

CHAPTER I

INTRODUCTION

Polymers and surfactants are often used together in industrial formulations to take advantage of their characteristically different properties. When present together they can interact to provide beneficial properties. Polymer-surfactant combinations in aqueous solutions which interact with each other can be broadly classified into three categories; namely uncharged polymer-ionic surfactant, oppositely charged polymer-surfactant and uncharged polymer-nonionic surfactant systems [Ananthapadmanabhan and Goddard, 1993]. Many studies deal with aqueous nonionic polymer and ionic surfactant systems or polyelectrolytes interacting with an oppositely charged surfactants. Adding a surfactant to a polymer solution and the formation of a polymer-surfactant complex can alter the physical properties of the starting polymer solution; for example, by imparting polyelectrolyte characteristics to a neutral polymer such as poly (ethylene oxide) (PEO), by addition of sodium dodecyl sulfate (SDS) [Brown et al., 1992].

In recent years a large number of studies have focused on hydrophobically-modified polymers (also termed amphiphilic polymers). These polymers usually consist of a water-soluble main chain (neutral or charged) to which is attached a small number of hydrophobic substituents. They are similar to micelle-like structures, where hydrophobic units form interior domains protected from the aqueous environment by an outer layer of water-soluble polymeric segments [Winnik, 1996]. The hydrophobically-modified polymers interact strongly with surfactants. Since the contact between the hydrophobic

groups and water is unfavorable, these polymers have a strong tendency to self-associate or to associate with surfactants.

Only a few studies concerning systems of water - soluble nonionic polymers and nonionic surfactants have been reported [Saito, 1987]. Generally the interaction for this system is very weak. However, a number of communications recently continue to appear detailing interactions between uncharged polymers and nonionic surfactants.

1.1 Background

1.1.1 Uncharged Polymer and Ionic Surfactant

The interactions between water soluble nonionic polymers and ionic surfactants have been extensively investigated in recent years [Carlsson et al., 1989]. These studies indicate a strong interaction with anionic surfactants. For example, Ricka et al., showed that the solubilization and conformational transitions of a polymer, poly (N - iso propylacrylamide), in dilute surfactant (SDS) solutions could be studied by dynamic light scattering. Dubin et al., [1992] studied the effects of ionic strength and PEO molecular weight on the complex of PEO-LDS (lithium dodecylsulfate) by using static light scattering, dynamic light scattering, electrophoretic light scattering, and dialysis equilibrium. With increasing surfactant concentration, no interaction between the polymers and the surfactants is detected until a critical aggregation concentration (cac) is reached. The cac is usually lower than the cmc in the absence of polymers. This is a clear indication of interaction between polymer and surfactant. Above the cac, surfactants form aggregates bound to polymer. The driving force for complex formation is the reduction in interfacial energy between the hydrocarbon core and the local solvent medium.

In general, nonionic polymers interact strongly with anionic surfactants, but weakly with cationic surfactants. This behavior has been explained as due to (a) the bulkiness of the cationic head group, (b) electrostatic repulsion between polymer and surfactant due to the possible protonation of the polymer, and (c) a more favorable interaction between anionic surfactants and the hydration shell of the polymers. If the hydrophobic character of the polymer is increased, a more pronounced interaction is observed with cationic surfactants. For example, Winnik et al., [1987] showed complex formation between hydroxypropyl cellulose (HPC) and hexadecyltrimethyl ammonium chloride (HTAC) micelles. Carlsson et al., [1989] also observed complex formation of ethyl(hydroxyethyl)cellulose (EHEC) with N-tetradecylpyridinium bromide (TDPB) or dodecyl trimethylammonium ions (DTA^+). Both an increase in ionic strength and a rise of temperature led to a more pronounced binding. Shirahama and co-workers [1987] also found binding of hexadecyltrimethyl ammonium bromide (HTAB) and hexadecyldimethyl-2-hydroxyethyl ammonium bromide (BINA) to poly(vinyl alcohol) (PVA) and PEO, which are hydrophilic polymers. On the other hand, if the hydrophobicity of surfactant is increased, interactions between nonionic polymers and cationic surfactants may also be enhanced.

1.1.2 Polyelectrolyte and Oppositely Charged Surfactant

The interaction between polyelectrolytes and oppositely charged surfactants is dominated by electrostatic forces, although hydrophobic interactions play a secondary role. Therefore, the interactions are significantly stronger than those in uncharged polymer-charged surfactant systems.

Abuin and Scaiano [1984] investigated the interaction between polystyrene sulfonate (PSS), a strong polyelectrolyte, and dodecyl trimethylammonium bromide (DTAB). The results showed the contraction of the polyelectrolyte chain, as deduced from viscosity measurement. Chu and

Thomas [1986] measured the aggregation numbers of the surfactant clusters formed in the system consisting of sodium polymethacrylate (NaPMA), a weak polyelectrolyte, and DTAB. They found the aggregation numbers in the complex are larger than the aggregation numbers in solutions of polymer-free surfactant micelles.

In general, the interactions between polyelectrolytes and oppositely charged surfactants start at a very low surfactant concentration (c_{ac}), usually a few orders of magnitude lower than the cmc of the free surfactant. Unlike the nonionic polymer-ionic surfactant system, the complex usually cannot coexist with free micelles because precipitation is observed as the addition of ionic surfactant brings the polyelectrolyte close to charge neutralization. However, further addition of ionic surfactant may resolubilize the precipitate [Winnik, 1996].

1.1.3 Uncharged Polymer and Non - ionic Surfactant

The interaction between nonionic polymers and nonionic surfactants is usually very weak. However, since the driving force for polymer-micelle interaction is the reduction in Gibbs energy of the total system, interaction could occur if hydrophobic polymer is used [Dubin, 1994]. Although nonionic surfactants have the same value for the cmc in the presence of the polymer as in water, this does not mean the absence of interaction. It probably means that the interactions do not involve the same type of binding of surfactant micelles to the polymer chain as in the ionic system [Brown, 1996]. The factors influencing the association between hydrated head groups and polymer segments and the favorable transfer of the hydrophobic polymer to the micellar environment, compensate each other resulting in a negligible change in total Gibbs energy. The dependence of complex structure upon the change in length, size, and concentration of polymers and surfactants is clearly important and not well understood.

Recently there has been a growing interest in studying polymer-surfactant interactions in aqueous neutral polymer and nonionic surfactant systems.

Boscher et al., [1983] described the interaction between nonionic surfactant and hydroxyethylcellulose (HEC) by light scattering measurement. Their result showed that the interactions occur in neutral polymer / nonionic surfactant systems.

Szmerekova et al., [1984] reported by gel permeation chromatography (GPC) on the interaction activity between a nonylphenol polyethylene glycol and PEO may well be due to an affinity of the aromatic phenol moiety. The presence of a surfactant in the system had two effects: lower PEO elution volumes, V_e , and the occurrence of negative vacant peak when compared with the chromatograms obtained with water as a mobile phase. The interaction between PEO and surfactant was confirmed by the above two factors.

Brackman et al., [1988] described microcalorimetric measurements on solutions of poly(propylene oxide) (PPO), containing the nonionic surfactant n-octylthioglucoside micelles (OTG). Although the cmc was identical with and without the polymer, the results showed that the enthalpy of the polymer-surfactant interaction is endothermic.

Winnik [1990] reported the interaction between pyrene-labeled hydroxypropyl cellulose (HPC) and OTG. The excimer formation of pyrene abruptly decreases at the cmc of the surfactant, implying an interaction between the modified HPC and the surfactant micelles. Again, no decrease in cmc was observed.

Lindmann et al., [1994] described the interaction between nonionic micelles ($C_{12}E_8$) and ethylhydroxyethyl cellulose (EHEC). They reported that the micelle diffusion is influenced by the polymer in two ways; obstruction due to the polymer network and association of micelles to the polymer chains.

The above authors brought forward the evidence for the existence of neutral polymer and neutral surfactant complexes. It is not excluded that complexes were formed but remained undetected by the measurements. Therefore, light scattering and viscometric measurements will be used to investigate the association of polyacrylamide (PAM) with micelles formed from the nonionic surfactant Triton X - 100 in this study.

1.2 Polyacrylamide (PAM)

Polyacrylamide belongs to the class of nonionic (neutral) polymers. It has the glass transition temperature (T_g) of 165°C. It is clear that PAM remains glassy to relatively high temperatures. Although PAM is slow to dissolve, it is soluble in water in all proportions. However, PAM solution viscosity shows a time dependence, attributed to intramolecular conformational changes. Very dilute solutions of pure PAM in water contain only individual, unassociated polymer coils. At higher concentrations, mechanical entanglements are sufficient to affect viscosity. Due to the enormous viscosity increase, PAM has been used as a thickening agent in tertiary oil recovery [Encyclopedia of Polymer Science and Engineering, 1985].

Large aggregates have been observed in dilute aqueous solutions of high molecular weight PAM. The aggregation increases with molecular weight but can be minimized by addition of salts. A solution of 41% methanol by volume in water is a theta solvent for PAM [Jacqueline, 1990].

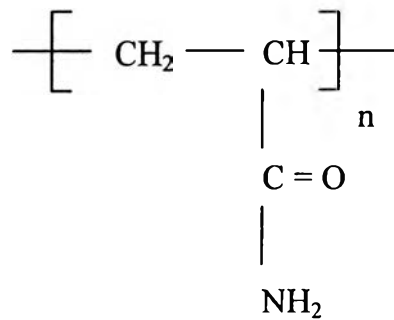


Figure 1.1 Chemical structure of PAM.

1.3 Nonionic Surfactant (Triton X - 100)

Surfactants have an amphiphilic character which contain both water-soluble (hydrophilic) and water-insoluble (hydrophobic) groups in the same molecule. Therefore, they tend to adsorb at interfaces. This adsorption gives rise to a decrease in surface tension until the interface is effectively saturated with surfactant molecules (Figure 1.2). After saturation surfactant molecules associate in submicronic aggregates called “ micelles ”. The hydrophobic part of the surfactant occupies the core of the micelles and the hydrophilic head groups are pointing outside toward the water. The concentration of the surfactant 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 [Christian and Scamehorn, 1995].

Triton X - 100 [p - 1,1,3,3 - tetramethylbutylphenoxy poly (oxyethylene)glycol] is a commercially available nonionic surfactant, has been widely used for solubilizing membrane bound enzymes and for stabilizing this class of enzymes in solution [Goddard, 1993 and Hasko Paradies, 1980]. It contains an average size of 9.5 oxyethylene units per molecule. Triton X - 100 is an excellent choice for studying amphiphile behavior over a wide range of

concentration. It forms micelles at relatively low solute concentrations. At low concentrations, Triton X - 100 forms micelles, at higher concentrations the system goes over from an isotropic liquid to a liquid crystalline phase [George D. J. Phillies, 1993]. The micellar shape and size distributions are dependent of the temperature and surfactant concentration.

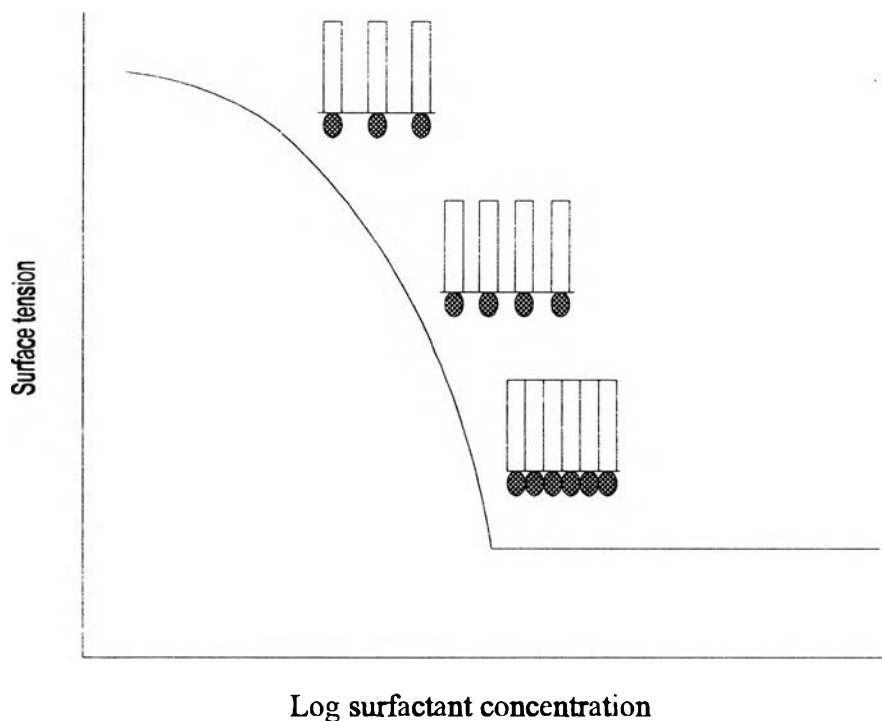


Figure 1.2 Surface tension versus bulk surfactant concentration [Eric G. Lomax, 1996].

1.4 Applications of the Polymer - Surfactant System

Complex formation between surfactants and polymers (including polyelectrolytes) has been the subject of intense research effort, because of both fundamental and technological interests. The study of polymer - surfactant interactions can be applied to important industrial and biological processes.

Some industrial situations in which polymers and surfactants are used conjointly in enhanced oil recovery systems by polymer - micelle flooding and rheology control [Goddard, 1993]. Alli and co-workers [1991] investigated the combination of polymers and surfactants as a medium for release of selected drugs in tablet form. The presence of surfactants was found in most cases to prolong the time of releasing drug from pharmaceutical tablets containing polymer. Acrylamide - based polymeric surfactants can be used as an associative thickeners. In addition, the polymer - surfactant complex can also be used in cosmetics formulations (e.g. film former for hair dressings, grooming aids, perfumes and colognes), food industrial and paint removers. [Mandel, M., 1985].

1.5 Objectives

Light scattering measurements provide a non - invasive means of probing conformational changes. Therefore, dynamic light scattering (DLS) and viscometric measurements are used to elucidate such changes in the interaction pattern in mixtures of a high molecular weight fraction of PAM and the non-ionic surfactant, Triton X - 100, in aqueous solutions.

The aim of this research are to identify the interactions between the polymer and the surfactant by measuring several physical properties of the binary systems (PAM in aqueous solution and Triton X - 100 in water) and ternary system (PAM / Triton X - 100 / water) and to examine the effect of polymer concentration, the surfactant concentration and the effect of molecular weight of polymer.