# CHAPTER I
# INTRODUCTION

Cotton is a kind of natural material, which is generally used in textile industry. Cotton has an advantage in comfort, soft, and flexibility. However cotton also has some drawbacks such as cotton can adsorb water well, soil can attach on the cotton surface easily, and flame resistance of cotton is too low.

Consequently, a method for the modification of cotton is needed. The demanded properties for an improvement of cotton at present are water-resistance, soil-repellence, and flame-retardation, respectively. A process, which is normally used to apply chemicals onto cotton surface, is coating with single or multifunctional groups of chemical such as acrylate polymers, fluorochemicals, and silicones. The treated fabric will have better performance than the original material. However, one of the disadvantages of the coating process is that the coated chemicals tend to block the gaps between fibers and yarns in the fabric such that the moisture can not ventilate out of the body as shown in Figure 1.1. The coated chemicals may also come off after several wash cycles. Therefore, a better method for cotton modification is desirable.


(a) (b)

**Figure 1.1** (a) A typical coating technique in the textile process and (b) A blocking problem in the product due to a technique.

Admicellar polymerization is an alternative process that can be used for chemical coating. In this process, a surfactant bilayer acts as a two-dimensional solvent for the formation of polymeric thin film onto substrate surface. The properties of the coated material will be different from the original material due to the coated layer of polymer on the surface. Monomers that have been used to produce thin film by admicellar polymerization are hydrocarbons and fluorocarbon derivatives, which are capable of polymerizing into thin film.

Recently, modification of cotton by the admicellar polymerization of styrene onto cotton surface has been studied (Methachan, 2000). The results show that the polymeric thin film was successfully formed on the cotton surface resulting in good water-repellency. In this work, admicellar polymerization of three different monomers on cotton was studied. Properties of the resulting coated fabric were tested for improvement in thermal stability, and dye ability.

## 1.1 Surfactant

Surfactant or surface active agent is a substance that is used in such fields as detergent, petroleum, and pharmacology. Surfactant has the property of adsorbing onto the boundary between any two immicible phases and of altering to a marked degree the surface or interface free energies of solid surface (Rosen, 1989).

A surfactant generally consists of two portions. A portion which solubilizes well in the aqueous solution or polar phase called hydrophilic or lypophobic. On the other hand, hydrophobic or lypophilic is the part of surfactant that can dissolve readily in the organic phase or nonpolar system. The typical class of surfactant depends on the charge of the polar group in the hydrophilic portion. Anionic surfactant is a surface active agent having a negative charge at the hydrophilic site. A surfactant, which is composed of positive charge, is cationic. Zwitterionic surfactant may have both positive and negative charge in the molecule. Nonionic surfactant demonstrates no apparent charge in the molecule. Moreover, there are some special features of surfactant that are organized in the specific field because of functional group in the hydrocarbon tail. Siloxane surfactants consist of a methylated siloxane hydrophobe coupled to one or more polar groups. Fluoro surfactant is composed of one or more fluorinated or partially fluorinated hydrophobic group that can show dramatically different properties to hydrophobic groups of hydrocarbon surfactants. Both types of surfactant are applied in areas where other kinds of surfactant are relatively ineffective.

Several types of surfactant aggregation can be formed at different concentrations of the supernatant as shown in Figure 1.2. At low concentration, surfactants are in molecular form in the solution. An admicelle or hemimicelle structure can be formed at surface or interface of the system when the concentration is higher. Finally, a micelle formation will occur when the concentration of surfactant is over a critical point.

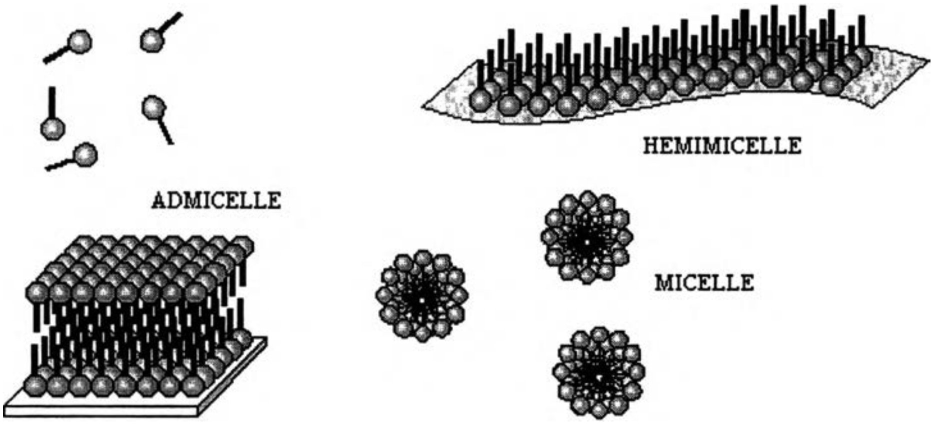


**Figure 1.2** The types of surfactant formation.

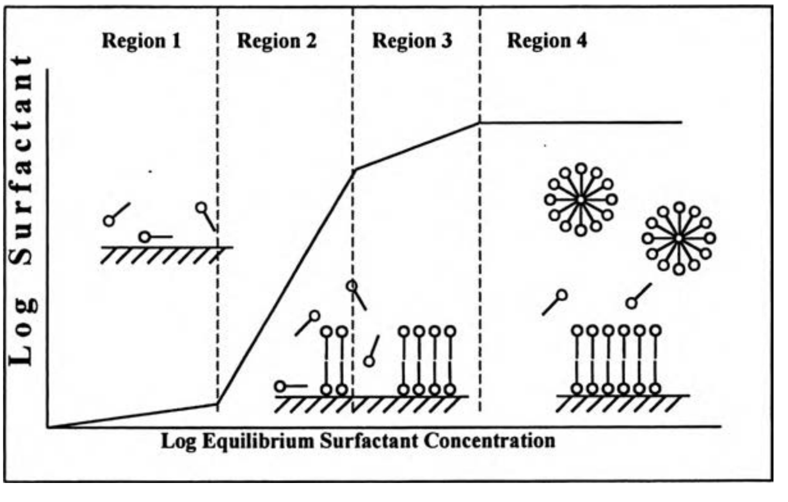


**Figure 1.3** Typical adsorption isotherm of surfactant on solid surface.

## 1.2 Adsorption Isotherm

Adsorption isotherm illustrates phenomena of surfactant at different concentrations in the equilibrium solution. From Figure 1.3, at region 1, the surfactant will dissolve in the solution in a form of single molecule. In region 2, surfactants form admicelle or hemimicelle at the substrate or the interface of the system. The concentration which admicelle or surfactant bilayer forms is known as critical admicelle concentration (CAC). When the concentration of surfactant is higher, the density of surfactant aggregation increases at the interface of system as shown in region 3. In the region 4, the surfactant forms micelles in the solution. This point is called critical micelle concentration (CMC).

## 1.3 Admicellar Polymerization

The admicellar polymerization is a novel technique that is modified from emulsion polymerization. The surfactant is adsorbed onto the solid surface and acts as a two-dimensional solvent for the formation of ultra polymeric thin film on the surface of material (Wu *et al.,* 1987a,1987b,1988). This template will control the monomer configuration before the polymerization takes place.

The admicellar polymerization is generally consisted of four steps.

Step1 - <u>Admicelle formation</u>

At an appropriate concentration of surfactant, the admicelle is formed along the surface and the surfactant in the solution is in the form of single molecules.

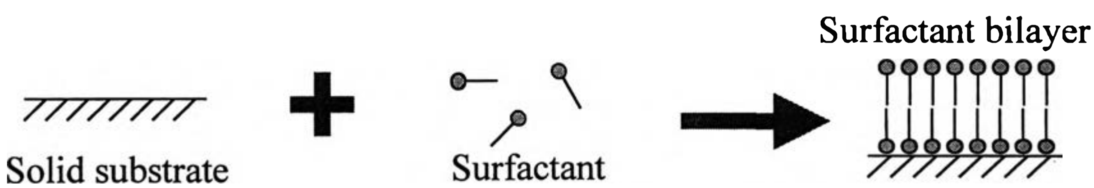


**Figure 1.4** Admicelle formation.

Step 2 - <u>Monomer adsolubilization</u>

The monomer is injected into the system. Some monomer dissolves in the solution and then solubilizes into the inner core of admicelle. This phenomena is called adsolubilization. At equilibrium the monomers will fill the inside of the surfactant bilayer.


**Figure 1.5** Monomer adsolubilization.

Step 3 - Polymerization

The monomer in the core of surfactant bilayer forms an ultra thin polymeric film by adding an initiator. The added initiator will diffuse into the hydrophobic zone of surfactant and will activate the polymerization of monomer to form a thin polymeric film.


**Figure 1.6** Polymerization of monomers.

Step 4 - Surfactant removal

The upper layer of the admicelle is removed after the polymerization is complete by washing-off with to expose the polymeric film on the surface.

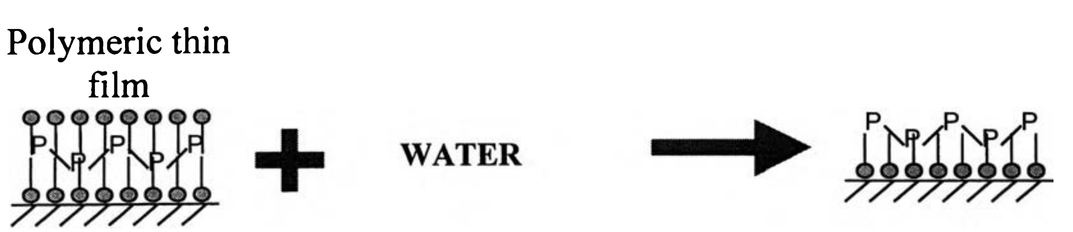


**Figure 1.7** Surfactant removal.

**1.4 Effect of pH**

pH has an important effect on the admicellar polymerization process since different materials have different charges on its surface. Thus, an alternation of charge by using acid or base solution will affect the charge on the interface of the substrate. At the point where acid or base causes the charge on the surface is called point of zero charge (PZC). The substrate surface has a positive charge at above this point and has a negative charge below the PZC as shown in Figure 1.8. Thus in case when the surfactant has a negative charge, the appropriate condition for a surfactant adsorption is to adjust the pH to below PZC to alter the surface charge of the substrate from negative to positive to increase surfactant adsorption.

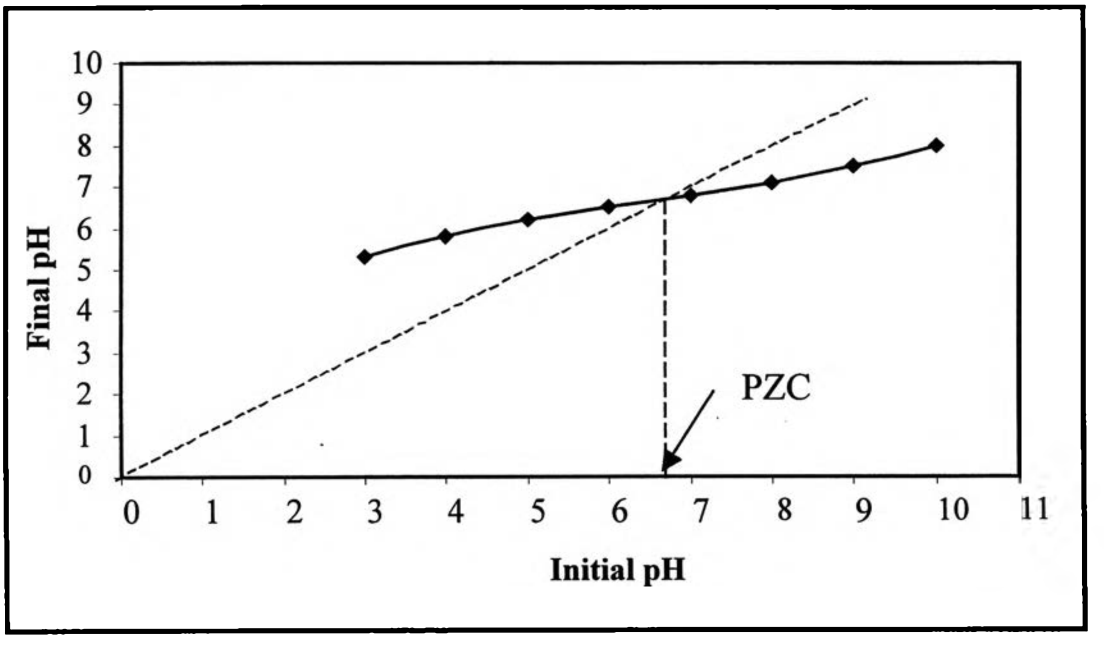


**Figure 1.8** The point of zero charge.

### 1.5 Effect of Salt

Salt can be added to enhance admicelle formation. The sodium ions from the salt molecules will shield the charge portion between surfactant-surfactant and surfactant-surface. These phenomena cause a reduction in repulsive force and create close packing between surfactant molecules as shown in Figure 1.9.

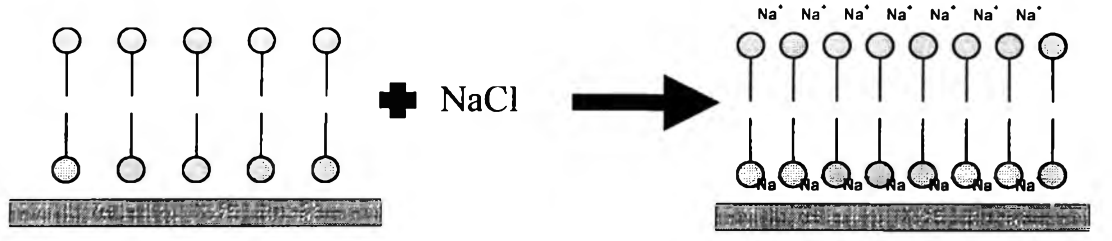


**Figure 1.9** Close packing of surfactant by adding salt.

## 1.6 Cotton Fabric

Cotton is composed of about 90 percent cellulose, about 6 percent moisture, and natural impurities. Each fiber in the cotton has flat, twisted and ribbon-shape with inner aperture. Cellulose is composed of many different molecular homologues, varying from 1,750 to 18,000 repeating cellobiose units, each of which contains three reactive hydroxyl groups (Seymour, 1988). Cellulose structure is demonstrated in Figure 1.10. Three hydroxyl groups in the cellulose can form a cross-linking with hydrogen bond between adjacent molecules as shown in Figure 1.11.

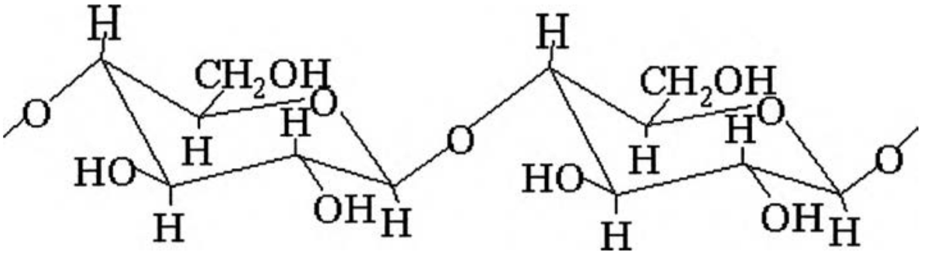

**Figure 1.10** Cellulose structure.

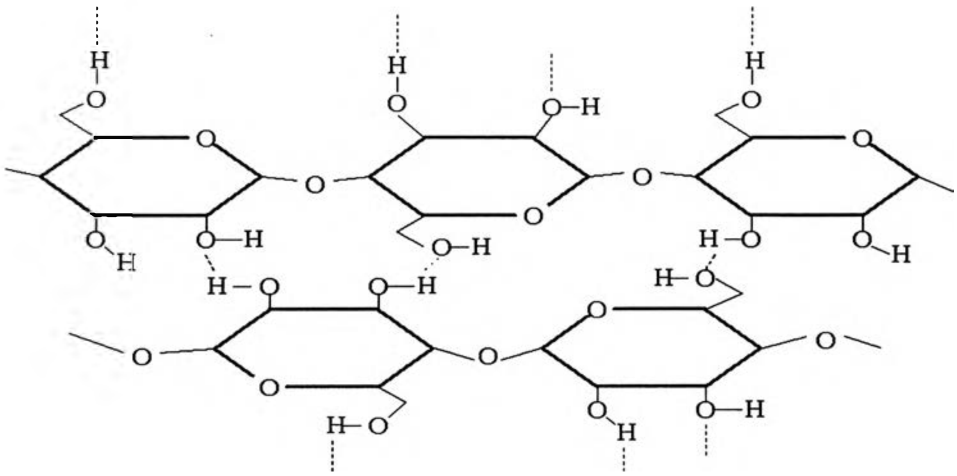


**Figure 1.11** Complex structure of cellulose in cotton.