



CHAPTER II

LITERATURE SURVEY

2.1 Interaction of Polymer-Surfactant Complexes in Dilute Solutions

2.1.1 Nonionic Polymer - Anionic Surfactant

A large number of studies have focused on polymer-surfactant interaction because of their numerous commercial and industrial applications. Most studies were carried out for water-soluble nonionic polymer and an ionic surfactant systems. Such systems are characterized by repulsive surfactant-surfactant interactions while the polymer-polymer interaction is typically more or less attractive (Goddard and Ananthapadmannabhan, 1993).

In 1957, Saito and Kolloid studied the pioneering work on polymer-surfactant interaction between poly(vinyl pyrrolidone) (PVP) and sodium dodecyl sulfate (SDS). He found two major observations: (i) an increase in viscosity of polymer solution upon addition of SDS; and (ii) an increase in solubilizing power of an SDS solution upon addition of PVP. It was suggested that the aggregation of surfactant molecules in the presence of polymer resembled with normal micellization. He proposed that the surfactant molecules bound individually to the polymer at low surfactant concentration. This binding occurred by dipolar interaction of the surfactant head groups with polar sites on the polymer. Later, much attention has been received on complex formation between uncharged polymers and anionic surfactants, especially on PEO-SDS system. In such a system, a number of different techniques have been used to study the nature of the complex formation, such as nuclear magnetic resonance (NMR) spectroscopy, viscometry, conductimetry, dialysis equilibrium, and static and dynamic light scattering.

Cabane (1977) described by NMR spectroscopy that the surfactant molecules exist freely in the solution below the critical aggregation concentration (c_{ac}). When the SDS concentration exceeds this level of concentration, a substantial amount of SDS is bound in the form of micelles to the polymer chain, although a proportion of SDS is still present in the bulk solution. Nagarajan and Kalpakci

(1985) examined the PEO with anionic surfactant (SDS), and cationic surfactant, didodecyl dimethyl ammonium bromide (DDAB) by viscometric measurement. They found that the extent of polymer-micelle association is large for anionic surfactant compared to cationic surfactant. It decreases with increasing bulkiness of the surfactant head groups. They concluded that the formation of polymer-micelle complexes is governed by the extent of augmented shielding from water provided by the polymer segments to the hydrocarbon core of the micelles and the steric and electrostatic interactions between the polymer segments and the surfactant head groups.

Chari *et al.* (1994) examined the effect of SDS on the conformation of PEO in water by viscometry and small angle neutron scattering (SANS) measurements. Their results indicated that only a small fraction of the total coil is in contact with the micelles at saturation. The polymer coil at saturation is slightly swollen compared to the unperturbed coil in a good solvent. Recently, Jiang and Han (2000) developed a new viscosity equation for PEG-SDS system in dilute aqueous solutions. They proposed that the polymer chains can be divided into two kinds of segments; the complex segments associated with surfactant micelle and the free segments. The complex segments are similar to the polyelectrolyte and the free segments exist in water and their properties are the same as polymer in pure water. Based on these considerations, they established a new viscosity equation by considering the partially stretched chain structure of the polymer-surfactant complex caused by the electrostatic repulsion of the resident charge. Brown *et al.* (1992) demonstrated the pronounced polyelectrolyte effect which is imparted to the neutral PEO chain on the formation of a charged complex with the ionic surfactant SDS by using static and dynamic light scattering. They found that the radius of gyration (R_g) changes with SDS concentration and the ionic strength of the solvent medium.

Norwood *et al.* (1998) determined the binding characteristics of aggregates formed between neutral polymer, poly(vinyl pyrrolidone) (PVP) and SDS by light scattering. They reported that the mass increase of the scattering aggregates by adding surfactant is reflected in higher scattered intensity. The majority of the scattering was observed due to PVP-SDS aggregates. These aggregates consist of single PVP chain with multiple bound SDS micelles.

Holmberg *et al.* (1992) investigated the hydrodynamic and thermodynamic behavior of the SDS-ethyl(hydroxyethyl) cellulose (EHEC) in water by means of viscosity and dialysis equilibrium. EHEC is a strongly hydrophobic water-soluble cellulosic polymer. The dialysis equilibrium showed strong adsorption of SDS at concentrations far below the critical micelle concentration (cmc) of SDS. The viscosity measurement revealed a drastic reformation of the polymer in dilute solution by combining with surfactant. At higher PEO concentrations, the viscosity passes through a sharp maximum by increasing SDS concentration. In 1994, Kamenka *et al.* investigated the interaction between SDS and EHEC at different temperatures by means of conductivity and time-resolved fluorescence quenching methods. They demonstrated that polymer-surfactant interaction is strengthened by means of a reduced critical micelle concentration, and a lowered micelle aggregation number as temperature is increased. In the absence of polymer, these quantities are apparently higher and approximately constant on temperature changes. Medeiros and Costa (1996) found, in steady state fluorescence measurement, that the critical micelle concentration of SDS is not significantly affected by temperature in the absence of polymer, but the critical aggregation concentration (cac) in the presence of EHEC polymer was found to decrease as the temperature was increased. Hoff *et al.* (2001) studied the effects of temperature and SDS concentration on the viscosity of dilute solutions of the nonionic cellulose ether EHEC. The viscosity results showed that a sharp collapse of the EHEC-SDS aggregates at SDS concentrations slightly above the critical aggregation concentration. At a moderate amount of SDS, the complexes expanded due to enhanced electrostatic repulsion between polymer chains cooperated with SDS. At a very high SDS concentration, the small contraction of the EHEC chain occurred and can be attributed to the screening of the electrostatic interactions. A temperature-induced shrinkage of the polymer chain was observed at low surfactant concentrations.

2.1.2 Nonionic Polymer - Cationic Surfactant

Hydroxypropylcellulose (HPC) is an interesting polymer with many commercial applications. Winnik *et al.* (1987) examined the interaction of dilute

aqueous solutions of HPC with a cationic surfactant, hexadecyl- trimethylammonium chloride (HTAC) by fluorescence measurement. The changes in the intensity ratio of the fluorescence of pyrene (probe) in aqueous solutions of HPC were measured as a function of HTAC concentration. Mixed micelle formation between HPC and HTAC is observed. Their results indicated that HTAC bound strongly to hydroxypropylcellulose. Large changes in the pyrene “excimer” fluorescence intensity and pyrene “monomer” fluorescence intensity indicated that polymer-polymer aggregates are broken up and the local conformation of the polymer is changed when HTAC interacts with HPC. Hormnirun *et al.* (2000) also investigated the complex formation between a semiflexible nonionic polymer HPC, and a cationic surfactant HTAB, by dynamic light scattering and viscometry. Their observations showed convincingly that a binding interaction occurs between HTAB surfactant micelles and HPC chains. Above the critical micelle concentration, charged micelles bind to the polymer resulting in a chain expansion and consequent rise in viscosity. They described the effect of electrostatic interaction on the viscosity of the polymer-surfactant system by a common scaling of the normalized interaction viscosity ($\eta_I/\eta_{I,max}$), i.e. the ratio of the interaction viscosity relative to its value at maximum binding, as a function of the surfactant/polymer concentration ratio.

Carlsson *et al.* (1989) performed a self-diffusion measurement on dodecyltrimethylammonium bromide (DoTAB) in aqueous solutions of EHEC by NMR self-diffusion technique. They demonstrated that an addition of salt or an increase in temperature promoted the binding of DoTAB to EHEC. The polymer molecules became increasingly more hydrophobic with increasing temperature, which was referred to as temperature-induced conformational changes in the polymer. At low temperature the OCCO groups in EHEC preferred to be in a polar, low energy conformation with low entropy. On heating, EHEC polymer became more hydrophobic, leading to the increase in binding of surfactant. Zana *et al.* (1992) investigated the interaction between EHEC and two cationic surfactants, hexadecyltrimethylammonium chloride and bromide (CTAC and CTAB) in aqueous solution as a function of temperature by means of electrical conductivity and time-resolved fluorescence quenching methods. The results indicated that, in the presence of EHEC, the critical micelle concentration (cmc) decreased, the micelle ionization

degree increased, and the micellar aggregation number (N) decreased upon increasing temperature. All these results suggested that the increase of the strength of the EHEC-cationic surfactant interaction with temperature. These findings gave significant insights into the mechanism of the systems; for example, a decreased cmc and a lower aggregation number with increasing temperature gave a larger number of micelles, thus promoting a micelle-induced cross-linking in the semidilute regime. Wang and Olofsson (1995) studied dilute solutions of EHEC with cationic surfactants, alkyltrimethylammonium halides; RTAX ($R = C_{12}, C_{14},$ and C_{16} and $X = Br$ and Cl) by using titration microcalorimetry and viscosity measurements. They found that an increase in temperature from 25 to 45°C has no significant effect on the critical aggregation concentration (cac), the saturation concentration (c_2), and the amount of polymer-bound surfactant. The results showed that the chloride counterion gave more strengthened interaction than the bromide counterion and the longer hydrocarbon chain length of surfactant interacted more strongly with polymer.

In 1994, Anthony and Zana investigated the effect of temperature on the interaction between poly(oxyethylene) (POE) and tetradecyltrimethylammonium bromide (TTAB) by means of conductivity, spectrofluorometry, and time-resolved fluorescence quenching methods. The results indicated that an interaction occurred at temperatures above 35°C, obtaining the formation of POE-bound TTAB micelles which were smaller and more ionized than free TTAB micelles. This behavior was attributed to the decreased polarity of POE upon increasing temperature. At 25°C, the conductivity data showed the same cmc and the cac values in the presence and in the absence of polymer, suggesting that no interaction occurred at that temperature.

2.1.3 Nonionic Polymer - Nonionic Surfactant

There is a little indication of nonionic surfactants with nonionic water-soluble polymers. In such systems, the interactions are very weak because the electrostatic repulsion between polar head groups is not strong in nonionic surfactants as in anionic ones. Boscher and Ouivoron (1983) reported the occurrence of an interaction between a nonionic polymer, hydroxyethylcellulose (HEC) and a nonionic surfactant, polyethylene oxide nonyl phenyl ether (NP₁₄ and NP₂₀) systems

through light scattering study. They determined the preferential adsorption coefficient (α) from the molecular weight measurements. The value of α was found to be positive which indicated a preferential adsorption of micelles around polymer chains. At higher surfactant concentrations, preferential adsorption was no longer observed. Owing to a greater steric hindrance for NP₂₀ micelles, the preferential adsorption maximum was reached at a lower concentration than for NP₁₄ micelles. These preliminary results demonstrated that interactions occurred between nonionic polymer and nonionic surfactant systems. Later, Szmerkova and Kralik (1984) reported the interaction between a nonylphenol polyethylene glycol and PEO by gel permeation chromatography (GPC). They suggested that the interaction activity might be due to an affinity of the aromatic phenol moiety and PEO. They reported that the presence of a surfactant in the mobile phase has two effects: lower PEO elution volumes, V_e , and the occurrence of negative vacant peaks when compared with the chromatograms obtained with water as a mobile phase. The shift in V_e value of PEO was explained by the strong interaction between PEO and the surfactant. Lower elution volumes may be regarded as a result of the formation of a stable polymer-surfactant complex.

In 1988, Brackman *et al.* provided the evidence for the formation of polymer-micelle complexes of the water-soluble nonionic polymers PEO, poly(propylene oxide) (PPO), PVP, and HPC with nonionic surfactants: n-octyl thioglucoside (OTG), n-octyltriethylene glycol ether (C₈E₃) by spectrophotometric and microcalorimetric measurements. One of the most convincing indications for polymer-micelle interactions has been a reduced value of the cmc in the presence of polymer. However, they proposed that this criterion appears not to be generally valid, the cmc of these surfactants was not influenced by the presence of polymer did not exclude polymer-micelle complexation. It was found that the cmc values of all surfactants were unchanged by the presence of polymer. The turbidity of PPO was reduced upon addition of OTG, presumably because of interaction between PPO and OTG micelles. The more hydrophilic PEO is insoluble in hydrocarbons, and PEO-OTG interaction would force the polymer to reside at the surface of the micelle. Again, Winnik (1990) confirmed the occurrence of the interaction between HPC and OTG by using fluorescence measurement.

Feitosa *et al.* (1996) examined the interaction between the nonionic surfactant, pentaethylene glycol mono-n-dodecyl ether ($C_{12}E_5$) and a high molar mass PEO in aqueous solution as a function of temperature by dynamic light scattering and fluorescence methods. They determined that the clusters of surfactant micelles formed within the PEO coil, leading to the chain expansion. The cmc of the surfactant remained unchanged with increase in PEO concentration. The hydrodynamic radius of the complex increased strongly with temperature as well as with the concentrations of surfactant and polymer. At high surfactant concentration, the complex coexisted with free surfactant micelles in the solution. At low surfactant concentrations, the aggregation number (N) of the surfactant micelles within the clusters was smaller than in the polymer free solution due to steric factors. N increased with increasing surfactant concentration in the presence of constant PEO concentration, to a plateau value. Mya *et al.* (1999) was studied on ternary mixture of high molecular weight polyacrylamide (PAM) and the nonionic surfactant, Triton X-100 (TX-100) in aqueous solution in terms of surfactant concentration, polymer concentration and the PAM molecular weight by using light scattering and viscometry. We found that the mean diffusion coefficient decreased slightly until reaching a minimum and then increased toward an asymptotic value which was identical to that of a single micelle. Near the cmc, the binding of the surfactant onto a PAM chain induced a slight chain expansion. Dynamic light scattering showed a relaxation peak corresponds to the free micelle at very high surfactant concentration which indicated the saturation point of binding between PAM and TX-100. We also found that the binding of surfactant to polymer is independent of polymer molecular weight.

2.1.4 Polyelectrolyte - Oppositely Charged Surfactant

Polyelectrolytes with oppositely charged surfactants can interact strongly due to the electrostatic interaction and the self-aggregation tendency of the surfactants. Therefore, polymer can induce micelle-type aggregation of the surfactant at concentrations well below the cmc. Such aggregation has been studied by light scattering, surface tension, turbidimetry, and fluorescence quenching methods.

Bahadur *et al.* (1995) studied the interaction of poly(4-vinylpyridine *N*-oxide) (PVPNO) with SDS in aqueous solutions by using surface tension and light scattering. This polymer has a high dipole and behaves as a hydrophilic nonionic polymer in water but can also be protonated to form a cationic polyelectrolyte at highly acidic pH. Surface tension measurement showed that the polymer began to interact with SDS at well below the cmc, similar to the behavior of nonionic polymer with ionic surfactant systems. They found that the phase separation occurred at low pH, presumably as a consequence of protonation of the polymer to form a polycation. The intensity results revealed that the saturation of the polymer with bound micelles at high SDS concentration and the light scattering measurement clearly showed two peaks; one corresponding to free micelles and the other to the complex. In 1996, Fundin *et al.* described the changes in the cationic polyelectrolyte, poly(*N,N,N*-trimethylammonio) ethyl acrylate (PCMA) conformation when the anionic surfactant, SDS was added in the presence of salt. The different surfactant/polymer mass concentration ratios were examined at different NaCl concentrations. They demonstrated that when the polyelectrolyte-surfactant complex was formed, the hydrodynamic radius (R_h) was smaller than that for the pure polymer as a result of a combination of electrostatic and hydrophobic interactions. A decrease in R_g was observed as the SDS/PCMA ratio was increased, in agreement with the change in R_h . The aggregation numbers (N) of the polyelectrolyte-bound micelles at different SDS/PCMA ratios were larger than those for SDS in the absence of PCMA at the same concentrations of NaCl.

Recently, Fundin *et al.* (1997) also studied the interaction between poly(acrylic acid) (PAA) and cetyltrimethylammonium bromide (CTAB) by light scattering, viscosity, and time-resolved fluorescence quenching techniques. Light scattering results showed that a single PAA chain bound several CTAB micelles to form a complex. At the concentration ratio of CTAB to PAA (β) was equal to 1, the complex was saturated with surfactant. The R_h of the complex was 75% smaller than the radius of the surfactant free PAA coil at $\beta < 1$. At higher β , the free micelles coexisted with the complex and the size approached the size of the pure PAA coil. The free micelles have a strong effect on the intercomplex interactions. They found,

by viscosity measurement, that no multipolymer complexes formed in the studied concentration range. In 1997, Antonietti *et al.* proposed a new class of highly ordered polyelectrolyte (PE)-surfactant complexes. They examined the solution and solid-state structure of PE-surfactant complexes. They found that the different lamellar modifications of complexes between poly(styrene sulfonate) (PSS) and various alkyltrimethylammonium counterions (C_{12} - C_{18}). A cylindrical mesophase structure was observed in the complex between poly(acrylic acid) (PAA) and dodecyltrimethylammonium counterions. Each cylinder consisted on the average of four polyelectrolyte chains, which was highly elongated.

2.2 Rheological Investigations on Polymer-Surfactant Complexes

Analysis of the rheological properties of a material provides useful information about the configurational rearrangements of the polymer and the long and short-range intermolecular interactions. Several authors have reported rheological studies on the influence of surfactant on the viscosity of aqueous solutions of polymer. Goddard and Ananthapadmannabhan (1993) studied on two cationic polymers: cationic cellulosic (polymer JR) and an acrylamide/ β -methacryloxyethyl trimethylammonium chloride copolymer (Reten) with SDS anionic surfactant. For the system of Reten copolymer with SDS surfactant, no change in viscosity was observed until the precipitation range. In contrast, the viscosity of polymer JR solution increased over 200-fold by adding surfactant. These results suggested that a little change in conformation when binding of SDS to Reten copolymer. On the contrary, the intermolecular association was observed in solution of the cationic cellulose with SDS at high surfactant concentration. When the polymer concentration was increased to 1%, it was observed to form a gel.

Lance-Gomez and Ward (1986) measured the stress relaxation after cessation of steady-state flow to investigate the viscoelastic properties of PEO in the presence of salt and surfactant solutions in terms of the effects of shear rate, PEO concentration, and molecular weight of polymer. He found that the shear rate did not have a significant effect on the stress relaxation while the PEO concentration had. Surprisingly, he observed that an increase or a decrease in stress relaxation upon an

addition of anionic surfactant. This effect was depending on the difference in molecular weight distribution of the polymer. The changes in viscosity and viscoelasticity of aqueous solutions of high molecular weight PEO was observed on addition of SDS proposed by Brackman (1991). The viscosity of the PEO solution at a fixed SDS concentration decreased with increasing shear rate, indicating the non-Newtonian behavior. At high SDS concentration and high shear rate, the normal stress difference, which is a measure of the viscoelasticity, became independent of shear rate. This behavior was proposed to arise from shear-induced breakdown of the polymer-micelle complex.

The rheological investigations revealed the formation of mixed micelles composed of a cellulose derivative water-soluble polymer (derivative of hydroxypropylcellulose) and an anionic surfactant, SDS (Zugenmaier and Aust, 1990). At low surfactant concentration, only few SDS molecules were adsorbed at the side group of the polymer. With a further addition of surfactant, a mixed micelle was formed at a certain SDS concentration.

Aqueous solutions of ethyl(hydroxyethyl) cellulose (EHEC) in the presence of ionic surfactants: anionic surfactant, SDS, and cationic surfactant, CTAB, formed a physically cross-linked gel in the semidilute concentration regime at elevated temperatures (Nystrom and Lindman, 1995; Nystrom *et al.*, 1995). Physical gels are built up by thermoreversibly cross-linked networks in which the junctions are formed by secondary forces. Measurements were performed by dynamic light scattering (DLS) and shear relaxation experiments at various temperatures. The relaxation processes were slow down as the gel evolves. The DLS results indicated two relaxation modes: an exponential at short times followed by a stretched exponential at longer relaxation times. The relaxation time of the fast mode decreased with increasing temperature and found to be diffusive at all temperatures, while the slow mode increased as the gel was formed. Both the rheological and the DLS measurements revealed that the interaction of the two systems was different and the level of chain association or entanglement was significantly higher for the EHEC/SDS system than for the EHEC/CTAB system.

Wang *et al.* (1997) recently studied the semidilute aqueous solutions of EHEC and SDS in the temperature range between 20-80°C by high-sensitivity

differential scanning calorimetry (HSDSC). In semidilute solutions, the hydrophobic association increased as the temperature was increased and addition of SDS at low concentrations induced the formation of cross-links. At certain concentrations, a polymer network developed and a gel was formed. The addition of SDS to solutions of gelling EHEC significantly changed the features of the differential scanning calorimetric (DSC) peaks, indicated that the surfactant changed the association behavior of the polymer.

2.3 Summary

Table 2.1 Literature studies of the interactions between polymers and surfactants

	Polymer	Surfactant	References	Methods
Nonionic polymers and anionic surfactants	PEO	SDS	Cabane (1977)	NMR spectroscopy
	PEO	SDS	Nagarajan & Kalpakci (1985)	Viscometry
	PEO	SDS	Brown <i>et al.</i> , (1992)	Static and dynamic light scattering
	EHEC	SDS	Holmberg <i>et al.</i> , (1992)	Viscosity and dialysis equilibrium
	PEO	SDS	Chari <i>et al.</i> , (1994)	Viscometry and SANS
	EHEC	SDS	Kamenka <i>et al.</i> , (1994)	Conductivity and fluorescence quenching
	EHEC	SDS	Medeiros & Costa (1996)	Fluorescence quenching
	PVP	SDS	Norwood <i>et al.</i> , (1998)	Light scattering
	PEG	SDS	Jiang and Han (2000)	Viscometry
	EHEC	SDS	Hoff <i>et al.</i> , (2001)	Viscometry

	Polymer	Surfactant	References	Methods
Nonionic polymers and cationic surfactants	PEO	DDAB	Nagarajan & Kalpakci (1985)	NMR spectroscopy
	HPC	HTAC	Winnik <i>et al.</i> , (1987)	Fluorescence
	EHEC	DoTAB	Carlsson <i>et al.</i> , (1989)	NMR self-diffusion
	PPO	HTAX (X = Cl ⁻ , Br ⁻)	Brackman & Engberts (1991)	Fluorescence and Conductivity
	PVME	HTAB, HTASal	Brackman & Engberts (1991)	Conductivity
	EHEC	CTAB, CTAC	Zana <i>et al.</i> , (1992)	Conductivity and fluorescence quenching
	POE	TTAB	Anthony & Zana (1994)	Conductivity, spectrofluorometry and fluorescence quenching
	EHEC	RTAB, RTAC (R = C ₁₂ , C ₁₄ , and C ₁₆)	Wang & Olofsson (1995)	Microcalorimetry and viscosity
	HPC	HTAB	Hormnirun <i>et al.</i> , (2000)	Light scattering and viscosity
Nonionic polymers and nonionic surfactants	HEC	NP ₁₄ and NP ₂₀	Boscher <i>et al.</i> , (1983)	Light scattering
	PEO	Slovafol 909	Szmerekova <i>et al.</i> , (1984)	Gel permeation chromatography
	PEO	C ₁₂ E ₅	Feitosa <i>et al.</i> , (1988)	Dynamic light scattering and fluorescence
	PAM	TX-100	Mya <i>et al.</i> , (1999)	Light scattering and viscosity

	Polymer	Surfactant	References	Methods
Polyelectrolytes and oppositely charged surfactants	PVPNO	SDS	Bahadur <i>et al.</i> , (1995)	Surface tension and light scattering
	PCMA	SDS	Fundin <i>et al.</i> , (1996)	Light scattering and fluorescence quenching
	PAA	CTAB	Fundin <i>et al.</i> , (1997)	Light scattering, viscosity, and fluorescence quenching
	PE	DTA ⁺	Antonietti <i>et al.</i> , (1997)	Small angle X-ray scattering

Table 2.2 Previous studies of physical parameters determination by static light scattering measurement

Method & systems	$M_{w,p}$	$M_{w,com}$	D'	f	$N_{s,b}/N_p$	# of chain
<u>I. Thermodynamic treatment method (using dialysis)</u>						
1. Protein – binary solvent system [β -lactoglobulin – water + methanol] (Inoue and Timasheff, <i>J. Amer. Chem. Soc.</i> , 1968)			✓			
2. Polymer – surfactant system [PVP – SDS] (Gilyani and Wolfram, <i>Microdomain in polymer solutions</i> , 1985)	✓	✓				✓
3. Protein – surfactant systems						
(i) [Lysozyme – SDS] (Valstar <i>et al.</i> , <i>Langmuir</i> , 1999)	✓					✓
(ii) [Bovine serum albumin – SDS] (Valstar <i>et al.</i> , <i>Langmuir</i> , 2000)	✓					✓

Method & systems	$M_{w,p}$	$M_{w,com}$	D'	f	$N_{s,b}/N_p$	# of chain
<u>II. Thermodynamic method</u>						
1. Polymer – surfactant systems						
(i) [HEC – water + surfactant binary mixture] (<i>Boscher et al., Polymer bulletin, 1983</i>)			✓			
(ii) [PVP – SDS] (<i>Norwood et al., Macromolecules 1998</i>)		✓		✓		
<u>III. Approximate methods</u>						
1. Polymer – surfactant systems						
(i) Poly(dimethyldiallylammonium chloride) – mixed micelles (SDS + TX – 100) (<i>Dubin et al., Macromolecules, 1990</i>)		✓				
(ii) Poly(N,N,N- trimethylammonio) ethyl acrylate chloride salt) – SDS (<i>Fundin et al., Macromolecules, 1996</i>)		✓				

In our work, we will investigate the above physical parameters by using thermodynamic treatment method including with equilibrium dialysis to determine the structures of the nonionic hydrophilic polymer PEO – cationic surfactant HTAC both in the presence and absence of salt. In addition, we will also study the structure of nonionic hydrophobic polymer HPC – amphoteric surfactant CADG in aqueous solution. All the finding parameters are shown in Table in 2.3.

Table 2.3 Investigation of physical parameters by static light scattering measurement

Method & systems	$M_{w,p}$	$M_{w,com}$	D'	f	$N_{s,b}/N_p$	# of chain
<u>Thermodynamic treatment method (using dialysis)</u>						
Polymer/surfactant/solvent system						
(i) PEO – HTAC – H ₂ O	✓	✓	✓	✓	✓	✓
(ii) PEO – HTAC – H ₂ O – Salt	✓	✓	✓	✓	✓	✓
(iii) HPC – CADG – H ₂ O	✓	✓	✓	✓	✓	✓

2.4 Rheological Studies on Flexible Elongated Micelles

The study of surfactants is a rapidly growing area of scientific research especially the rheological properties of surfactants are of great interest. Dilute surfactant solutions usually behave as Newtonian liquids with viscosities slightly greater than that of water. In contrast to these simple fluids there are viscoelastic surfactant systems which can assemble reversibly into flexible wormlike micelles that can form a viscoelastic fluid. These aggregates can break and recombine continuously in course of time. Despite the existence of breaking time (τ_{break}), the behavior of surfactant solutions is similar to that of ordinary polymer chains in solution. Aqueous solutions of surfactants with strongly binding counterions exhibit gellike properties. In 1988, Rehage and Hoffmann investigated the viscoelastic behavior of cationic surfactant, cetylpyridinium chloride (CPyCl) in sodium salicylate (NaSal) solution. They examined the zero shear viscosity, the shear modulus, and the stress relaxation time as functions of surfactant and salt concentrations. They found that the shear modulus did not depend on the salt concentration, which implied that the micellar structures were not changed upon

changing salt concentration. However, the stress relaxation time was strongly influenced by the ionic strength. At higher surfactant concentrations, the gel-like supermolecular structure was observed. Later, the rheological behavior of flexible elongated micelles was studied on aqueous solutions of cetylpyridinium chloride (CPyCl) and sodium salicylate (NaSal) in brine solution (Ponton *et al.*, 1998). The isotropic phase of wormlike micelles was investigated as functions of surfactant mass fraction (ϕ) and temperature ranging from 25 to 39°C. The results were explained by the Cates model (Cates, 1990) which predicted a decrease of the micellar length when the temperature increased. In addition, a master curve was constructed for temperature superposition of viscosity curves at various temperatures by using appropriate reduced variables.

Imae and Ikeda (1987) provided the information about the worm-like micelles by static light scattering measurement. They studied the cetyltrimethylammonium chloride (CTAC) cationic surfactant in aqueous sodium chloride (NaCl) solutions and demonstrated that rod-like micelles were formed above the threshold NaCl concentration of sphere to rod transition. Rodlike micelles became very long in aqueous solutions of high NaCl concentrations. The aggregation number of rodlike micelles increased markedly with increasing NaCl concentration. Long rodlike micelles are semiflexible and behave as worm-like chains. Their contour length and persistence length were calculated as 630 and 46.4 nm, respectively, at very high NaCl concentration.

In 1989, Candau *et al.* proposed the rheological properties of semidilute and concentrated aqueous solutions of cetylmethylammonium bromide (CTAB) in the presence of potassium bromide (KBr). They investigated that the stress relaxation function was found to be a single-exponential decaying function and yielded the value of the longest viscoelastic relaxation time T_R . The viscosity and relaxation time followed the power law behavior, suggesting that the changes of micelle size on the time scale of micellar reptation. The variation of viscosity with temperature was found that only in a restricted range of temperature following the Arrhenius like behavior. However, the temperature dependence of the stress relaxation time and the breaking time (τ_{break}) followed the Arrhenius law for CTAB/KBr system proposed by

Cates and Candau (1990). Alternatively, the frequency-dependent shear modulus of semidilute aqueous solutions of CTAB in KBr was measured as functions of surfactant concentration and temperature (Kern *et al.*, 1992). Their results provided the estimation of τ_{break} from the comparison between the experimental data and the results from the computer simulation. At a moderately low concentration range, the value of calculated τ_{break} was well agreement with that value obtained from the experimental data. At high concentrations, the unexpected increase of τ_{break} was observed. It was tentatively attributed to the fact that the persistence length of the wormlike micelles became larger than the mesh size of the transient network of entangled micelles, which corresponded to the concentrated regime of wormlike polymers. Makhloufi and Cressely (1992) investigated the non-Newtonian viscosity of aqueous CTAB solutions in the presence of KBr. At high surfactant concentrations, it was found that an increase of the viscosity with temperature due to the increase of the entanglement with concentration coupled with the temperature.

In 1995, Cappelaere *et al.* determined the linear and non-linear rheological properties of concentrated aqueous solutions of CTAB in the absence of salt. They reported that CTAB in the absence of salt was not Maxwellian fluid characterized by a single exponential stress relaxation and therefore the behavior of surfactant system without salt was evidently different from the system in the presence of salt. It was suggested that the effect of salt concentration is important in determining the dependence of average micellar size on surfactant concentration. It is necessary to make modifications of existing theories in order to explain their experimental results obtained in both linear and non-linear regimes.

Recently, Raghavan and Kaler (2001) examined two cationic surfactants which have long mono-unsaturated tails: erucyl bis-(hydroxyethyl) methylammonium chloride (EHAC) and erucyl trimethylammonium chloride (ETAC) in the presence of salt. Both solutions exhibited very high viscosity at room temperature and ETAC reduced the viscosity at high temperatures. They found that the cationic surfactant EHAC in water gave rise to highly viscoelastic or gellike solution on addition of salt, and these solutions retained appreciable viscosity up to

high temperatures above 90°C. The summary for the previous studies on elongated worm-like micelles is shown in Table 2.4.

Table 2.4 Summary for the rheological studies of elongated worm-like micelles

System	References	Measured parameters
Cetylpyridinium chloride (CPyCl) in sodium salicylate (NaSal)	Rehage & Hoffmann, (1988)	η_0 , G' and G'' , τ
Cetyltrimethylammonium bromide (CTAB) in potassium bromide (KBr)	Candau <i>et al.</i> , (1989)	η_0 and τ_R
Cetyltrimethylammonium bromide (CTAB) in potassium bromide (KBr)	Cates & Candau, (1990)	τ_R and τ_{break}
Cetyltrimethylammonium bromide (CTAB) in potassium bromide (KBr)	Kern <i>et al.</i> , (1992)	G' , G'' and τ_{break}
Cetyltrimethylammonium bromide (CTAB) in potassium bromide (KBr)	Makhloufi & Cressely, (1992)	η^*
Cetyltrimethylammonium bromide (CTAB) in aqueous solution	Cappelaere <i>et al.</i> , (1995)	τ_R and η^*