

CHAPTER II

BACKGROUND

2.1 Surfactant Structure

Surfactant is an abbreviation of “surface active agent”. Surfactants are a very versatile class of chemical compounds due to their chemical structure. A surfactant molecule consists of a hydrophilic group made of a soluble species hydrophobic tail made of organic derivative groups, usually with the carbon number greater than eight. This structure is known as amphiphilic, and surfactants are considered to be amphiphiles. Depending on the nature of the hydrophilic group, surfactants are classified as nonionic or zwitterionic (Rosen, 1989).

2.2 Micellization

Micellization or micelle formation is a fundamental surfactant phenomenon where a large number of separate surfactant molecules (monomer) assemble to form a closed aggregate in solution. At low concentrations, surfactant molecules are present in the form of monomers. Due to their amphiphilic structure, surfactants will concentrate at the liquid-air interface. The hydrophobic parts will be directed away from the aqueous solution while the hydrophilic parts participate into the aqueous phase. At sufficiently high concentration, surfactant molecules simultaneously aggregate in the bulk solution to form clusters called micelles. The concentration at which micelle first form is the critical micelle concentration (CMC). The surfactant molecules organize in such a fashion that their hydrophilic groups are oriented directed

toward the aqueous phase and the hydrophobic groups are directed toward the interior of the micelle and thereby shielded from water. The gathering at the liquid-air interface and micellization of surfactants both provide mechanisms to reduce the free energy of the system by removing hydrophobic groups from contact with the water. The average number of monomers that incorporate into one micelle is called the aggregation number. The aggregation number can vary anywhere from several to hundreds depending on the surfactant and system conditions.

2.3 Solubilization

Solubilization is one of the most important properties of surfactants that is directly related to micelle formation. 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. Depending on the nature of the material solubilized(the solubilize), solubilization can occur at 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. In general, solubilization capacity depends on the structure of both the surfactant and solubilize. Some other factors that affect the extent of solubilization capacity of a micelle include temperature, added electrolytes and organic additives.

2.4 Surfactant Adsorption

Numerous studies have been made on the adsorption of ionic surfactant on an oppositely charged surface. When a mineral oxide is brought into the aqueous solution, the adsorption of H_3O^+ or OH^- ions from the solution onto the surface can cause a variation on the surface charge. If the pH of the aqueous solution is increased, a solid surface will become more negative or less positive because OH^- ions adsorb onto the surface. Thus, the adsorption of cationic surfactant increase and the adsorption of anionic surfactant decrease. The opposite is true when the pH of solution is lowered. So that, change in the pH has a great effect on the surface charge as well as the surfactant adsorption. The surface can bear positive or negative charge depending on the pH of the solution. At a certain pH, the net surface charge will be zero. The pH at which the surface charge becomes zero is known as the point of zero charge (PZC). At a pH below the point of zero charge, the surface will have a net positive charge, and at a pH above the point of zero charge, the surface will have a net negative charge.

Adsorption data have usually been represented as log-log plot of the surfactant adsorption (amount of surfactant adsorbed per gram of adsorbent) versus the equilibrium bulk concentration of surfactant. The adsorption isotherm usually takes on a very characteristic shape.

Figure 2.1 is a schematic representation of a typical adsorption isotherm of ionic surfactant on an oppositely charged substrate. In region 1, the surfactants adsorb as individual molecules on the surface. This adsorption is due to the electrostatic attraction between the surfactant head groups and the oppositely charged surface. The interactions between surfactant molecules are

considered to be neglectgible in this region. This region of the surfactant adsorption isotherm is called the Henry's law region.

Region 2 is characterized by a very rapid increase in adsorption and is known to be a result of the cooperative interaction between hydrocarbon tails of the adsorbed surfactant molecules. The slope of the isotherm increases in this region. The surface aggregates so formed are called hemimicelle or admicelles.

In region 3, adsorption increases more slowly because of competition between admicelles and the slope of the isotherm decreases. The adsorption now must overcome electrostatic repulsion between the oncoming ions and the similarly charged surface(Rosen, 1990).

Region 4 is referred to as the Plateau Adsorption Region. In this region, micelles begin to form and added surfactant monomers result in the formation of more micelles. Adsorption remains fairly constant with the increase in equilibrium concentration above the critical micelle concentration(CMC).

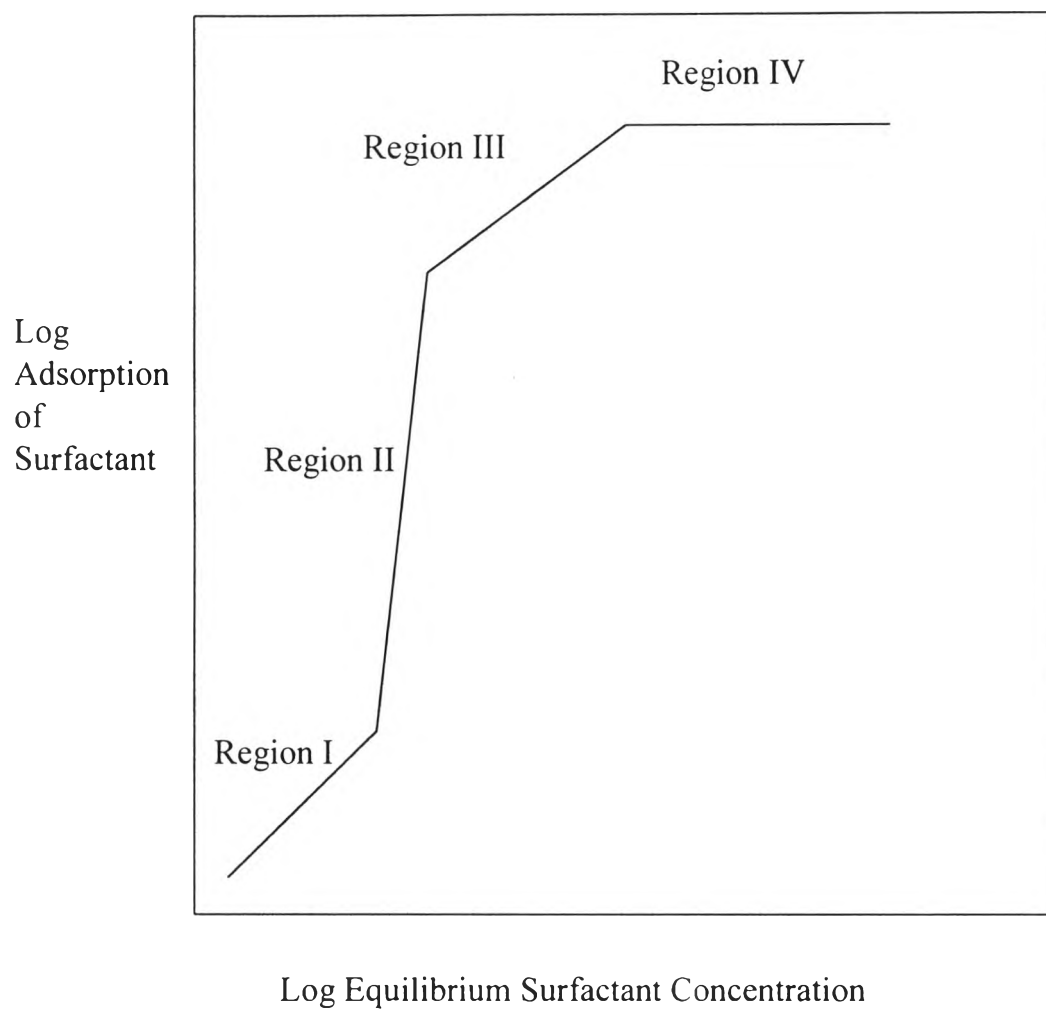


Figure 2.1 A typical Adsorption Isotherm for an Ionic Surfactant on an Oppositely Charged Substrate.

2.5 Adsolubilization

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 2.2. Adsolubilization is defined as “the incorporation of compounds into the surfactant aggregates adsorbed on surfaces, which compounds would not be in excess at the solid - solution interface in the absence of the surfactant”(Scamehorn and Harwell, 1986).

Nunn et al.(1982) first incorporated the dye pinacyanol chloride into surfactant aggregates adsorbed at the alumina-aqueous solution interface. The color change of the dye showed a micelle-like environment on the surface and partitioning of 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) studied the adsolubilization of alcohols and alkanes 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 micelles.

Wu et al.(1987) and Esumi et al.(1991) used surfactant adsorbed on mineral oxide surfaces as a reaction solvent to produce polystyrene films on the solid via polymerization of styrene within surfactant bilayers. Valsaj(1992) attempted to solubilize volatile organic compound into admicelles of sodium

dodecyl sulphate on alumina. They found that in many cases surfactant-coated alumina was a better adsorption surface for hydrophobic organic compounds than natural soils and sediments. Kitiyanan et al.(1995) studied the adsolubilization of styrene and isoprene in adsorbed surfactant bilayers of cetyltrimethylammonium bromide on precipitated silica. They found a significant synergistic interaction between the styrene and isoprene during the adsolubilization process.

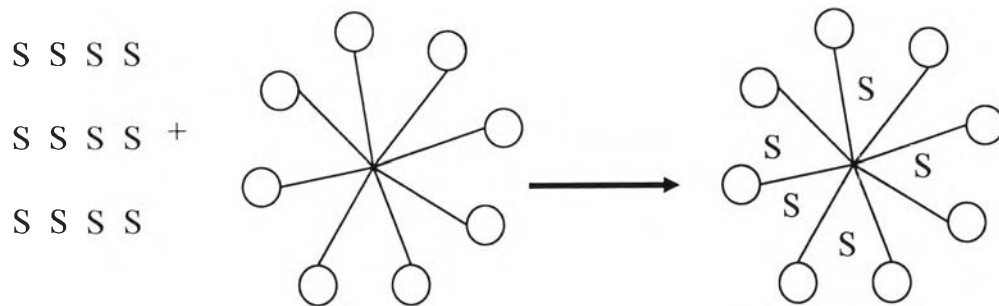
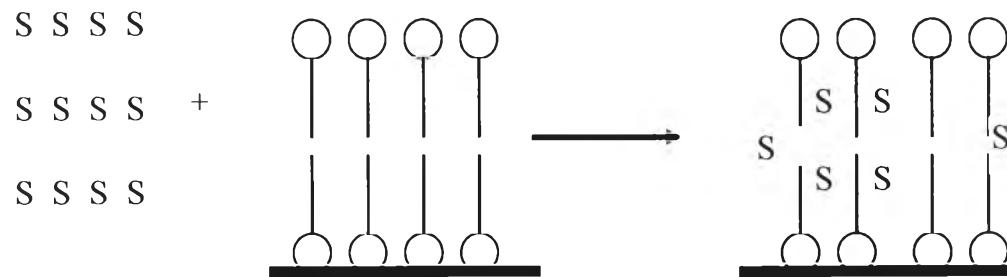
SOLUBILIZATION**ADSOLUBILIZATION**

Figure 2.2 A comparison of solubilization to adsolubilization.

2.6 Ultra-Thin Film Formation

Wu; et. al(1987 a,c) manipulated the formation of admicelles on the solid surface, and the adsolubilization of organic monomer of interest into admicelles, and developed a novel method of ultra-thin film formation using the organized structure of admicelles and chemical solvent. They demonstrated the feasibility of this concept by developing thin films of polystyrene on gamma-alumina using admicelles of anionic surfactant, sodium dodecyl sulphate(SDS) as a two dimensional solvent.

The formation of ultra-thin polymer films consists of four basic steps. Step 1 consists of admicelle formation by adsorption of a surfactant bilayer onto the surface substrate. Adsorption is accomplished through the use of suitable surfactant under appropriate charge(PZC) for the substrate provides information on the pH ranges in which cationic or anionic surfactants maybe utilized. The instability or dissolution of components in certain pH ranges may further define the range of useful operating conditions, and hence, surfactant type.

Step 2 in the process is the solubilization of monomer into the bilayer of surfactant. This phenomenon is called adsolubilization. Many organic monomers are nearly insoluble in water. So that, at equilibrium, they prefer to partition themselves into the hydrophobic interior of the admicelle. This process can occur after admicelles formation, or concurrently with surfactant adsorption. In these cases, the presence of micelles promote the solubility of the monomer in the feed solution, increase the rate of the adsolubilization of the monomer in the admicelles, and help prevent the formation of emulsions. When

this feed solution is contacted with the substrate, the adsorption of the micelle is thought to carry the solubilized monomer onto the substrate surface.

Step 3 is the in-situ polymerization of monomer. For free radical polymerization, this is accomplished by the generation of radicals capable of initiating the polymerization reaction. In some cases, the compatibility of the initiator system with anionic or cationic surfactants may also affect the choice of an appropriate surfactant and suitable reaction conditions. To reduce the chance of competing polymerization in the bulk solution, a detailed study of adsolubilization and adsorption isotherms are made to insure that the system equilibrates with the surfactant concentration in the bulk solution below the critical micelle concentration(CMC).

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 of the outer surfactant layer as possible in order to expose the polymer film.

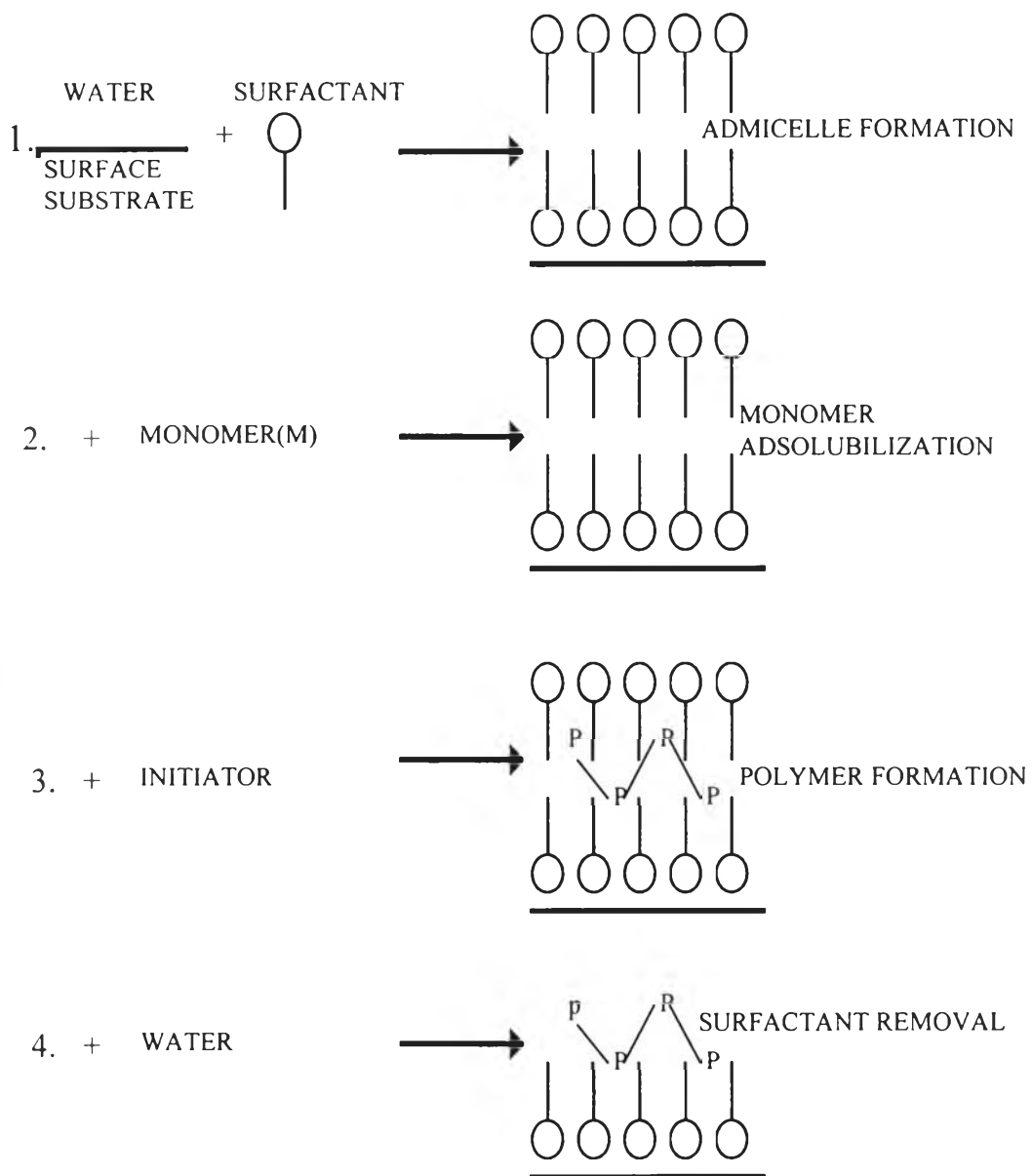


Figure 2.3 The 4 steps surface modification process.