CHAPTER I

INTRODUCTION

A great number of aqueous based systems in nature and commerce contain one or more polymer and surfactant in the same solution. In these, any interaction between polymer and surfactant, as well as property changes conferred by any resulting "complex", can be of considerable importance. Included in this category are a multitude of biological systems, e.g.,membranes (structure and functioning), a variety of other systems including pharmaceutics, cosmetics, detergents, and various chemical treating systems. A knowledge of the interaction characteristics of a particular polymer and a surfactant will greatly aid the understanding and facilitate optimization of the properties of a system [Ananthapadmanabhan and Goddard, 1993]. So until now, a number of different techniques have been employed to study the nature of formed complex. Light scattering technique is highly sensitive and noninvasive method for investigating changes in the conformation of the complex but, surprisingly, have been little employed in this context. So, light scattering and viscometric investigations are used to reveal interesting properties of the polymer-surfactant complex in this study.

1.1   Hydroxypropyl Cellulose (HPC)

Hydroxypropyl cellulose (HPC) is an interesting nonionic polymer with many commercial applications It is soluble in a wide variety of solvents, including water from which it precipitates when heated above 42° C. At high concentrations in several solvents, it forms liquid crystalline phases. The HPC

is a largely hydrophobic polymer. At temperatures above $0°C$ in water, it has a tendency to form aggregates and these become sufficiently extensive at elevated temperatures which lead to phase separation above the lower critical solution temperature [Winnik et al., 1987].
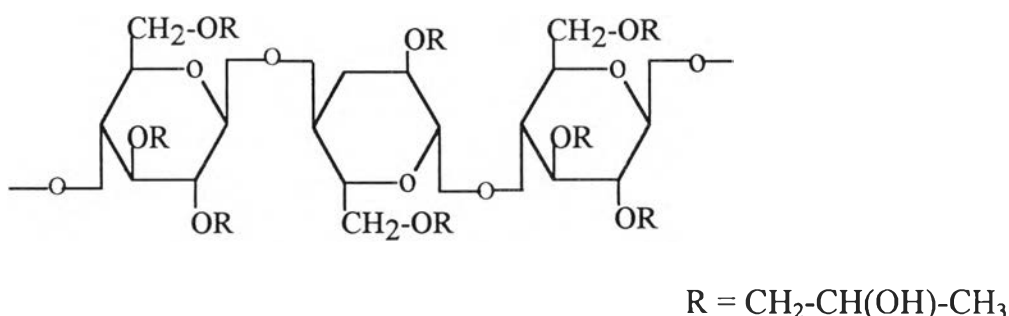

$$R = CH_2\text{-}CH(OH)\text{-}CH_3$$

Figure 1.1 Chemical structure of HPC.

1.2 **Hexadecyltrimethylammonium Bromide (HTAB)**

Hexadecyltrimethylammonium bromide (HTAB) is a cationic surface active agent or surfactant characterized by having a hydrophilic (waterloving with positive charge) group and a hydrophobic (waterhating with hydrocarbon chain) group in the same molecule as shown in figure 1.2 .
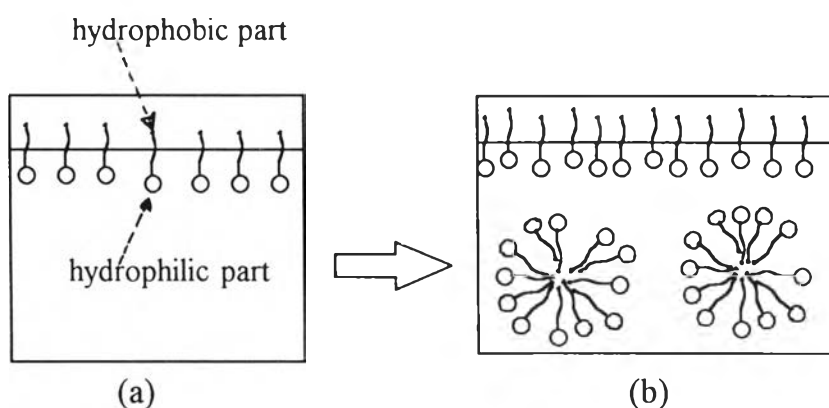

Figure 1.2 Schematic representations of cationic surfactant in aqueous solution (a) C_{HTAB} < cmc , (b) C_{HTAB} > cmc.

When the surfactant is present at low concentrations in a system, it has the property of adsorbing onto the interface of the system by turning the hydrophilic part into the water . Once the interface is saturated when the amount of surfactant increases, micelle formation will take place as shown in fig. 1.2. The concentration of the surfactant in the bulk phase at which the formation of surfactant cluster or micelle begins to occur is called the critical micelle concentration (cmc). The chief driving force for micellization is a reduction of the hydrocarbon/water contact area of alkyl chains of dissolved surfactants.

1.3   Uncharged Polymer and Ionic Surfactant

The interaction between water soluble nonionic polymers and ionic surfactants has become a field of intense research in recent years [Carlsson et al., 1989]. Such studies mainly deal with the action of anionic surfactants, while cationic species are inferred to interact comparatively weakly with nonionic polymers. This behavior has been illustrated as owing to :

(a) the bulkiness of the cationic head group [Nagarajai, 1985 and Ruckenstein et al., 1987]

(b) the electrostatic repulsion between polymer and surfactant due to the possible positive charge of polymer upon protonation [Moroi et al., 1977]

(c) more favorable interaction between anionic surfactants and the hydration shell of the polymers [Witte and Engberts, 1989].

Moreover, if a more hydrophobic polymer is used, a more pronounced interaction between nonionic polymer and cationic surfactant is observed. For example, the complex formation between HPC and hexadecyltrimethylammonium chloride (HTAC) micelles [Winnik et al., 1987], ethyl (hydroxyethyl) cellulose (EHEC) and N-tetradecylpyridinium

bromide (TDPB) or dodecyltrimethylammonium ions (DTA$^+$) [Carlsson et al., 1989], poly (vinyl alcohol) (PVOH) containing 88% acetate groups and HTAB [Tadros,1974] have been shown by using different techniques. The latest system has been investigated by surface tension, conductance, and cloud point techniques.

1.3.1 Critical Concentrations in Polymer-Surfactant Solutions

In the absence of the polymer, the surfactant micellization occurs when the total surfactant concentration exceeds the critical micelle concentration (cmc) of the surfactant. However, in the presence of the polymer, the nature of the partitioning of the available surfactant into the free surfactant, the polymer-bound surfactant and the micellized surfactant depends on the interplay between the model parameters. In a system of fixed polymer concentration with increases in the amount of surfactant, no interaction between the polymers and the surfactants is detected until a critical aggregation concentration, known as thecac is reached [Lindman and Thalberg, 1993]. So, cac is a surfactant concentration at which interaction between polymers and surfactants takes place and complex begins to form. The cac value can be detected by a variety of techniques such as conductivity, surface tension, and fluorescence. However, the cac values from different techniques may be different. The cac is usually lower than the normal cmc in the absence of the polymers. This is a clear indication of interaction between polymer and surfactant.

1.3.2 The Main Driving Force

The competitive processes that exist in polymer/surfactant/water systems are mainly surfactant micellization and polymer-surfactant

association. The process of micellization of ionic surfactant represents a delicate balance between several forces favoring and resisting aggregation. One of the main forces resisting self-aggregation is the crowding together of the ionic head groups at the periphery of the micelle. Because of the electrostatic interactions which are particularly susceptible to change, even quite small modifications of 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 interactions. This is the reason why ionic surfactants in general interact strongly with polymers, while nonionic surfactants interact quite weakly or insignificantly.

The role of the polymer must also be considered. An important suggestion comes from the polymer "reactivity" series of Breuer and Robb (1972) where reactivity increases with polymer hydrophobicity. Several available experimental results indicate that "the more hydrophobic on polymer, the greater is the binding of the surfactant onto it [Arai and Horin, 1969; Saito, 1967; and Lewis, 1970]."

The favorable polymer-surfactant association arises from

(a) a reduction of the hydrophobic part/water interface area of both hydrophobic polymer segments and alkyl chains of surfactant by contacting of polymer hydrophobic areas with exposed hydrophobic areas of developing surfactant aggregates

(b) a more favorable free energy, as manifested in a lower cac than normal cmc

(c) an increase in ionic dissociation of the aggregates that leads to reducing in charge density at the periphery zones

1.3.3 Structure of Polymer-Surfactant Complexes

Some of the recent neutron scattering [Chen and Teixeira, 1986], quasi-elastic light scattering [Tanner et al., 1982], and fluorescence/dynamic fluorescence results appear to support the pearl-necklace model of polymer-surfactant complexes where the surfactant micellar beads decorate along the polymer "string" or chain.

The interaction between a nonionic polymer and an ionic surfactant could take one or more of the following forms [Holmberg et al., 1992]:

(1) redistribution of the surfactant between the bulk solution and coil regions

(2) surfactant molecules bound individually along the polymer chain

(3) surfactant molecules clustered around hydrophobic sites on the polymer

(4) polymer segments partially penetrate and wrap around the hydrophilic micellar surfaces
the

The interaction type (3) is fairly similar to (4). However, there are conceptual differences in the initial step between the two, as described below

The "*site clustering*" (type 3) characters

(a) implies a strongly cooperative surfactant-polymer interaction

(b) starts well below the regular cmc

(c) occurs over a range of surfactant concentrations

(d) such as cellulose derivative and ionic surfactant interactions

(Nilsson S., 1995)

The "*mixed micelle*" (type 4) characters

(a) implies the formation of a micelle in a normal fashion, though at a bulk concentration lower than cmc and with aggregation number lower, but of the same order of magnitude as that of a regular micelle

(b) backbone flexibility is a favorable factor

(c) requires a minimum M_w for reacting with the surfactant clusters

(d) such as PEO/SDS/water system [Goddard, 1986 and Shirahama, 1974]
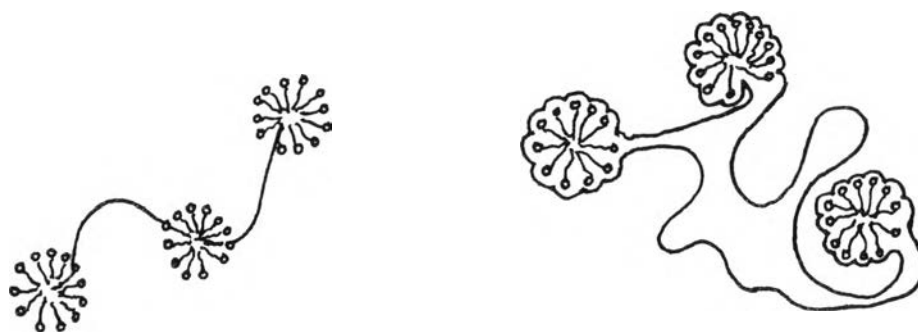
Figure 1.3 Schematic representations of interaction between a nonionic polymer and an ionic surfactant, *site clustering* type (left) and *mixed micelle* type (right).

We expect that the interaction between HPC-HTAB may be represented by the "*site clustering*" cooperative manner. This is because of the fact that

(1). the stiff backbone character of HPC [Mandel, 1985] may obstruct loop formation around the micellar head groups.

(2). the largely hydrophobic behavior of HPC is known to lead to strongly cooperative polymer-surfactant interaction as manifested by the lower cac of HPC-SDS than of PEO-SDS [Winnik et.al., 1987].

1.3.4 How can we know when polymer-surfactant complexes form?

Systems of a nonionic polymer and ionic surfactant are characterized by the charging up of the polymer chains when the ionic surfactants interact with the polymer. This can be observed by the increases in both hydrodynamic radius and viscosity. These phenomena are reasonably explained that micellelike clusters of bound HTAB molecules are arranged statistically along the HPC chain and that the complex behaves like polyelectrolyte.

1.3.5 Applications of The HPC-Ionic Surfactant System

The major application for the HPC-ionic surfactant complex formation is in pharmaceutical field. To find the most efficient pharmaceutical formulation, it is essential to understand how a certain drug is released from a matrix such as a tablet, and how the drug is then transported into the systemic circulation. Both these events are influenced by diffusion processes which can be studied by dynamic light scattering technique.

Alli and co-workers (1991) have investigated the combination the HPC and various anionic surfactants as a medium for release of selected drugs in tablet form. The presence of SDS and other ionic surfactants was found in most cases to prolong the time of releasing drug from a tablet containing HPC.

In addition to pharmaceutics, the HPC-ionic surfactant complex can be used in cosmetics (e.g. film former for hair dressings, grooming aids, perfumes and colognes), food industrial and paint removers [Mandel, 1985].

1.4   <u>Literature Reviews</u>

The amphiphilic character of surfactants makes them interesting agents in polymer chemistry. For instance, the hydrophobic part of such a molecule will have a marked tendency to interact in associative sense with hydrophobic polymers and at the same time give the polymer new properties due to the hydrophilic coating introduced. Phenomena of this type have been extensively studied, and the literature on the subject is vast.

Effect of Surfactant Concentration

Brown et al. (1992) investigated PEO-SDS complex by static light scattering (SLS) and dynamic light scattering (DLS). The complex chains expand with an initial increase in SDS concentration and reaches a maximum at saturation point of weight concentration ratio $C_{SDS}/C_{PEO} = 5$. Then the chains collapse with further increase in the SDS concentration.

Cabane and Duplessix (1982) showed that the complex of PEO-SDS is stoichiometric by using small-angle neutron scattering.

Effect of Salt

Gilanyi and Wolfram (1985) investigated Poly (vinylpyrrolidone), PVP-SDS in 0.1 M NaNO$_3$ system by using SLS. They observed that while the M_w of the complex increased steadily as SDS is added, radius of gyration (R_g) of the complex decreased first and then increased, in agreement with their viscosity measurement.

Dubin et al. (1992) used SLS , DLS , electrophoretic light scattering , and dialysis equilibrium to study the effects of ionic strength in the PEO-lithium dodecyl sulfate (LDS) system. They proposed two effects of the addition of salt ; (a) it weakens the simultaneous binding of the counterion Li^+ to oxygen and LDS, and (b) it also diminishes intermicellar repulsion promoting more micelles to bind.

Effect of Counterions

Dubin and coworkers (1992) studied the influence of micelle counterions (Na^+, Li^+, and NH_4^+) of dodecyl sulfate micelles on the interactions between micelles and PEO using dye solubilization and DLS. Their results suggested that the cation interacts simultaneously with the micelle through electrostatic forces and with the polymer via coordination complexation.

Interactions between Nonionic Polymers and Cationic Surfactants

The weaker interaction between uncharged water soluble polymers with cationic surfactants than anionic surfactants is suggested by several investigators. For example, no interaction has been observed between HTAC and PVP, both of which form mixed micelles with SDS [Winnik el al., 1987 and Chari et al., 1990]. However, the hydrophobicity of polymer is increased, interactions between nonionic polymers and surfactants may be enhanced.

Recently, interactions between nonionic polymers and cationic surfactants have been observed, as shown in the table 1.

Table 1. Literature studies of the interactions between nonionic polymers and cationic surfactants.

Nonionic polymers	Cationic surfactants	References
HPC	HTAC	Winnik et al., (1987)
PVA and PEO	HTAB and BINA	Shirahama et al., (1987)
EHEC	TDPB and DTA$^+$	Carlsson et al., (1989)
PPO	HTAX (X$^-$ for Cl$^-$, Br$^-$, ClO$_3^-$, and NO$_3^-$)	Witte and Engberts (1987), Brackman and Engberts (1991), Sierra and Rodenas (1993), and De Schryver et al., (1991)
PVME	HTAB, HTASal, and HTATs	Brackman and Engberts (1991)
PVOH-Ac	HTAX	De Schryver (1993)

Glossary

polymers ;

PVA	poly (vinyl alcohol)
PEO	poly (ethylene oxide)
EHEC	ethyl (hydroxyethyl) cellulose
PPO	poly (propylene oxide)
PVME	poly (vinylmethylether)
PVOH-Ac	poly (vinyl alcohol)-poly (vinylacetate)

cationic surfactants ;

HTAC   hexadecyltrimethylammonium chloride

HTAB   hexadecyltrimethylammonium bromide

BINA   hexadecyldimethyl-2-hydroxyethylammonium bromide

TDPE   N-tetradecylpyridinium bromide (TDPB)

DTA^+ dodecyltrimethylammonium ion

HTASal   hexadecyltrimethylammonium salicylate

HTATs   hexadecyltrimethylammonium tosylate

1.5   Objectives

Dynamic light scattering and viscometry investigations are used to reveal interesting properties of HPC-HTAB interactions. These methods yield information on the conformational changes of HPC-HTAB charged complex whereby polyelectrolyte properties are imparted to the neutral HPC chain.

The purposes of this research are to elucidate the effects of the surfactant concentration, the polymer concentration, and the gram ratio of the surfactant to the polymer on the complex formation of HPC and HTAB. The modification of the charged complex in the presence of a simple salt is also investigated.