CHAPTER I

INTRODUCTION

Polymers and surfactants are often used together in industrial formulations to take advantage of their characteristically different properties. When present together they can interact to provide beneficial properties. Such interactions can occur in both aqueous and nonaqueous systems. Owing to their industrial importance, aqueous system have been studied much more in detail than nonaqueous systems.

Polymer-surfactant combinations in aqueous solutions which interact with each other can be broadly classified into three categories, namely uncharged polymer-ionic surfactant, oppositely charged polymer-surfactant and hydrophobe-modified polymer-surfactant systems. While the dominant forces responsible for interactions in the latter two systems can be readily identified, the reasons for the interaction between nonionic polymer and charged surfactant are less clear (Goddard and Ananthapadmannabhan, 1993). In all cases, the interaction of polymers with surfactants, unlike that with other small molecules is made complex by the key role played by the self aggregation or micellization properties of the surfactant.

Polymer-surfactant complexes have found applications in many industrial products, such as foods, phamaceutics, cosmatics, detergents and various chemical treating systems (Goddard and Ananthapadmannabhan, 1993).

1.1 Surfactant Solutions

1.1.1 Characteristic Features of Surfactant

A fundamental property of a surfactant is the presence of both water-soluble and water-insoluble group in its molecule. The water-soluble group is known as a hydrophilic group, while the water-insoluble is called a hydrophobic group. The gerneral structure of sufactant molecule is shown in Figure 1.1. The hydrophilic group can be charged or polar such as anionic, cationic or zwitterionic. On the other hand, the hydrophobic group is usually hydrocarbon, aliphatic chains, polycyclic moieties or aromatic groups that are sparingly soluble in water (Lichtenberg *et al.*, 1982).

Hydrophilic   Hydrophobic
   group   group
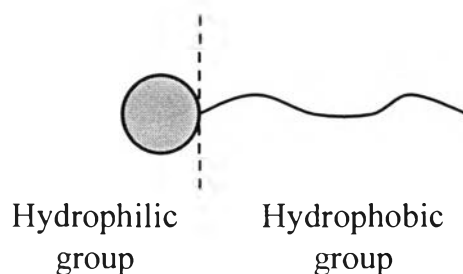
Figure1.1 The general structure of surfactant molecule.

Because surfactants contain both water-soluble and water-insoluble groups, they tend to adsorb at the interface with their hydrophobic groups away from water and their hydrophilic groups in solution. A consequence of this is that some of the water molecules at the interface will be replaced by hydrocarbon or other nonpolar groups. Since the interaction force between water molecules and nonpolar groups is less than between water molecules, adsorption of surfactants at the interface results in a reduction in the surface tension of the solution (Goddard and Ananthapadmannabhan, 1993; Lamax, 1996). The dual tendency is responsible for adsorption of surfactants at interfaces and for the formation of such aggregates as micelles (Rosen, 1989).

1.1.2 Micelle Formation

Surfactant molecules in aqueous solution at concentration above their critical micelle formation (CMC) aggregate to form fairly uniformed sized structures referred to as micelles. The micelle formation depends on the two opposing forces of interaction between surfactant molecules (Porter, 1994).

1.1.2.1 Hydrophilic repulsion

Hydrophilic repulsion may be electrical in the case of ionic groups, or steric in the case of nonionic groups. The greater this charge, the larger is the repulsion and the less tendency to form micelles. If large nonionic hydrophiles come into close proximity, there will be a tendency for water molecules to move toward the lower water concentration around the chains or a tendency to hydrate them. Either effect results in the moving apart the hydrophiles. Then the surfactant molecules will be difficulty to form micelles (Lamax, 1996).

1.1.2.2 Hydrophobic attraction

Hydrophobic attraction is the bond attracting of hydrophobic groups. The reason for this is complex and due to enthalpy and entropy changes when an alkyl group is transferred from a hydrocarbon environment to solution in water. This is basically the hydrophobic effect (Lamax, 1996).

If hydrophilic repulsion is large compared with hydrophobic attraction, the molecules will not aggregate until forced to by increase in concentration. Such aggregation may be seen as more transient and less stable. Thus the CMC is high.

If hydrophilic repulsion is small compared with hydrophobic attraction, the molecules will aggregate easily at low concentration. This means that the CMC is low (Lamax, 1996).

1.1.3 Type of Surfactants

Surfactant can be classified into four classes; anionic surfactants, cationic surfactants, nonionic surfactants and amphoteric surfactants. The classification is used on the chemical structure of hydrophilic group (Goddard and Ananthapadmannabhan, 1993).

1.1.3.1 Anionic surfactants

The surface-active part of the molecule carries a negative charge, e.g. $C_{12}H_{25}COO^-Na^+$, and has a long chain hydrophobe carrying the negative charge

1.1.3.2 Cationic surfactants

The surface-active part of the molecule carries a positive charge, e.g. $C_{12}H_{25}N^+(CH_3)_3Cl^-$.

1.1.3.3 Nonionic surfactants

The surface-active part of the molecule apparently carries no charge.

1.1.3.4 Amphoteric surfactants

The surface-active part of the molecule can carry a positive or a negative charge or both, depending on the conditions, e.g. $C_{12}H_{25}N^+$ $(CH_3)_2-CH_2COO^-$.

1.1.4 General properties of amphoteric surfactants

1.1.4.1 General

The charge of amphoteric surfactant was varied from anionic via zwitterionic to cationic by adjusting the pH, or ionization state of their molecules which is depend on the pH of solution (Folmer *et al.*, 1997; Alargova *et al.*, 1996). Zwitterionic in which both its ionic groups show equal ionization at a specific pH, is at the isoelectric point or area. The most

common anionic group and cationic group are the carboxyl (COOH) and the amine (NH), respectively (Winter, 1989).

When butyloxypropylamine (BOPA), denoted by AH_2, is solubilized in water it forms the zwitterion H^+AH^-. When one equivalent weight of aqueous HCl is added to the latter, it forms the cation $H^+AH_2Cl^-$. When one equivalent weight of aqueous NaOH is added to the zwitterion, it forms the monoanion $H^+A^{2-}Na^+$, and with another equivalent of NaOH it forms the dianion $A^{2-}(Na^+)^{2-}$ (Max *et al.*, 1998).

1.1.4.2 Adsorption

The adsorption gives rise to a decrease in surface tension because surfactants contain both water-soluble and water-insoluble groups, they tend to absorb at interfaces. Packing of molecules at the interface depends on their ability to remain in close proximity. Since amphoteric surfactants consist of anion and cation, the cationic group gives rise to decrease repulsion between negative charges, while the anionic group can act to decrease repulsion between positive charges, promoting closer packing. Packing varies with pH because the effect of pH on the size of head group of amphoteric surfactant (Lamax, 1996).

1.1.4.3 Solubility

Water solubility depends on the presence of water soluble groups in the molecules. The solubility is very slight until a critical concentration is reached at which the solubility increases approximately linearly with the concentration of surfactant (Rosen, 1989). Mixture of surfactant and water is generally a liquid with a high viscosity because formed micelle at and above CMC.

Lin *et al.* (1994) studied the viscosity of sodium dodecyl sulfate (SDS) in water as function of its concentration. They found that the viscosity of aqueous solution is constant until critical micelle concentration is reached at which the viscosity increases with concentration of SDS.
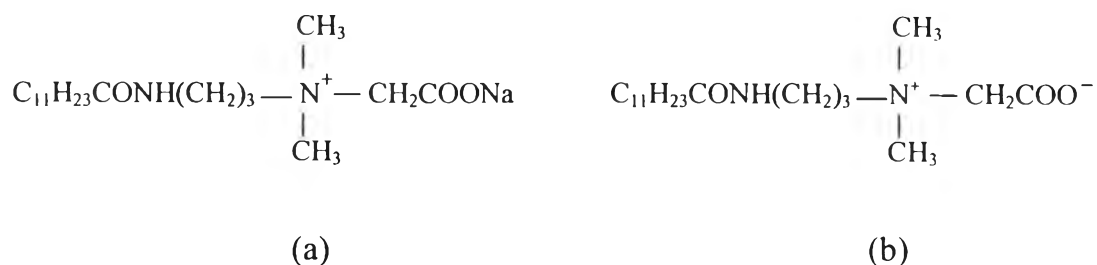
The solubility of these surfactants depends on the relative strength of anionic and cationic groups. Amphoteric surfactants have both anionic and cationic groups so will be soluble over wide pH because of this ability; there is a growing demand for this kind of surfactant (Max, 1996).

Isoelectric area or point in a condition in which molecule has equal positive and negative charges, the solubility shows minimum in this area because interaction between their anionic and cationic groups is of equal strength. Isoelectric area or point of amphoteric surfactants are neutral pH.

Zwitterionic surfactants, whose hydrophilic polar heads carry both a positive or negative charge, are interesting in several respects. They exhibit pH dependent behavior, display a high foam stability, and are less irritating to skin than many ionic surfactants (Shiloach and Blankschtein, 1997). Because of these useful characteristics, zwitterionic surfactants are often combined with anionic or cationic surfactants in many consumer products, such as shampoo and detergents. Mixtures of zwitterionic and ionic surfactants also exhibit interesting rheology behavior.

1.1.5 Cocamidopropyl dimethyl glycine (CADG)

Cocamidopropyl dimethyl glycine or cocamidopropyl betaine is one type of amphoteric surfactants. Surface-active betaines differ from other amphoteric surfactants owing to the presence of the quaternary nitrogen which prevents the molecule from existing as an anionic surfactant in alkaline solutions. They therefore exist only in the zwitterionic or cationic form (Max, 1996). The advantage of this type of amphoteric surfactant is that it is stable when exposed to air. The disadvantage is the allergy to skin. The structure of CADH is shown in Figure 1.2.

$$CH_3$$
$$|$$
$$C_{11}H_{23}CONH(CH_2)_3 — N^+ — CH_2COONa$$
$$|$$
$$CH_3$$

$$CH_3$$
$$|$$
$$C_{11}H_{23}CONH(CH_2)_3 — N^+ — CH_2COO^-$$
$$|$$
$$CH_3$$

(a)   (b)

Figure 1.2 Chemical structure of cocamidopropyl dimethyl glycine (CADG): (a) in solid form, (b) in aqueous solution.

1.2 Polymer Solutions

Water plays a key role in determining the properties of aqueous solutions. Solvation of polymer chains may result from the interaction of ionic, polar, or hydrogen-bonded hydrophilic segments with water. Some water-soluble polymers contain monomers that have amphiphilic character themselves. In this case, solvation of the polymer may involve the hydrophobic interaction, in which the local structure of water in the neighborhood of the hydrophobic portion of the segment is though to play a role (Goddard and Ananthapadmannabhan, 1993).

Polymer used in this study is nonionic water-soluble polymer. In general, water solubility in nonionic polymers derives from strong polarity or hydrogen-binding functionality in the monomer units, leading to favorable interactions with water molecules. Addition of other solution components, such as salt, cosolvents, or surfactants, or changing the molecular weight of the polymer, can effect the solubility strongly (Goddard and Ananthapadmannabhan, 1993).

1.2.1 Hydroxypropylcellulose (HPC)

Hydroxypropylcellulose is an interesting in many commercial applications. It is a water-soluble ether of native cellulose. It is soluble in many solvents, including water, at room temperature. Nevertheless, it is a largely hydrophobic polymer. It precipitates when aqueous soluiton of HPC is heated above 40^0C. In nonpolar solvents, this polymer tend to extend intramolecular hydrogen bonding where as in water, hydrogen bonding with solvent predominant. The general structure of HPC is shown in Figure 1.3.

$R = CH_2\text{-}CH(OH)\text{-}CH_3$
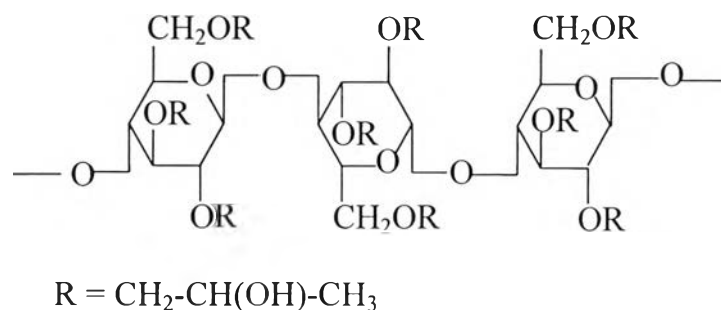
Figure 1.3 Chemical structure of hydroxypropylcellulose (HPC).

1.3 Polymer-Surfactant Interactions

The mechanisms for the formation of stable polymer-surfactant complexes may include one or a few of the following : minimization of the free energy, electrostatic interaction between charged polymers and charged surfactants, hydrophobic interaction, dispersion forces, hydrogen bonding, hydration of the polymer and the head groups, steric repulsion, and electrostatic effect between surfactant head groups (Goddard and Ananthapadmannabhan, 1993).

1.3.1 Driving forces

This force in polymer-surfactant systems comes from the hydrophobic interactions between surfactant molecules. Because of energetically delicate balance, even quite small modifications of the free energy of normal micellization and small contributions from the other interactions can have dramatic influences on the self-assembly and induce important surfactant-polymer interaction. Interaction between ionic surfactants and polymers is stronger than interaction of nonionic surfactants with polymers because electrostatic interaction in ionic surfactants (Goddard and Ananthapadmannabhan, 1993).

1.3.2 Binding Isotherms

The characterization of the surfactant binding to the polymer at a fixed polymer concentration can be obtained and is usually presented as a binding isotherm. A typical binding isotherm is shown in Figure 1.4. The isotherm indicated of cooperative binding, and the onset of surfactant binding often occurs at a critical aggregation concentration (cac) (Goddard and Ananthapadmannabhan, 1993).
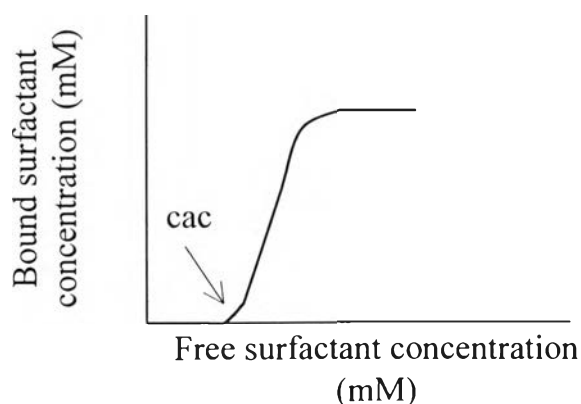
Figure 1.4 A typical binding isotherm for the binding of a surfactant to a Polymer (cac = critical aggregation concentration)

1.3.3 Strength of Interaction

The free energy of micellization can be written as (Goddard and Ananthapadmannabhan, 1993).

$$\Delta G_m = RT \ln cmc \qquad (1.1)$$

where ΔG_m is the free energy of surfactant micellization, R is the gas constant, T is the absolute temperature, and cmc is the critical micelle concentration. The free energy of surfactant binding to a polymer is expressed as (Goddard and Ananthapadmannabhan, 1993),

$$\Delta G_b = RT \ln cac \qquad (1.2)$$

where ΔG_b is the free energy of polymer-bound micelle and cac is the critical aggregation concentration. Therefore, the free energy per mole surfactant for the reaction : free micelle $\leftrightarrow$ polymer-bound micelle , can be derived as (Goddard and Ananthapadmannabhan, 1993).

$$\Delta G_{PS} = \Delta G_b - \Delta G_m = RT \ln (cac / cmc) \qquad (1.3)$$

This quantity is a measure of the strength of the interaction between the surfactant and the polymer. In particular, it is pointed out that it is impossible to have a cac which is higher than the cmc of the surfactant in that case the surfactant molecules would prefer to form free micelles instead of polymer-bound ones and surfactant binding to the polymer will not occur. If the polymer preferentially interacts with a micelle, the free energy of the micelle, and thus the cmc, should be lowered.

The strength of the interaction varies between the different type of polymer-surfactant systems. Generally, the interaction between a polyelectrolyte and an oppositely charged surfactant is very strong (Goddard and Ananthapadmannabhan, 1993).

1.4 Polymer-Surfactant Structures

The interaction between polymer and surfactant could take one or more of the following forms (Holmberg et al., 1992): (a) redistribution of the surfactant molecules between the bulk solution and the polymer coil regions; (b) surfactant molecules bound along the polymer chain; (c) surfactant molecules start to bind as a cluster or micelle on the hydrophobic sites of the polymer chain; and (d) polymer segments penetrate and wrap around the polar head group regions of surfactant micelles.

The interaction types (c) and (d) are called site clustering and mixed micelle, respectively. The (c) step is fairly similar to the (d) step. However, there are conceptual differences in the initial step between them. The site clustering and mixed micelle interaction are shown in Figure 1.5. The site clustering characters implies a strongly cooperative surfactant-polymer interaction, starting below the normal the CMC and occurring over a range of surfactant concentration.

The mixed micelle character is the formation of micelle in the normal fashion, although at a bulk concentration lower than the CMC of magnitude as that of a normal micelle.
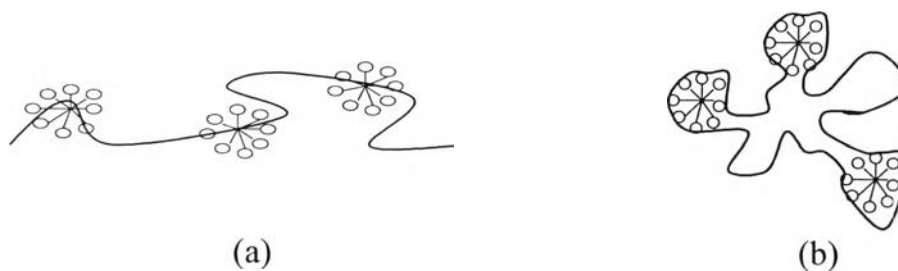
Figure 1.5 Schematic diagram of polymer-surfactant complex; (a) site clustering and (b) mixed micelle.

1.5 Applications of Polymer-Surfactant Systems

A great number of polymer-surfactant complexes are very useful in biological systems, e.g., membranes, carriers and a variety of other systems including foods, phamaceutics, cosmetics, detergents, various chemical treating system such as viscosity enhancement, rheology control, seperation and purification (Goddard and Ananthapadmannabhan, 1993).

When an uncharged polymer binds with an ionic surfactant, the polymer will acquire a charge and therefore, on the basic of polyelectrolyte effect, an increase in viscosity would be anticipated. An interesting applications of the polymer-surfactant complexs are a seperation and purification such as seperation sucrose from enzyme lipase (Rosen, 1989).

The combination of nonionic polymer and various anionic surfactants are also used as a medium for drug release. The presence of surfactants to prolong the releasing time of drug from a tablet. The mechanism of prolongation is attributed to increase viscosity of a gel layer which forms on the surface of the tablet when it contacts an aqueous medium.