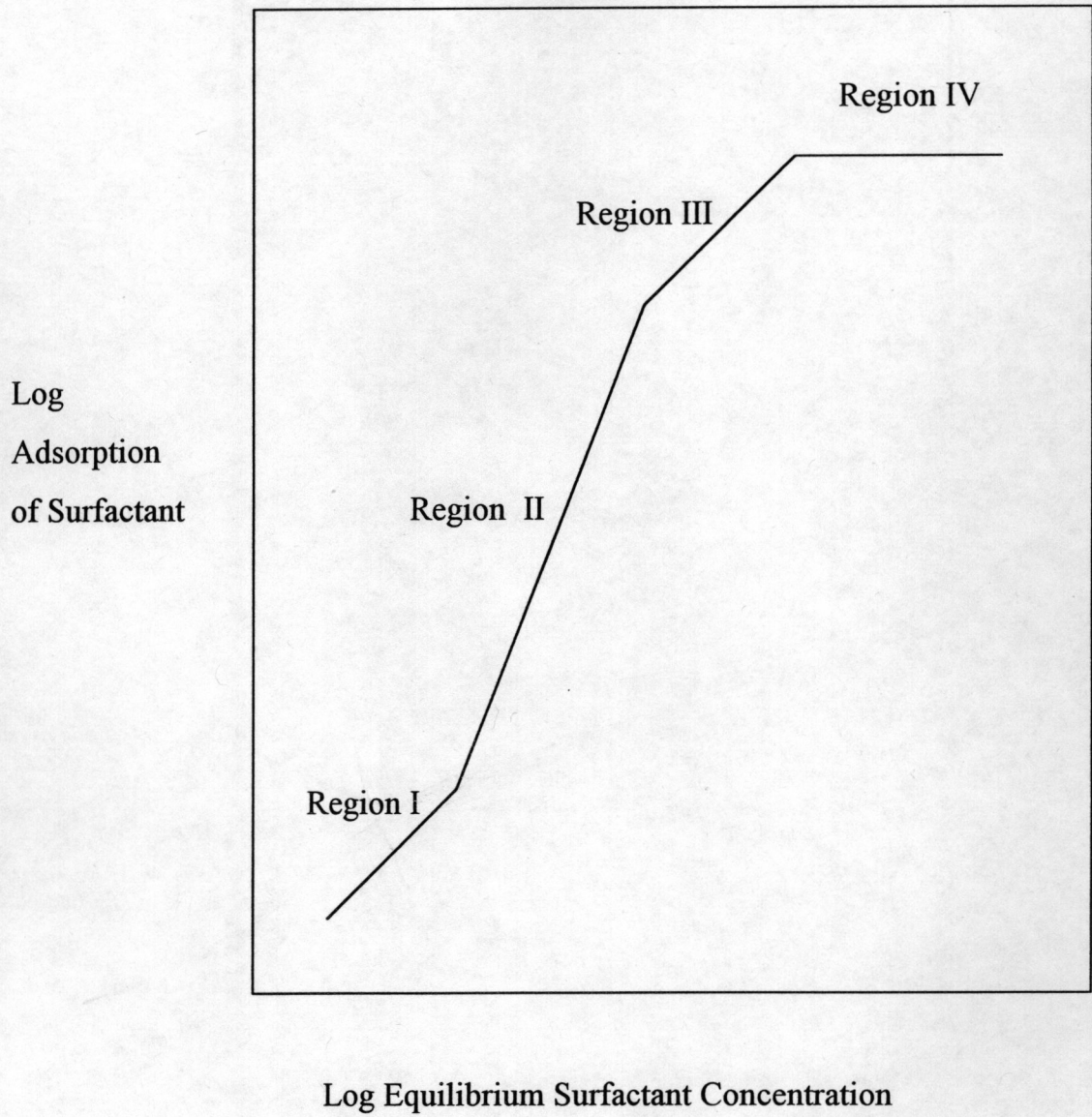


Figure 2.1 A Typical Adsorption Isotherm for an Ionic Surfactant on an Oppositely Charged Substrate.

are viewed as local bilayers or monolayers. The equilibrium concentration at which the admicelle or hemimicelle first forms is called the critical admicelle concentration (CAC) or hemimicelle concentration (HMC), respectively, and represents the transition point from region I to region II. During aggregate formation, the original charge on the solid is neutralized and eventually reversed. Therefore, by the end of this region, the solid surface has the same sign on its overall charge as the surfactant ions.

In region III, higher equilibrium concentrations are required for the surfactant to continue to adsorb. Additional adsorption becomes more difficult because of electrostatic repulsion between the oncoming surfactant ions and the like-charged head groups on the surface. In addition, the most energetic patches available for adsorption are fewer in number as compare to region II. As these patches become filled, lower energy patches become energetically more favorable for adsorption at slightly higher equilibrium surfactant concentration. This causes a rapid decrease in the slope of the isotherm in this region.

Region IV is referred to as the Plateau Adsorption Region, having almost constant surfactant adsorption with increasing surfactant concentration. When the adsorption is complete, micelle begin to form and added surfactant monomer results in the formation of more micelles. Either the surface concentration of surfactant has reached saturation or the chemical potential of surfactant has become roughly independent of concentration because of the formation of the micellar pseudo-phase. Typically, the equilibrium surfactant concentration at the transition point from region III to IV is approximately at the critical micelle concentration (CMC).

2.4 Adsolubilization

Analogous to the solubilization of organics into micelles, organic molecules can be incorporated into admicelles. Admicellar solubilization is defined as "the incorporation of compounds into surfactant aggregates adsorbed on surfaces, which compounds would not be in excess at the solid-solution interface in the absence of surfactant" (Scamehorn and Harwell, 1986).

While solubilization has been examined in great detail, adsolubilization has received relatively little attention. Nunn et al (1982) first studied the dye pinacyanol hydrochloride adsolubilized into surfactant aggregates adsorbed at the alumina-aqueous phases interface. The color change of the dye showed a micelle-like environment on the surface and partitioning of the dye into the admicelles. Levitz et al (1984) further studied the fluorescence decay of pyrene molecules adsolubilized into the adsorbed nonionic surfactant aggregates at the solid-solution interface.

Yeskie et al (1987) did an extensive study on adsolubilization of alkanes and alcohols in the admicelles of sodium dodecyl sulphate on alumina. Yeskie and coworkers suggested the possibility that the structure of the admicelle changes with the increase in adsolubilization and showed that adsolubilization was thermodynamically similar to solubilization in micelle.

Wu et al (1987) and Esumi et al (1991) used surfactant adsorbed onto mineral oxide surface as reaction solvents to produce polystyrene films on solids via polymerization of styrene within surfactant bilayers. In another study, Valsaraj (1992) attempted to solubilize volatile organic compounds into admicelles of sodium dodecyl sulfate on alumina and concluded that in many

cases surfactant-coated alumina was a better adsorption surface for hydrophobic organic compounds than natural soils and sediments. O'Haver, et al (in preparation) studied the adsolubilization of styrene and butadiene in adsorbed bilayers of cetyltrimethylammonium bromide on precipitated silica. They found that pore condensation, as well as adsolubilization, had to be considered when using microporous substrates. Kitiyanan, et al., (accepted for publication by Langmuir) studied the adsolubilization of styrene and isoprene in adsorbed bilayers of cetyltrimethylammonium bromide on precipitated silica. They found a significant synergistic interaction between the styrene and isoprene during the adsolubilization process.

2.5 Thin Films

Conventionally, a film having thickness of less than a micron is termed a thin film. The usefulness of thin films in various applications have made them the subject of study for many researchers. Corrosion inhibition, separation processes and surface modification are some of the applications of thin films.

Although the number of thin film studies have increased in recent years, monolayer experiments were performed in the time of Benjamin Franklin. In the 1920s, Langmuir first demonstrated the tendency of amphiphiles to align in a monolayer on the air-water interface with their hydrophobic tails extending into the air. Now a molecular film at the air-water interface is widely known as a Langmuir film. Blodgett extended this idea to form Langmuir monomolecular layers on to a solid substrate, which is called a Langmuir-Blodgett film (Blodgett et al, 1935). This Langmuir-Blodgett technique has been the source of recent studies in the thin film area because of the wide variety of their applications.

A portion of recent research has been directed to the formation of self-assembling thin films. Sagiv and coworkers have used a novel technique for developing organized molecular layers of bifunctional silane terminated surfactants as an alternative to the Langmuir-Blodgett technique (Sagiv et al, 1980 ; Netzer et al, 1983). This process is a two-step process. Monolayers were constructed by bringing surfactants into contact with a hydroxylated surface and then introducing chemical activation. Multilayers can be constructed monolayer by monolayer.

The use of polymerizable surfactants in forming thin films has also received considerable attention. Esumi et al have studied the use of a polymerizable surfactant in forming thin films on a solid substrate (Esumi et al, 1989). The method they employed consists of two steps. First, a bilayer of the surfactant is formed on the solid substrate by varying the surface charge density. This bilayer is then polymerized by UV radiation in the second step.

Another recent, novel method was developed by Harwell and O'Rear (1987) for the formation of ultrathin polymeric films on solid surface. Films formed by this method are ultra-thin in dimension, thermodynamically stable, possess a high degree of uniformity and can be formed on geometrically irregular surfaces. A variety of amphiphilic surfactants and solid substrates can be used for the purpose depending upon the application. Wu et al, (1987) demonstrated the feasibility of this concept by forming ultra-thin films of polystyrene on alumina using admicelles of anionic surfactant, sodium dodecyl sulphate, as a chemical reaction solvent. This study was expanded by Lai (1992), who studied the formation of polytetrafluoroethylene on alumina, by Chen (1992) who formed polystyrene on titanium dioxide, and by O'Haver, et al, who formed various homo- and copolymer modified precipitated silicas

(1993 and 1994). Application of these films as ion exchange resins was tested and the results from that study exhibited promising results.

2.6 Admicellar Polymerized Thin Film Formation

The method used for the modification of inorganic powders by the construction of a polymeric ultrathin films on the solid substrate via admicellar polymerization consists of four basic steps as show in Figure 2.2. Step 1 consists of admicelle formation by the adsorption of surfactant bilayer onto the surface of the substrate. Harwell et al (1985) proposed that ionic surfactant adsorption on oppositely charged surfaces actually proceeded by patchwise formation of surfactant bilayers on the surface. These local, bilayered surfactant aggregates were called admicelles, to emphasize the simultaneous formation of the first and second surfactant layers. The admicellar interior exhibits a highly organic-like environment, forming a favorable space for the solubilization of organic species. Care must be taken to keep the bulk concentration of surfactant at equilibrium below the surfactant's critical micelle concentration (CMC) in order to prevent solubilization in micelles and to reduce the possibility of emulsion polymerization. The most critical parameter in admicelle formation is the pH of the solution relative to the pH at which the oxide exhibits a net surface charge; of zero (point of zero charge, or PZC). At pH values below the PZC, the surface becomes protonated and more positively charged ; above the PZC the surface is negatively charged. As a result anionic surfactants adsorb well below the PZC, while cationics adsorb well above the PZC (Wu, Harwell and O'Rear, 1988). The choice of surfactant is influenced by the point of zero charge of the substrate, the chemical nature of the polymer to be formed, and the chosen polymerization initiator system (O'Haver, 1995). A study of the point of zero charge (PZC) for the substrate provides information on the pH ranges in which cationic or

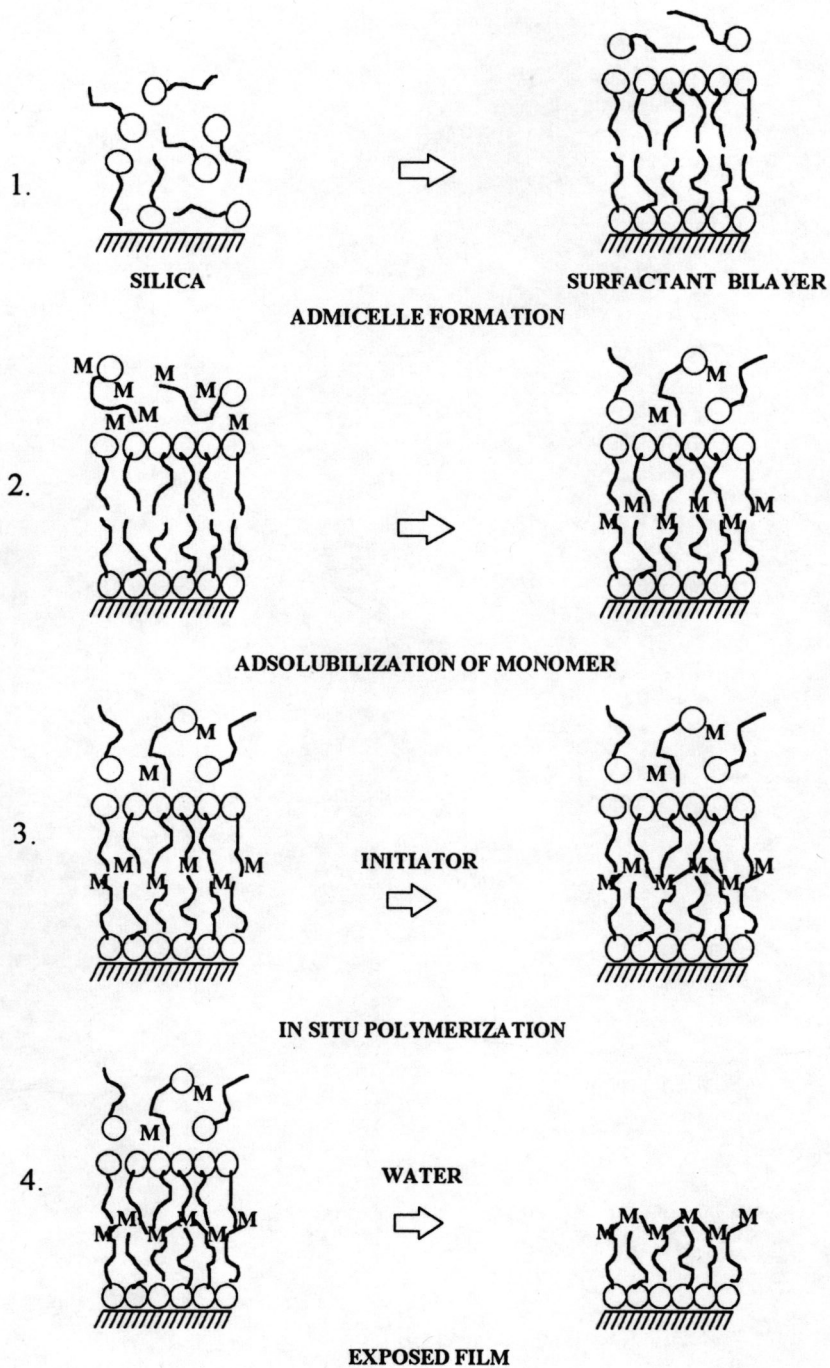


Figure 2.2 Ultra-Thin Film Formation.

anionic surfactants may readily be utilized.

Step 2 in the process is the solubilization of monomer into the organic-like admicellar interior. Many organic monomers are nearly insoluble in water. Thus, when introduced into the solution, they preferentially partition into the hydrophobic interior of the admicelle. This process can occur after the formation of admicelles or concurrently with surfactant adsorption; i.e., the first and second steps can be performed concurrently or sequentially.

Step 3 is the *in-situ* polymerization of the adsolubilized monomer. The monomer is polymerized in a manner similar to emulsion polymerization except that the polymer formation occurs in the admicelle instead of in micelles. This is accomplished by the addition of initiators to the system and then increasing the temperature or exposure to light. Once the reaction has started, additional monomer from the bulk solution diffuses into the admicelle. If the reaction is continued for a sufficient length of time, virtually all monomer can be converted to polymer.

Step 4 is the washing of the treated powder to remove as much as possible of the excess surfactant in order to expose the polymer film, constituting the final step of the process for the *in-situ* formation of ultrathin films.

With the various combinations of surfactant and monomers possible in the four-step process, a great variety of feasible ways exist to form a film on a substrate and to construct films with desirable characteristics. Additionally, films can be formed on highly irregular surfaces, including the extreme case of forming polymer films on the internal surface of porous solids.