CHAPTER I INTRODUCTION

The study of polymer-surfactant interactions is of great interest for many physico-chemical as well as biological phenomena. Polymer-surfactant complexes have found applications in many industrial products, such as paints and coating, laundry detergents, and cosmetic products, and they also play a role in ternary oil recovery. In recent years, studies of polymer-surfactant solutions have been reviewed extensively (Goddard and Anathapadmanabhan, 1993; Winnik, 1996). The foundations of today's activities on mixed polymer/surfactant systems were laid in work carried out in two separate areas. The first, in the 1940s and 1950s, involved protein/synthetic ionic surfactant pairs. The second, in the 1950s and 1960s, involved water-soluble synthetic polymers which were uncharged and surfactants which were charged. It should be pointed out that interest in charge pairs has again developed in the 1970s, 1980s, and early 1990s, but more in system in which the polyelectrolyte is synthetic, including various acid and basic polypeptide.

Past as well as current studies on aqueous polymer-surfactant solutions can be broadly classified into three groups depending upon their objectives. The first concerns with the structure or the topology of the polymer-surfactant complexes in solution. Hardly any direct studies probing the structure of complexes have been carried out in the past, primarily due to the paucity of experimental techniques. Only recently, a number of modern instrumental techniques such as nuclear magnetic resonance (NMR), neutron scattering, fluorescence spectroscopy, and light scattering have been utilized. These techniques have provided interesting preliminary results on the topology of the nonionic polymer-surfactant complexes and on the size of the polymer-bound micelles.

The second group of investigations have focused on a quantitative measurement of the amount of surfactant complexing with the polymer molecules. In addition, the occurrence of critical phenomena in solution properties has been examined. In these studies, classical techniques such as dialysis, surface tension, viscosity, electrical conductivity, dye solubilization, specific ion activity, etc., have been employed. Indeed, they form an overwhelming majority of investigations to date, because of the simplicity of the classical experimental techniques. Results from these studies show that some surfactants do not associate at all with nonionic polymers while others do so significantly. Also, the solution properties exhibit critical behavior at one or two surfactant concentrations in some systems but not in others. While qualitative rationalizations of these results have been presented in these studies, no attempt has been made to quantitatively model the results in term of the molecular features of the surfactant and the polymer.

The third group of investigations relate to the phase behavior of the polymer-surfactant solutions with or without the presence of additional components like electrolytes, oil, etc. The phase properties are of direct interest to applications such as enhanced oil recovery. Very few experimental measurements of phase diagrams exits and no absolutely suitable theory is available even for simpler aqueous polymer solutions. It is evident that systematic studies of polymer-surfactant solutions, both experimental and theoretical, along the three groups outlined above, are only in their infancy.

In this study, we provide strong evidence for the association or nonassociation of nonionic water-soluble polymer hydroxypropylcellulose (HPC) with the micelles of the nonionic surfactant n-octyl β -D-thioglucopyranoside (OTG) and the cationic surfactant cetyltrimethylammonium bromide (CTAB) by using viscosity and dynamic light scattering measurements because the formation of a polymer-surfactant complex usually gives rise to gross conformation changes in the polymer molecule so a measurement of the solution viscosity provides the simplest means for monitoring polymer-surfactant association. Dynamic light scattering is also chosen to elucidate such changes in the polymer-surfactant solution since these measurements provide a non-invasive means of probing conformation changes.

1.1 Background

1.1.1 Surfactant Solutions

1.1.1.1 General Structure Features and Behavior of Surfactants. The word SURFACTANT is a concentration term of SURFace ACTive AgeNT. Surfactants have a characteristic molecular structure consisting of a structural group that has very little attraction for the solvent, known as a *lyophobic group* (solvent-hating), together with a group that has a strong attraction for the solvent called the *lyophilic group* (solvent-loving). This is known as an amphipatic structure.

The existence of groups with opposing characteristics is responsible for all the special properties of surfactants. The behavior of surfactants in aqueous solution is determined by their tendency to seclude their hydrophobic part from solution and expose their hydrophilic part towards the solution. The dual tendency is responsible for adsorption of surfactants at interfaces and for the formation of such aggregates as micelles (Rosen, 1989).

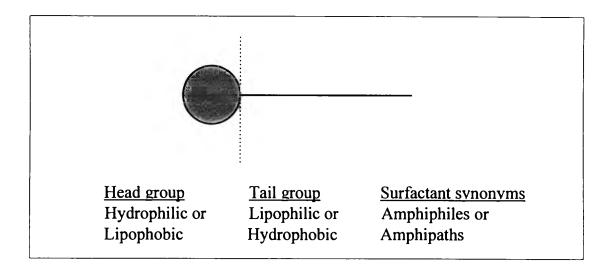


Figure 1.1 Surfactant architecture.

1.1.1.2 Why do surfactants have a CMC? The critical micelle concentration (CMC) is due to two opposing forces of interaction between the surfactant molecules (Porter, 1994):

<u>Force 1:</u> The polar groups in water if ionic will repel one another due to mutual charge repulsion. The larger this charge, the greater is the repulsion and the less tendency to form micelles. The hydrophilic groups may also have a strong affinity for water and there will be a tendency for them to be spaced out to allow as much water as possible to solvate the hydrophilic group.

Force 2: The hydrophobic groups act as if there is a bond attracting them together. 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. A diagram illustrating the two forces is shown in Figure 1.2. When the molecules are very far apart (very low concentration) then both forces above are weak. When the concentration increases, i.e. the surfactant molecules get closer, the two interactions described above will increase. If Force 1 exerted by the hydrophilic group is very much greater than Force 2 exerted by the

hydrophobic group, then the molecules will probably not aggregate; they will remain monodisperse in solution at high concentration. This is the situation when the hydrophobic effect is very small and the molecule will be very soluble.

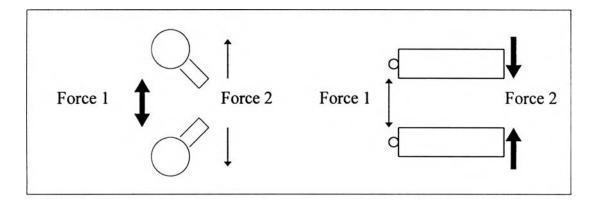


Figure 1.2 Forces between surfactant molecules in solution.

If Force 1 exerted by the hydrophilic group is very much smaller than Force 2 exerted by the hydrophobic group, then the molecules will aggregate together (Force 2 >Force 1) at very low concentrations. This is the situation when the hydrophobic effect is very large; aggregation is easy and the molecule is practically insoluble. There will probably be weak that they will be difficult to detect.

The relative strength of Force 1 and Force 2 determines the CMC. At a particular concentration Force 1 will be equal to Force 2 and the molecules will aggregate. For this to occur the hydrophobic and hydrophilic effects must have a similar order of magnitude. In comparing two surfactants, the one with the larger hydrophilic effect will have a higher CMC than the other.

1.1.1.3 Classes of Surfactants. Surfactants can be classified into three classes (Ananthapadmanabhan, 1993): anionic surfactants; cationic surfactants; and nonionic surfactants. The classification given is based on the chemical structure of the hydrophilic group.

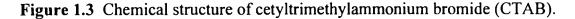
- <u>Anionic</u>-the surface-active part of the molecule carries a negative charge,
 e.g. C₁₂H₂₅CO-O⁻Na⁺, and has a long chain hydrophobic carrying the negative charge.
- <u>Nonionic</u>-the surface-active part of the molecule apparently carries no charge, e.g. C₁₂H₂₅-O-(CH₂CH₂O)7-H.
- <u>Cationic</u>-the surface-active part of the molecule apparently carries a positive charge, e.g. C₁₂H₂₅N(CH3)₃⁺Cl⁻.

The surfactants used in this study are cationic surfactant cetyltrimethylammonium bromide (CTAB) and nonionic surfactant n-octyl β -D-thioglucopyranoside (OTG).

Cetyltrimethylammonium bromide (CTAB)

Cetyltrimetthylammonium bromide or hexadecyltrimethylammonium bromide ($C_{16}N(CH_3)_3Br$) is one type of cationic surfactants. It is a quaternary ammonium salt. The advantages of this type of cationic surfactant is that it is unaffected by pH changes; positive charge remains in acidic, neutral, and alkaline media. The disadvantage is they are more easily removed from surfaces onto which they may be adsorbed since water solubility is retained at all pHs (Rao *et al.*, 1987).

$$CH_{3}(CH_{2})_{15} \xrightarrow[]{(H_{3})}{}^{CH_{3}}_{N} CH_{3}Br^{\Theta}$$



n-Octyl β-D-thioglucopyranoside (OTG)

n-Octyl β -D-thioglucopyranoside is a new nonionic surfactant. It is an excellent detergent for solubilization and reconstitution of membrane proteins. One of the characteristics is its solubility because generally the thioether bond is more stable than the ether bond. On the other hand, it could be stored as solution for at least several months without losing its ability to give reproducible results of solubilization and reconstitution of membrane protein (Saito and Tsuchiya, 1984; Saito and Tsuchiya, 1985).

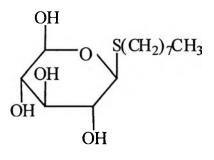


Figure 1.4 Chemical structure of n-octyl β -D-thioglucopyranoside (OTG).

1.1.2 Polymer Solutions

Polymer used in this study is nonionic water-soluble polymer. Polymers exhibiting water solubility are not limited to polyelectrolytes but a diverse class of important structures, both ionic and nonionic, of both synthetic and biological origins. Water plays a key role in determining the properties in 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 thought to play a role. Addition of other solution components, such as salt, cosolvents, or surfactants, or changing the molecular weight of the polymer, can affect the solubility strongly.

Hvdroxypropylcellulose (HPC)

Hydroxyproplycellulose is an interesting polymer with many commercial applications. It is a water-soluble ether of native cellulose (Wirick and Waldman, 1970). It is soluble in a wide variety of solvents, including water from which it precipitates when heated above ca. 40 °C (Werbwyj and Gray, 1980). At high concentrations in several solvents, it forms liquid crystalline phase above 42 % by weight of HPC. In nonpolar solvents, HPC experiences extensive intramolecular hydrogen bonding, whereas in water, hydrogen bonding with solvent molecules predominates. Nevertheless, HPC is a largely hydrophobic polymer. At temperature above 0 °C in water, it has a tendency to form aggregates, and these become sufficiently extensive at elevated temperatures to lead to phase separation. Phase separation has been described in terms of a lower critical temperature (LCST) (Winnik *et al.*, 1987; Guido, 1995).

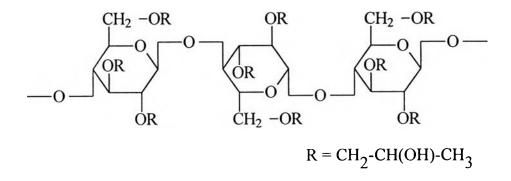


Figure 1.5 Chemical structure of hydroxypropylcelllulose (HPC).

1.1.3 Polymer-Surfactant Solutions

1.1.3.1 Classification of the Polymer-Surfactant Systems. A convenient classification of polymer-surfactant system is offered by the presence or absence of charges on the interactions and the type of charges (Lindman and Thalberg, 1993):

- (a) nonionic polymer-anionic surfactant
- (b) nonionic polymer-cationic surfactant
- (c) nonionic polymer-nonionic surfactant
- (d) anionic polymer-anionic surfactant
- (e) anionic polymer-cationic surfactant
- (f) anionic polymer-nonionic surfactant
- (g) cationic polymer-anionic surfactant
- (h) cationic polymer-cationic surfactant
- (I) cationic polymer-nonionic surfactant

1.1.3.2 Driving force. The main driving force for polymersurfactant interaction is believed to be reduction of the interfacial area between the hydrophobic polymer segments and the solvent water by association of these segments with the exposed hydrophobic parts of aggregation surfactants. Here the hydrophobicity of the polymer chain plays a major role, although steric requirement at the micellar surface and the perturbation of the hydration sheath by the surfactant head groups and counterions may influence the free energy transfer of the polymer from the aqueous to the micellar phase. Since the hydrophobic polymer strands are believed to replace water molecules structured around the micellar head groups, stabilization of the micelle upon binding to a polymer strand results from a reduction of interfacial tension between the hydrophobic core and water. Furthermore, specific interactions such as hydrogen bonding between the polymer and headgroups may also play a role (Reekmans, 1993). 1.1.3.3 Critical Aggregation Concentration (CAC). In a system of fixed polymer concentration with increasing amount of surfactant, no interaction between the polymer and surfactant is detected until a critical aggregation concentration (CAC) is reached. Therefore, the CAC is a surfactant concentration at which interaction between polymer and surfactants takes places and complex starts to form.

It is generally accepted (Lindman and Thalberg, 1993) that an ionic surfactant interacts with the polymer chain as small micellar aggregates, which are first formed at the critical aggregation concentration; the latter is substantially lower than the critical micelle concentration (CMC) of the pure surfactant in solution. The interactions may include electrostatic, hydrophobic, and steric interactions, which together serve to considerably modify the overall coil conformation of the original polymer chain. In general, there is a much stronger affinity between anionic surfactant and nonionic polymer compared to cationic surfactant and nonionic polymer. The interaction between nonionic polymer and nonionic surfactant is also usually very weak.

1.1.3.4 Modeling of Polymer-Surfactant Interaction. Several approaches to model the interactions between a polymer and a surfactant in solution have been put forward during the last decade, and the majority deal with nonionic polymer-ionic surfactant system. Nagarajan (Nagarajan, 1985) and Ruckenstein (Ruckenstein, 1987) developed detailed model in order to explain and quantify the influence of surfactant headgroup structure on interaction with polymer. Both authors stressed the important of the relative contributions of stabilization of the water-hydrophobic core interface by the polymer on one hand and the unfavorable interaction between the surfactant headgroups and the polymer segment on the other. According to Nagarajan (1985), the latter interaction stems from steric repulsion; according to Ruckenstein (1987), the interfacial tension between headgroups and water is unfavorably influenced by polymer association.

The Nagarajan theory

Nagarajan (Nagarajan, 1985) has proposed a simple model which considers that surfactant aggregates are adsorbed into the "free space" of the coil macromolecules. The latter participates in the formation of aggregates via segments that penetrates the interfacial of the micelles. The model equations show that the competition between free micellization and complexation is critically governed by the nature of interactions at the micellar surface. Together they determine whether polymer-bound micelles would form or not. Of course, in all cases, the formation of free micelles would occur if a sufficient amount of surfactant is available. The essential difference between the behavior of ionic surfactant and nonionic surfactant is attributed to the bulky nature of the headgroup of nonionic surfactant and the consequent importance assumed by the steric repulsion at the presence of the polymer. In the case of nonionic surfactant, the decrease in interfacial free energy provided by the polymer segments does not compensate the increase in the steric repulsion at the micellar surface. In contrast, for ionic surfactant, the decrease in free energy is more significant compared to the increase in the steric repulsion, the permitting polymer-surfactant complexation.

The Ruckenstein theory

Ruckenstein (Ruckenstein, 1987) has proposed the model for surfactant aggregation in the presence of the macromolecules that involves the adsorption of micellar aggregate in the "free space" of the coiled macromolecules. It is well-known that the surfactant molecules aggregate in dilute solution if their concentration is greater than the critical micelle

concentration. The hydrophobic bonding, which tends to minimize the contact between the hydrocarbon chains and water constitutes the main driving force for the aggregation. While the headgroups remain exposed to water, the extent of exposure to water of the hydrocarbon chains is reduced to the residual contact between water and the hydrocarbon core of the aggregates. Obviously, the free energy of the formation of the hydrocarbon-water interface constitutes the positive contribution to the free energy of the formation of micelle. The formation of aggregates that are bound to polymer changes the microenvironment of the former. The interfacial tension between the water located in the free space of the macromolecular coil is expected to be lower than that of the water free of polymer. However, while the new more hydrophobic environment has stronger interaction with the hydrocarbon core of the aggregates, it has weaker interactions with the headgroups. If the crosssectional area of the headgroup is large enough, the latter effect can dominate and the resulting free energy of the formation of the aggregate becomes greater than that in the aqueous environment free of polymer. In other word, in such cases only the regions occupied by solvent alone will be preferred for the formation of micelles. In contrast, if the cross-sectional area of the headgroup is small, the first effect dominates and micelles that are bound to the macromolecules will form before those in the regions occupied by the solvent alone form. The nonionic surfactants as well as the cationic surfactants have large headgroups. This explains why their aggregation is not stimulated by the presence of polymer. In contrast, the anionic surfactants have small headgroups. Therefore, the presence of macromolecules can cause in such cases earlier micellization in the form of bound micelles.

1.1.3.5 The Polymer-Surfactant Structure. The interaction between a nonionic polymer and an ionic surfactant could take one or more of the following forms (Holmberg *et.al.* 1992): (a) redistribution of the surfactant between the bulk solution and the coil regions; (b) surfactant molecules cluster around hydrophobic sites on the polymer chain; (c) polymer molecules wrap around surfactant micelles in such a way that the polymer segments partially penetrate and wrap around the polar headgroup regions of the of the micelles.

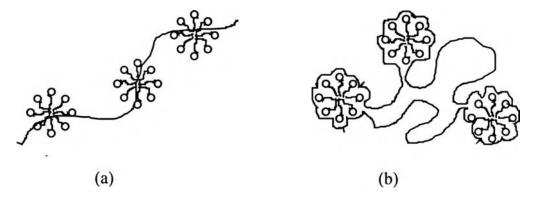


Figure 1.6 Schematic diagram of polymer-surfactant complex (a) site clustering; (b) mixed micelle.

The interaction types (c) and (d) are fairly similar as far as the final effect of the interaction is concerned. However, there are conceptual difference in the initiation step between the two. The "site clustering" (c) implies a strongly cooperative surfactant-polymer interaction, starting well below the normal CMC and occurring over a range of surfactant concentrations. The "mixed micelle" approach (d) implies the formation of a micelle in the normal fashion, albeit at a bulk concentration lower than the CMC of magnitude as that of a normal micelle. The polymer is wrapped around this micelle, with it hydrophobic parts inserted between the surfactant molecules (Cabane, 1977).

Other systems may well involve a combination of models (c) and (d), with (d) as the second step in the interaction process: micelle-like clusters are first formed in hydrophobic sites, and then other hydrophobic sites of the chain attach to these clusters. At higher polymer concentrations, hydrophobic parts of neighboring chains can compete for binding with these clusters. This will lead to the formation of cross-links and, eventually, of three dimensional structures accompanied by a considerable increase in viscosity.

Shirahama *et al.* (Shirahama *et al.*, 1974) proposed an alternative model of the complex according to which micelle-like aggregates formed along the protein or the polymer. This model, called "necklace model", assume a flexible chain which is free draining with respect to the solvent.

The "necklace and bead" structure of the proteinsurfactant complex deduced from SANS results (Gue *et al.*, 1990; Tamer *et al.*, 1982) is similar to the results obtained by Cabane (Cabane, 1977) for the PEO/SDS/water system. This is consistent with Shirahama's observation that the protein-surfactant complexes behaved similarly in their free boundary electrophoresis studies. It is clear that many protein-surfactant and polymersurfactant complexes have similar structure.

1.2 Literature Review

1.2.1 Nonionic Polymer and Cationic Surfactant

The interaction between nonionic water-soluble polymer and cationic surfactants has been observed to be nonexistent or very weak, contrary to the case of anionic surfactants where many investigations have shown clear evidence of interaction (Hayakana and Kwak, 1991). This behavior has been explained as due to (a) the bulkiness of the cationic headgroup (Nagarajan, 1985), (b) the electrostatic repulsion between polymer and surfactant due to the possible positive charge of polymer upon protonation (Moroi *et al.*, 1982) and possible difference in interaction of anions and cations with the hydration shell of the polymer which favors interaction with anionic surfactant (Witte and Engberts, 1989).

Winnik *et al.* (Winnik *et al.*, 1987) showed complex formation between hydroxypropylcellulose (HPC) and hexadecyltrimethyammonium chloride (HTAC) micelles, using fluorescence probe and fluorescence label experiments.

The interaction between ethyl (hydroxyethyl) cellulose (EHEC) and two cationic surfactants, hexadecyltrimethylamonium chloride and bromide (CTAC and CTAB), have been investigated in aqueous solution as a function of temperature, by means of electrical conductivity and chloride ion self-diffusion measurement for CTAC and by time-resolved fluorescence quenching for CTAC and CTAB. The results indicate that, in the presence of EHEC, the critical micelle concentration (CMC) decreases, the micelle ionization degree increases, and the micelle aggregation number N decreases upon increasing temperature. All these results are in line with the proposed increase of the strength of the EHEC-cationic surfactant interaction with temperature (Zana *et al.*, 1992).

Reekmans *et al.* (Reekman *et al.*, 1993) showed complex formation between nonionic polymer PPO and cetyltrimethylammonium surfactant molecules (CTAX, $X^- = Cl^-$, ClO₃⁻, NO₃⁻) which were investigated by means of photophysical techniques. The presence of polymer gives rise to a CAC lower than CMC, a higher micellar ionization degree, and a smaller N for the bound micelle in the presence of PPO. They also suggested that polymer chains wrap around several micelles and disturb only the Stern layer of the micelles by means of its penetrating segments, which renders the polymerbound micelle more hydrophobic and a better solubilizing agent, even though the surfactant aggregate is smaller. The viscosity results also indicated expansion of the polymer coil due to CTAX micelle binding to poly (vinylalcohol)-poly (vinyl acetate). Brackman and Engberts (Brackman and Thalberg, 1991) studied the influence of polymers on the micellization of cetryltrimethylammonium salts. The critical micelle concentration values and aggregation numbers of the cetyltrimethylammonium bromide (CTAB) micelles were measured in the presence and absence of the polymers poly (vinyl methyl ether) (PVME), and poly (vinyl pyrrolidone) (PVP). Association of the micelles with the polymers PVME and PPO is apparent from a reduction in both the CMC and the aggregation number, PEO and PVP do not influence these properties. From their viscosity measurements in the presence of PVME, rodlike micelles of hexadecyltrimethylammonium salicylate (HTASal) and tosylate (HTATS) change to spherical polymer-bound micelle.

1.2.2 Nonionic Polymer and Nonionic Surfactant

The interaction between nonionic polymer and nonionic surfactants is usually very weak. However, since the driving force for polymermicelle interaction is the reduction in Gibbs free evergy of the total system, interaction between nonionic polymer and nonionic surfactant could occur if a sufficiently hydrophobic polymer is used.

According to the review of Saito (Saito, 1987), typically hydrophilic nonionic polymer such as PVA, PEO, and PYP show no sign of interaction with polyoxyethylated nonionic surfactants by the dye solubilization, viscosity, and surface tension methods. No binding between PVP and Triton X-100 ((EO)9 octylphenyl ether) was found by the ultraviolet absorption method at the CMC. By calorimetric measurement PVP did not display binding of alkyldimethylphosphine oxide, a nonionic surfactant. By gel permeation chromatography it was found that PEO and PEO nonylphenyl ether have a weak interaction. However, mildly hydrophobic nonionic polymer such as polypropylene oxide (PPO) and partially hydrolyzed polyvinylacetate (PVA-Ac), which has large hydrophobic patches, have interaction with nonionic surfactants. This was easily demonstrated, for example, by the rise of cloud points of these hydrophobic polymers affected by addition of nonionic surfactants. As the nonionic surfactant solutions alone developed no clouding in the temperature range studied, the rise of cloud point, a hydrophilization of the PVA-Ac or PPO, was clearly attributed to the binding of nonionic surfactant to these polymers.

Brackman *et al.* (Brackman *et al.*, 1988) reported that the formation of complexes between a neutral water-soluble polymer, poly (propylene oxide) (PPO, MW 1000) and a neutral surfactant n-octyl β -D-thioglucopyranoside (OTG). An important feature of this work is that it was the first account of the unambiguous detection of complexes between nonionic polymers and nonionic surfactants. Until now it was generally believed that nonionic surfactants are indifferent toward nonionic polymers. They detected polymer-surfactant complexes by microcalorimetry and turbidity measurements and they also reported that the surfactant has the same critical micelle concentration (CMC) in the presence of PPO as it does in water. This is in contrast to the situation encountered with all ionic surfactants, for which association with neutral polymer is always accompanied by a decrease in CMC. Although the CMC was identical with and without polymer, the results gave clear evidence for an endothermic interaction between the components.

Winnik (Winnik, 1990) studied the interaction between pyrenelabeled hydroxypropylcellulose and OTG using fluorescence measurements. From measurements of the ratio of the pyrene monomer emission to the pyrene excimer emission intensity and its changes with surfactant concentration, the author reported the first unambiguous detection of complex formation between the nonionic polymer and the nonionic surfactants. The solution properties of polymeric component may still be strongly changed in the presence of the surfactant since polymer-polymer interactions are disrupted and the conformation of the polymer is modified.

Feitosa et al. (Feitisa et al., 1996) studied the interaction between the nonionic surfactant $C_{12}E_5$ and poly (ethylene oxide) by using dynamic light scattering and fluorescence quenching. Dynamic light scattering measurements showed that an addition of a low concentration of the nonionic surfactant C₁₂E₅ to binary solution of high molecular weight PEO inhibits formation of PEO clusters, which are the well-known feature of aqueous solutions of this polymer, by incorporating hydrophobic residue into the micellar core. Above minimum concentration of C12E5 and PEO, depending on the temperature, the correlation functions are bimodal. The fast components is consistent with the size of the free micelles of surfactant and the slow formation of a complex made up of cluster of $C_{12}E_5$ micelles stabilized within PEO coil. Since the micelles are close to their overlap point, the formation of the latter is promoted by the exclude volume effect of the high molar mass PEO. Rh for the C12E5/PEO complex increases strongly with surfactant concentration from an initial value corresponding to the energy aggregation number of C12E5 increases significantly on addition of the high molar mass PEO.

Alami *et al.* (Alami *et al.*, 1996) studied the interaction of hydrophobically end-capped poly (ethylene oxide) with nonionic surfactants in aqueous solution by using fluorescence and light scattering measurements. They found that in the ternary mixture of an associative polymer (AP), hydrophobically end-capped poly (ethylene oxide), $C_{12}EO_{460}C_{12}$, and the nonionic surfactant, $C_{12}E_6$, hydrophobic microdomain are formed at much lower concentrations than the CAC and CMC of the binary system.

Also for the uncharged semipolar surfactant n-dodecyldimethyl amine oxide, Brackman and Engberts (Brackman and Engberts, 1992) reported

binding to poly (propylene oxide) (PPO) in particular inferred from a marked increase in cloud point. The isomeric polymer poly (vinyl methyl ether) (PVME), on the other hand, showed no significant change in cloud point when mixed with this surfactant. Both polymers, however, induce a slight decrease in the aggregation number of the micelles. Again, the CMC of the surfactant was unaltered by the presence of the polymers.

1.3 Objectives

In this study, the interactions of nonionic water-soluble polymer hydroxypropylcellulose (HPC) with cationic surfactant cetyltrimethylammonium bromide (CTAB) and nonionic surfactant n-octyl β -D-thioglucopyranoside (OTG) will be studied. The complex binding between nonionic watersoluble polymer and these two different types of surfactants are not wellexplored or understood when comparing to the anionic surfactant. Since the dynamic light scattering measurement provides a non-invasive means of probing conformation change we choose to apply dynamic light scattering to elucidate such changes in the interaction. Furthermore, we also choose viscosity measurement in this study.

The aims of this research are:

1. To elucidate the effect of the surfactant concentration, the polymer concentration, and the concentration ratio of the surfactant to the polymer on the HPC/OTG/water system and the HPC/CTAB/water system.

2. To compare the interaction of the HPC/OTG/water system with the interaction of the HPC/CTAB/water system.

3. To study the effect of ionic strength on the HPC/CTAB/water system.