CHAPTER I

INTRODUCTION

The association of surfactants and polymers in aqueous solution has been a focus of intense fundamental and applied research activities. Attention to this topic is driven by the numerous industrial applications of mixtures of polymers and surfactants in solution. They are found in fluids for enhanced oil recovery, food preparations, cosmetic formulations, and pharmaceutical compositions. Present fundamental studies are directed towards elucidating detailed aspects of the structure and conformation of aggregates and mechanisms of the association phenomena [Winnik and Regismond, 1996]. Light scattering, viscosity and rheological properties were used in this study to investigate the changes in conformation of the complex.

There are quite different types of aqueous polymer-surfactant systems. Of major significance is the presence of charged groups on the polymer and/ or on the surfactant then they can be broadly classified into three categories, namely uncharged polymer-ionic surfactant, oppositely charged polymer-surfactant and hydroprobe-modified polymer-surfactant systems. The dominant forces responsible for interactions in the latter two systems can be readily identified but the reasons for the interaction between nonionic polymer and charged surfactant are less clear. [Ananthapadmannabhan and Goddard, 1993]. This is why this thesis concentrates on studying complex formations of a nonionic polymer and ionic surfactants.
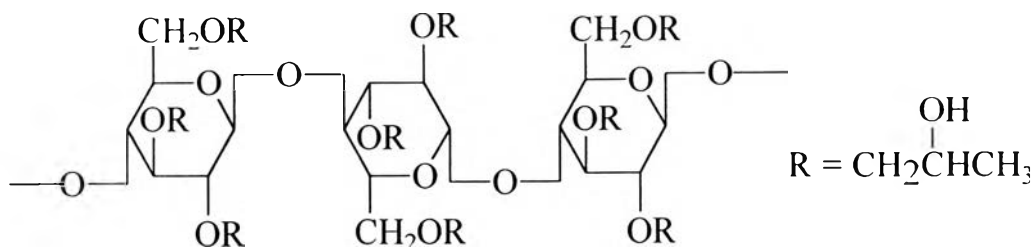
1.1 Hydroxypropylcellulose (HPC)

Hydroxypropylcellulose or HPC is a semi-flexible, nonionic polymer chain. It can be prepared by the based catalyzed reaction of propylene oxide with alkali-cellulose stirred with an aliphatic hydrocarbon and alcohol or propylene oxide as shown in Figure 1.1.

$$RcellOHNaOH + nCH_3CH\overset{O}{\overbrace{}}CH_2 \longrightarrow Rcell(OCH_2CHCH_3)_nOH + NaOH$$
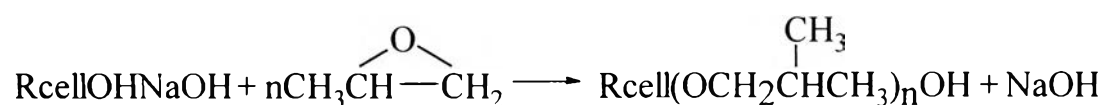
Figure 1.1 Preparation of hydroxypropylcellulose.

Hydroxypropylcellulose is soluble in many solvents, including water, at room temperature. In nonpolar solvents, this polymer tends to extend intramolecular hydrogen bonding whereas in water, hydrogen bonding with solvent predominant. Nevertheless, it is a largely hydrophobic polymer. When aqueous solution of HPC is warmed to about 40°C, a phase separation occurs with a sharp increase in turbidity and decrease in viscosity [Klug, 1971].

HPC forms as an order liquid-crystalline phase with cholesteric structure in excess of 40% w/v [Werbowyj, 1980]. At temperature above 0°C in water, it has a tendency to form aggregates and they become sufficiently extensive at elevated temperatures to lead to phase separation above the lower critical solution temperature, LCST [Winnik *et al.*, 1987].

CH$_2$OR   OR   CH$_2$OR

OH
R = CH$_2$CHCH$_3$

Figure 1.2 Chemical structure of hydroxypropylcellulose.

1.2 Hexadecyltrimethylammonium Bromide (HTAB)

Quaternary ammonium salt (usually called quats) are one of cationic surfactant that carries a net positive charge in solution. It can be made in simple equipment under mild conditions by reacting on appropriate tertiary amine with an organic halide or organic sulfate. (Figure 1.3)

$$R_2-\overset{R_1}{\underset{R_3}{N}} + R_4Br \longrightarrow \left[R_2-\overset{R_1}{\underset{R_3}{N}}-R_4 \right]^+ Br^-$$
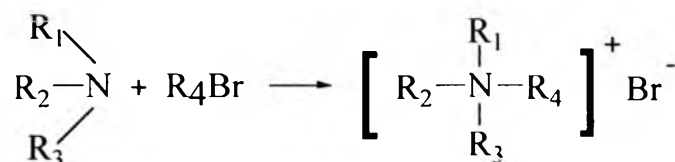
Figure 1.3 Preparation of quaternary ammonium salts.

Quats are soluble in water when there is only one long hydrophobic group. When the number of long hydrophobic chains increases, the products become dispersible in water and soluble in organic solvent [Porter, 1994]. They can adsorb strongly onto negatively charge surfaces. Adsorption of cations on surfaces modifies their properties by

(a) making surfaces more greasy (feel sticker) or lipophilic (a property used for improving the adhesion of asphalt onto aggregates)

(b) helping to reduce static charge buildup (key property for hair and fabric softeners)

(c) interfering with microbial activity (biocides, sanitizers)

However these surfactants cannot be used at temperature higher than $100^{\circ}C$ because they will decompose [Lange, 1994].

HTAB is the one of the most widely studied quaternary ammonium salt because of its availability, low odor and relatively low toxicity. It starts to form micelles in aqueous solution when concentration of HTAB equals to 0.92 mM at 25°C [Rosen, 1989]. At higher concentrations, the cylindrical micelles or rod-like micelles occur. They will cause the significant increase in viscosity [John and Edward, 1994].

$$\left[\; C_{16}H_{34}-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{N}}-CH_3 \; \right]^{+} \; Br^{-}$$
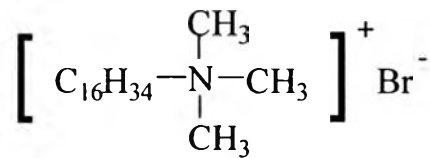
Figure 1.4 Structure of hexadecyltrimethylammonium bromide.

1.3 The Interaction between Uncharged Polymer and Ionic Surfactant

The interaction between water soluble nonionic polymers and ionic surfactants has become a topic of intense research interest in recent years [Carlsson et al., 1989]. In general, nonionic polymers interact strongly with anionic surfactants, but weakly with cationic surfactants. This behavior was explained due to:

(a) the bulkiness of the cationic head group [Ruckenstein, 1987];

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

(c) a more favorable interaction between anionic surfactant and the hydration shell of polymer. As the hydrophobicity of polymer or surfactant increases, the binding of surfactants to polymer is more favorable. [Witte and Engberts, 1989].

In a system of fixed polymer concentration but increasing surfactant concentration, no polymers and surfactants formation is detected until reaching a critical aggregation concentration, cac. [Lindman and Thalberg, 1993]. It has to be noted that the cac can be determined by a variety of techniques such as surface tension, conductivity, and fluorescence. The cac value from different means can be different. Normally, the cac of nonionic polymer-ionic surfactant complex is lower than a critical micelle concentration, cmc, in the absence of polymers [Fishman and Eirich, 1971]. Above the cac, surfactant form micelles bound onto a polymer chain and the chain becomes saturated with surfactant micelles at a constant concentration.

1.4 The Main Driving Force

The competitive processes that exist in ternary (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 modification 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 where reactivity increases with polymer hydrophobicity. Several available experimental results indicate that "the more hydrophobic the polymer, the greater is the binding of the surfactant onto it" [Saito, 1967].

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.

The association between HPC and HTAB usually leads to a stabilization of the interface between hydrocarbon core and water. However, in the case of HTAB, the bulky head groups already shield most of the core from contact with water. Furthermore steric repulsion between head groups and polymer segments may produce an unfavorable contribution to the free energy of formation of polymer-bound micelles. Therefore only some HPC chains will interact with HTAB micelles because of the additional reduction in free energy due to the transfer of polymer segments from the aqueous to the micellar surroundings.

1.5 Structure of Polymer-Surfactant Complexes

When polymer-surfactant complex occurs, it should take one or more of the following forms [Holmberg et al., 1992]:

(a) redistribution of the surfactants between the bulk solution and the polymer coil regions;

(b) individual surfactant molecules bound along the polymer chain only;

(c) surfactant molecules aggregate around hydrophobic sites of the polymer or called "site clustering" ;

(d) polymer segments partially penetrate and wrap around the polar head group regions of micelle surface or called "mixed micelle".

The interaction type (c) is fairly similar to (d). However, there are conceptual differences in the initial step between them.
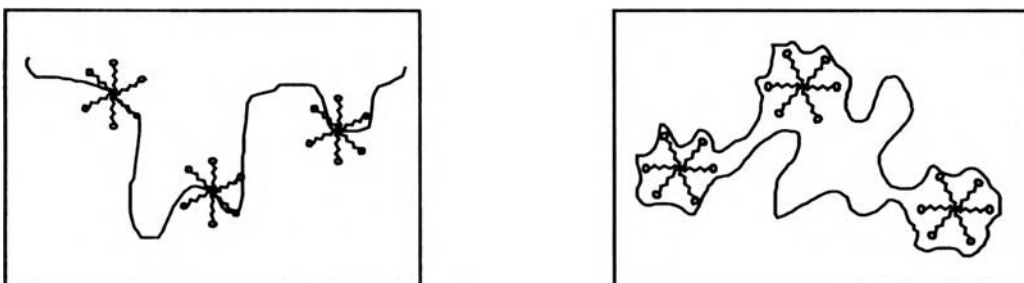
The site clustering characters:

(1) implies a strongly cooperative surfactant-polymer interaction;

(2) starts well below the regular cmc;

(3) occurs over a range of surfactant concentrations.

Cellulose derivative and ionic surfactant interactions is one of complexes which have this structure [Nilsson, 1995].

The mixed micelle characters:

(1) implied 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;

(2) backbone flexibility is a favorable factor;

(3) requires a minimum molecular weight for reacting with the surfactant clusters.

The example of this structure is PEO-SDS complex in aqueous system [Goddard, 1986].

Figure 1.5 The models of site clustering type (left) and mixed micelle (right).

For HPC-HTAB system, the interaction should be represented by the site clustering structure. The reasons for this hypothesis are:

(a) HPC is semi-flexible polymer [Mandel, 1985]. Its structure will obstruct loop formation around the micelle head groups;

(b) the largely hydrophobic behavior of HPC leads complex starting to form below the regular cmc [Nilsson, 1995].

1.6 Gelation

A polymer gel point (GP), the critical gel, is a transition state between liquid and solid. The liquid polymer before the GP is called a sol because it is soluble in good solvents. The polymer beyond the GP is called a gel, which is not soluble, even in a good solvent.

Polymer systems around the gel point are just beginning to be explored. They are of interest for applications such as gel processing, and the development of new materials (adhesive, adsorbents, porous catalysts, membranes etc.). They are also important beyond the polymer field, for example, in food industries or in blood clotting. For many applications in polymer processing, it is sufficient to know when the liquid-solid transition occurs for the purpose of avoiding it.

In chemical gelation, the molecules cross-link into larger clusters by forming covalent bonds. However, molecular networks can also form by physical gelation in which the molecules associate each other by physical forces.

The principal differences between chemical and physical gels lie in the lifetime and the functionality of the network junctions. Chemical bonds are considered to be permanent while the physical junctions have finite lifetimes.

The chemical gel forms continuously with increasing extent of reaction whereas the physical gelation process depends on the type of transition. Defining GP of a physical gel is difficult because its molecular weight is finite even if it forms infinite clusters and it is soluble even beyond GP. Therefore, it is common to use mechanical properties to define GP.

1.7 Applications of Hydroxypropylcellulose and Cationic Surfactants

The HPC-cationic surfactant complex plays an important role in many technical applications especially in pharmaceutical formulations. It may serve as a part of a regulating system for the release rate, as a stabilizer in emulsion, as a neutral substance to provide adequate flow properties, as an adsorbent for the drug. and so on [Nilsson. 1995]

In cosmetic industries, this kind of complex is used in hair conditioners. It will adsorb on hair with cations of hydrophilic group while hydrophobic group oriented away from hair. Polymer will act as a thickener. Both of them give softness and antistatic properties.

In addition to pharmaceutics and cosmetics, the polymer-cationic surfactant complexes can also be used in food, detergents, paint, textile, biocides. etc. [Ananthapadmannabhan and Goddard, 1993].

1.8 Literature Reviews

1.8.1 Interaction between Nonionic Polymers and Ionic Surfactants

The association between nonionic polymers and ionic surfactants has been studied by many types of techniques.

Using small-angle neutron scattering (SANS) to study complexation between poly(ethylene oxide), PEO and sodium dodecylsulfate, SDS, Cabane and Duplessix (1982) identified an intrapolymer complex, which contains one PEO macromolecule whose radius of gyration (R_g) is comparable to that of the free PEO coil. Therefore, the interaction between PEO and SDS does not produce a change in size of the PEO coils. By using the contrast variation method, they also showed from the SANS results at the Guinier region that with the SDS binding the complex has the same R_g as that of the PEO. Therefore, the SDS must be distributed throughout the polymer coil. The SDS molecules form micelles of about 2 nm in radius.

Maltesh and Somasundaran (1992) studied the conformation change of PEO upon the association with SDS using fluorescence of either pyrene end-labeled PEO or pyrene probe. Initial binding of SDS causes PEO to contract whereas at the saturation of the polymer by SDS the coiled PEO chains stretch out. They also found that the stronger the binding of the cation to PEO, the less the interaction between PEO and SDS. Quina *et al.* (1990) and Winnik *et al.* (1990) also investigated this complex by using fluorescence technique. The results showed lower cac compare to SDS-PEO. It should be note that the pyrene-labeled PEO represents a hydrophobically modified system and is no longer the same as PEO.

Complex formation of PVME-HTAB by using mainly conductivity. viscosity, and fluorescence has been reported by Brackman and Engberts (1991). They observed that the presence of polymer gives rise to cac

lower than cmc. a higher micellar ionization degree, and a smaller N for the bound micelle in presence of PPO. Besides this kind of surfactant, Brackman and Engberts also studied interactions between PVME and HTASal and HTATs. They found that in presence of PVME, rodlike micelles of HTASal and HTATs change to spherical polymer-bound micelles. The change of rodlike micelles to spherical micelles in the presence of PVME has been reported by using ^{13}C NMR [Wong et al., 1992] and diffusion-ordered 2D NMR [Morris et al., 1994]

Dubin et al. (1992) studied the effects of ionic strength, and PEO molecular weight on the complex of PEO-LDS by using static light scattering, electrophoretic light scattering, and dialysis equilibrium. They concluded that adding the simple salt (a) weakens the binding counterions, Li^+, to PEO and SDS (b) reduces intermicellar repulsion so the number of LDS micelles bound to PEO chain will be increased. Brown et al. (1992) reported a study of interaction between PEO and SDS by using static and dynamic light scattering. Their results indicated that the neutral PEO chain, on formation of a charged complex with ionic surfactant SDS, expands. This was illustrated by changing in R_g and relative viscosity. The saturation point of this system is about $C_{SDS}/C_{PEO} = 5$. Above this point chain contracts because of screening effect by free counterions from excess SDS.

The interaction of surfactants and cellulose polymer especially EHEC continues to be a special interest in view of industrial processes. Zena et al. (1992) described that EHEC interact with cationic surfactant such as CTAX (X = Cl⁻, Br⁻) by means of conductivity and fluorescence. They showed that the polymer-micelles association has a larger degree of micelle ionization and to be at the lower aggregation number than free micelles. These cause the cac to be lower than cmc. The EHEC-surfactant interaction will be stronger with increasing temperature. Kamenka et al. (1994) proceeded to study the

interactions of EHEC with anionic surfactant. Fluorescence quenching measurements were carried out and they found that the polymer bound micelles are much smaller than free SDS micelles. Another systems, SDS with HPMC, was investigated over and extended composition interval from infinite dilution to a polymer concentration above the critical overlap concentration, C^*. The aim of this experiment was to characterize the redistribution (adsorption) of surfactant to polymer. Fluorescence measurements were used to monitor the onset of interactions and to determine number of aggregation of the bound clusters SDS ranging from 50 for solutions of 0.2% HPMC to 20-25 for infinitely dilute solution. In Carlsson *et al.* (1989) work, self-diffusion measurements were performed on $DoTA^+$ from DoTAB in aqueous solutions of EHEC by the Fourier transform NMR self-diffusion technique. Furthermore, it was shown that an addition of salt or an increase in temperature promotes the binding of $DoTA^+$ to EHEC. The finding of an increased attraction between surfactant and EHEC at evaluated temperatures demonstrates that the polymer molecules become increasingly more hydrophobic with increasing temperature, which is referred to as temperature-induced conformational changes in the polymer.

1.8.2 Gelation

Sol-gel transition can be monitored by the change in viscosity or in elasticity, the growth of cluster size by light scattering technique and also the rheological aspects.

For chemical gelation, Walter *et al.* (1988) studied the dynamically critical behavior during chemical gelation and vulcanization in context of polymeric fractals. The results showed that at the critical point power laws of the complex viscosity and the storage modulus appear. Viscosity and modulus were calculated around the critical point and as functions of the

extent of reaction. The power law was interpreted in terms of the fractal dimension of the cluster, and it was shown that this agrees with experiment if one takes swelling phenomena into account.

Unlike chemical gelation, physical gelation is less understood. Berghams et al. (1987) reported the thermoreversible of syndiotactic PMMA solutions in o-xylene by using calorimetric and rheometric techniques. Their results indicated that the temperature domain of the sol-gel transition is independent of the overall tacticity and polymer concentration. The extent of gelation increases with increasing tacticity. A minimum degree of tacticity, corresponding to a minimum average sequence length, is needed. The combination of infrared and calorimetric data with rheological observations reveals a two step mechanism. Gelation is induced by a fast conformational changes, followed by an intermolecular association. Klaas and Winter (1989) used rheological measurement to study the mechanical properties at the GP of PVC solution. They found that the mechanical behavior of PVC plastisols has the same evolution as chemically cross-linking systems. From the analogy between the physical and chemical gelation, the PVC plastisol is at gel point when it exhibits power law relaxation. This makes it possible to measure the GP directly by using simple rheological test. The gel equation for the stress can be used to model the flow of PVC plastisol gels for processing. Lin et al. (1997) also studied PVC gelation. Lin described that increasing the polymer concentration gradually from the liquid state to the solid state allowed the rheological observation of the sol-gel transition. The scaling exponent n and gel strength were constant (n = 0.75, S_g/GP = $1.27 \times 10^{-2} Pa.s^{0.75} g^{-1} L$) and independent of PVC molecular weight. These results suggest a unique character and structure at the GP of the gelling system. In Jamieson et al. (1993) work, they concluded that the dynamical exponent of gelatin has a unique value (n = 0.69 ± 0.02) over the wide concentration range, 1-14% w/v, and is independent

of ionic strength, pH and denaturant. The critical cluster is a percolation network of dimension $d_f = 2.5$.

In ternary system. Jaan Roots *et al.* (1992) studied static and dynamic properties of a thermoreversible gelling system (EHEC/CTAB/water) by application of the light scattering technique. The time-dependent correlation functions were probed over a temperature interval where the semidilute system passed from a sol to a gel. The decay of the correlation function is shifted towards longer times with increasing temperature. During the gelation process the relaxation of the cooperative mode is only slightly affected, whereas the long relaxation time exhibits a drastic change. The pronounced slowing down of the motion of individual chains when approaching the gelation threshold is associated with a reptation-like behavior as a mechanism of relieve local constrains. Lindman *et al.* (1995) described the systems of EHEC/SDS and EHEC/CTAB that undergo temperature induced sol-gel transitions. The GP has been found to decrease with increasing EHEC concentration, and this trend is stronger for the EHEC/SDS system. At GP, the gel strength parameter increases considerably with increasing EHEC concentration for both EHEC/ surfactant systems, but the increase is more pronounced for EHEC/CTAB system. This difference in behavior probably reflects that these two surfactants generate a different interaction situation. It was observed that the value of *n* for EHEC/CTAB system exhibits only slightly decrease (0.43-0.38) with increasing polymer concentration, while *n* increases strongly (0.24-0.41) for the EHEC/SDS system.

Glossary

<u>Polymers</u>

EHEC	Ethyl(hydroxy ethyl)cellulose
HPMC	Hydroxy(propyl methyl)cellulose
PEO	Poly(ethylene oxide)
PMMA	Poly(methyl methacrylate)
PPO	Poly(propylene oxide)
PVC	Poly(vinyl chloride)
PVME	Poly(vinyl methylether)

<u>Surfactants</u>

CTAB	Cetyltrimethylammonium bromide
CTAC	Cetyltrimethylammonium chloride
DoTAB	Dodecyltrimethylammonium bromide
DoTA$^+$	Dodecyltrimethylammonium ion
HTAB	Hexadecyltrimethylammonium bromide
HTASal	Hexadecyltrimethylammonium silicate
HTATs	Hexadecyltrimethylammonium tosylate
LDS	Lithium dodecylsulfate
SDS	Sodium dodecylsulfate

1.9 Objectives

The aims of this research are divided into 3 mains topics which are:

(1) To investigate complex formation between HPC and HTAB in terms of polymer concentration and surfactant concentration;

(2) To find the maximum binding conditions for polymer/surfactant complex in terms of C_{HTAB}/C_{HPC} when C_{HTAB} is surfactant concentration and C_{HPC} is polymer concentration;

(3) To investigate the conditions and properties at the sol-gel transition of the HPC/HTAB at the gel point.