CHAPTER I

INTRODUCTION

The interactions between various types of polymer and different kinds of surfactant have gained attention over a decade because of both fundamental and technological interest. From a fundamental point of view, most studies have focused on the structure of the polymer-surfactant complexes and how the properties of a surfactant solution change upon the addition of polymer. From a practical point of view, the properties of the polymer-surfactant complex are crucial to their optimal use in formulations for paints and coatings, cosmetic products, food, laundry detergents, and pharmaceutical products (Goddard and Ananthapadmannabhan, 1993; Herb and Prud'homme, 1994). Polymer-surfactant interaction also plays an important role in enhanced oil recovery technology. Many of these products are based on dispersion systems which require the simultaneous presence of polymers and surfactants, in which the surfactants provide emulsification capacity, interfacial tension control, and colloidal stability (Chattopadhyay and Mittal, 1996).

1.1 Types of Polymer-Surfactant Complexes

Several different combinations of polymer-surfactant systems are possible:

1) Uncharged polymer with anionic surfactant
2) Uncharged polymer with cationic surfactant
3) Uncharged polymer with nonionic surfactant
4) Polyelectrolyte with oppositely charged surfactant

The binding efficiency and the driving force for polymer-surfactant interaction differ substantially between these different systems.

1.1.1 Uncharged Polymer with Anionic Surfactant

The majority of studies of polymer-surfactant systems deal with the interactions between nonionic polymers and anionic surfactants (Cabane, 1977;

Brown, 1992; Chari, *et al.* 1994; etc.) (for more detailed discussion, see Chapter II). These studies indicate that anionic surfactants exhibit significantly stronger interactions than cationic surfactants having the same hydrophobic surfactant chain lengths. For example, surfactant binding to polyethylene oxide studies indicate (Whitte and Engberts, 1987) that the interaction mechanism probably involves a partially positive charge transfer to the ether oxygen group, and consequently an increased attraction of the hydrophilic group of the anionic surfactant. The size of the surfactant headgroup may also influence the interaction between polymer and surfactant.

1.1.2 Uncharged Polymer with Cationic Surfactant

Various studies (Whitte and Engberts, 1988; Nystrom and Lindman, 1995; Brackman and Engberts, 1992) convincingly demonstrate that nonionic polymers interact weakly with cationic surfactants. This is interpreted as due to the bulkiness of the cationic headgroup (Ruckenstein *et al.*, 1987), to a more favorable interaction between anionic surfactants and the hydration shell of the polymers (Whitte and Engberts, 1987), or to an electrostatic repulsion between the polymer and the surfactant due to protonation of the polymer (Moroi *et al.*, 1977). However, Carlsson *et al.* (1989) reported that for more hydrophobic polymers, a greater binding of cationic surfactant to polymer occurs.

1.1.3 Uncharged Polymer with Nonionic Surfactant

The interaction between an uncharged polymer and an uncharged surfactant is generally considered to be very weak, e.g. various polymers show no interaction with polyethoxylated nonionic surfactants (Saito, 1987). However, recent studies (Winnik, 1990; Zhang *et al.*, 1994; Feitosa *et al.*, 1996; Mya *et al.*, 1999) suggest that there can be a significant interaction in water-soluble neutral polymer and nonionic surfactant systems.

1.1.4 Polyelectrolyte with Oppositely Charged Surfactant

The association between oppositely charged polyelectrolytes and surfactants is strong due to the dominant electrostatic forces, leading to irreversible phase separation above the point at which the polyelectrolyte is saturated with surfactant. The reason for the cooperative binding is the electrostatic stabilization of the micelles, which depends on the charge density, chain flexibility, and hydrophobic character of the polyelectrolyte chain (Goddard and Ananthapadmannabhan, 1993). Supramacromolecular complexes are formed through association of the alkyl groups of surfactant ions bound to different polymer molecules. Such a structure has pronounced shear-thinning characteristics, thus providing opportunities for rheology control. Recently, light scattering studies (Fundin *et al.*, 1996; and Ruela *et al.*, 2000) have demonstrated that there is a large mass excess of polyions associated with each surfactant micelle, even in the limit that the weight ratio of the micelle to polyion is very low, as a result of a combination of electrostatic and hydrophobic interactions.

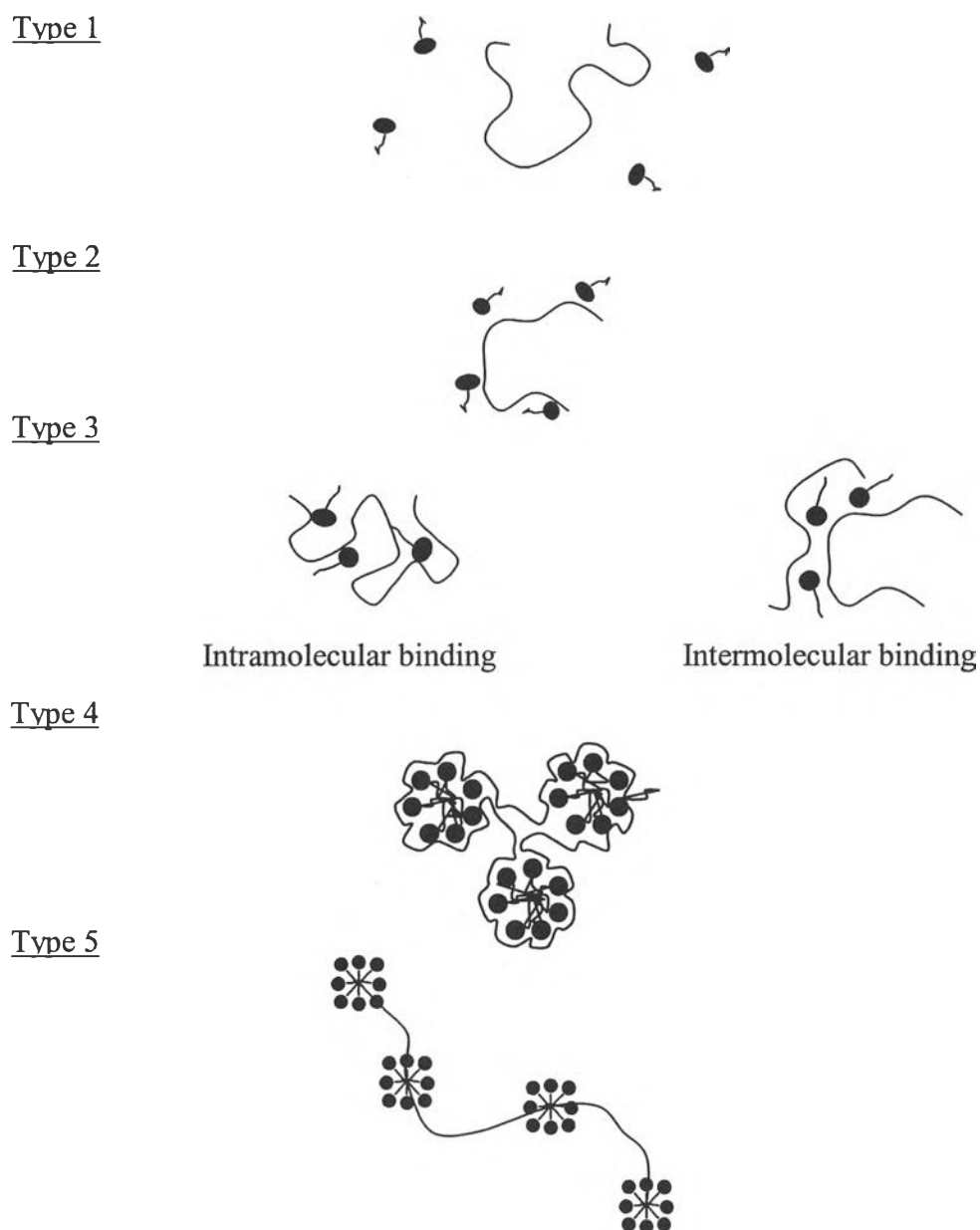## 1.2 Structures of Polymer-Surfactant Complex

Various structures of polymer-surfactant complexes have been proposed, depending on the nature of the interaction forces operative among the solvent, the surfactant and the polymer and also based on their stereo-chemical features. Schematic representations of different types of polymer-surfactant complexes are shown in Figure 1.1.

Type 1

No surfactant is bound to the polymer and the latter remains as free polymer in solution. This type is observed below the critical aggregation concentration (cac), i.e. the concentration at which polymer-surfactant aggregation starts to occur. In this concentration range, there is no binding between polymer and surfactant.

Type 2

Single surfactant molecules are bound linearly along the length of the polymer molecules.

Type 1

Type 2

Type 3

Intramolecular binding   Intermolecular binding

Type 4

Type 5

Figure 1.1 Schematic representations of structures of polymer-surfactant complexes (Nagarajan and Kalpakci, 1985; and Cabane, 1977).

Type 3

An individual surfactant molecule binds at more than one binding sites of a single polymer molecule, giving rise to intramolecular binding. Alternatively, a single surfactant molecule binds to more than one polymer molecules giving rise to intermolecular binding.

Type 4 (Mixed-Micelle Model)

The polymer segments partially penetrate and wrap around the polar head group region of the surfactant micelles. This type of structure is visualized as the polymer molecule wrapping around spherical surfactant micelles with the polymer segments partially penetrating the polar head group region of the micelles. The mixed-micelle model is proposed for interactions between nonionic hydrophilic polymers and cationic surfactants, and between nonionic polymers and nonionic surfactants. Cabane (1977) proposed the interaction between poly(ethylene oxide)(PEO) and sodium dodecyl sulfate (SDS) occurs via the mixed-micelle model in which the polymer is sited close to the surface of the SDS aggregates and the chain segments mainly interact in the surfactant head group region.

Type 5 (Pearl-Necklace or Site-Clustering Model)

The structure can be described as a series of spherical micelles binding along the polymer chain. The surfactant micelles bind cooperatively between the polymer segment and their hydrophobic tail groups. The pearl-necklace model was originally proposed for complexes formed between nonionic hydrophobic polymers and anionic surfactants, and between polyelectrolytes and oppositely charged surfactants. However, Shirahama et al. (1974) found that the interaction between hydroxypropyl cellulose (HPC) and cationic surfactant; hexadecyltrimethylammonium bromide (HTAB) can be represented by the site-clustering model. This is because the stiff backbone of HPC may obstruct loop formation around the micellar head groups, and the highly hydrophobic character of HPC, which leads to a strongly cooperative polymer-surfactant interaction.

1.3 General Aspects of Interactions

Polymers and surfactants are often used together in industrial formulations to take advantage of their uniquely different characteristics. When present together they can interact to provide beneficial properties. The mechanisms responsible 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

oppositely charged polymer and surfactant, hydrophobic interaction, dispersion forces, hydrogen bonding, hydration of the polymers and head groups, steric repulsion, and electrostatic interaction between surfactant headgroups (Winnik and Regismond, 1996).

1.3.1 Binding Isotherms

Quantitative characterization of surfactant binding to polymer can be determined through dialysis equilibrium or electrical conductivity, which monitor the amount of polymer-bound surfactant as a function of the total surfactant concentration, to generate a so-called binding isotherm. A typical binding isotherm is shown in Figure 1.2. The isotherm typically has a marked sigmoidal shape, which is an indication of cooperative binding, and the onset of surfactant binding often occurs at a certain surfactant concentration, which is denoted as the critical aggregation concentration (cac). This notation indicates that the surfactant molecules form aggregates upon interaction with the polymer, as suggested by Chu and Thomas (1986). In general, a steep binding isotherm is expected when a strongly cooperative binding occurs between polymer and surfactant. The transition point, which corresponds to the surfactant concentration where binding begins to occur, is dependent on the alkyl chain length of the surfactant. An asymptotic value of the binding isotherm at higher surfactant concentration is due to the saturation of the polymer with surfactant, which indicates the maximum amount of surfactant that can bind to polymer.
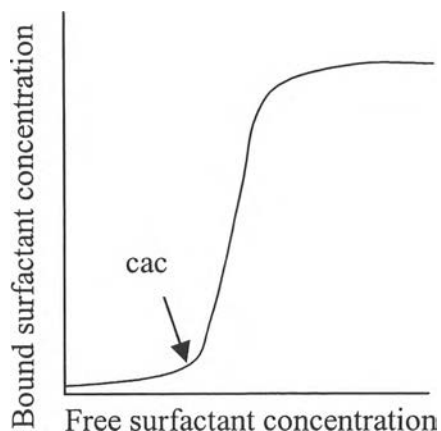
Figure 1.2 A typical isotherm for the binding of a surfactant to a polymer.

For many systems, however, this asymptote is not reached due to phase separation or obscured by the formation of free micelles. The transition point can shift to lower surfactant concentration as the molecular weight of the polymer increases. This effect broadens the binding isotherm for polydisperse polymers.

1.3.2 Strength of Interaction

The degree to which the cac is lower than the cmc of the surfactant alone depends on the strength of the polymer-surfactant interaction; both local and long-range interactions may cause a major lowering of the cac. The free energy of micellization can be written as,

$$\Delta G_m = RT \ln \text{cmc}, \quad \text{(nonionic)} \quad (1.1)$$

$$\Delta G_m = (2 - \alpha) RT \ln \text{cmc}, \quad \text{(ionic)} \quad (1.2)$$

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. α is the fraction of charges on the micelles neutralized by the counterions. When fully ionized, $\alpha = 1$, in this case the free energy of surfactant micellization for the nonionic and ionic surfactant systems will be the same.

$$\Delta G_m = RT \ln \text{cmc}, \quad \text{(fully ionized ionic)} \quad (1.3)$$

The free energy of surfactant binding to a polymer may be similarly expressed as,

$$\Delta G_b = RT \ln \text{cac}, \quad (1.4)$$

where ΔG_b is the free energy of polymer-bound micelle and cac is the critical aggregation concentration and therefore, the free energy per mole surfactant for the reaction can be derived as,

$$\Delta G_{PS} = RT \ln (\text{cac/cmc}). \qquad\qquad (1.5)$$

This quantity is measure of the strength of the interaction between the surfactant and the polymer. It has been pointed out that it appears to be impossible to have a cac which is higher than the cmc of the surfactant (Lindman and Thalberg, 1993). If the surfactant molecules prefer to form free micelles instead of polymer-bound micelles, surfactant binding to the polymer will not occur. The interaction strength varies between the different types of polymer-surfactant systems. In particular, the strength of interaction between neutral polymer with nonionic surfactant system is very weak, and thus the value of cac will be approximately the same as the cmc value; however, the interaction between a polyelectrolyte and an oppositely charged surfactant is thermodynamically favored, and therefore a decrease of the cac relative to the cmc by several orders of magnitude is observed. Table 1.1 shows the cmc and cac values for some surfactants and polymer-surfactant systems.

1.4 Technical Applications of Polymer-Surfactant Complexes

Polymer-surfactant complexes have many applications in the pharmaceutical, cosmetics, detergents, food and various chemical treatment industries, including viscosity enhancement, rheology control, separation and purification.

1.4.1 Rheology Control

When a neutral polymer binds to an ionic surfactant, the polymer will acquire a charge and hence, on the basis of the polyelectrolyte effect, the viscosity will be increased. Supramacromolecular complexes are formed through the association of the alkyl groups of surfactant bound to different polymer molecules. Such a structure has a pronounced shear-thinning behavior, thus providing a rheology control.

Table 1.1 The cmc values for surfactant micelles in water and the corresponding cac values in the presence of polymer

Surfactant/ polymer-surfactant	cmc (mM)	cac (mM)	Methods	References
SDS	8		Equilibrium dialysis	Shirahama et al., (1974)
PEO-SDS		5	Binding isotherm Surface tension	Fishman & Eirich (1971)
PEG-SDS		3.8	Conductivity	Schwuger (1973)
HTAB	0.95		Surface tension	Brackman & Engberts (1991)
HTAB	0.85		Conductivity	Hormnirun et al., (2000)
HPC-HTAB		0.85	Pyrene-labelled fluoresence	Hormnirun et al., (2000)
HTAC	1.3		Conductivity	Winnik et al., (1987)
HTAC	1.02		Conductivity	Zana et al., (1992)
EHEC-HTAC		0.5		Zana et al., (1992)

1.4.2 Pharmaceutical Applications

In pharmaceutical systems, the combination of neutral polymer and various ionic surfactants is used as a medium for drug release. The presence of surfactant in polymer prolongs the release time of drug from a tablet. The mechanism of prolongation is attributed to an increase in viscosity of a gel layer, which forms on the surface of the tablet when it contacts with an aqueous medium. In the presence of polymer, the aggregation of surfactant can occur at concentrations lower than the critical micelle concentration (cmc). This means that the maximum concentration of surfactant is reduced. An irritation to skin is caused by exposure to surfactant and therefore the lower concentration of surfactant can reduce irritation.

1.4.3 Cosmetic Formulation

As noted above, an irritation to skin is generally caused by surfactants, in particular anionic surfactants. Rhien *et al.*, (1986) suggest that a lower surfactant concentration is required to reduce skin irritation. The cmc value for the aggregation of surfactant molecules is lower in the presence of polymer, which means that the required surfactant concentrations in certain cosmetic products can be reduced by an addition of polymer and hence cause a lesser skin irritation (Ward and Sperandia, 1964).

1.4.4 Solubilization

It is well known that polymer can increase the solubility of the surfactant since the monomer concentration required for aggregation of the surfactant is lowered in the presence of polymer. Likewise, surfactant can increase the solubility of a polymer. For example, polyvinyl acetate of very low solubility could be solubilized in the presence of sodium dodecyl sulphate (Isemura and Imanishi, 1958). Polyelectrolytes can precipitate with oppositely charged surfactants at certain ratios. Such precipitates can be solubilized in the presence of excess surfactant, allowing the preparation of commercial formulations.

1.4.5 Detergency

1.4.5.1 Increasing Soil Removal:

During laundering, surfactants loosen oily and particulate soils from the fabric surface. Polymers aid this process by absorbing the loosened soil, dispersing it into the wash bath, and thus increase soil removal (Lange, 1994).

1.4.5.2 Dye Transfer Inhibition

Dyes released from dark fabric can interact with light or white fabrics during washing. Polymers such as poly(vinylpyrrolidone) or poly (vinylimidazole) can form strong complexes with dyes in aqueous solution, and prevent them from transferring to fabrics during washing (Lange, 1994). The complexes are formed through H- bonding, even though hydrophobic attraction and vander Waals forces may occur.

1.4.5.3 Preventing Particulate Soil Redeposition

During laundering, soil is removed from fabrics and remains in the wash bath. Charged polymer (e.g. polyacrylic acid) can adsorb onto the particulate soil surface, increasing its overall negative charge and reducing the tendency of the soil to redeposit on the cleaned fabric surface (Lange, 1994).

1.5 Rheology

Rheology is a study of the deformation and flow of materials. Polymeric materials exhibit both elastic and viscous characteristics, i.e., they possess viscoelastic behavior.

1.5.1 Viscoelastic Properties of Polymeric Materials

The viscoelasticity of polymer is related to molecular structure, the rate of the configurational rearrangements, and the disposition and interaction of the polymer molecules in both their short-range and long-range interrelations (Ferry, 1970). Rearrangements on a local scale (kinks) are relatively rapid, while those on a long-range scale (convolutions) are very slow. The long-range and short-range contour relationships in a flexible polymer molecule are represented in Figure 1.3.

Monomer unit
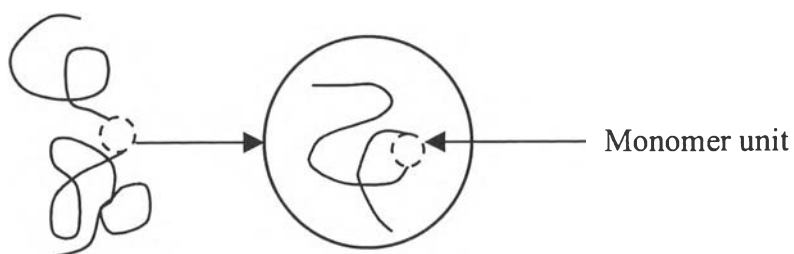
Figure 1.3 Symbolic representation of long-range and short-range contour relationships in a flexible polymer molecules.

Under stress, a new conformation of the polymer chain is obtained; the response to the local aspects of the new distribution is rapid while the long-range aspects is slow and therefore there is a continuous range of time scale covering the

response of such a system to external stress. Generally, the viscoelastic properties of a polymer can be described in terms of the moduli, which are the storage and loss moduli as a function of time or frequency. The storage modulus (G') is defined as the stress in phase with the strain in a sinusoidal shear deformation divided by the strain; it is a measure of the energy stored and recovered per cycle of sinusoidal deformation. The loss modulus (G") is the stress 90° out of phase with the strain divided by the strain; it is a measure of the energy dissipated as heat per cycle of sinusoidal deformation.

Investigation of viscoelastic properties of polymers has been greatly stimulated by the practical importance of mechanical behavior in the processing and utilization of rubbers, plastics, and fibers. As a result, a very high proportion of all studies on viscoelasticity have been devoted to the viscoelasticity of polymers.

1.5.2 Viscoelastic Properties of Surfactant Solutions

Surfactant amphiphiles self-assemble into aggregates such as spherical micelles, worm-like micelles, vesicles, and bilayers (Larson, 1999). At high enough concentrations, such aggregates can form ordered structures like nematic, hexagonal, smectic, or cubic forms. The surfactant solutions containing spherical micelles do not show viscoelastic behavior. However, the entangled solutions of worm-like micelles show pronounced viscoelastic effect.

The behavior of entangled worm-like micelles is similar to that of entangled flexible polymers, suggesting that relaxation theories for entangled polymers might be applicable to solutions of wormy micelles. However, long wormy micelles can break and recombine continuously (Larson, 1999). At equilibrium, the typical time for breakage of a micelle must equal the time for reconnection. The former process predominates at low ionic strength because the electrostatic repulsions prevent the micelles from interconnecting with each other, whereas at high ionic strength, the micelles intersect more easily. Cates (1990) proposed a model based on the reptation theory of polymer and including the process of micellar breakage. In the linear regime the result depends on the relative values of τ_{rep}, the reptation time for average micellar length L, and τ_{break}, the average time of micelles

to break into two shorter worm-like micelles. When τ_{break} is large compared to τ_{rep} ($\tau_{break} \gg \tau_{rep}$), the stress relaxation function is strongly non-exponential. In this case, the reptation theory of polydisperse polymers should apply. On the other hand, if $\tau_{rep} \gg \tau_{break}$, Cates theory predicts a pure exponential form of the stress relaxation time τ_R which is given by,

$$\tau_R = \left(\tau_{break} \cdot \tau_{rep}\right)^{1/2} \qquad (1.6)$$

and the zero shear viscosity (η_0) is:

$$\eta_0 = G_0\,\tau_R \qquad (1.7)$$

where G_0 is the plateau shear modulus. The moduli are close to that predicted by a single-relaxation time Maxwell model, for which,

$$G' = \frac{G_0\omega^2\tau^2}{1+\omega^2\tau^2}, \qquad (1.8)$$

and

$$G'' = \frac{G_0\omega\tau}{1+\omega^2\tau^2}. \qquad (1.9)$$

In some systems (Shikata *et al.*, 1988; and Rehage and Hoffmann, 1988), the stress relaxation function changes from a non-exponential form to a pure exponential decaying function by increase of the ionic strength of the solution. The departure from purely exponential relaxation can be presented in the form of a Cole-Cole plot, in which the imaginary part of the complex modulus (the loss modulus G") is plotted against the real part (the storage modulus G'). If the stress relaxation function is single-exponential, a Cole-Cole plot is observed as a semicircle passing through $\mu''(\omega)$ [$G''(\omega)/G_0(\omega)$] = 0 and $\mu'(\omega)$ [$G'(\omega)/G_0(\omega)$] = 1 as shown in Figure 1.4. However, when the reptation time (τ_{rep}) is compared to the breaking time (τ_{br}), a

semicircular Cole-Cole plot fits the data only in the low frequency regime and the plot deviates from semicircular shape at high frequencies.
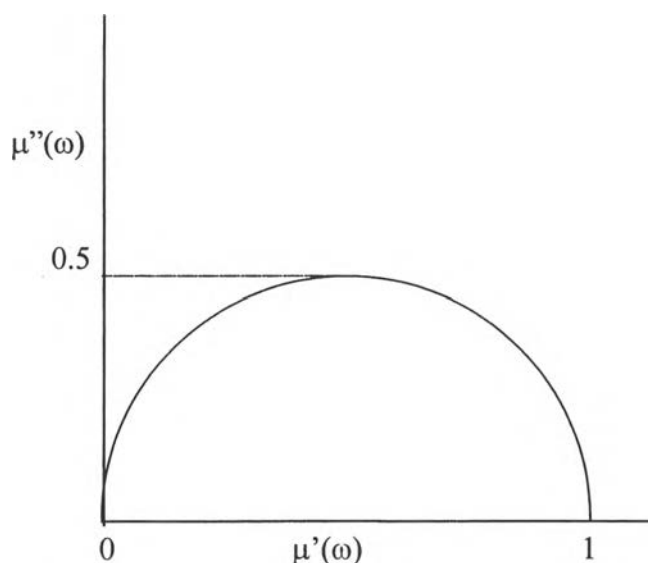
**Figure 1.4** Schematic representation of a Cole-Cole plot.

1.6 Polymers

1.6.1 Poly(Ethylene Oxide) (PEO)

Poly(ethylene oxide) (PEO) is a semi-crystalline, thermoplastic, nonionic water soluble polymer with the general formula $(-CH_2CH_2O-)_n$. In PEO, the hydrophobic and hydrophilic character is provided by the alternating ethylene units (hydrophobic) and ether oxygens (hydrophilic) in the polymer chain. PEO is miscible in water at room temperature in all proportions, and also can readily dissolve in common organic solvents (Kroschwitz, 1990). Phase separation occurs close to the boiling point of water but the precipitation temperature (cloud point) depends on molecular weight and concentration. The structure of PEO in water is interpreted in terms of an association between ether oxygen and water molecules. Increasing the temperature can cause a disruption of hydrogen bonding and allows polymer-polymer interaction.

1.6.2 Hydroxypropyl Cellulose (HPC)

Hydroxypropylcellulose (HPC) has many technical applications. It is a nonionic water-soluble biopolymer with large hydrophobic groups. It is soluble in many solvents even at room temperature. It can precipitate when an aqueous solution of HPC is heated above $40^{\circ}C$. In nonpolar solvents, HPC tends to form intramolecular hydrogen bonding but in polar solvent (water), hydrogen bonding with solvent predominates. The general structure of HPC is shown in Figure 1.5.


$R = CH_2\text{-}CH(OH)\text{-}CH_3$
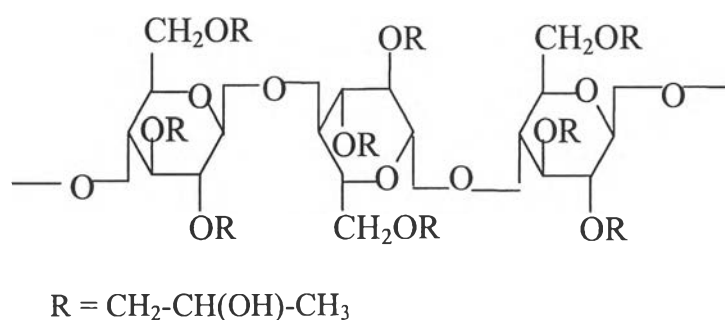
Figure 1.5 Chemical structure of hydroxypropylcellulose (HPC).

1.7 Surfactant Solutions
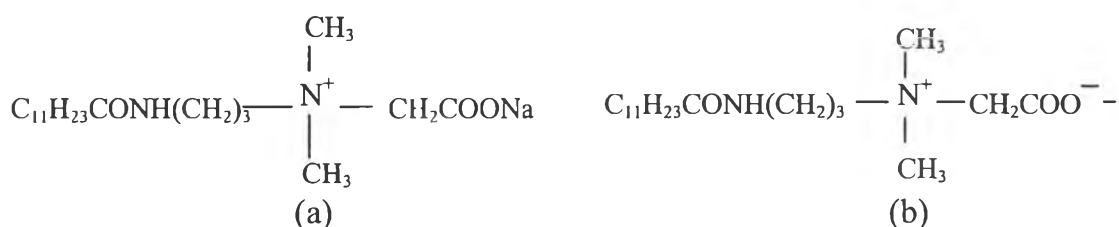
1.7.1 Hexadecyltrimethylammonium Chloride (HTAC)

Hexadecyltrimethylammonium chloride (HTAC) is a cationic surfactant, which has a positively charged quaternary ammonium compound group. These compounds are odorless and have no deleterious adverse effect on a variety of synthetic materials, including plastics, rubber, ceramic and stainless steel (Cross and Singer, 1994). This type of cationic surfactant is used in laundry applications as fabric softeners and antistatic agents. It is also used as an antiseptic for injuries to the skin and as preservatives in skin product formulations. These quaternary ammonium surfactants retain their cationic character at any pH. The chemical structure of HTAC is shown in Figure 1.6.

$$C_{16}H_{33} \quad CH_3$$
$$\diagdown \quad \diagup$$
$$N^+ \quad Cl^-$$
$$\diagup \quad \diagdown$$
$$CH_3 \quad CH_3$$
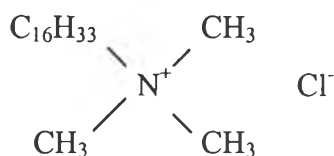
Figure 1.6 Chemical structure of hexadecyltrimethylammonium chloride (HTAC).

1.7.2 Cocamidopropyl Dimethyl Glycine (CADG)

Cocamidopropyl dimethyl glycine (CADG) or cocamidopropyl betaine is an amphoteric surfactant. The advantage of CADG is that it is stable when exposed in air. The structure of CADG is shown in Figure 1.7.

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

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

Figure 1.7 Chemical structure of cocamidopropyl dimethyl glycine (CADG): (a) in solid form, (b) in aqueous solution.

1.8 Objectives

The tasks of this research work are as follows.

1) To identify the interaction between nonionic polymer and cationic surfactant by determining several physical parameters, such as changes in viscosity and light scattering characteristics, and to explore the effect of surfactant (HTAC) concentration, polymer (PEO) concentration, the mass concentration ratio of surfactant to polymer (c_{HTAC}/c_{PEO}), temperature, polymer molecular weight, and the effect of salt.

2) To investigate the structure of the polymer-surfactant complex in aqueous solution by determining the molecular weight of PEO-HTAC complex, the number of HTAC molecules in the complex, and the number of PEO chains in the complex.

3) To study the effect of ionic strength on the structure of PEO-HTAC complex, by comparing the molecular weight of PEO-HTAC complex in salt solution at the maximum binding point.

4) To determine the rheological properties of pure surfactant (HTAC) and PEO-HTAC complex in the presence and absence of salt.

5) To our knowledge, there is no report on interaction between polymer and amphoteric surfactant, which behaves as a nonionic surfactant at a certain pH. Therefore, it is difficult to bind with neutral polymer and amphoteric surfactant, especially with nonionic hydrophilic polymer, e.g. PEO. In this work, we try to investigate the interaction between a water-soluble nonionic hydrophobic polymer, hydroxypropyl cellulose (HPC), and the amphoteric surfactant, cocamidopropyl dimethyl glycine (CADG) through light scattering and viscometric measurements.